Supporting Information

Contents:

1. General Information

Unless otherwise noted, all catalytic reactions were set up in a nitrogen-filled glovebox, using glassware that was oven-dried (120 °C) and evacuated while hot prior to use. Proton Sponge® was recrystallized from EtOH prior to use.[1] LiOAc was dried under reduced pressure at 120 °C overnight prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a nitrogen atmosphere. Solvents were sparged with argon and purified by elution through a column of activated alumina under argon before use and were stored in a nitrogen-filled glovebox over activated 3 Å molecular sieves; molecular sieves were dried at 200 °C overnight under vacuum prior to use. CD_2Cl_2 was distilled over CaH_2 under nitrogen and stored in a bulb with a Teflon tap over activated 3 Å molecular sieves. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Microwave vials and caps were purchased from Biotage® with part numbers 351521 and 352298 respectively. Product purification was performed by either flash column chromatography with SiliaFlash® P60 (230-400 mesh) silica gel or preparative thin-layer chromatography with plates from Analtech (1 mm SiO_2, 20 x 20 cm).

NMR spectra were recorded on Agilent DD2 400, 500, or 600 MHz spectrometers between 20–25 °C unless otherwise indicated, with chemical shifts (in ppm) referenced to residual protio solvent peaks (^{1}H), deuterated solvent peaks (^{13}C{^{1}H}), or external $CFCl_3$ (^{19}F). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet, with all coupling constants (*J*) reported in Hertz (Hz). IR spectra were collected on a FTIR Shimadzu IRTracer-100 spectrometer. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) or dual ion source (DUIS, combining ESI and atmospheric pressure chemical ionization, APCI) on a time of flight (TOF) mass spectrometer. Melting points are reported uncorrected.

2. Preparation of Starting Materials

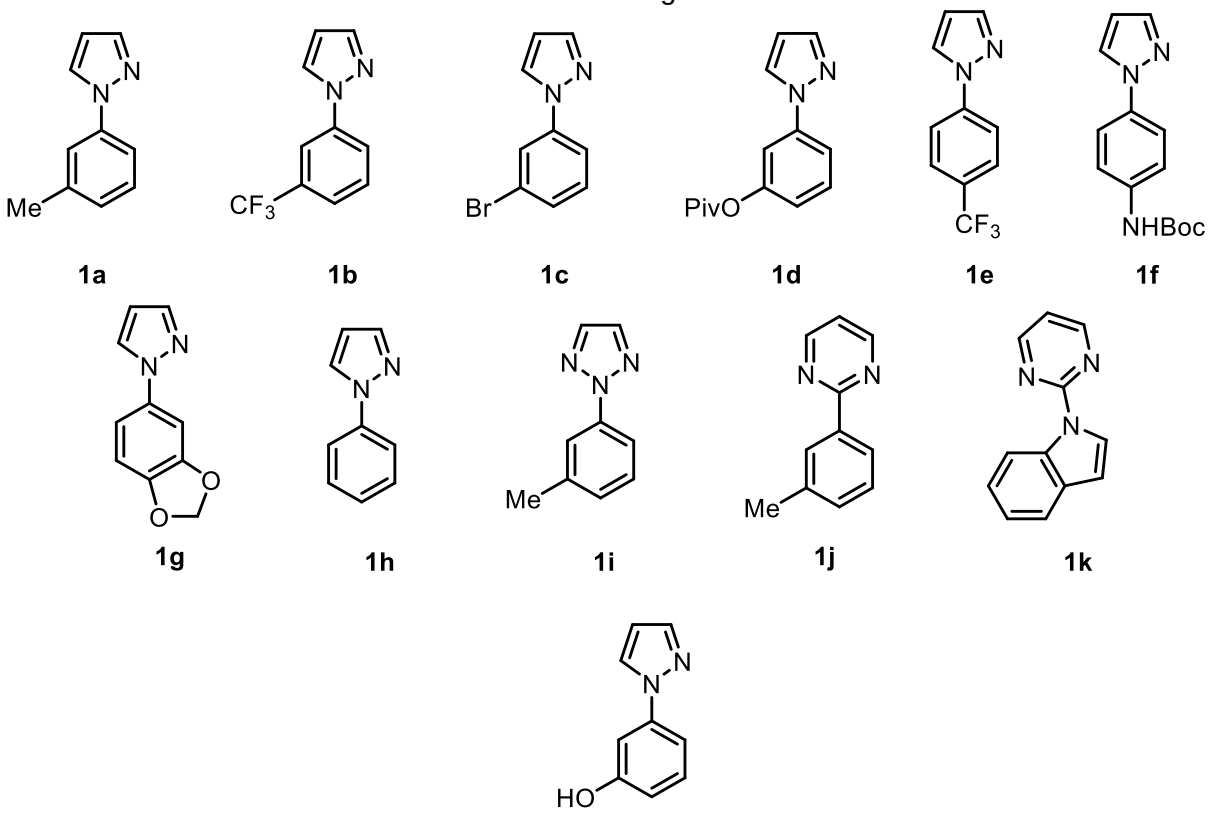
2a. Preparation of Catalysts

$[Cp^*Co(C_6H_5)][B(C_6F_5)_4]_2$,[2] $[Cp^*Co(C_6H_5)(PF_6)_2$,[3] $[Cp^*Co(CO)I_2]$,[4] $[Cp^*Co(MeCN)_3](SbF_6)_2$,[5] and $[Cp^*RhCl_2]_2$[6] were prepared according to literature procedures.

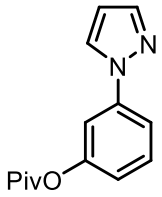
2b. Preparation of C–H Bond Substrates

1-(*m*-Tolyl)-1*H*-pyrazole (**1a**),[7] 1-(3-(trifluoromethyl)phenyl)-1*H*-pyrazole (**1b**),[7] 1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (**1e**),[7] *tert*-butyl (4-(1*H*-pyrazol-1-yl)phenyl)carbamate (**1f**),[8] 1-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-pyrazole (**1g**),[7, 9] 2-(*m*-tolyl)-2*H*-1,2,3-triazole (**1i**),[10] 2-(*m*-tolyl)pyrimidine (**1j**),[11] and 1-(pyrimidin-2-yl)-1*H*-indole (**1k**)[12] were prepared according to literature procedures. 1-(3-bromophenyl)-1*H*-pyrazole (**1c**) and 1-phenyl-1*H*-pyrazole (**1h**) were purchased from commercial sources and used as received.

Chart S1. C–H bond substrates used in this investigation.



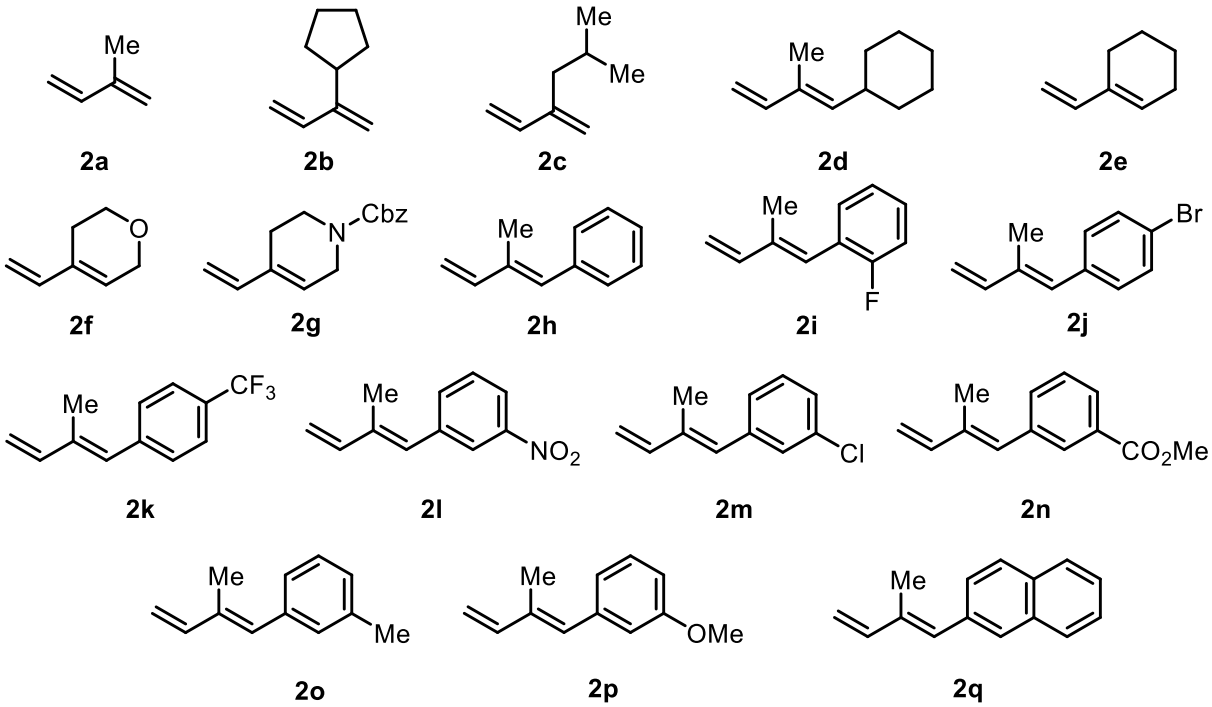
<u>3-(1*H*-Pyrazol-1-yl)phenol (intermediate to C-H bond substrate **1d**)</u>**.** This procedure was adapted from the literature.[13] An oven-dried 100 mL round bottom flask was charged with Cu_2O (71.5 mg, 0.500 mmol, 0.1 equiv), pyrazole (0.511 g, 7.50 mmol, 1.5 equiv), and Cs_2CO_3 (2.44 g, 7.50 mmol, 1.5 equiv). Then, to the degassed flask were added 3-bromophenol (0.53 mL, 5.00 mmol, 1.0 equiv) and anhydrous DMF (1 mL). The solution was placed in a pre-heated oil bath set to 110 °C and stirred at this temperature under nitrogen for 18 h (unoptimized). After this time, the flask was removed from the bath and allowed to cool to room temperature. The heterogenous mixture was diluted with CH_2Cl_2 (20 mL) and filtered through silica, rinsing the silica plug with EtOAc (100 mL). The filtrate was concentrated, and the resulting residue was purified via flash chromatography on silica gel (40% EtOAc in hexanes), affording the title compound as a white solid (49.3 mg, 62%). M.p. 90–02 °C. **IR** (neat): 3013, 2939, 2822, 2689, 2579, 1597, 1523, 1491, 1428, 1404, 1363, 1332, 1224, 1190, 1158, 1057, 1046, 968, 869, 826, 764, 691, 652, 625, 607, 532, 463 cm^{-1}. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.74 (s, 1H), 8.38 (d, J = 2.8 Hz, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.24–7.18 (m, 3H), 6.67–6.65 (m, 1H), 6.47 (t, J = 2.2 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6): δ 158.8, 141.3, 141.2, 130.7, 128.1, 113.6, 109.3, 108.1, 106.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_9H_9N_2O^+$, 161.0709; found, 161.0713.



3-(1*H*-Pyrazol-1-yl)phenyl pivalate (**1d**). This procedure was adapted from the literature.[13] A flame-dried 100 mL round bottom flask was charged with 3-(1*H*-pyrazol-1-yl)phenol (128 mg, 8.02 mmol, 1.0 equiv) and CH_2Cl_2 (24 mL). Then, under nitrogen, NEt_3 (1.20 mL, 8.82 mmol, 1.1 equiv) and PivCl (1.10 mL, 8.82 mmol, 1.1 equiv) were consecutively added dropwise via syringe to the stirring solution at 0 °C. The resulting solution was gradually warmed to room temperature over 3 h. Upon completion of the reaction (as determined by TLC analysis), the solution was diluted with 5% v/v aq. HCl (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The resulting residue was purified via flash chromatography on silica gel (20% EtOAc in hexanes), affording the title compound as a pale-yellow oil (190.8 mg, 98%). **IR** (neat): 2974, 1748, 1608, 1521, 1490, 1392, 1277, 1252, 1183, 1159, 1104, 1044, 1001, 952, 874, 746, 678, 655, 611, 564 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.71 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.46–7.41 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.46 (s, 1H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 176.8, 151.9, 141.3, 141.0, 130.1, 126.9, 119.5, 115.9, 112.9, 107.9, 39.1, 27.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{14}H_{17}N_2O_2^+$, 245.1285; found, 245.1285.

2c. Preparation of Dienes

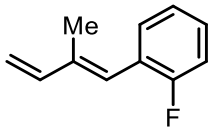
Chart S2. 1,3-Dienes used in this investigation.



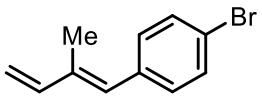
Isoprene (**2a**) was purchased from commercial sources, purified according to the literature,[1] and stored in the freezer (−25 °C) in a nitrogen-filled glovebox. All synthesized dienes were stored in

microwave vials under nitrogen at −78 °C. For use in catalytic reactions, the vials were allowed to warm to room temperature, then transferred into the glovebox to minimize exposure of the dienes to air. Buta-1,3-dien-2-ylcyclopentane (**2b**),[14] 5-methyl-3-methylenehex-1-ene (**2c**),[15] (*E*)-(2-methylbuta-1,3-dien-1-yl)cyclohexane (**2d**),[16] 1-vinylcyclohex-1-ene (**2e**),[17] 4-vinyl-3,6-dihydro-2*H*-pyran (**2f**),[18] benzyl 4-vinyl-3,6-dihydropyridine-1(2*H*)-carboxylate (**2g**),[19] (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**2h**),[20], (*E*)-1-(2-methylbuta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (**2k**),[21] and (*E*)-1-chloro-3-(2-methylbuta-1,3-dien-1-yl)benzene (**2m**)[16] were prepared according to literature procedures. (*E*)-2-(2-Methylbuta-1,3-dien-1-yl)naphthalene (**2q**) was prepared according to General Procedure A (see below), and the spectroscopic data were in agreement with those previously reported.[22]

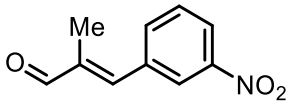
General Procedure for the Synthesis of 1-Aryl-2-methyl Dienes (General Procedure A). This procedure was adapted from the literature.[21] A flame-dried 250 mL three-neck flask containing a magnetic stir bar was charged with $MePPh_3Br$ (1.0 equiv). The flask was sealed with two septa and a vacuum inlet adapter, connected to a Schlenk line, and evacuated and degassed with N_2 three times. THF (V = (moles aldehyde/0.17 M) – 5 mL) was added via syringe, and the cloudy white mixture was cooled to −78 °C (acetone/dry ice). *n*-BuLi (2.5 M solution in hexanes, 1.0 equiv) was then added dropwise via syringe to the cooled mixture, affording a cloudy, bright yellow mixture upon complete addition. The flask was removed from the −78 °C bath and placed in a 0 °C bath (water/ice), and the mixture was stirred at this temperature for 1 h. After this time, the mixture was cooled to −78 °C, where a solution of (*E*)-α,β-unsaturated aldehyde in 5 mL of THF (prepared in a separate, flame-dried round bottom flask under nitrogen) was added to the cooled mixture dropwise via syringe. The reaction mixture was then removed from the −78 °C bath, placed in a 0 °C bath, and the mixture was stirred and allowed to warm up to room temperature over 18 h (unoptimized). The next day, the reaction mixture was transferred to a separatory funnel and quenched with saturated aq. NH_4Cl (20–50 mL). The aqueous layer was extracted with Et_2O (3 x 50–100 mL). The Et_2O fractions were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via flash chromatography on silica gel to afford the indicated 1-aryl-2-methyl diene products.



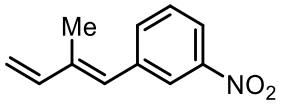
(*E*)-1-Fluoro-2-(2-methylbuta-1,3-dien-1-yl)benzene (**2i**). General Procedure A was followed using $MePPh_3Br$ (7.395 g, 20.7 mmol, 1.0 equiv), *n*-BuLi (8.3 mL of 2.5 M solution in hexanes, 20.7 mmol, 1.0 equiv), and (*E*)-3-(2-fluorophenyl)-2-methylacrylaldehyde[23] (3.350 g, 20.7 mmol, 1.0 equiv) in THF (120 mL total). After flash chromatography on silica gel (hexanes), the title compound was obtained as colourless oil (2.361 g, 71%). **IR** (neat): 1601, 1483, 1452, 1233, 1099, 1061, 1034, 988, 849, 797, 750 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32–7.30 (m, 1H), 7.25 –7.20 (m, 1H), 7.14–7.10 (m, 1H), 7.08–7.03 (m, 1H), 6.59 (dd, *J* = 17.4, 10.7 Hz, 1H), 6.52 (br s, 1H), 5.34 (d, *J* = 17.4 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 1.94 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 160.4 (d, J_{CF} = 247.5 Hz), 141.5, 138.1, 130.9 (d, J_{CF} = 3.4 Hz), 128.6 (d, J_{CF} = 8.1 Hz), 125.6 (d, J_{CF} = 14.5 Hz), 124.1 (d, J_{CF} = 3.1 Hz), 123.7 (d, J_{CF} = 3.5 Hz), 115.5 (d, J_{CF} = 22.4 Hz), 113.8, 13.6 (d, J_{CF} = 1.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −114.48 – −114.52 (m). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{11}H_{12}F^+$, 163.0918; found, 163.0916.



(*E*)-1-Bromo-4-(2-methylbuta-1,3-dien-1-yl)benzene (**2j**). General Procedure A was followed using $MePPh_3Br$ (3.574 g, 10.0 mmol, 1.0 equiv), *n*-BuLi (4.0 mL of a 2.5 M soln in hexanes, 10.0 mmol, 1.0 equiv), and (*E*)-3-(4-bromophenyl)-2-methylacrylaldehyde[23a] (2.252 g, 10.0 mmol, 1.0 equiv) in THF (60 mL total). After flash chromatography on silica gel (pentane), the title compound was obtained as a colourless oil that solidified to a white solid under reduced pressure (1.466 g, 66%). **M.p**.: 54–55 °C. **IR** (neat): 3086, 1599, 1578, 1483, 1361, 1074, 995, 887, 815, 799, 711, 671, 517 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48–7.45 (m, 2H), 7.18–7.15 (m, 2H), 6.56–6.50 (m, 1H), 6.44 (br s, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 1.97 (d, *J* = 1.3 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 141.7, 136.8, 136.7, 131.4, 130.9, 130.5, 120.6, 113.7, 13.3. **HRMS-APCI (*m/z*)**: $[M]^{+\bullet}$ calc'd for $C_{11}H_{11}Br^{+\bullet}$, 222.0039; found, 222.0042.

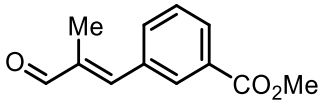


(*E*)-2-Methyl-3-(3-nitrophenyl)acrylaldehyde (intermediate to **2l**). This procedure was adapted from the literature.[24] A 500 mL, single-necked round-bottom flask containing a magnetic stir bar was charged with 3-nitrobenzaldehyde (6.045 g, 40.0 mmol, 1.0 equiv), followed by 50% aq. EtOH (240 mL), affording a cloudy yellow mixture. The flask was sealed with a rubber septum, the reaction mixture was placed under nitrogen, and propionaldehyde (3.0 mL, 41.6 mmol, 1.04 equiv) was added via syringe with no apparent change. Then, aq. NaOH solution (0.440 g in 10.8 mL distilled H_2O) was added slowly via syringe pump (over ~20 min; flow rate = 0.54 mL/min). During the addition, the solid (benzaldehyde) dissolved affording an orange solution. About halfway through the addition, an off-white solid precipitated. Upon complete addition, the now cloudy, off-white mixture was stirred for 1 h at room temperature. After this time, the precipitated, off-white solid was collected by vacuum filtration on a medium fritted funnel, washed with distilled H_2O (3 x 20 mL), and dried under vacuum over P_2O_5 overnight. Yield: 5.829 g (76%). The title compound has been reported previously,[25] but full characterization data were not provided. **M.p**.: 87–88 °C. **IR** (neat): 3065, 2864, 1670 1624, 1516, 1472, 1414, 1352, 1288, 1186, 1096, 1016, 908, 843, 806, 735, 696, 669 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 8.36 (t, *J* = 2.0 Hz, 1H), 8.25–8.22 (m, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 2.09 (d, *J* = 1.5 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 194.8, 148.5, 146.2, 140.7, 136.7, 135.5, 129.9, 124.4, 124.0, 11.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{10}H_{10}NO_3^+$, 192.0655; found, 192.0655.

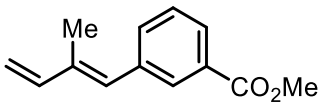


(*E*)-1-(2-Methylbuta-1,3-dien-1-yl)-3-nitrobenzene (**2l**). General Procedure A was followed using $MePPh_3Br$ (5.605 g, 15.7 mmol, 1.0 equiv), *n*-BuLi (6.3 mL of a 2.5 M soln in hexanes, 15.7 mmol, 1.0 equiv), and (*E*)-2-methyl-3-(3-nitrophenyl)acrylaldehyde (3.0 g, 15.7, 1.0 mmol) in THF (90 mL total). After flash chromatography on silica gel (~800 mL pentane, then 5% EtOAc in hexanes), the title compound was obtained as an opaque yellow oil (2.563 g, 87%). **IR** (neat): 3090, 2803, 1603, 1524, 1346, 1307, 1080, 1057, 986, 901, 824, 733 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (t, *J* = 2.0 Hz, 1H), 8.09–8.06 (m, 1H), 7.59 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.52–7.48 (m, 1H), 6.58–6.51 (overlapping m, 2H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.23 (d, *J* = 10.6 Hz, 1H), 2.01 (d,

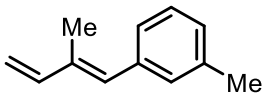
J = 1.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 148.3, 141.1, 139.5, 138.7, 135.2, 129.2, 129.0, 123.9, 121.5, 115.0, 13.3. **HRMS-APCI (*m/z*)**: $[M]^{+\bullet}$ calc'd for $C_{11}H_{11}NO_2^{+\bullet}$, 189.0784; found, 189.0788.



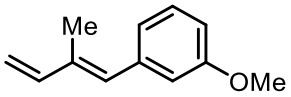
Methyl (*E*)-3-(2-methyl-3-oxoprop-1-en-1-yl)benzoate (intermediate to **2n**). This procedure was adapted from the literature.[26] A flame-dried 200 mL Schlenk flask was charged with methyl 3-formylbenzoate (1.720 g, 10.5 mmol, 1.0 equiv), 2-(triphenylphosphoranylidene)propionaldehyde (4.335 g, 13.6 mmol, 1.3 equiv), and a magnetic stir bar. The flask was sealed with a septum and connected to a Schlenk line and evacuated and backfilled with nitrogen three times. Toluene (52 mL) was added affording a cloudy, beige mixture. The septum was replaced with a reflux condenser against a positive pressure of nitrogen, the flask was placed in a pre-heated oil bath set to 80 °C, and the mixture was stirred at this temperature for 48 h, after which time NMR spectroscopic analysis of an aliquot indicated complete conversion. The flask was removed from the bath and allowed to cool to room temperature. The mixture was transferred to a 500 mL round-bottom flask and the volatiles were removed under reduced pressure. The resulting residue was suspended in Et_2O (50 mL) and filtered through Celite, rinsing the additional Et_2O (100 mL) until the filtrate ran colourless. The volatiles were removed from the clear, yellow filtrate, affording a yellow-orange residue, which was purified via flash chromatography on silica gel (15% MTBE in hexanes), affording an off-white solid. The solid was washed with 5% MTBE in pentane (3 x 3 mL), affording the title compound as a white solid (0.679 g, 32%). **M.p**.: 49–50 °C. **IR** (neat): 2967, 2851, 1717, 1674, 1624, 1429, 1400, 1364, 1292, 1207, 1190, 1105, 1086, 1016, 966, 833, 820, 750, 711, 687 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 8.19 (t, J = 1.8 Hz, 1H), 8.05 (dt, J = 7.8, 1.5 Hz, 1H), 7.70 (dt, J = 7.8, 1.6 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 1.7 Hz, 1H), 3.94 (s, 3H), 2.08 (d, J = 1.5 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 195.4, 166.6, 148.4, 139.5, 135.5, 134.1, 131.1, 130.9, 130.5, 129.0, 52.5, 11.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{12}H_{13}O_3^+$, 205.0859; found, 205.0860.



Methyl (*E*)-3-(2-methylbuta-1,3-dien-1-yl)benzoate (**2n**). General Procedure A was followed using $MePPh_3Br$ (1.155 g, 3.2 mmol, 1.0 equiv), *n*-BuLi (1.3 mL of 2.5 M solution in hexanes, 3.2 mmol, 1.0 equiv), and (*E*)-3-(2-methyl-3-oxoprop-1-en-1-yl)benzoate (0.660 g, 3.2 mmol, 1.0 equiv) in THF (19 mL total). After flash chromatography on silica gel (5% Et_2O in hexanes), the title compound was obtained as an opaque colourless oil (0.423 g, 65%). **IR** (neat): 3088, 2999, 2951, 1721, 1608, 1580, 1437, 1271, 1206, 1107, 1084, 988, 897, 862, 748, 696, 633 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98 (d, J = 1.8 Hz, 1H), 7.90 (dt, J = 7.8, 1.5 Hz, 1H), 7.48 (dt, J = 7.8, 1.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 6.58–6.53 (m, 2H), 5.34 (d, J = 17.4 Hz, 1H), 5.17 (d, J = 10.7 Hz, 1H), 3.92 (s, 3H), 2.00 (d, J = 1.3 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 167.2, 141.7, 138.1, 137.2, 133.6, 130.6, 130.4, 130.2, 128.3, 127.8, 113.8, 52.3, 13.3. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{13}H_{15}O_2^+$, 203.1067; found, 203.1071.



(*E*)-1-methyl-3-(2-methylbuta-1,3-dien-1-yl)benzene (**2o**). General Procedure A was followed using $MePPh_3Br$ (3.751 g, 10.5 mmol, 1.0 equiv), *n*-BuLi (4.2 mL of a 2.5 M solution in hexanes, 10.5 mmol, 1.0 equiv) (*E*)-2-methyl-3-(*m*-tolyl)acrylaldehyde[23a] (1.681 g, 10.5 mmol, 1.0 equiv) in THF (62 mL total). After flash chromatography on silica gel (pentane), the title compound was obtained as a colourless oil (1.134 g, 68%). **IR** (neat): 3090, 3007, 2947, 2918, 2862, 1607, 1581, 1487, 1356, 1063, 988, 891, 860, 779, 764, 746, 698, 453 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27–7.23 (m, 1H), 7.14–7.12 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.56 (dd, *J* = 17.3, 10.6 Hz, 1H), 6.51 (br s, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.14 (d, *J* = 10.6 Hz, 1H), 2.37 (s, 3H), 2.02 (d, *J* = 1.3 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 142.1, 137.8, 137.8, 136.0, 131.9, 130.1, 128.1, 127.5, 126.4, 112.9, 21.6, 13.3. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{12}H_{15}^+$, 159.1168; found, 159.1166.



(*E*)-1-Methoxy-3-(2-methylbuta-1,3-dien-1-yl)benzene (**2p**). General Procedure A was followed using $MePPh_3Br$ (4.798 g, 13.4 mmol, 1.0 equiv), *n*-BuLi (5.4 mL of a 2.5 M soln in hexanes, 13.4 mmol, 1.0 equiv), and (*E*)-3-(3-methoxyphenyl)-2-methylacrylaldehyde[27] (2.367 g, 13.4 mmol, 1.0 equiv) in THF (80 mL total). After flash chromatography on silica gel (1% EtOAc in hexanes), the title compound was obtained as a colourless oil (0.959 g, 58%). **IR** (neat): 3088, 2833, 1607, 1596, 1574, 1487, 1425, 1290, 12677, 1258, 1155, 1049, 986, 889, 874, 775, 694 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 2.2 Hz, 1H), 6.83–6.80 (m, 1H), 6.61–6.53 (overlapping m, 2H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 3.83 (s, 3H), 2.04 (d, *J* = 1.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 159.5, 141.9, 139.2, 136.4, 131.6, 129.2, 121.9, 114.9, 113.2, 112.3, 55.3, 13.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{12}H_{15}O^+$, 175.1117; found, 175.1125.

2d. Preparation of Formylating Agents

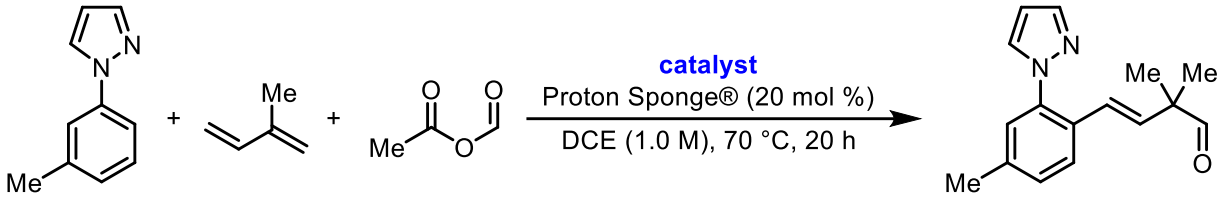
Acetic formic anhydride[28] (**3**, 200 mmol scale) and formic pivalic anhydride[29] were prepared according to the literature and stored in the freezer (−25 °C) in a nitrogen-filled glovebox. 4-nitrophenylformate and 2,4,6-trichlorophenylformate were purchased from commercial suppliers and used as received.

3. Reaction Optimization

General Procedure for Catalytic Screening Reactions. In a nitrogen-filled glovebox, a 0.5–2 mL Biotage® microwave vial was consecutively charged with additive (if solid; 0.0200 mmol, 0.1 equiv), catalyst (0.0400 mmol, 0.2 equiv), solvent, 1-(m-tolyl)-1*H*-pyrazole (15.8 mg, 0.100 mmol, 1.0 equiv), acetic formic anhydride (26.4 mg, 0.300 mmol, 3.0 equiv), and isoprene (40.0 µL, 0.400 mmol, 4.0 equiv), followed by a magnetic stir bar. The vial was sealed, removed from the glovebox, and placed in a pre-heated oil bath set to the indicate temperature. The reaction mixture was stirred at this temperature for 20 h (unoptimized), after which time it was removed from the bath and allowed to cool room temperature. The vial was then uncapped, diluted with EtOAc (1 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (1 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 1 mL). The organic

fractions were combined, dried over Na_2SO_4, filtered, and concentrated. Trimethyl(phenyl)silane (0.100 mmol, 1.0 equiv) was added and the reaction mixture was analyzed by NMR spectroscopic methods in $CDCl_3$.

Table S1. Catalyst screening for the three-component sequential C–H bond addition to isoprene and acetic formic anhydride.

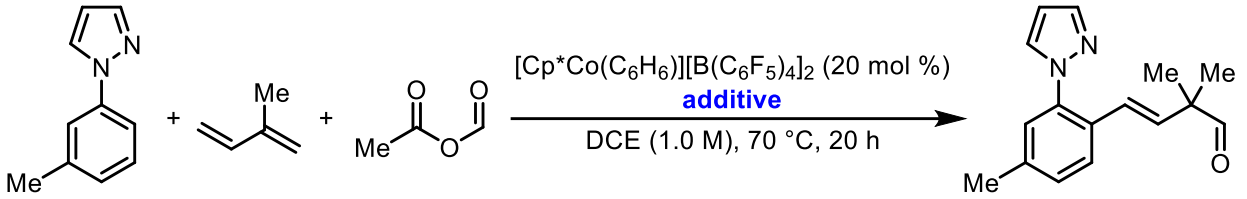


1a 1.0 equiv | **2a** 4.0 equiv | **3** 3.0 equiv | **4a**

Entry	Catalyst	Yield of 4a (%)[a]
1	$[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (20 mol %)	71
2	$[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (15 mol %)	61
3	$[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (10 mol %)	47
4	$[Cp^*Co(C_6H_6)](PF_6)_2$ (20 mol %)	20
5	$Cp^*Co(CO)I_2$ (20 mol %)+ $AgSbF_6$ (40 mol %)	50
6	$Cp^*Co(CO)I_2$ (20 mol %)+ $AgNTf_2$ (40 mol %)	45
7	$Cp^*Co(CO)I_2$ (20 mol %)+ $AgSbF_6$ (40 mol %)	38
8	$[Cp^*RhCl_2]_2$ (5 mol %) + $AgSbF_6$ (20 mol %)	0
9	None	0

[a]Yield determined by crude ^1H NMR spectroscopic analysis relative to trimethyl(phenyl)silane as standard.

Table S2. Additive screening for the Co(III)-catalysed sequential C–H bond addition to isoprene and acetic formic anhydride.

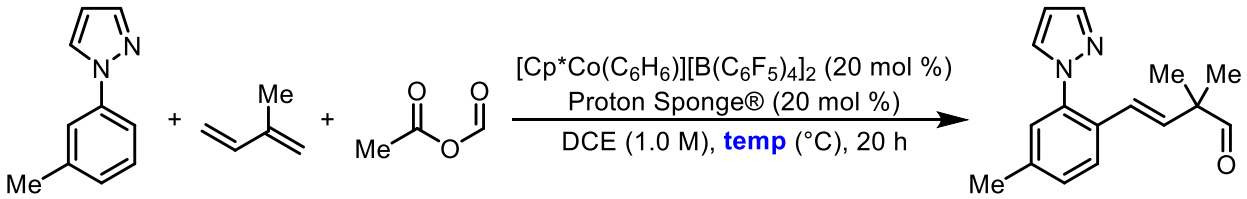


1a 1.0 equiv | **2a** 4.0 equiv | **3** 3.0 equiv | **4a**

Entry	Additive	Yield of 4a (%)[a]
1	Proton Sponge® (20 mol %)	71
2	None	51
3	Proton Sponge® (10 mol %)	59
4	Proton Sponge® (30 mol %)	4
5	Proton Sponge® (50 mol %)	0
6	4-Dimethylaminopyridine (20 mol %)	20
7	*i*-Pr_2NEt (20 mol %)	49
8	2,6-Di-*tert*-butylpyridine (20 mol %)	48
9	LiOAc (20 mol %)	22
10	HOAc (20 mol %)	44

[a]Yield determined by crude ^{1}H NMR spectroscopic analysis relative to trimethyl(phenyl)silane as standard.

Table S3. Temperature screening for the Co(III)-catalysed sequential C–H bond addition to isoprene and acetic formic anhydride.

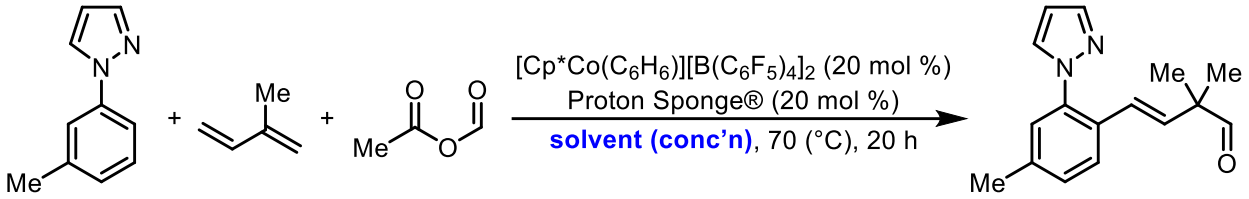


1a 1.0 equiv | **2a** 4.0 equiv | **3** 3.0 equiv | **4a**

Entry	Temperature (°C)	Yield of 4a (%)[a]
1	70	71
2	30	13
3	50	75
4[b]	50	35
5	90	56

[a]Yield determined by crude ^{1}H NMR spectroscopic analysis relative to trimethyl(phenyl)silane as standard. [b]Using 6.0 equiv (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**2h**) in place of **2a**.

Table S4. Concentration and solvent screening for the Co(III)-catalysed sequential C–H bond addition to isoprene and acetic formic anhydride.

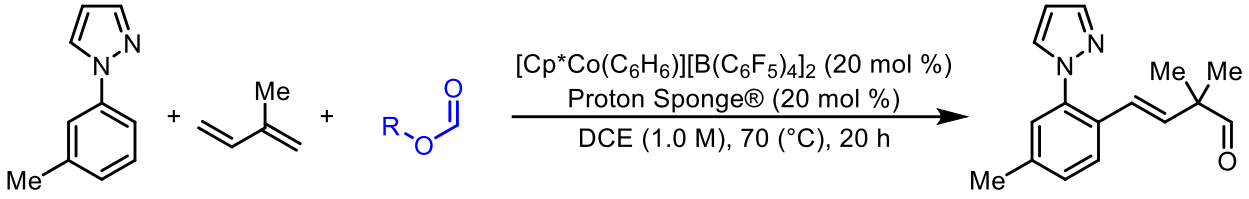


1a 1.0 equiv | **2a** 4.0 equiv | **3** 3.0 equiv | **4a**

Entry	Solvent	Concentration (M)	Yield of 4a (%)[a]
1	DCE	1.0	71
2	DCE	0.5	73
3	toluene	1.0	75
4	1,4-dioxane	1.0	62
5	CH_2Cl_2	1.0	76
6	PhCl	1.0	74
7	MeCN	1.0	12

[a]Yield determined by crude ^{1}H NMR spectroscopic analysis relative to trimethyl(phenyl)silane as standard.

Table S5. Formylating agent screening for the three-component Co(III)-catalysed sequential C–H bond addition to isoprene and alkyl formic anhydride.



1 1.0 equiv | **2** 4.0 equiv | 3.0 equiv | **4a**

Entry	Formylating Agent (R =)	Yield of 4a (%)[a]
1	Ac (acetic formic anhydride, **3**)	71
2	Piv (formic pivalic anhydride)	62
3	4-nitrophenyl	0
4	2,4,6-trichlorophenyl	0

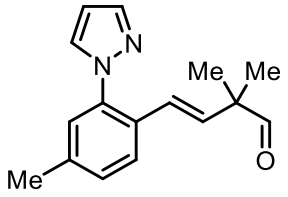
[a]Yield determined by crude ^{1}H NMR spectroscopic analysis relative to trimethyl(phenyl)silane as standard.

4. Procedure for Catalytic Reactions and Characterization of Three-Component Products

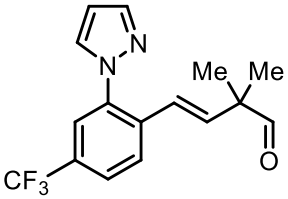
General Procedure for the Co(III)-catalyzed Three-Component Coupling of C–H Bond Substrates, Dienes, and Acetic Formic Anhydride (General Procedure B). In a nitrogen-filled glovebox, a 2–5 mL Biotage® microwave vial was consecutively charged with Proton Sponge (8.6 mg, 0.0400 mmol, 0.2 equiv), $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.0400 mmol, 0.2 equiv), solvent (200 µL, 1.0 M in C–H bond substrate), C–H bond substrate (0.200 mmol, 1.0 equiv), acetic formic anhydride (52.8 mg, 0.600 mmol, 3.0 equiv), and diene (0.800 mmol, 4.0 equiv *or*

1.20 mmol, 6.0 equiv), followed by a magnetic stir bar. The vial was sealed, removed from the glovebox, and placed in a pre-heated oil bath set to 70 °C. The reaction mixture was stirred at 70 °C for 20 h (unoptimized), after which time it was removed from the bath and allowed to cool room temperature. The vial was then uncapped, diluted with EtOAc (5 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 5 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via flash chromatography on silica gel (typical column dimensions: 6-inch length × 1-inch diameter).

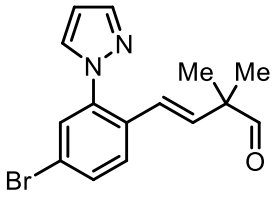
Note: aldehyde products were found to decompose under acidic conditions (e.g., silica gel), so two eluent systems or a gradient were often chosen in order to remove starting material quickly and rapidly elute the product to minimize decomposition.



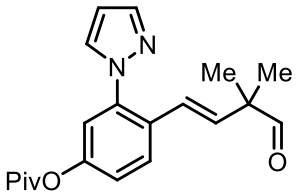
(*E*)-2,2-Dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4a**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (36.6 mg, 72%). **IR** (neat): 2969, 1722, 1615, 1516, 1458, 1392, 1328, 1192, 1098, 973, 950, 884, 808, 751, 622 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.27 (d, *J* = 16.3 Hz, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 2.37 (s, 3H), 1.20 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 202.1, 140.7, 138.8, 138.5, 132.9, 131.3, 129.7, 129.3, 126.9, 126.8, 126.8, 106.6, 49.1, 21.5, 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{16}H_{19}N_2O^+$, 255.1492; found, 255.1490.



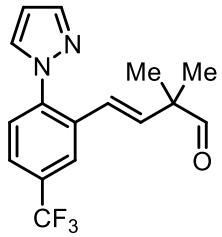
(*E*)-4-(2-(1*H*-Pyrazol-1-yl)-4-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal (**4b**). General Procedure B was followed using DCE as solvent, 1-(3-(trifluoromethyl)phenyl)-*1H*-pyrazole (42.4 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20%, then 50 mL of 30%, 40%, and 50% Et_2O in hexanes), the title compound was obtained as a colorless oil (41.6 mg, 67%). **IR** (neat): 2974, 2935, 2874, 2805, 2705, 1726, 1645, 1622, 1578, 1520, 1457, 1402, 1340, 1308, 1278, 1233, 1168, 1123, 1101, 1075, 1029, 975, 942, 895, 825, 757, 704, 651, 627 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.71– 7.70 (m, 2H), 7.64–7.61 (m, 2H), 6.50 (t, *J* = 2.1 Hz, 1H), 6.37 (d, *J* = 16.3 Hz, 1H), 6.22 (d, *J* = 16.3 Hz, 1H), 1.24 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.6, 141.3, 138.6, 136.4, 135.9, 131.3, 130.5 (q, *J* = 33.4 Hz), 127.6, 125.7, 124.9 (q, *J* = 3.7 Hz), 123.45 (q, *J* = 272 Hz), 123.39 (q, *J* = 3.9 Hz), 107.3, 49.2, 21.4. **^{19}F NMR** (471 MHz, $CDCl_3$): δ −62.7 (s). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{16}H_{16}F_3N_2O^+$, 309.1209; found, 309.1216.



(*E*)-4-(4-Bromo-2-(1*H*-pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal (**4c**). General Procedure B was followed using DCE as solvent, 1-(3-bromophenyl)-*1H*-pyrazole (44.6 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (42.2 mg, 66%). **IR** (neat): 2969, 2931, 2871, 2807, 2704, 1722, 1590, 1517, 1482, 1399, 1192, 1100, 1081, 1027, 972, 940, 878, 809, 751, 624 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.73 (s, 1H), 7.59–7.58 (m, 2H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 6.28 (d, *J* = 16.4 Hz, 1H), 6.10 (d, *J* = 16.3 Hz, 1H), 1.21 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.7, 141.1, 139.3, 134.5, 131.39, 131.37, 131.2, 129.1, 128.2, 125.9, 121.4, 107.0, 49.1, 21.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{15}H_{16}BrN_2O^+$, 319.0441; found, 319.0440.

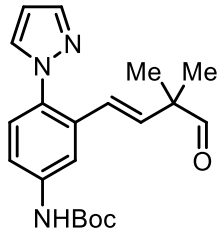


(*E*)-4-(3,3-Dimethyl-4-oxobut-1-en-1-yl)-3-(1*H*-pyrazol-1-yl)phenyl pivalate (**4d**). General Procedure B was followed using DCE as solvent, 3-(*1H*-pyrazol-1-yl)phenyl pivalate (48.8 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (30% Et_2O in hexanes), the title compound was obtained as a white solid (46.1 mg, 68%). **IR** (neat): 2973, 2935, 2875, 2812, 2718, 1747, 1723, 1607, 1514, 1456, 1404, 1278, 1241, 1195, 1168, 1113, 1031, 980, 906, 763, 628 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.72 (s, 1H), 7.61 (d, *J* = 2.6 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 6.32 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 1.33 (s, 9H), 1.21 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.8, 176.7, 150.7, 140.9, 139.0, 133.9, 131.3, 129.7, 127.8, 126.2, 121.6, 119.4, 106.8, 49.0, 39.1, 27.1, 21.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{20}H_{25}N_2O_3^+$, 341.1860; found, 341.1857.

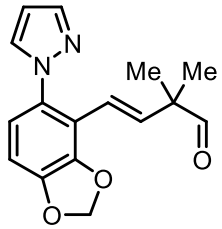


(*E*)-4-(2-(1*H*-Pyrazol-1-yl)-5-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal (**4e**). General Procedure B was followed using DCE as solvent, 1-(4-(trifluoromethyl)phenyl)-*1H*-pyrazole (42.4 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv) at 50 °C. After flash chromatography (150 mL of 20%, then 50 mL of 30%, 40%, and 50% Et_2O in hexanes), the title compound was obtained as a white solid (34.7 mg, 56%). M.p. 131–132 °C. **IR** (neat): 3096, 2975,

2930, 2874, 2808, 2707, 1726, 1616, 1517, 1395, 1334, 1316, 1271, 1159, 1107, 1081, 972, 934, 893, 836, 766, 625, 507 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 6.49 (t, *J* = 2.1 Hz, 1H), 6.41 (d, *J* = 16.4 Hz, 1H), 6.21 (d, *J* = 16.4 Hz, 1H), 1.25 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.6, 141.4, 140.9, 135.7, 132.8, 131.2, 130.4 (q, J_{CF} = 32.7 Hz), 126.4, 126.0, 125.1 (q, J_{CF} = 3.6 Hz), 124.4 (q, J_{CF} = 3.8 Hz), 123.7 (q, J_{CF} = 273 Hz),107.3, 49.1, 21.5. **^{19}F NMR** (471 MHz, $CDCl_3$): δ −62.6 (s). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{16}H_{16}F_3N_2O^+$, 309.1209; found, 309.1211.

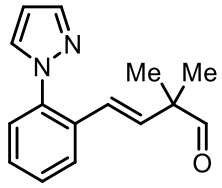


***tert*-Butyl (*E*)-(3-(3,3-dimethyl-4-oxobut-1-en-1-yl)-4-(1*H*-pyrazol-1-yl)phenyl)carbamate** (**4f**). General Procedure B was followed using DCE as solvent, *tert*-butyl (4-(1*H*-pyrazol-1-yl)phenyl)carbamate (51.8 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). The compound was purified via flash column chromatography (30% EtOAc in hexanes) on silica gel, followed by C18 reverse phase column chromatography. The crude mixture was loaded with 0.4 mL of 25% CH_3CN in H_2O containing 0.1% TFA and 0.2 mL of DMSO and was purified with 5.5 g of reverse phase media and a 56 column volume gradient from 20–100% CH_3CN/H_2O containing 0.1% TFA. The presence of the desired product was confirmed by LC-MS, and the relevant fractions were combined and concentrated. The compound was diluted with saturated aq. $NaHCO_3$ and extracted with EtOAc (5 x 3 mL). The combined organic layers washed with brine (50 mL), dried over Na_2SO_4, and concentrated, affording the title compound as a yellow foam (34.8 mg, 49%). **IR** (neat): 3296, 2974, 2934, 1721, 1612, 1587, 1520, 1393, 1366, 1314, 1234, 1153, 1101, 1051, 1051, 1020, 970, 937, 889, 837, 752, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 50 °C): δ 9.36 (s, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.29–7.27 (m, 2H), 6.80 (s, 1H), 6.41 (t, *J* = 2.1 Hz, 1H), 6.22 (d, *J* = 16.3 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 1.52 (s, 9H), 1.17 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 25 °C): δ 201.9, 152.7, 140.5, 138.7, 134.0, 133.6, 133.5, 131.4, 127.0, 126.4, 118.3, 116.0, 106.4, 80.8, 49.0, 28.3, 21.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{20}H_{26}N_3O_3^+$, 356.1969; found, 356.1964.

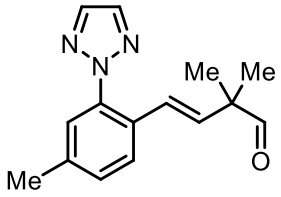


(*E*)-4-(5-(1*H*-Pyrazol-1-yl)benzo[*d*][1,3]dioxol-4-yl)-2,2-dimethylbut-3-enal (**4g**). General Procedure B was followed using DCE as solvent, 1-(benzo[*d*][1,3]dioxol-5-yl)-*1H*-pyrazole (37.6 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 40% Et_2O in hexanes, then 150 mL of 60% Et_2O in hexanes), the title compound was obtained as a yellow solid (41.2 mg, 72%). **IR** (neat): 2974, 1719, 1456, 1395, 1362, 1308, 1252, 1192, 1161, 1119, 1074, 1045, 1026, 962, 934, 870, 812, 756, 621 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.34 (s, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 6.87 (d,

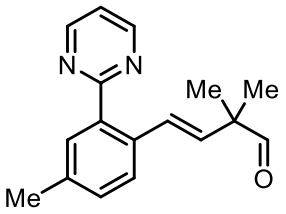
J = 8.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.42–6.38 (m, 2H), 6.09 (s, 2H), 5.88 (d, *J* = 16.5 Hz, 1H), 1.15 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$): δ 201.9, 147.7, 145.5, 140.4, 137.2, 133.1, 131.6, 121.3, 120.3, 117.1, 106.7, 106.3, 101.9, 49.4, 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{16}H_{17}N_2O_3^+$, 285.1234; found, 285.1233.



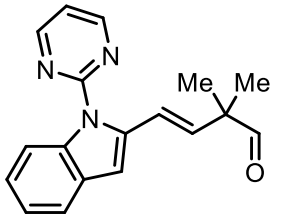
(*E*)-4-(2-(1*H*-Pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal (**4h**). General Procedure B was followed using DCE as solvent, 1-phenyl-1*H*-pyrazole (26.4 µL, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv) at 50 °C. After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (33.2 mg, 69%). **IR** (neat): 2969, 2930, 2872, 2806, 2705, 1721, 1631, 1602, 1576, 1517, 1487, 1462, 1394, 1330, 1192, 1096, 1044, 1020, 970, 936, 915, 891, 752, 691, 660, 622, 584 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.59–7.57 (m, 2H), 7.40–7.33 (m, 3H), 6.44 (t, *J* = 2.1 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 6.07 (d, *J* = 16.3 Hz, 1H), 1.20 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$): δ 202.0, 140.8, 138.7, 133.9, 132.7, 131.3, 128.53, 128.46, 127.0, 126.8, 126.3, 106.7, 49.1, 21.5. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{15}H_{17}N_2O^+$, 241.1335; found, 241.1338.



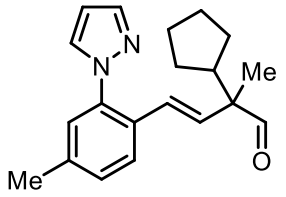
(*E*)-2,2-Dimethyl-4-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)but-3-enal (**4i**). General Procedure B was followed using 1,2-dichlorobenzene as solvent, 2-(*m*-tolyl)-2*H*-1,2,3-triazole (31.8 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). The remaining solvent was removed through distillation under vacuum after work-up. After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (34.0 mg, 67%). **IR** (neat): 2970, 2930, 2870, 2806, 2706, 1722, 1616, 1506, 1462, 1412, 1362, 1152, 961, 880, 812, 773, 584 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.84 (s, 2H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.39 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H), 1.20 (s, 6H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$): δ 202.0, 138.6, 137.9, 135.3, 132.9, 129.9, 129.2, 126.9, 126.8, 126.0, 49.0, 21.4, 20.9. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{15}H_{18}N_3O^+$, 256.1444; found, 256.1443.



(*E*)-2,2-Dimethyl-4-(4-methyl-2-(pyrimidin-2-yl)phenyl)but-3-enal (**4j**). General Procedure B was followed using PhCl as solvent, 2-(*m*-tolyl)pyrimidine (34.0 mg, 0.200 mmol, 1.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv). After flash chromatography (100 mL of 30% Et_2O in hexanes, then 40% Et_2O in hexanes), the title compound was obtained as an orange oil (27.7 mg, 52%). **IR** (neat): 3032, 2968, 2926, 2870, 2805, 2706, 1721, 1568, 1553, 1418, 1395, 966, 804, 731, 634, 583 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.84 (d, *J* = 4.9 Hz, 2H), 7.68 (br s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.24–7.23 (m, 2H), 6.97 (d, *J* = 16.1 Hz, 1H), 5.99 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H), 1.24 (s, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 202.4, 167.1, 157.0, 137.8, 136.9, 133.6, 131.3, 130.9, 130.8, 127.0, 118.8, 49.1, 21.7, 21.2. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{17}H_{19}N_2O^+$, 267.1492; found, 267.1489.

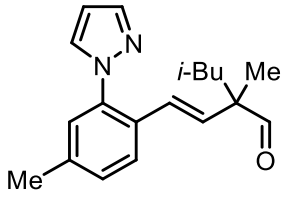


(*E*)-2,2-Dimethyl-4-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)but-3-enal (**4k**). General Procedure A was followed using toluene as solvent, 1-(pyridin-2-yl)-1*H*-indole (38.8 mg, 0.200 mmol, 1.0 equiv), and isoprene (120 µL, 1.200 mmol, 6.0 equiv). After flash chromatography (150 mL of 40% Et_2O in hexanes, then 150 mL of 70% Et_2O in hexanes), the title compound was obtained as an orange oil (31.0 mg, 53%). **IR** (neat): 3048, 2968, 2930, 2870, 2803, 2704, 1721, 1572, 1560, 1450, 1418, 1346, 1209, 1150, 959, 891, 804, 739, 629, 600 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.80 (d, *J* = 4.8 Hz, 2H), 8.30 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.58 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.28–7.25 (m, 1H), 7.23–7.19 (m, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.06 (dd, *J* = 16.1, 0.9 Hz, 1H), 6.85 (s, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 1.32 (s, 6H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ δ 202.1, 158.3, 158.1, 138.1, 137.2, 132.0, 129.3, 124.0, 123.7, 122.4, 120.5, 117.4, 114.2, 105.6, 49.2, 21.7. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{18}H_{18}N_3O^+$, 292.1444; found, 292.1441.

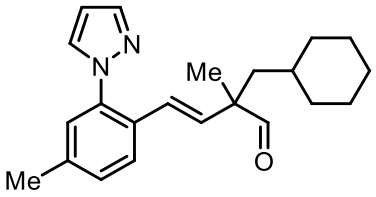


(*E*)-2-Cyclopentyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4l**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and buta-1,3-dien-2-ylcyclopentane (98.7 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 40% Et_2O in hexanes), the title compound was obtained as a colourless oil (35.2 mg, 57%). **IR** (neat): 2951, 2868, 1721, 1616, 1516, 1452, 1391, 1329, 1192, 1098, 1038, 974, 949, 808, 750, 623 cm^{-1}. **^{1}H NMR** (500 MHz,

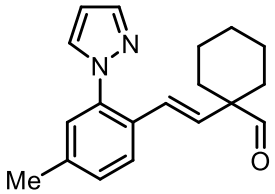
$CDCl_3$): δ 9.45 (s, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.43 (t, *J* = 2.2 Hz, 1H), 6.23 (d, *J* = 16.4 Hz, 1H), 6.12 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H), 2.26–2.19 (app pent, 1H), 1.71–1.62 (m, 2H), 1.58–1.49 (m, 4H), 1.33–1.23 (m, 2H), 1.12 (s, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): δ 202.8, 140.7, 138.7, 138.4, 131.7, 131.3, 130.1, 129.3, 127.5, 126.9, 126.8, 106.5, 55.0, 44.7, 27.3, 27.2, 25.7, 25.6, 21.1, 16.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{20}H_{25}N_2O^+$, 309.1961; found, 309.1961.



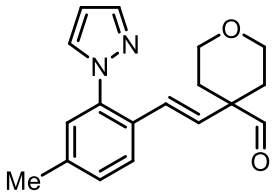
(*E*)-2,4-Dimethyl-2-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)pentanal (**4m**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and 5-methyl-3-methylenehex-1-ene (88.2 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 15% Et_2O in hexanes, then 150 mL of 30% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (27.2 mg, 46%). **IR** (neat): 2957, 2926, 2870, 1722, 1616, 1516, 1456, 1329, 1099, 1038, 974, 949, 808, 750, 623 cm^{-1}. **^1H NMR** (600 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 6.24 (d, *J* = 16.4 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H), 1.73–1.66 (m, 1H), 1.59 (d, *J* = 6.4 Hz, 2H), 1.18 (s, 3H), 0.89–0.85 (overlapping d, 6H). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$): δ 202.5, 140.7, 138.7, 138.5, 132.7, 131.4, 129.9, 129.4, 126.85, 126.84, 126.76, 106.6, 52.6, 45.3, 24.8, 24.4, 24.2, 21.1, 19.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{19}H_{25}N_2O^+$, 297.1961; found, 297.1962.



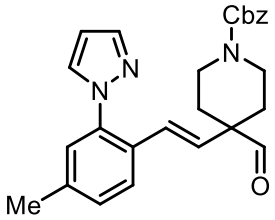
(*E*)-2-(Cyclohexylmethyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4n**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-(2-methylbuta-1,3-dien-1-yl)cyclohexane (180.3 mg, 1.20 mmol, 6.0 equiv). After flash chromatography (150 mL of 15% Et_2O in hexanes, then 150 mL 30% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (23.7 mg, 41%). **IR** (neat): 2920, 2849, 1721, 1616, 1516, 1449, 1329, 1099, 1038, 972, 949, 808, 748, 623 cm^{-1}. **^1H NMR** (500 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 6.25 (d, *J* = 16.4 Hz, 1H), 6.06 (d, *J* = 16.4 Hz, 1H), 2.38 (s, 3H), 1.66–1.59 (m, 4H), 1.56 (d, *J* = 6.1 Hz, 2H), 1.36–1.26 (m, 2H), 1.22–1.08 (overlapping m, 6H), 0.95–0.85 (m, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): δ 202.5, 140.7, 138.7, 138.5, 132.8, 131.4, 130.0, 129.4, 126.9, 126.8, 126.8, 106.6, 52.5, 44.0, 34.9, 34.7, 34.1, 26.4, 26.4, 26.3, 21.1, 19.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{22}H_{29}N_2O^+$, 337.2274; found, 337.2274.



(*E*)-1-(4-Methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde (**4o**). General Procedure B was followed using PhCl as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and 1-vinylcyclohex-1-ene (86.5 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL 50% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (50.5 mg, 86%). **IR** (neat): 3127, 3046, 2934, 2920, 2851, 2797, 2687, 1717, 1616, 1568, 1516, 1456, 1449, 1387, 1327, 1192, 1099, 1038, 974, 947, 818, 808, 766, 745, 623 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.16 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.25 (d, *J* = 16.4 Hz, 1H), 5.80 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 1.91–1.87 (m, 2H), 1.58–1.52 (m, 4H), 1.47–1.32 (m, 4H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ 202.0, 140.6, 138.8, 138.4, 132.0, 131.3, 129.8, 129.3, 128.0, 126.8, 126.7, 106.6, 53.1, 31.0, 25.7, 22.4, 21.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{19}H_{23}N_2O^+$, 295.1805; found, 295.1810.

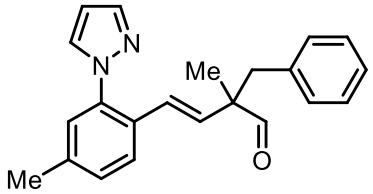


(*E*)-1-(4-Methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde (**4p**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and 4-vinyl-3,6-dihydro-2H-pyran (88.1 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL 50% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (36.7 mg, 62%). **IR** (neat): 3134, 3055, 2970, 2918, 2860, 1711, 1614, 1510, 1456, 1402, 1383, 1329, 1304, 1287, 1240, 1193, 1103, 1036, 978, 949, 939, 816, 770, 750, 658, 625 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.72 (s, 1H), 7.57–7.56 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.44 (br s, 1H), 6.30 (d, *J* = 16.4 Hz, 1H), 5.80 (d, *J* = 16.4 Hz, 1H), 3.78–3.73 (m, 2H), 3.57–3.52 (m, 2H), 2.38 (s, 3H), 2.04–1.99 (m, 2H), 1.78–1.73 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 200.4, 140.8, 139.2, 138.6, 131.2, 130.1, 129.5, 129.4, 129.2, 126.9, 126.8, 106.7, 64.4, 51.0, 30.9, 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{18}H_{21}N_2O_2^+$, 297.1598; found, 297.1605.

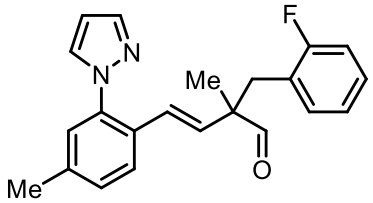


Benzyl (*E*)-4-formyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)piperidine-1-carboxylate (**4q**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and benzyl 4-vinyl-3,6-dihydropyridine-1(2H)-carboxylate (194.6 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 30% EtOAc in hexanes, then 150 mL

50% EtOAc in hexanes), the title compound was obtained as a pale-yellow oil (70.5 mg, 82%). **IR** (neat): 2945, 2922, 2860, 1719, 1694, 1616, 1516, 1429, 1277, 1238, 1157, 1142, 1098, 970, 949, 908, 810, 752, 727, 696 cm^{-1}.**^{1}H NMR** (500 MHz, $CDCl_3$, 50 °C): δ 9.31 (s, 1H), 7.71 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37–7.29 (m, 5H), 7.21–7.18 (m, 2H), 6.44 (s, 1H), 6.33 (d, *J* = 16.5 Hz, 1H), 5.76 (d, *J* = 16.4 Hz, 1H), 5.13 (s, 2H), 3.67–3.62 (m, 2H), 3.37–3.32 (m, 2H), 2.38 (s, 3H), 2.00–1.95 (m, 2H), 1.73–1.67 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 50 °C): δ 200.0, 155.4, 140.8, 139.3, 138.8, 137.0, 131.1, 129.8, 129.7, 129.6, 129.4, 128.6, 128.1, 128.0, 127.0, 126.9, 106.8, 67.3, 51.7, 40.8, 30.4, 21.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{26}H_{28}N_3O_3^+$, 430.2125; found, 430.2133.

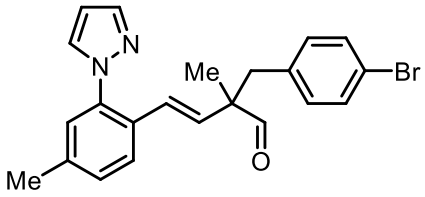


(*E*)-2-Benzyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4r**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (173.1 mg, 1.20 mmol, 6.0 equiv). After flash chromatography (100 mL of 20% Et_2O in hexanes, then 200 mL 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (43.6 mg, 66%). **IR** (neat): 3028, 2974, 2920, 2710, 1721, 1616, 1516, 1497, 1452, 1400, 1329, 1038, 974, 949, 808, 750, 700, 623, 484 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.52 (s, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.28–7.22 (m, 4H), 7.20–7.18 (m, 1H), 7.10–7.09 (m, 2H), 6.34 (t, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 16.3 Hz, 1H), 6.08 (d, *J* = 16.3 Hz, 1H), 2.96, 2.95 (ABq, J_{AB} = 13.6 Hz, 2H), 2.38 (s, 3H), 1.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 202.0, 140.7, 139.0, 138.5, 136.5, 131.6, 131.4, 130.5, 129.5, 129.3, 128.3, 127.9, 126.9, 126.8, 126.7, 106.6, 53.7, 42.4, 21.1, 18.3. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{22}H_{23}N_2O^+$, 331.1805; found, 331.1825.

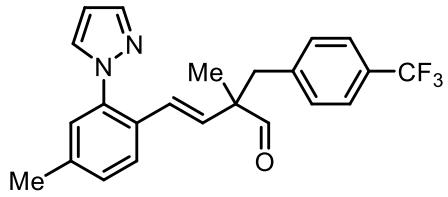


(*E*)-2-(2-Fluorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4s**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-fluoro-2-(2-methylbuta-1,3-dien-1-yl)benzene (129.8 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL 50% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (41.7 mg, 60%). **IR** (neat): 2974, 2926, 2810, 2710, 1721, 1616, 1584, 1516, 1491, 1454, 1229, 1036, 974, 949, 880, 808, 752, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.52 (s, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.22–7.18 (overlapping m, 2H), 7.10 (td, *J* = 7.6, 1.9 Hz, 1H), 7.05–6.98 (m, 2H), 6.35 (t, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 16.3 Hz, 1H), 6.11 (d, *J* = 16.3, 1H), 3.01, 2.99 (dABq, J_{AB} = 13.6 Hz, J_{HF} = 1.6 Hz, 2H), 2.38 (s, 3H), 1.16 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 201.5, 161.4 (d, J_{CF} = 246 Hz), 140.7, 138.9, 138.5, 132.8 (d, J_{CF} = 5.0 Hz), 131.4, 131.2, 129.4, 129.3, 128.7 (d, J_{CF} = 9.0 Hz), 128.0, 126.9, 126.7, 123.9 (d, JCF = 4.0 Hz), 123.6 (d, J_{CF} = 16.0 Hz), 115.5 (d, J_{CF} = 23.0 Hz), 106.6, 53.7, 34.9, 21.1,

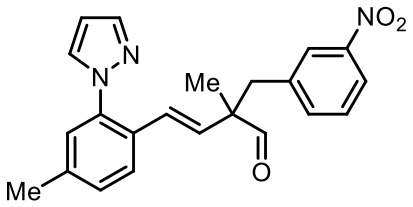
18.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ −115.09 to −115.14 (m). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{22}H_{22}FN_2O^+$, 349.1711; found, 349.1714.



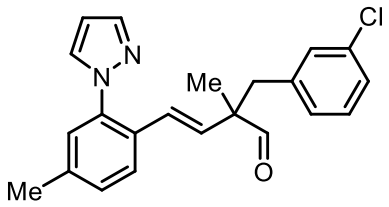
(*E*)-2-(4-Bromobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4t**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and methyl (*E*)-1-bromo-4-(2-methylbuta-1,3-dien-1-yl)benzene (178.5 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (100 mL 20%, Et_2O in hexanes, then 200 mL 50% Et_2O in hexanes), the title compound was obtained as a pale yellow oil (41.5 mg, 51%). **IR** (neat): 2972, 2922, 2806, 2708, 1721, 1614, 1516, 1487, 1456, 1402, 1099, 1072, 1037, 1011, 974, 949, 808, 752, 731, 621, 490 cm^{-1}.**^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38–7.35 (overlapping m, 3H), 7.24 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.38 (t, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 16.3 Hz, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 2.91, 2.87 (ABq, J_{AB} = 13.6 Hz, 2H), 2.38 (s, 3H), 1.12 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.6, 140.8, 139.1, 138.5, 135.6, 132.2, 131.3, 131.3, 131.0, 129.4, 129.3, 128.4, 126.9, 126.8, 120.8, 106.7, 53.5, 41.5, 21.1, 18.3. **HRMS-ESI (*m/z*)**: $[M+H+2]^+$ calc'd for $C_{22}H_{22}BrN_2O^+$, 411.0892; found, 411.0898.



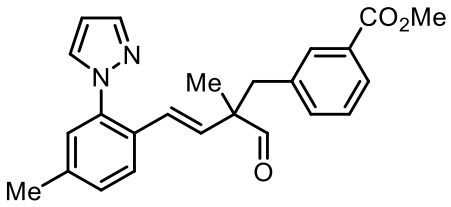
(*E*)-2-Methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(4-(trifluoromethyl)benzyl)but-3-enal (**4u**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-(2-methylbuta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (254.7 mg, 1.20 mmol, 6.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL 50% Et_2O in hexanes), the title compound was obtained as a pale yellow oil (43.4 mg, 54%). **IR** (neat): 2974, 2926, 1724, 1618, 1518, 1456, 1323, 1163, 1119, 1067, 1018, 908, 808, 754, 729, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.23–7.19 (overlapping m, 4H), 6.35 (t, *J* = 2.1 Hz, 1H), 6.21 (d, *J* = 16.3 Hz, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 3.02, 2.98 (ABq, J_{AB} = 13.5 Hz, 2H), 2.39 (s, 3H), 1.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 201.3, 140.9, 140.8, 139.2, 138.6, 131.2, 130.9, 130.8, 129.38, 129.35, 129.1 (q, J_{CF} = 32.5 Hz), 128.6, 126.85, 126.82, 125.1 (q, J_{CF} = 3.7 Hz), 124.3 (q, J_{CF} =272 Hz), 106.6, 53.5, 41.8, 21.1, 18.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ −62.4 (s). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{23}H_{22}F_3N_2O^+$, 399.1679; found, 399.1684.



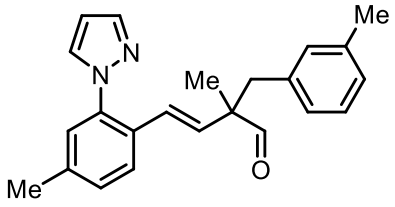
(*E*)-2-Methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-nitrobenzyl)but-3-enal (**4v**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-(2-methylbuta-1,3-dien-1-yl)-3-nitrobenzene (151.4 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (50 mL each of 20%, 40% and 50% Et_2O in hexanes, then 150 mL 60% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (52.4 mg, 70%). **IR** (neat): 2972, 2924, 2872, 1721, 1616, 1521, 1506, 1456, 1348, 1328, 1192, 1098, 1037, 974, 948, 804, 754, 731, 696, 621, 588 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.08 (dt, *J* = 7.4, 2.1 Hz, 1H), 7.99 (br s, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.45–7.40 (m, 4H), 7.21–7.19 (m, 2H), 6.38 (t, *J* = 2.1 Hz, 1H), 6.23 (d, *J* = 16.3 Hz, 1H), 5.98 (d, *J* = 16.3 Hz, 1H), 3.07, 3.03 (ABq, J_{AB} = 13.7 Hz, 2H), 2.39 (s, 3H), 1.15 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 200.9, 148.1, 140.8, 139.3, 138.9, 138.6, 136.8, 131.1, 130.3, 129.5, 129.4, 129.17, 129.16, 126.89, 126.86, 125.3, 121.9, 106.7, 53.5, 41.5, 21.1, 18.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{22}H_{22}N_3O_3^+$, 376.1656; found, 376.1656.



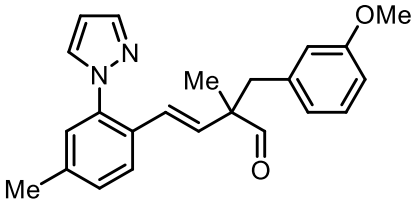
(*E*)-2-(3-Chlorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4w**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-chloro-3-(2-methylbuta-1,3-dien-1-yl)benzene (142.9 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (100 mL 20% Et_2O in hexanes, then 200 mL 50% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (36.2 mg, 50%). **IR** (neat): 2972, 2713, 1721, 1616, 1597, 1572, 1516, 1456, 1391, 1329, 1192, 1099, 1080, 1038, 974, 849, 881, 808, 791, 752, 731, 708, 685, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.21–7.16 (overlapping m, 3H), 7.11–7.10 (m, 1H), 6.97 (dt, *J* = 7.1, 1.6 Hz, 1H), 6.38 (t, *J* = 2.1 Hz, 1H), 6.20 (d, *J* = 16.3 Hz, 1H), 6.00 (d, *J* = 16.3 Hz, 1H), 2.93, 2.91 (ABq, J_{AB} = 13.6 Hz, 2H), 2.39 (s, 3H), 1.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 201.5, 140.8, 139.1, 138.7, 138.5, 134.1, 131.3, 131.1, 130.6, 129.5, 129.4, 129.4, 128.7, 128.4, 127.0, 126.9, 126.8, 106.6, 53.5, 41.8, 21.1, 18.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{22}H_{22}ClN_2O^+$, 365.1415; found, 365.1420.



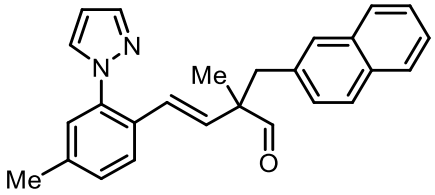
Methyl (*E*)-3-(2-formyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)benzoate (**4x**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and methyl (*E*)-3-(2-methylbuta-1,3-dien-1-yl)benzoate (161.8 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL 15%, EtOAc in hexanes, then 150 mL 30% EtOAc in hexanes), the title compound was obtained as a yellow oil (48.5 mg, 62%). **IR** (neat): 2951, 2924, 1717, 1686, 1614, 1516, 1447, 1433, 1281, 1202, 1099, 1038, 976, 951, 914, 808, 746, 731, 702, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.90 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.80 (t, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.35 (t, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 16.3 Hz, 1H), 6.04 (d, *J* = 16.3 Hz, 1H), 3.89 (s, 3H), 3.01, 2.99 (ABq, J_{AB}= 13.6 Hz, 2H), 2.38 (s, 3H), 1.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.5, 167.1, 140.7, 139.1, 138.5, 137.0, 135.0, 131.5, 131.3, 131.2, 130.2, 129.5, 129.3, 128.4, 128.4, 128.1, 127.0, 126.7, 106.6, 53.6, 52.3, 41.9, 21.1, 18.3. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{24}H_{25}N_2O_3^+$, 389.1860; found, 389.1852.



(*E*)-2-Methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-methylbenzyl)but-3-enal (**4y**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-methyl-3-(2-methylbuta-1,3-dien-1-yl)benzene (126.6 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (38.4 mg, 56%). **IR** (neat): 3025, 2971, 2919, 2858, 2809, 2711, 1721, 1608, 1517, 1456, 1401, 1391, 1328, 1192, 1098, 1037, 973, 949, 916, 881, 870, 844, 807, 792, 751, 701, 622 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.53 (s, 1H), 7.69 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.26 (s, 1H), 7.20–7.13 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.91–6.89 (m, 2H), 6.36 (t, *J* = 2.1 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 2.92 (s, 2H), 2.39 (s, 3H), 2.30 (s, 3H), 1.15 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 202.0, 140.6, 138.8, 138.4, 137.7, 136.3, 131.7, 131.3, 131.2, 129.4, 129.1, 128.1, 127.6, 127.44, 127.39, 126.8, 126.5, 106.4, 53.5, 42.3, 21.4, 21.0, 18.2. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{23}H_{25}N_2O^+$, 345.1961; found, 345.1964.

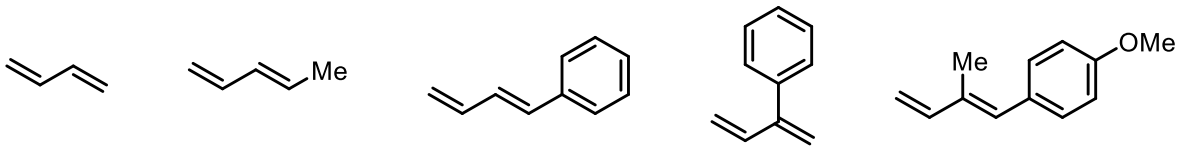


(*E*)-2-(3-Methoxybenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal (**4z**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-1-methoxy-3-(2-methylbuta-1,3-dien-1-yl)benzene (139.4 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (50 mL each of 20%, 40% and 50% Et_2O in hexanes, then 150 mL 60% Et_2O in hexanes), the title compound was obtained as a pale-yellow oil (36.6 mg, 51%). **IR** (neat): 2961, 2934, 2836, 2712, 1721, 1601, 1584, 1516, 1489, 1454, 1263, 1155, 1040, 974, 949, 750, 729, 698, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.19–7.15 (m, 2H), 6.77 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.66–6.65 (m, 1H), 6.36 (t, *J* = 2.1 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 6.08 (d, *J* = 16.3 Hz, 1H), 3.75 (s, 3H), 2.93 (br s, 2H), 2.38 (s, 3H), 1.15 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.9, 159.5, 140.7, 138.9, 138.5, 138.1, 131.7, 131.4, 129.5, 129.24, 129.21, 127.9, 126.9, 126.7, 122.9, 116.3, 112.0, 106.5, 55.2, 53.6, 42.4, 21.1, 18.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{23}H_{25}N_2O_2^+$, 361.1911; found, 361.1904.



(*E*)-2-Methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(naphthalen-2-ylmethyl)but-3-enal (**4aa**). General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and (*E*)-2-(2-methylbuta-1,3-dien-1-yl)naphthalene (155.4 mg, 0.800 mmol, 4.0 equiv). After flash chromatography (150 mL of 20% Et_2O in hexanes, then 150 mL of 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (35.8 mg, 47%). **IR** (neat): 3053, 2977, 2925, 2860, 2812, 2709, 1722, 1615, 1517, 1507, 1456, 1371, 1328, 1240, 1192, 1098, 1038, 973, 949, 907, 858, 814, 750, 733, 622, 475 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.81–7.77 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.48–7.43 (m, 3H), 7.24–7.18 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 6.14–6.11 (m, 2H), 3.14, 3.11 (ABq, J_{AB} = 13.6 Hz, 2H), 2.38 (s, 3H), 1.20 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 201.9, 140.6, 138.8, 138.4, 134.0, 133.3, 132.2, 131.5, 131.2, 129.3, 129.1, 129.0, 128.8, 128.0, 127.63, 127.60, 127.59, 126.9, 126.5, 126.1, 125.7, 106.3, 53.7, 42.4, 21.0, 18.4. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{26}H_{25}N_2O^+$, 381.1961; found, 381.1956.

Chart S3. Unsuccessful 1,3-diene substrates tested (<5% NMR yield of aldehyde product in each case).

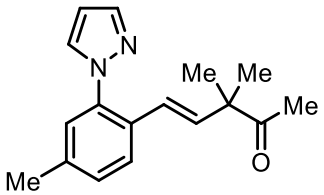


5. Carboformylation Mechanistic Experiments

5a. Co(III)-Catalyzed Sequential C–H Bond Addition Reactions with Isoprene and CO Gas (Scheme 2A, top)

General Procedure. In a nitrogen-filled glovebox, an oven-dried pressure tube equipped with a Teflon tap containing a magnetic stir bar was consecutively charged with additive (0.0200 mmol, 0.2 equiv), $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (32.6 mg, 0.0200 mmol, 0.2 equiv), DCE (100 µL, 1.0 M in C–H bond substrate), 1-(*m*-tolyl)-1*H*-pyrazole (15.8 mg, 0.100 mmol, 1.0 equiv), acetic formic anhydride (26.4 mg, 0.300 mmol, 3.0 equiv), and isoprene (40 µL, 0.400 mmol, 4.0 equiv). The tube was sealed, removed from the glovebox, and attached to a Schlenk line connected to a CO gas cylinder. The sidearm of the flask was evacuated and backfilled with CO three times. Then, under a positive pressure of CO, the Teflon tap was removed and quickly replaced with a septum with an outlet needle. The tube was flushed with CO for 5 min, after which time the septum was removed and quickly replaced with the Teflon tap under a positive pressure of CO. The tube was sealed and placed in a pre-heated oil bath set to 70 °C. The reaction mixture was stirred at 70 °C for 20 h, after which time it was removed from the bath and allowed to cool room temperature. The tube was then opened, diluted with EtOAc (2 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (2 mL) was added, and the layers were separated. The aqueous layer was then extracted with EtOAc (3 x 2 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. Trimethyl(phenyl)silane (0.100 mmol) was added as a standard and the residue was analyzed via NMR spectroscopic methods.

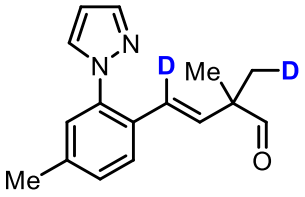
5b. Co(III)-Catalyzed Sequential C–H Bond Addition to Isoprene and Acetic Anhydride (Scheme Scheme 2A, bottom)



(*E*)-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-one (**6**). In a nitrogen-filled glovebox, a 2–5 mL Biotage® microwave vial was consecutively charged with Proton Sponge (8.6 mg, 0.0400 mmol, 0.2 equiv), $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.0400 mmol, 0.2 equiv), DCE (200 µL, 1.0 M in C–H bond substrate), 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), acetic anhydride (56.8 µL, 0.600 mmol, 3.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv), followed by a magnetic stir bar. The vial was sealed, removed from the glovebox, and placed in a pre-heated oil bath set to 110 °C. The reaction mixture was stirred at 110 °C for 20 h (unoptimized), after which time it was removed from the bath and allowed to cool room temperature. The vial was then uncapped, diluted with EtOAc (5 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (5 mL) was added, and the layers were separated. The aqueous layer was then extracted with EtOAc (3 x 5 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via preparative thin-layer chromatography (20% EtOAc in hexanes), affording the title compound as a yellow oil (12.4 mg, 23%). **IR** (neat): 2970, 2926, 2870, 1705, 1616, 1516, 1458, 1391, 1352, 1192, 1123, 1099, 1038, 972, 949, 808, 750, 623, 584 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 6.11 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H), 2.11 (s, 3H), 1.23 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 211.0, 140.7, 138.6, 138.5, 136.0, 131.3, 130.1,

129.4, 126.9, 126.8, 125.3, 106.6, 50.9, 25.8, 24.0, 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{14}H_{21}N_2O^+$, 269.1648; found, 269.1650.

5c. Co(III)-Catalyzed Sequential C–H Bond Addition to d_2-Isoprene and Acetic Formic Anhydride (Scheme 2B)



***d*$_2$-4a**. General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), and d_2-isoprene[30] (52.8 mg, 0.800 mmol, 4.0 equiv). After flash chromatography on silica gel (150 mL 20% Et_2O in hexanes, then 150 mL 50% Et_2O in hexanes), the title compound was obtained as a yellow oil (40.7 mg, 79%). **IR** (neat): 2968, 2930, 2805, 2710, 1722, 1616, 1516, 1456, 1391, 1327, 1192, 1101, 1040, 949, 885, 826, 750, 621 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.01 (t, J_{HD} = 2.2 Hz, 1H)., 2.37 (s, 3H), 1.19 (s, 3H), 1.18 (t, J_{HD} = 1.7 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 202.1, 140.6, 138.8, 138.5, 132.8, 131.3, 129.6, 129.3, 126.8, 126.7, 126.4 (t, J_{DC} = 23.9 Hz), 106.6, 49.0, 21.5, 21.4 (t, J_{DC} =17.6 Hz), 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{16}H_{17}D_2N_2O^+$, 257.1617; found, 257.1621.

Figure S1. ^{1}H NMR spectrum of ***d*$_2$-4a** (500 MHz, $CDCl_3$).

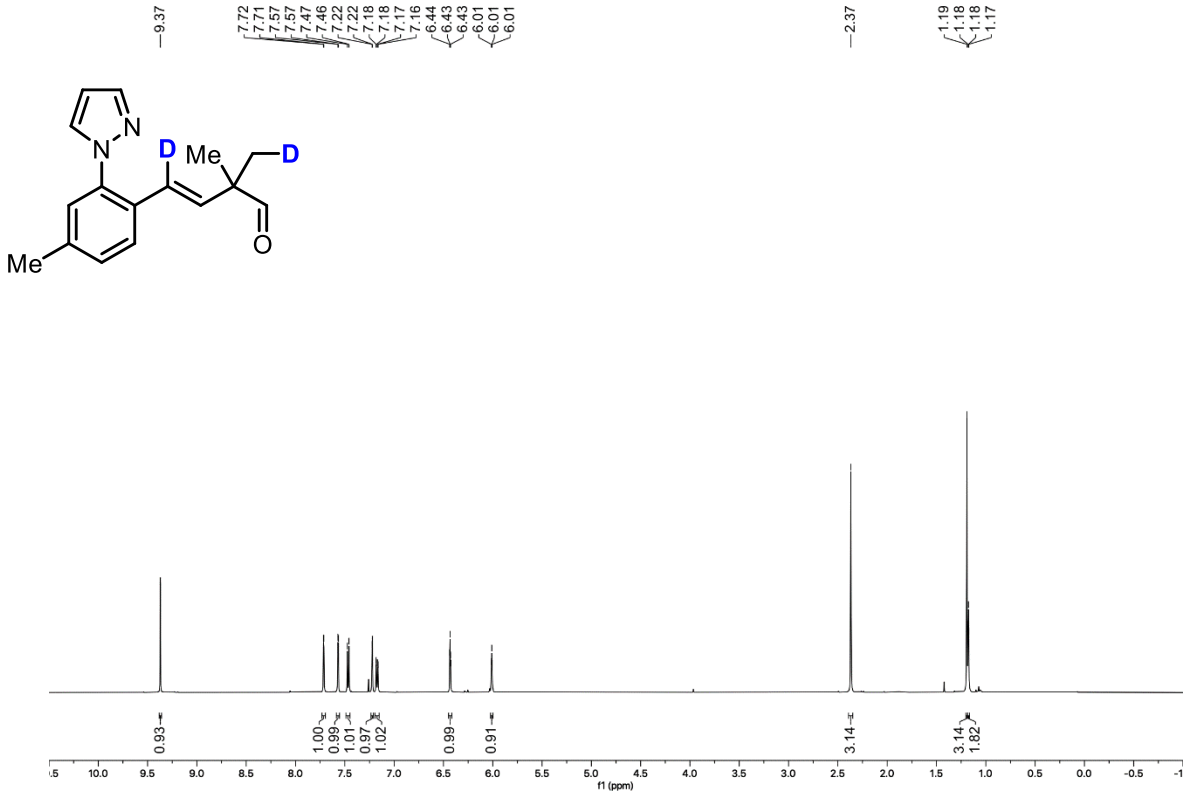


Figure S2. $^{13}C\{^{1}H\}$ spectrum of ***d*$_2$-4a** (126 MHz, $CDCl_3$).

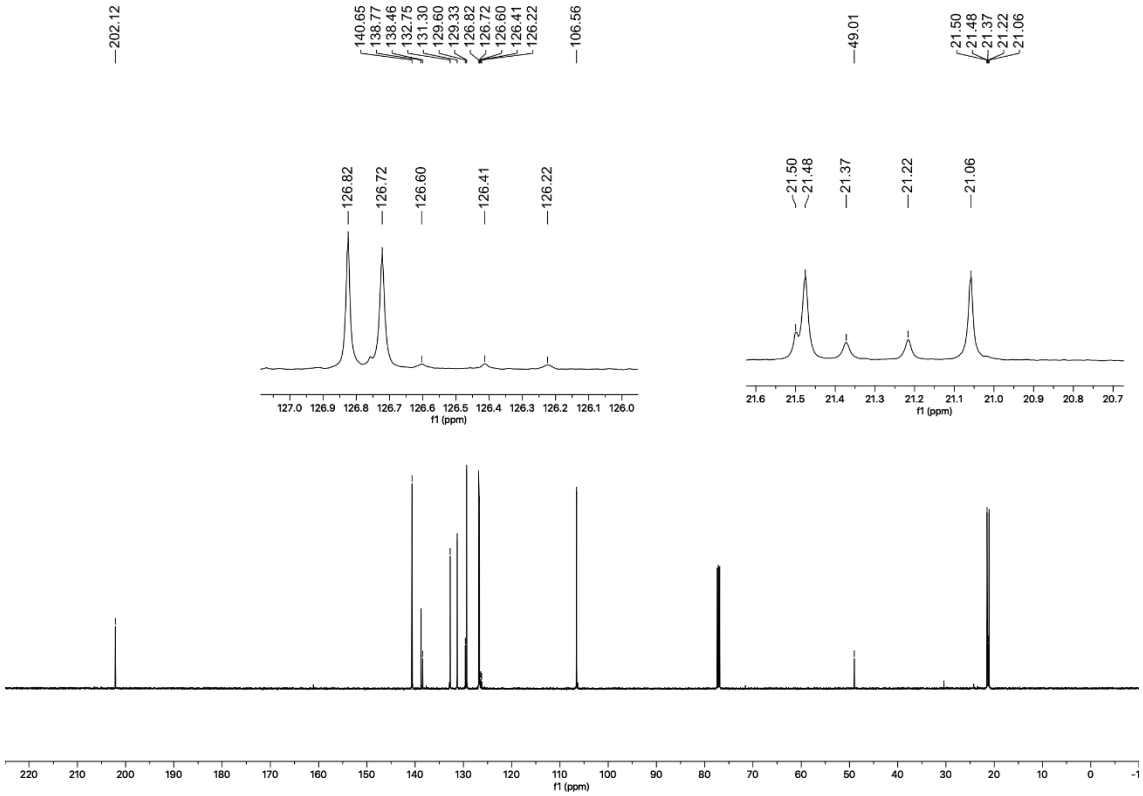
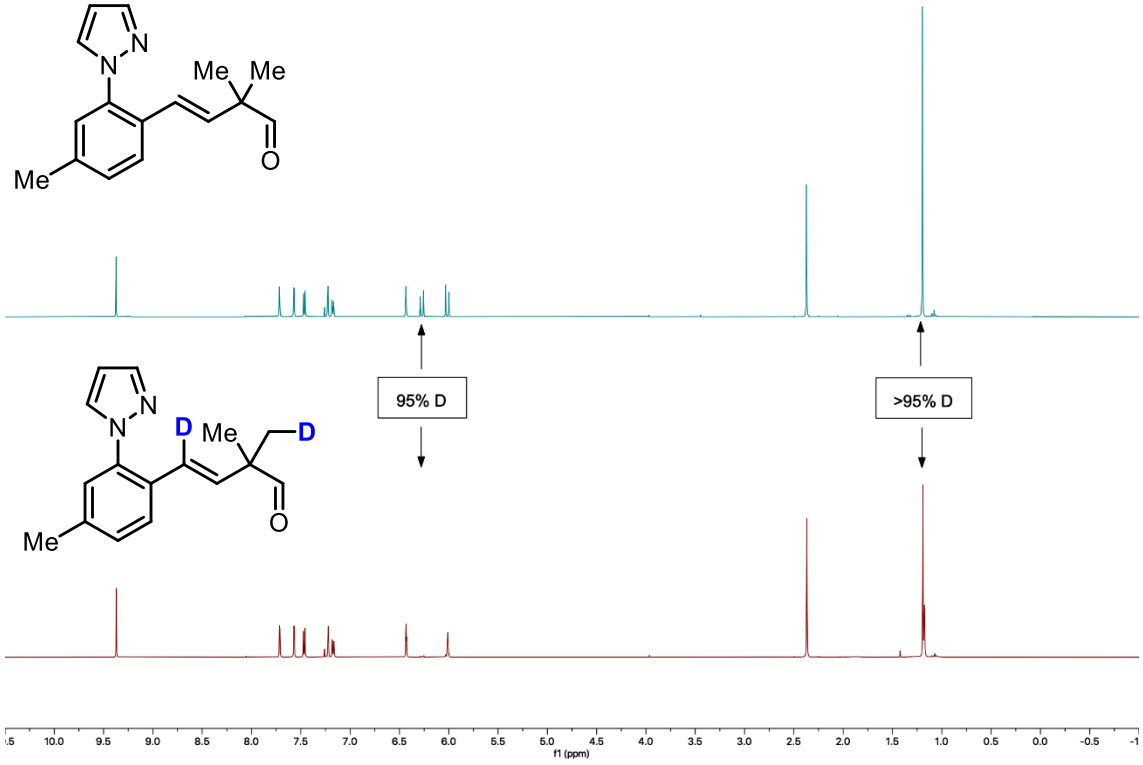


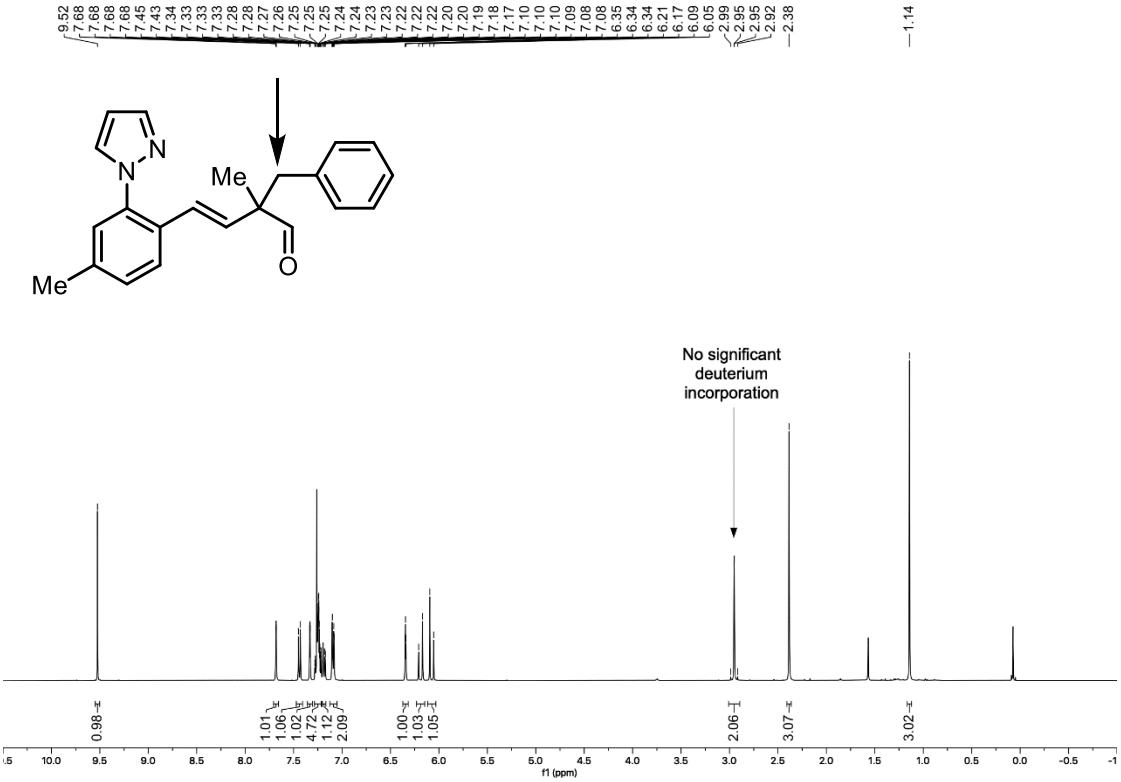
Figure S3. Comparison of the ^{1}H NMR spectra of (*E*)-2,2-Dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4a** (500 MHz, $CDCl_3$), and ***d*$_2$-4a** (500 MHz, $CDCl_3$).



5d. Crossover Diene Reaction: Addition of 1.0 equiv (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**2h**) to the Co(III)-Catalyzed Sequential C–H Bond Addition of d_2-Isoprene and Acetic Formic Anhydride (Scheme 2C)

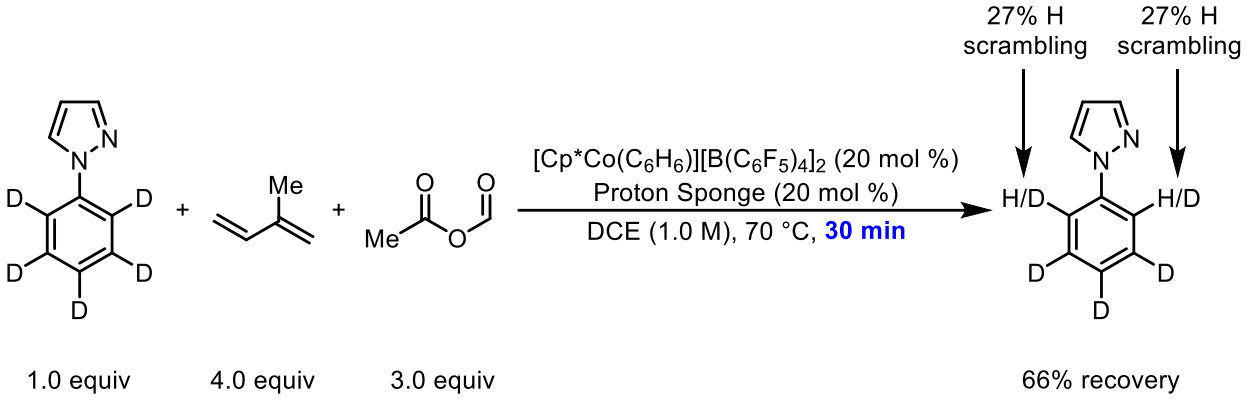
General Procedure B was followed using DCE as solvent, 1-(*m*-tolyl)-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), d_2-isoprene (52.8 mg, 0.800 mmol, 4.0 equiv), and (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**2h**; 28.8 mg, 0.200 mmol, 1.0 equiv). After flash chromatography on silica gel (5% Et_2O in benzene), aldehyde **4r** was obtained as a colourless oil (7.7 mg, 12%) and aldehyde d_2-**4a** was obtained as a yellow oil (19.9 mg, 39%). NMR spectroscopic data for **4r** and d_2-**4a** are consistent those reported in Section 4 (**4r**) and above (d_2-**4a**).

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of aldehyde **4r** showing no deuterium incorporation at the expected benzylic position.



5e. Reversibility of C–H Activation: Co(III)-Sequential C–H Bond Addition to Isoprene and Acetic Formic Anhydride Using 1-(Phenyl-d_5)-1*H*-pyrazole at Short Reaction Times

Scheme S1. Co(III)-catalyzed sequential C–H bond addition to isoprene and acetic formic anhydride using 1-(phenyl)-d_5-1H-pyrazole at short reaction times.



In a nitrogen-filled glovebox, a 2–5 mL Biotage® microwave vial was consecutively charged with Proton Sponge (8.6 mg, 0.0400 mmol, 0.2 equiv), $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.0400 mmol, 0.2 equiv), DCE (200 µL, 1.0 M in C–H bond substrate), 1-(phenyl-d_5)-1*H*-pyrazole[31] (29.8 mg, 0.200 mmol, 1.0 equiv), acetic formic anhydride (52.8 mg, 0.600 mmol, 3.0 equiv), and isoprene (80 µL, 0.800 mmol, 4.0 equiv), followed by a magnetic stir bar. The vial was sealed, removed from the glovebox, and placed in a pre-heated oil bath set to 70 °C. The reaction mixture was stirred at 70 °C for 30 min, after which time it was removed from the bath and allowed to cool room temperature. The vial was then uncapped, diluted with EtOAc (5 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 5 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via flash chromatography on silica gel (150 mL 20% Et_2O in hexanes, then 200 mL 50% Et_2O in hexanes), affording the three-component product as a colourless oil (9.0 mg, 18%) and 19.6 mg (66%) of recovered C–H bond substrate. NMR spectroscopic analysis of the recovered C–H bond substrate indicated 27% H incorporation at both *ortho* sites (see spectra below).

Figure S5. ^{1}H NMR spectrum of recovered 1-(phenyl-d_5)-1*H*-pyrazole (600 MHz, $CDCl_3$).

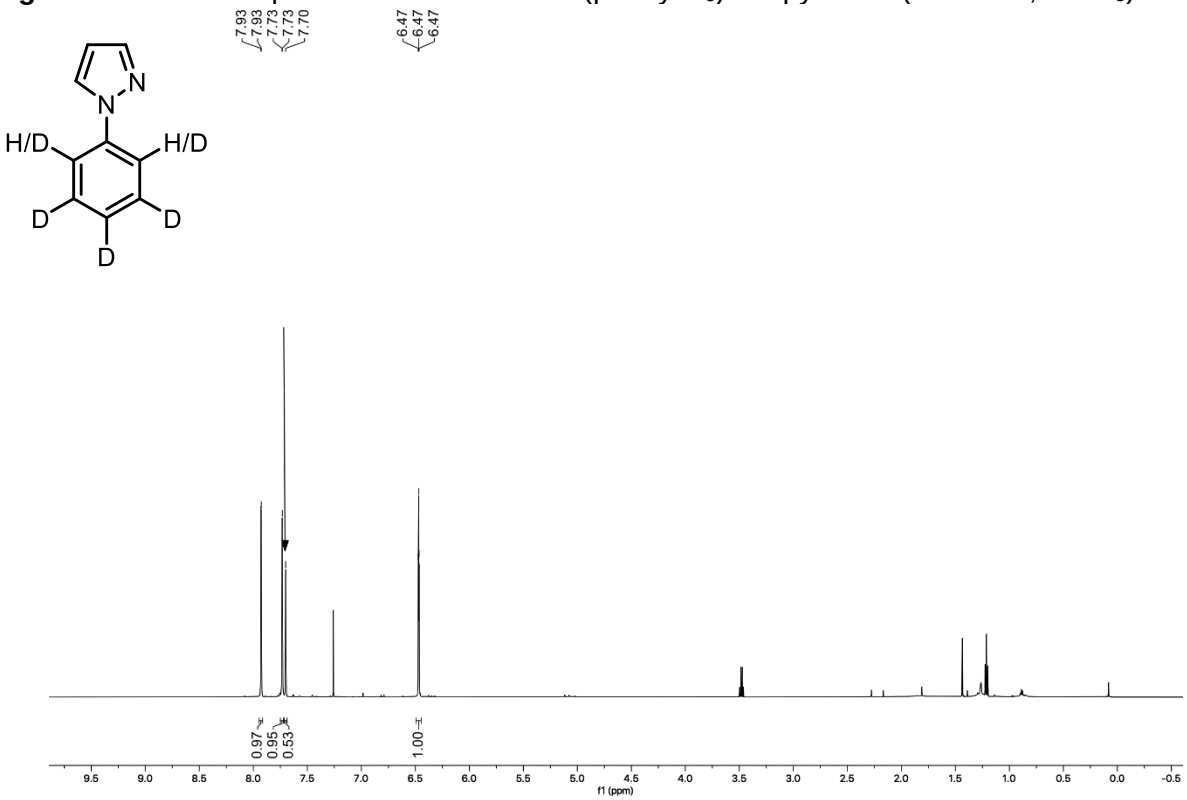


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of recovered 1-(phenyl-d_5)-1*H*-pyrazole (151 MHz, $CDCl_3$).

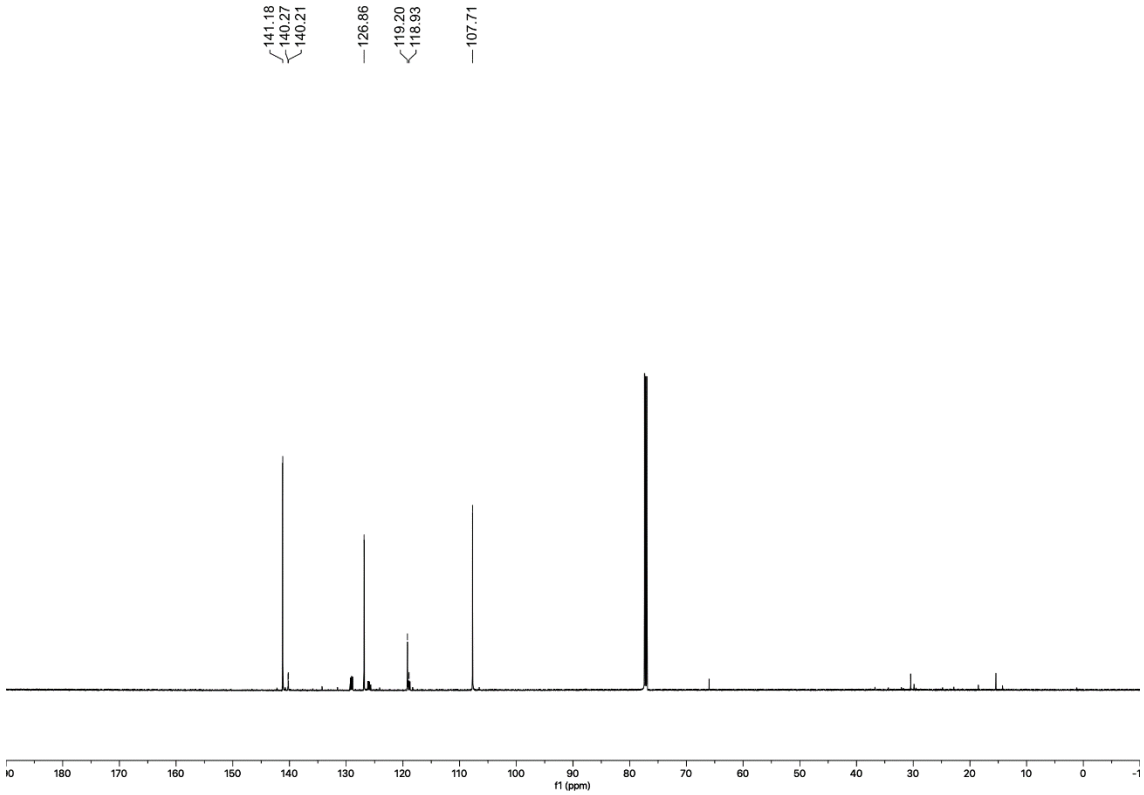


Figure S7. $^{1}H–^{1}H$ COSY NMR spectrum of recovered 1-(phenyl-d_5)-1*H*-pyrazole ($CDCl_3$).

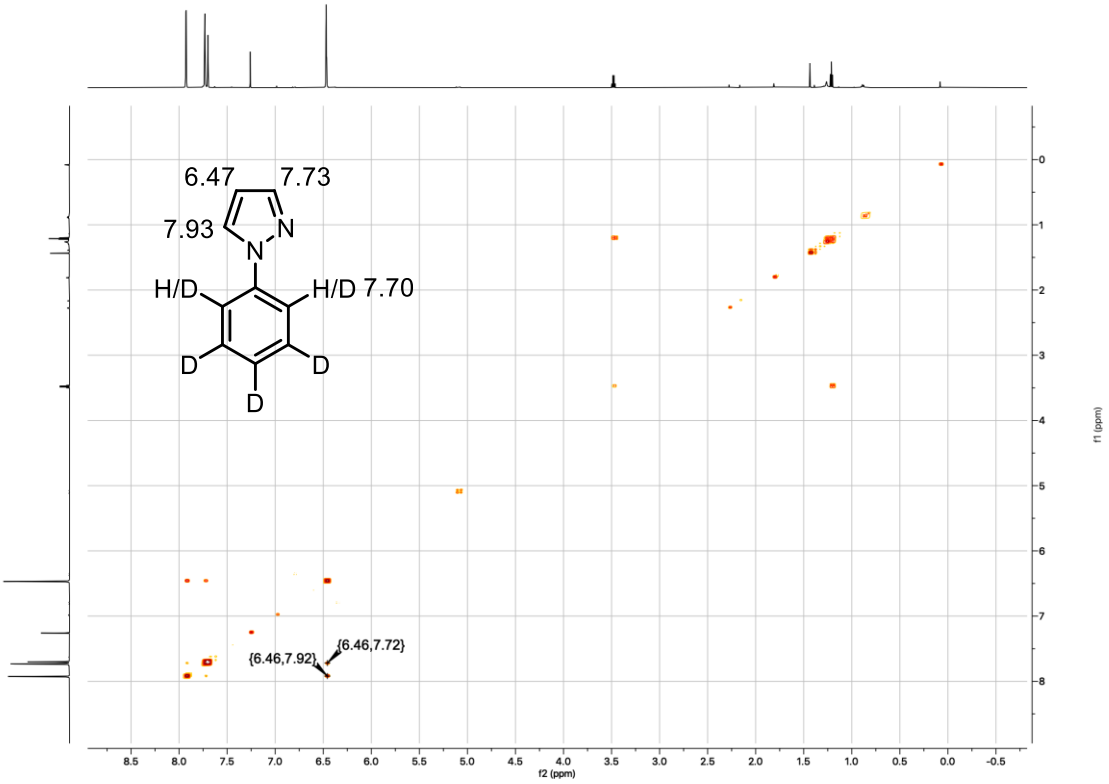


Figure S8. $^{1}H–^{13}C\{^{1}H\}$ HSQC NMR spectrum of recovered 1-(phenyl-d_5)-1*H*-pyrazole ($CDCl_3$).

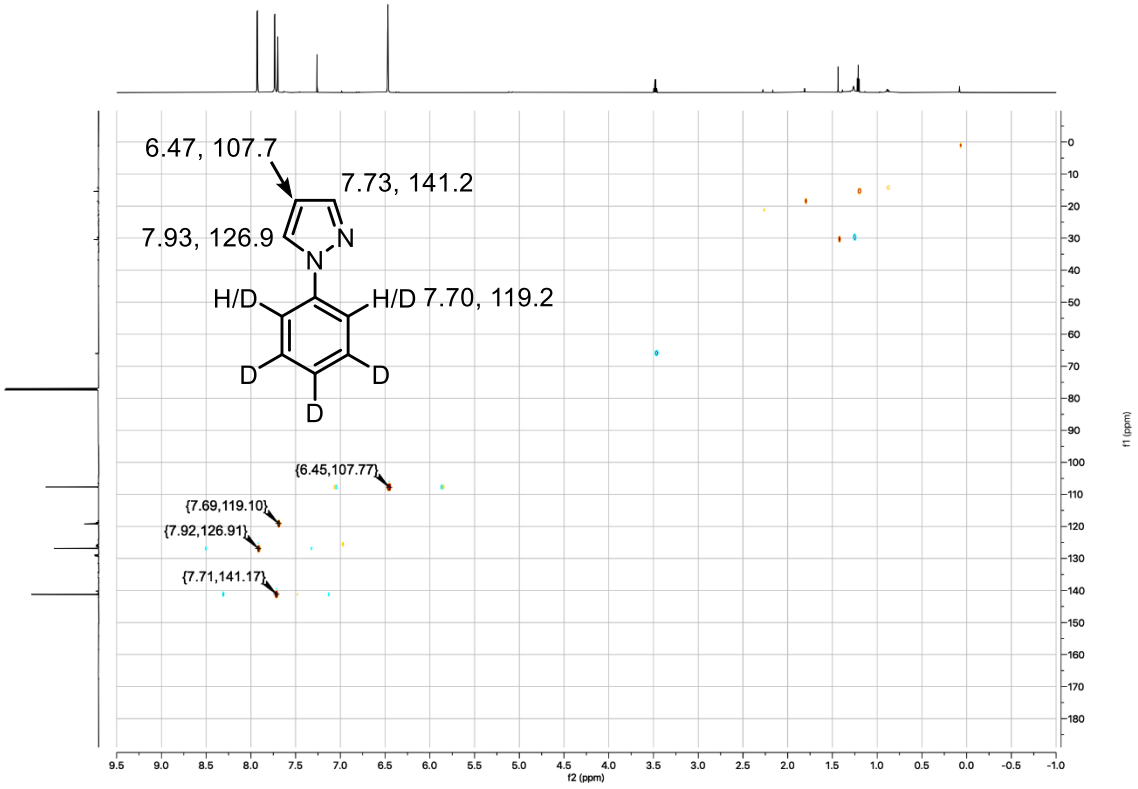
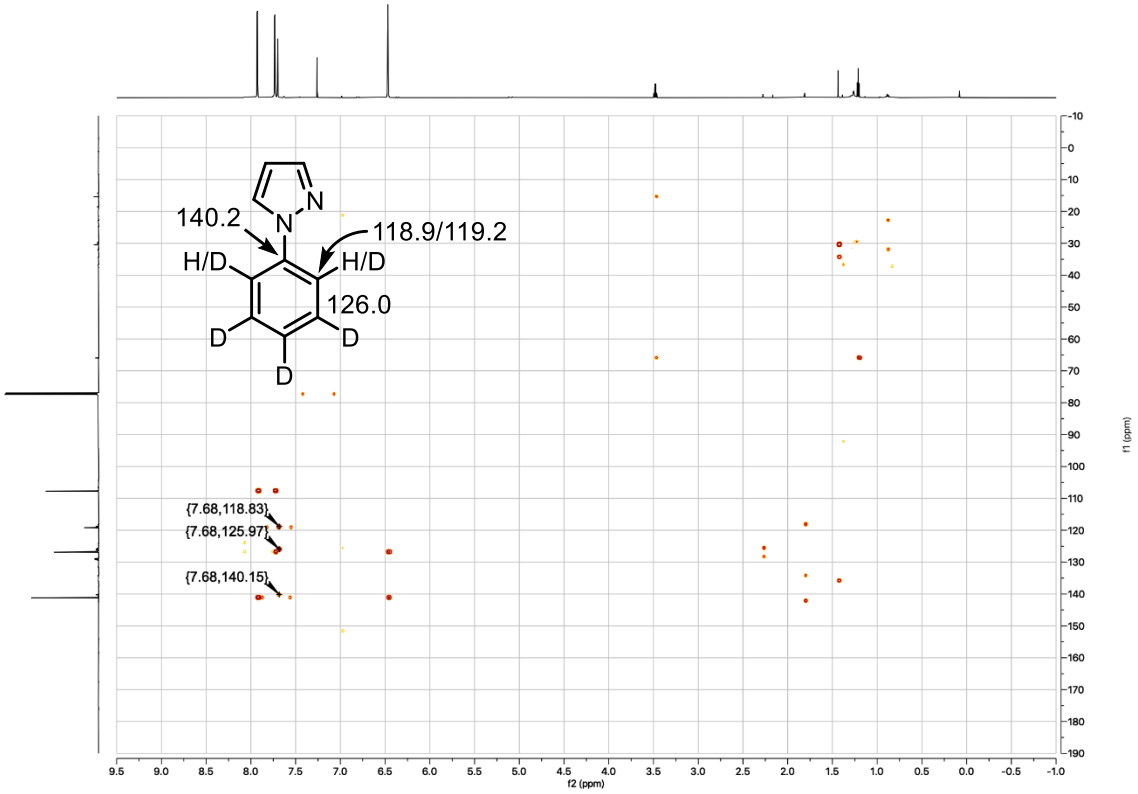


Figure S9. $^{1}H–^{13}C\{^{1}H\}$ HMBC NMR spectrum of recovered 1-(phenyl-d_5)-1*H*-pyrazole ($CDCl_3$).



6. Mechanistic Experiments Involving Co-1

6a. Reaction of $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® – Identification of **Co-1** (Scheme 2D).

In a nitrogen-filled glovebox, a 2 mL vial was charged with Proton Sponge® (8.6 mg, 0.040 mmol, 1.0 equiv) and dissolved in CD_2Cl_2 (100 µL). The vial was sealed with a cap with a PTFE septum, removed from the glovebox, and placed under N_2 on a Schlenk via a needle. Separately, on the benchtop, a 5 mL Schlenk flask was charged with $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.040 mmol, 1.0 equiv) and a magnetic stir bar. The flask was sealed with a septum, attached to a Schlenk line, and evacuated and backfilled with N_2 three times. Then, CD_2Cl_2 (100 µL) was added, and the green heterogeneous mixture was cooled to −50 °C. The Proton Sponge® solution was then transferred via syringe to the cold (−50 °C) Cp*Co(III) mixture, affording an intensely coloured red-orange solution upon complete addition. Additional CD_2Cl_2 (2 x 100 µL) was used to ensure quantitative transfer of Proton Sponge®. The reaction mixture was stirred at −50 °C for 2 h, after which time the reaction mixture was transferred to an oven-dried J-Young NMR tube under N_2 cooled to −50 °C, rinsing with additional CD_2Cl_2 (2 x 100 µL). Mesitylene standard solution (50.0 µL of a 0.267 M solution in CD_2Cl_2, 0.0133 mmol, 0.333 equiv) was then added, the tube was sealed under N_2, and the reaction mixture was analyzed using NMR spectroscopic methods at −50 °C, revealing a 26% NMR yield of **Co-1**. NMR characterization data for **Co-1**: **^{1}H NMR** (500 MHz, CD_2Cl_2, −50 °C): δ 6.13 (s, 6H), 3.91 (s, 2H), 1.99 (s, 6H), 1.29 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, −50 °C): δ 140.5, 102.0, 98.3, 84.8, 84.7, 11.7, 10.5. **^{19}F NMR** (471 MHz, CD_2Cl_2, −50 °C): δ −132.44 (d, *J* = 19.0 Hz), −161.73 (t, *J* = 21.2 Hz), −165.35 (d, *J* = 20.8 Hz).

Figure S10. ^{1}H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® with **Co-1** peaks identified (500 MHz, CD_2Cl_2, −50 °C).

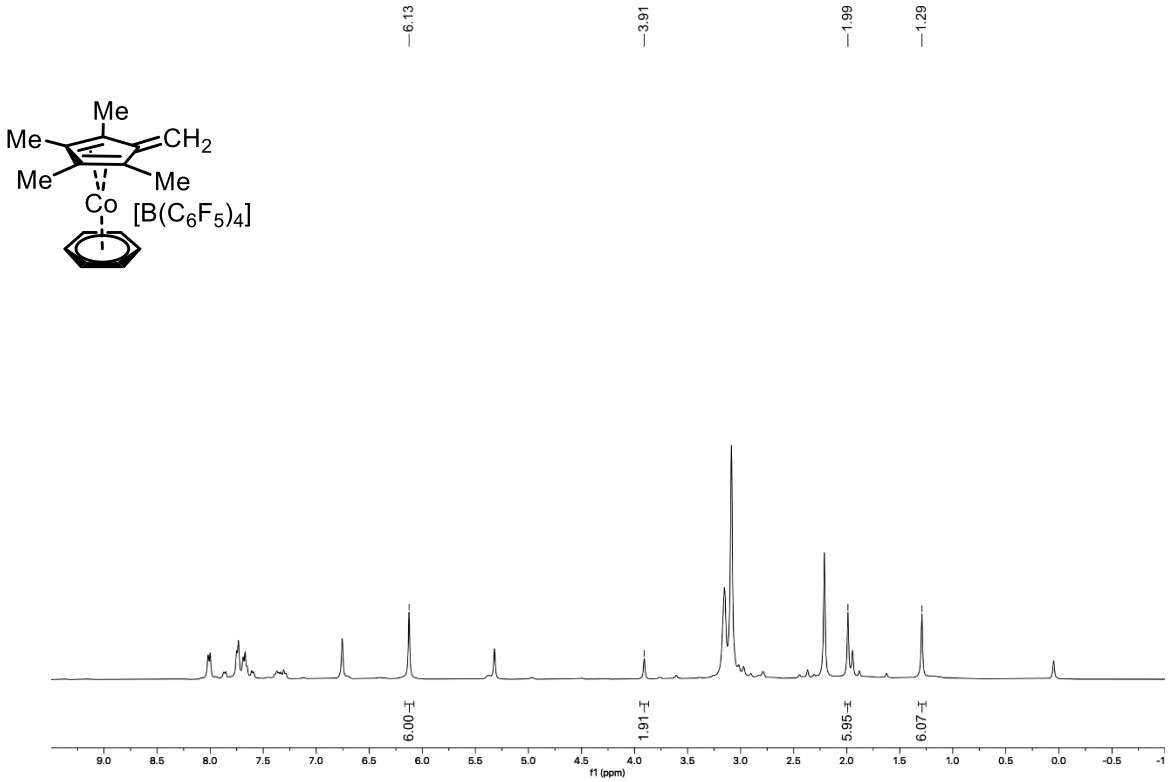


Figure S11. ^{1}H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® – NMR Yield with **Co-1** and mesitylene peaks identified (500 MHz, CD_2Cl_2, −50 °C).

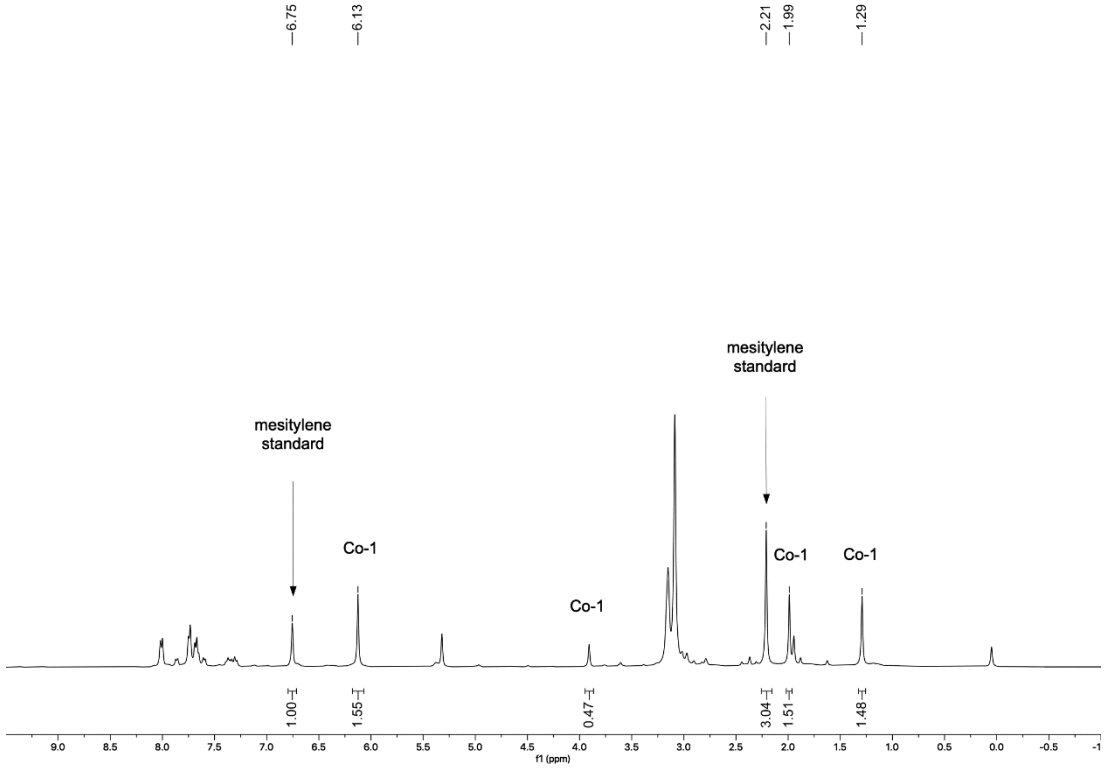


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® with **Co-1** peaks identified (126 MHz, CD_2Cl_2, −50 °C).

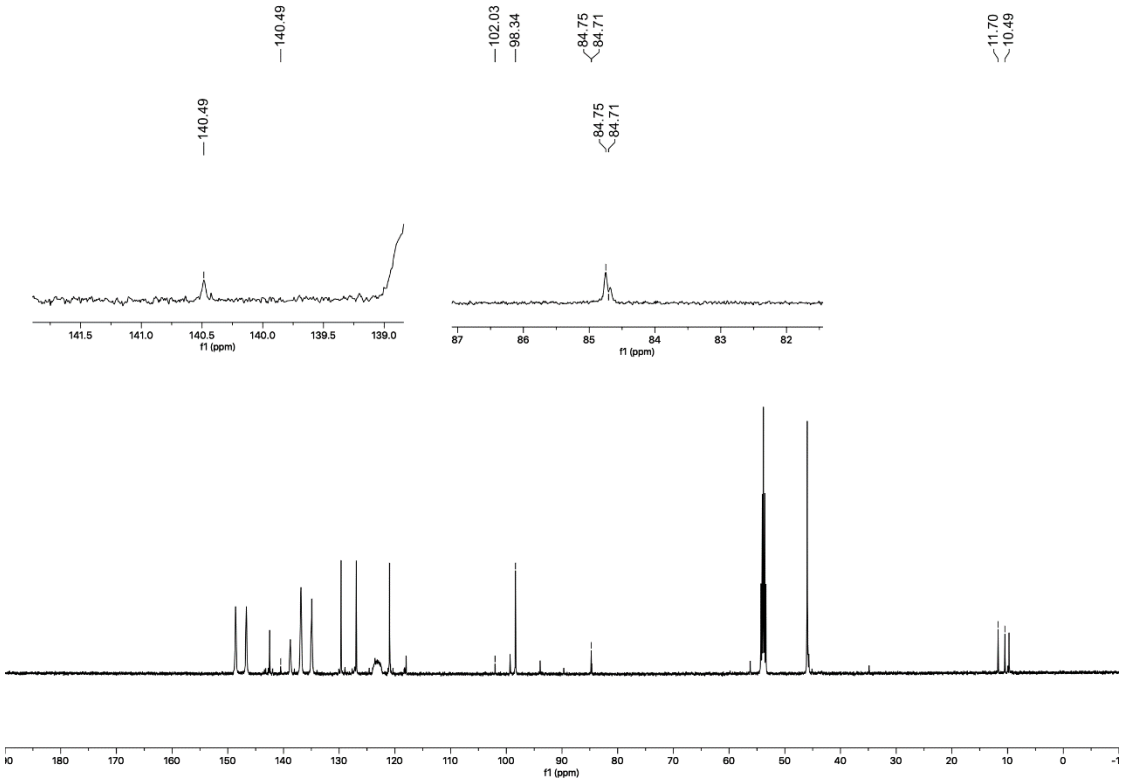


Figure S13. $^{1}H–^{13}C\{^{1}H\}$ HSQC NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® with **Co-1** peaks identified (CD_2Cl_2, −50 °C).

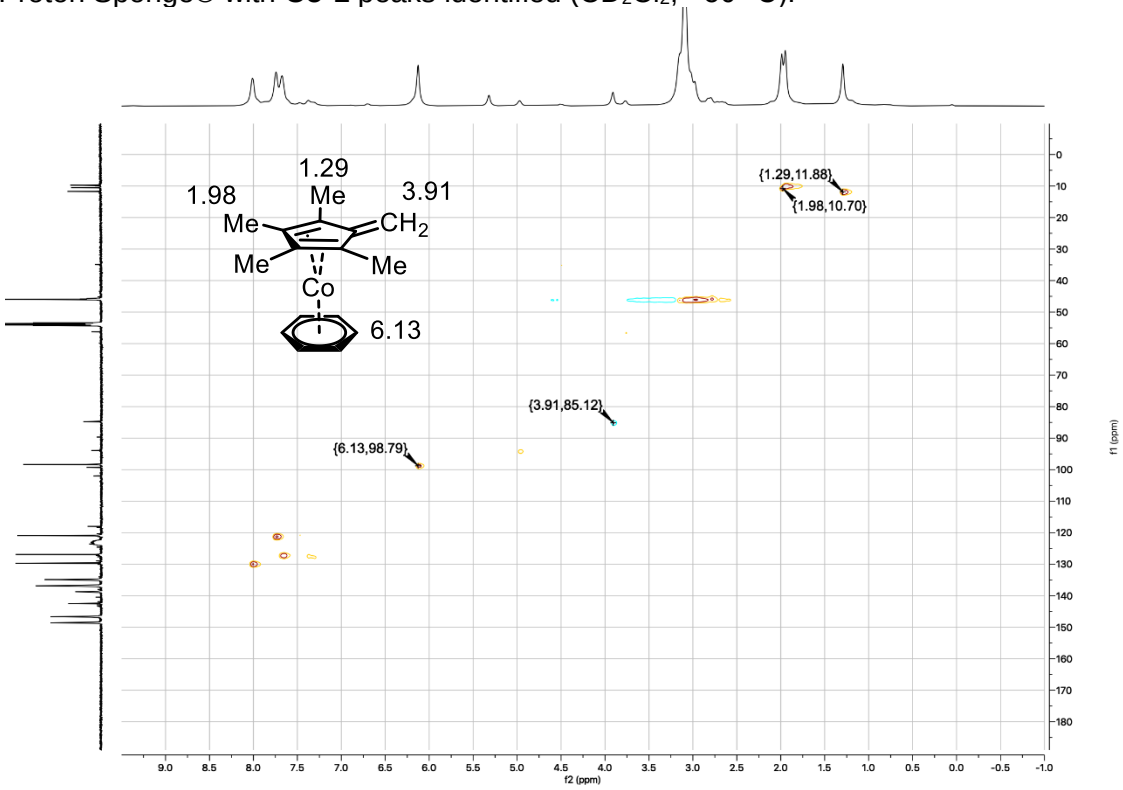


Figure S14. $^{1}H–^{13}C\{^{1}H\}$ HMBC NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® with **Co-1** peaks identified (CD_2Cl_2, −50 °C).

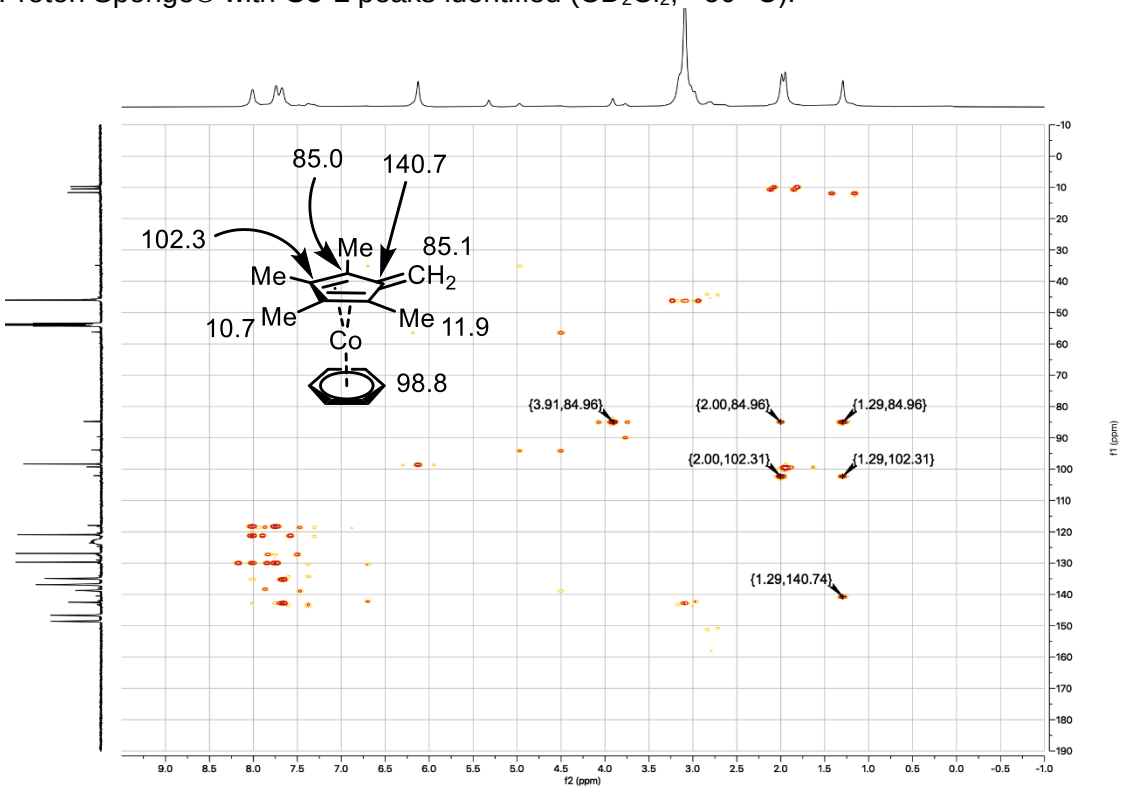
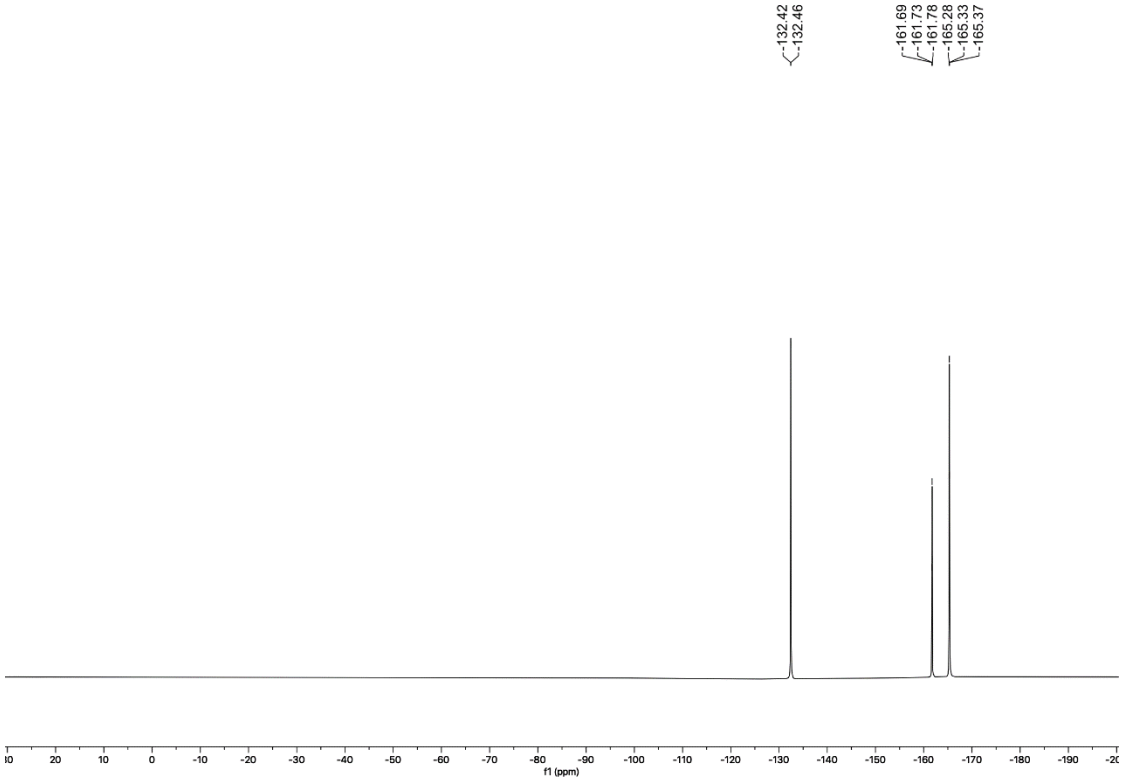
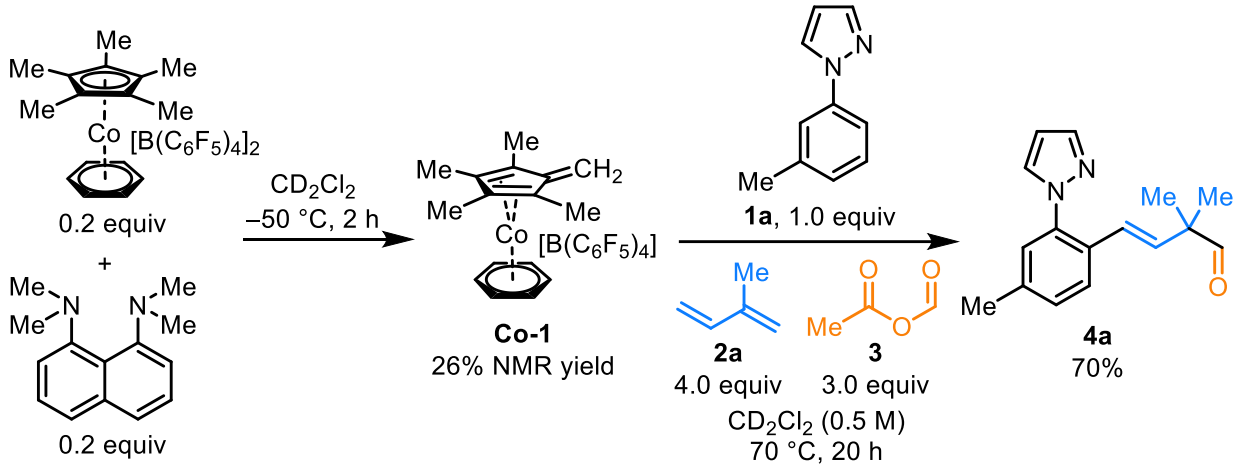


Figure S15. ^{19}F NMR spectrum of the of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® (471 MHz, CD_2Cl_2, −50 °C).



6b. Co(III)-Catalyzed Sequential C–H Bond Addition to Isoprene and Acetic Anhydride using **Co-1** as Catalyst

Scheme S2. Co(III)-catalyzed sequential C–H bond addition to isoprene and acetic formic anhydride using **Co-1** as catalyst.

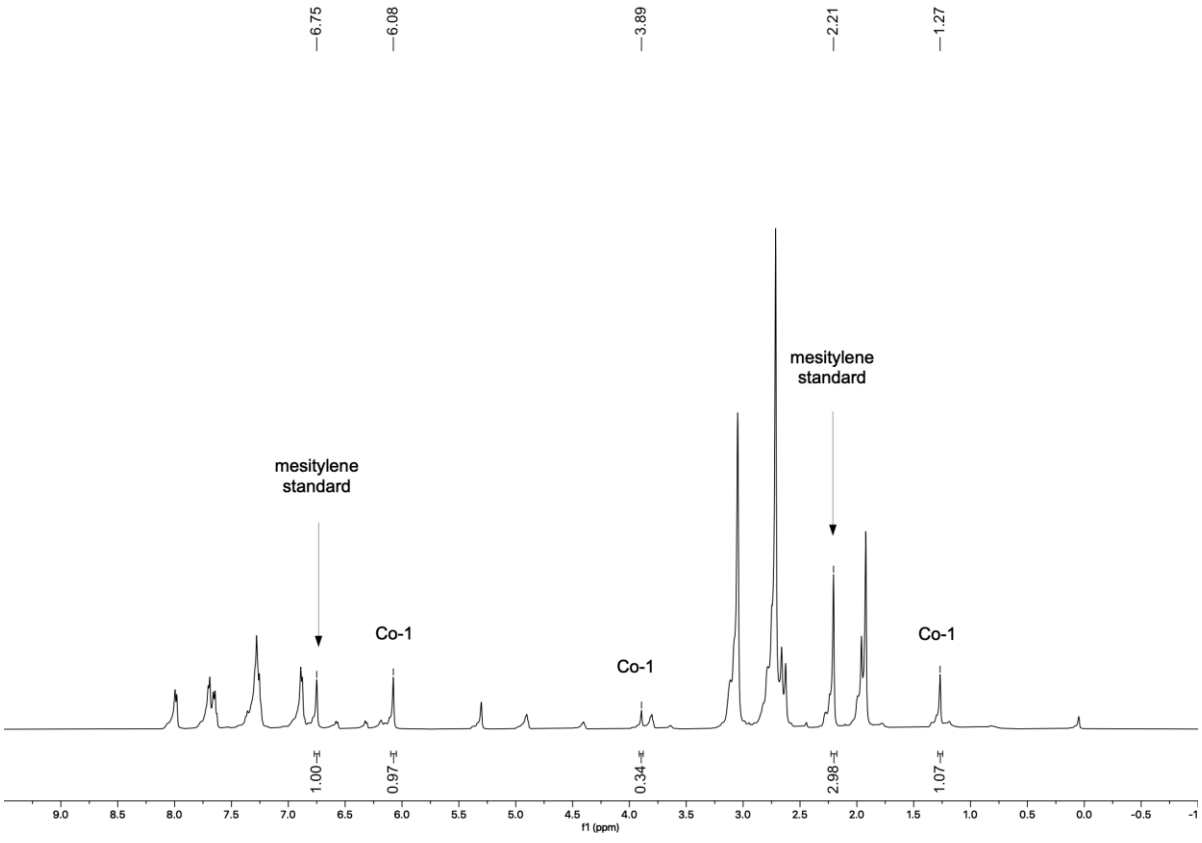


In a nitrogen-filled glovebox, separate 2 mL vials were charged with Proton Sponge® (8.6 mg, 0.040 mmol, 0.2 equiv), 1-(*m*-tolyl)-1*H*-pyrazole (**1a**; 31.6 mg, 0.200 mmol, 1.0 equiv), and acetic formic anhydride (**3**; 52.8 mg, 0.600 mmol, 3.0 equiv), and each compound was dissolved in CD_2Cl_2 (50 µL). Another 2 mL vial was charged with isoprene (**2a**; ~100 µL). All the vials were sealed with caps containing PTFE septa, removed from the glovebox, and placed under N_2 on a Schlenk line via needle. Separately, on the benchtop, a 0.5–2 mL Biotage® microwave vial was charged with $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.0400 mmol, 0.2 equiv) and a magnetic stir bar. The vial was sealed, attached to a Schlenk line via a needle, and evacuated and backfilled with N_2 three times Then, CD_2Cl_2 (100 µL) was added, and the green heterogeneous mixture was cooled to −50 °C. The Proton Sponge® solution was transferred via syringe to the cold (−50 °C) Cp*Co(III) mixture, affording an intensely coloured red-orange solution upon complete addition. Additional CD_2Cl_2 (50 µL) was used to ensure quantitative transfer of Proton Sponge®. The reaction mixture was stirred at −50 °C for 2 h, after which time the 1-(*m*-tolyl)-1*H*-pyrazole solution, acetic formic anhydride solution, and isoprene (80.0 µL, 0.800 mmol, 4.0 equiv) were sequentially added to the reaction mixture via syringe (using additional CD_2Cl_2 (2 x 50 µL) to ensure quantitative transfer of **1a** and **3**; total volume = 400 µL, [**1a**] = 0.5 M). The vial was then *very quickly* uncapped and re-capped under N_2 and placed in a pre-heated 70 °C oil bath. The reaction mixture was stirred at 70 °C for 20 h, after which time it was removed from the bath and allowed to cool room temperature. The vial was uncapped, diluted with EtOAc (5 mL), and transferred to a separatory funnel. Saturated aq. $NaHCO_3$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 5 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via flash chromatography on silica gel (typical column dimensions: 6-inch length × 1-inch diameter), affording **4a** as a pale-yellow oil (0.0359 g, 70%). NMR spectroscopic data are consistent with those reported in Section 4.

6c. Reaction of $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with 2.0 equiv Proton Sponge®

In a nitrogen-filled glovebox, a 2 mL vial was charged with Proton Sponge® (17.1 mg, 0.080 mmol, 2.0 equiv) and dissolved in CD_2Cl_2 (100 µL). The vial was sealed with a cap with a PTFE septum, removed from the glovebox, and placed under N_2 on a Schlenk via a needle. Separately, on the benchtop, a 5 mL Schlenk flask was charged with $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.040 mmol, 1.0 equiv) and a magnetic stir bar. The flask was sealed with a septum, attached to a Schlenk line, and evacuated and backfilled with N_2 three times. Then, CD_2Cl_2 (100 µL) was added, and the green heterogeneous mixture was cooled to −50 °C. The Proton Sponge® solution was then transferred via syringe to the cold (−50 °C) Cp*Co(III) mixture, affording an intensely coloured red-orange solution upon complete addition. Additional CD_2Cl_2 (2 x 100 µL) was used to ensure quantitative transfer of Proton Sponge®. The reaction mixture was stirred at −50 °C for 2 h, after which time the reaction mixture was transferred to an oven-dried J-Young NMR tube under N_2 cooled to −50 °C, rinsing with additional CD_2Cl_2 (2 x 100 µL). Mesitylene standard solution (50.0 µL of a 0.267 M solution in CD_2Cl_2, 0.0133 mmol, 0.333 equiv) was then added, the tube was sealed under N_2, and the reaction mixture was analyzed using NMR spectroscopic methods at −50 °C, revealing a 16% NMR yield of **Co-1**.

Figure S16. ^1H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with 2.0 equiv of Proton Sponge® – NMR Yield with **Co-1** and mesitylene peaks identified (500 MHz, CD_2Cl_2, −50 °C).



6d. Reaction of $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge® – Addition of 1.0 equiv of 1-(*m*-Tolyl)-1*H*-pyrazole (**1a**), Isoprene (**2a**), or Acetic Formic Anhydride (**3**)

In a nitrogen-filled glovebox, a 2 mL vial was charged with Proton Sponge® (8.6 mg, 0.040 mmol, 1.0 equiv) and dissolved in CD_2Cl_2 (50 µL). Additionally, a 2 mL vial was charged with either:

a) 1-(*m*-tolyl)-1*H*-pyrazole (**1a**; 6.3 mg, 0.040 mmol, 1.0 equiv) in 50 µL CD_2Cl_2;
b) isoprene (**2a**; ~50 µL); or
c) a solution of acetic formic anhydride (**3**; 3.5 mg, 0.040 mmol, 1.0 equiv) in 50 µL of CD_2Cl_2

The vials were sealed with caps containing PTFE septa, removed from the glovebox, and placed under N_2 on a Schlenk line via needle. Separately, on the benchtop, a 5 mL Schlenk flask was charged with $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.040 mmol, 1.0 equiv) and a magnetic stir bar. The flask was sealed with a septum, attached to a Schlenk line, and evacuated and backfilled with N_2 three times. Then, CD_2Cl_2 (100 µL) was added, and the green heterogeneous mixture was cooled to −50 °C. The Proton Sponge solution was transferred via syringe to the cold (−50 °C) Cp*Co(III) mixture, affording an intensely coloured red-orange solution upon complete addition. Additional CD_2Cl_2 (2 x 50 µL) was used to ensure quantitative transfer of Proton Sponge®. The reaction mixture was stirred at −50 °C for 2 h, after which time

a) the 1-(*m*-tolyl)-1*H*-pyrazole solution;
b) isoprene (4.0 µL 4.0 µL, 0.040 mmol, 1.0 equiv) and CD_2Cl_2; or
c) the acetic formic anhydride solution

was/were added to the reaction mixture (using additional CD_2Cl_2 (2 x 50 µL) to ensure quantitative transfer of **1a** and **3**; total volume in each reaction = 400 µL). The reaction mixture was stirred at −50 °C for 1 h, after which time the reaction mixture was transferred to an oven-dried J-Young NMR tube under N_2 cooled to −50 °C, rinsing with additional CD_2Cl_2 (2 x 100 µL). Mesitylene standard solution (50.0 µL of a 0.267 M solution in CD_2Cl_2, 0.0133 mmol, 0.333 equiv) was then added, the tube was sealed under N_2, and the reaction mixture was analyzed using NMR spectroscopic methods at −50 °C.

Figure S17. ^{1}H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ and Proton Sponge® after addition of **1a**. Amount of **Co-1**: 21% vs 26% before addition of **2a** (500 MHz, CD_2Cl_2, −50 °C).

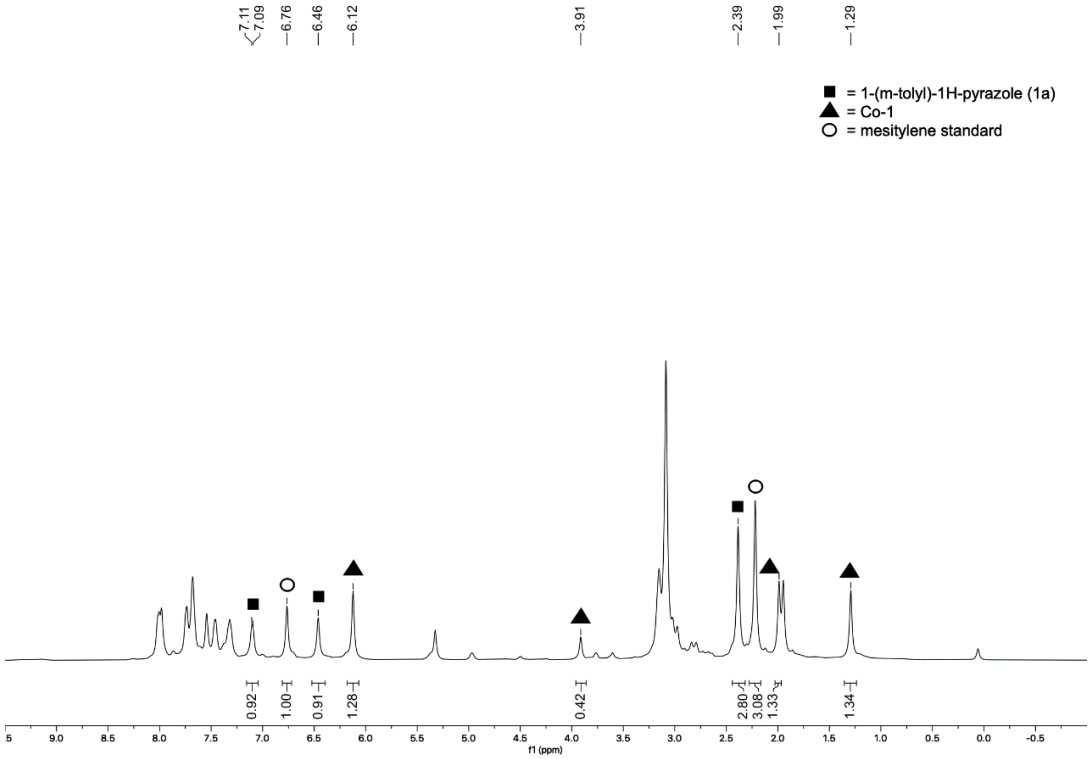


Figure S18. ^{1}H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ and Proton Sponge® after addition of **2a**. Amount of **Co-1**: 27% vs 26% before addition of **2a** (500 MHz, CD_2Cl_2, −50 °C).

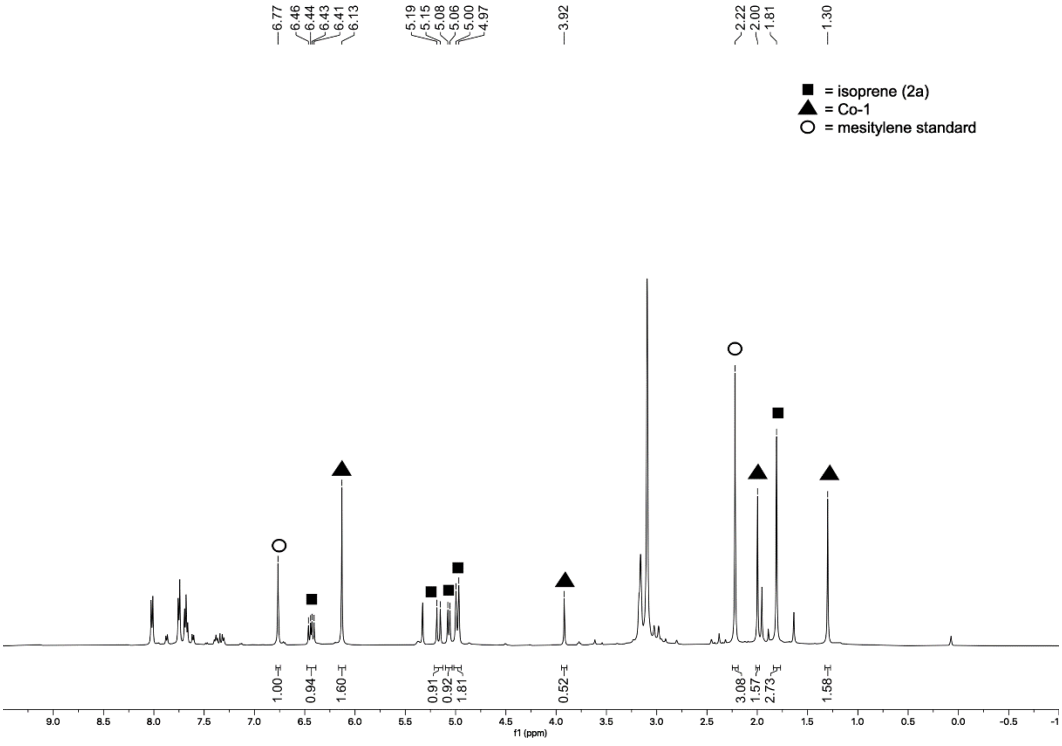
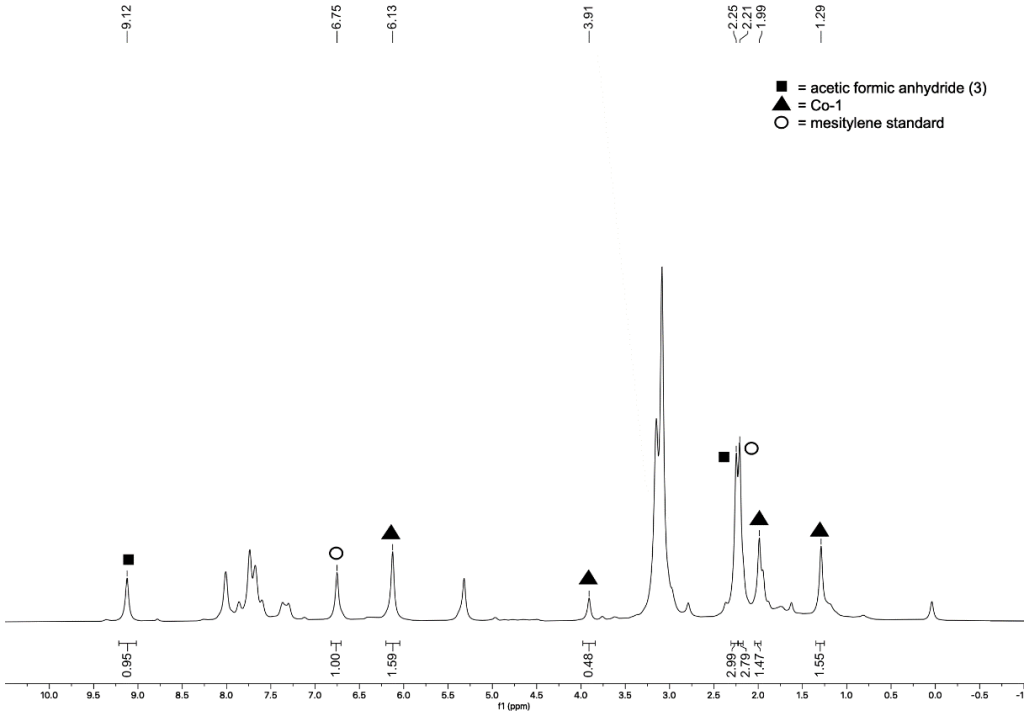


Figure S19. ^{1}H NMR spectrum of the reaction between $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ and Proton Sponge® after addition of **3**. Amount of **Co-1**: 26% vs 26% before addition of **3** (500 MHz, CD_2Cl_2, −50 °C).



6e. Reaction of $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ with Proton Sponge®, 1-(*m*-Tolyl)-1*H*-pyrazole (**1a**), Isoprene (**2a**), and Acetic Formic Anhydride (**3**)

In a nitrogen-filled glovebox, three 2 mL vials were charged with Proton Sponge® (8.6 mg, 0.040 mmol, 1.0 equiv), 1-(*m*-tolyl)-1*H*-pyrazole (**1a**; 6.3 mg, 0.040 mmol, 1.0 equiv), and acetic formic anhydride (**3**; 3.5 mg, 0.040 mmol, 1.0 equiv). Each compound was dissolved in CD_2Cl_2 (50 µL). Another 2 mL vial was charged with isoprene (**2a**; ~50 µL). All the vials were sealed with caps containing PTFE septa, removed from the glovebox, and placed under N_2 on a Schlenk line via needle. On the benchtop, a 5 mL Schlenk flask was charged with $[Cp^*Co(C_6H_6)][B(C_6F_6)_4]_2$ (65.2 mg, 0.040 mmol, 0.2 equiv) and a magnetic stir bar. The flask was sealed with a septum, attached to a Schlenk line, and evacuated and backfilled with N_2 three times. Then, CD_2Cl_2 (100 µL) was added and the green heterogeneous mixture was cooled to −50 °C. The Proton Sponge® solution was transferred via syringe to the cold (−50 °C) Cp*Co(III) mixture, affording an intensely coloured red-orange solution upon complete addition. Additional CD_2Cl_2 (50 µL) was used to ensure quantitative transfer of Proton Sponge®. The reaction mixture was stirred at −50 °C for 2 h, after which time the 1-(*m*-tolyl)-1*H*-pyrazole solution, acetic formic anhydride solution, and isoprene (**2a**; 4.0 µL, 0.040 mmol, 4.0 equiv) were sequentially added to the reaction mixture via syringe (using additional CD_2Cl_2 (2 x 50 µL) to ensure quantitative transfer of **1a** and **3**; total volume = 400 µL). The reaction mixture was stirred at −50 °C for 1 h, after which time the reaction mixture was transferred to an oven-dried J-Young NMR tube under N_2 cooled to −50 °C, rinsing with additional CD_2Cl_2 (2 x 100 µL). Mesitylene standard solution (50.0 µL of a 0.267 M solution in CD_2Cl_2, 0.0133 mmol, 0.333 equiv) was then added, the tube was sealed under N_2, and the reaction mixture was analyzed using NMR spectroscopic methods at −50 °C. After this analysis, the reaction mixture was transferred back to the Schlenk flask under N_2 and allowed to warm to 0 °C over 2 h. Then, the reaction mixture was transferred to an oven-dried J-Young NMR tube under N_2 cooled to 0 °C and analyzed using NMR spectroscopic methods at 0 °C.

Figure S20. ^{1}H NMR spectrum of the reaction between [Cp*Co(C_6H_6)][$B(C_6F_5)_4$]$_2$, Proton Sponge®, 1-(*m*-tolyl)-1*H*-pyrazole (**1a**), isoprene (**2a**), and acetic formic anhydride (**3**) at −50 °C (500 MHz, CD_2Cl_2).

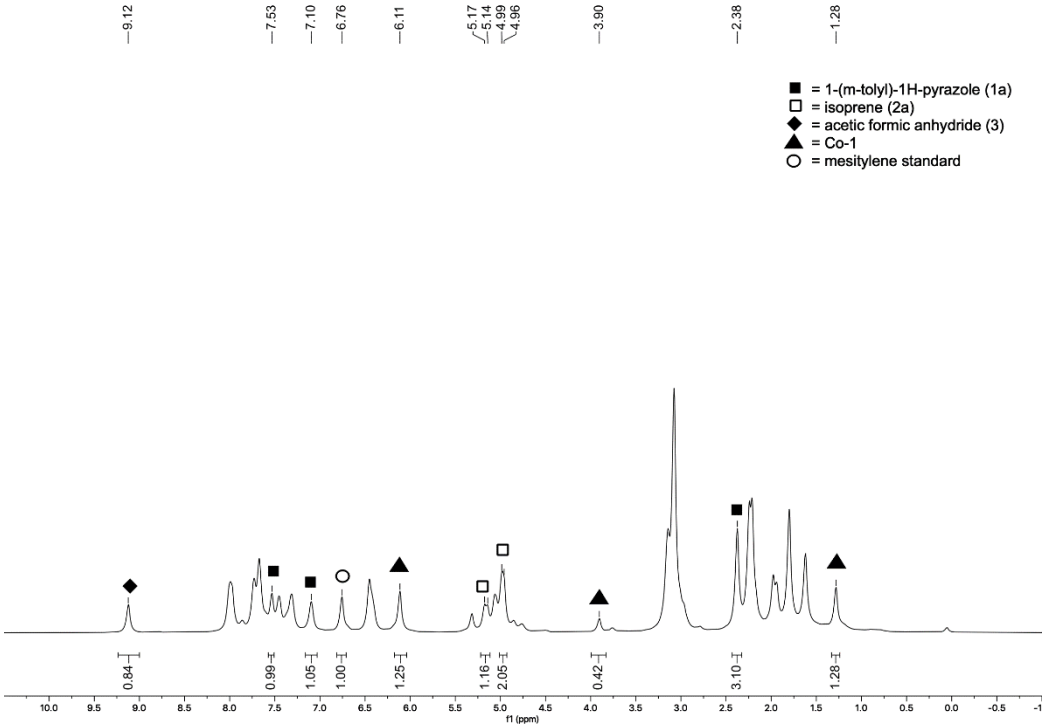
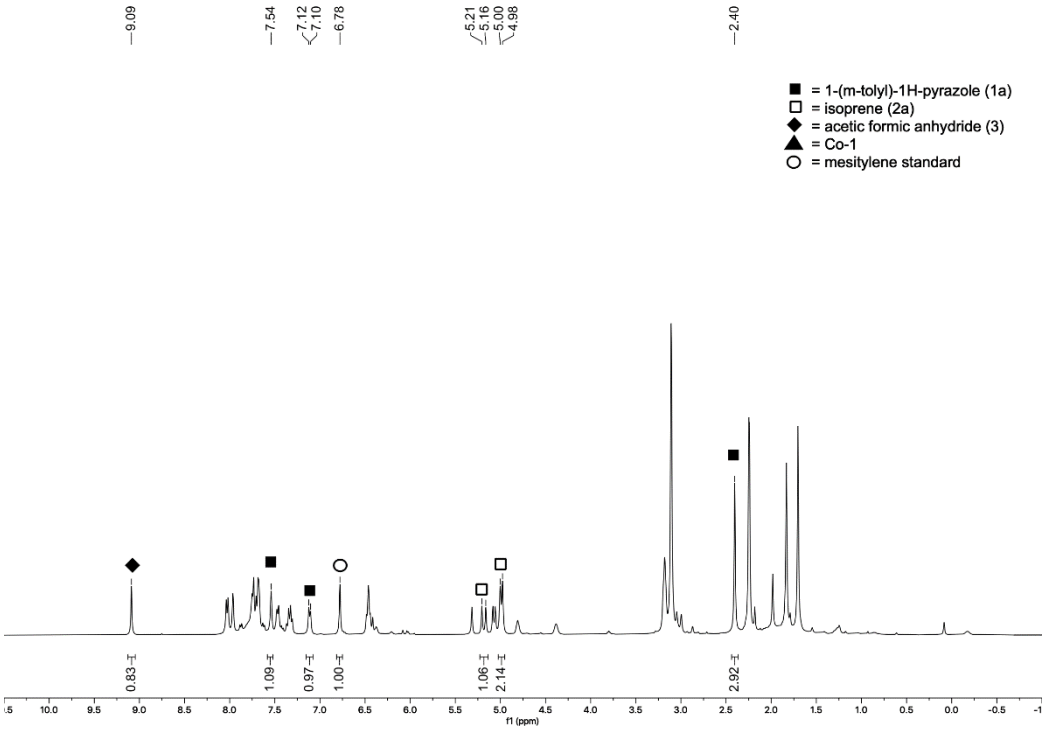


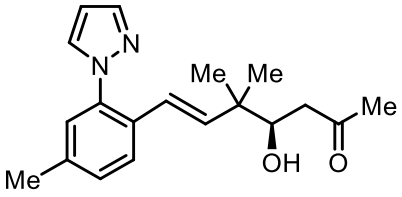
Figure S21. ^{1}H NMR spectrum of the reaction between [Cp*Co(C_6H_6)][$B(C_6F_5)_4$]$_2$, Proton Sponge®, 1-(*m*-tolyl)-1*H*-pyrazole (**1a**), isoprene (**2a**), and acetic formic anhydride (**3**) at 0 °C (400 MHz, CD_2Cl_2). Note the absence of **Co-1** peaks, as well as no appreciable change in the amounts of **1a**, **2a**, and **3**.



6f. Summary of Results from Experiments in Section 6d and 6e

Complex **Co-1** does not react with 1.0 equiv of either 1-(*m*-tolyl)-1*H*-pyrazole (**1a**), isoprene (**2a**), or acetic formic anhydride (**3**) at –50 °C, as evidenced by NMR spectroscopic analysis (see Figures S17–S19). Additionally, combining 1.0 equiv each of $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$, Proton Sponge®, **1a**, **2a**, and **3** in CD_2Cl_2 at –50 °C and reacting over 2 h does not appreciably impact the amount of **Co-1** formed (21% NMR yield vs 26% NMR yield in the absence of **1a**, **2a**, and **3**). Warming this reaction mixture to 0 °C decreases the amount of **Co-1** but causes no corresponding change in the amounts of **1a**, **2a**, and **3** (see Figure S20–S21). HRMS analysis of the reaction mixture at this temperature did not identify any obvious cobalt-containing species.

7. Diversification Reactions

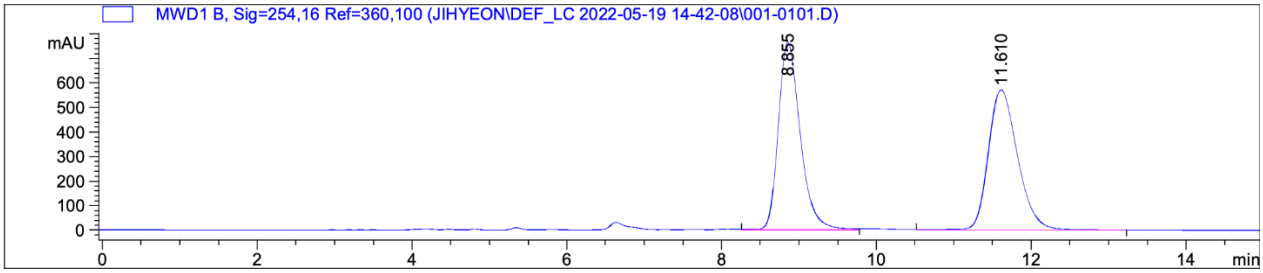


Synthesis of (*R*,*E*)-4-Hydroxy-5,5-dimethyl-7-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hept-6-en-2-one (**7**). This procedure was adapted from the literature.[32] In an oven-dried 0.5–2.0 mL Biotage® microwave vial, aldehyde **4a** (56.3 mg, 0.221 mmol, 1.0 equiv) was dissolved in 4:1 ratio of acetone (0.89 mL) and chloroform (0.22 mL) at 30 °C under nitrogen. Then, *S*-proline (5.1 mg, 0.044 mmol, 0.2 equiv) was added to the solution with no apparent change. After 3 days, the mixture was diluted with H_2O (5 mL) and Et_2O (5 mL) and transferred to a separatory funnel where the layers were separated. The aqueous layer was extracted with Et_2O (3 x 3 mL), and the organic layers were combined, dried over Na_2SO_4, and concentrated. The resulting residue was purified via a flash column chromatography on silica gel (40% EtOAc in hexanes), affording the title compound as a colorless oil (45.7 mg, 66%, 99:1 er). **IR** (neat): 3404, 2963, 1707, 1616, 1516, 1460, 1387, 1360, 1327, 1283, 1192, 1165, 1072, 1043, 976, 951, 808, 752, 623, 590 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.18 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.41 (t, *J* = 2.1 Hz, 1H), 6.15 (d, *J* = 16.4 Hz, 1H), 6.03 (d, *J* = 16.3 Hz, 1H), 3.82 (d, *J* = 10.0 Hz, 1H), 3.12 (s, 1H), 2.54 (dd, *J* = 17.0, 2.4 Hz, 1H), 2.44 (dd, *J* = 17.1, 10.1 Hz, 1H), 2.35 (s, 3H), 2.14 (s, 3H), 1.01–1.00 (overlapping s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 210.0, 140.4, 138.5, 138.0, 137.9, 131.1, 130.5, 129.2, 126.8, 126.5, 124.1, 106.3, 74.2, 45.5, 40.6, 30.8, 23.4, 22.8, 20.9. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{19}H_{25}N_2O_2^+$, 313.1911; found, 313.1907.

The configuration of the stereocenter was assigned by analogy to the product of the proline-catalyzed asymmetric aldol addition of acetone to trimethylacetaldehyde as described in the literature.[32]

Figure S22. er determination for **7**.

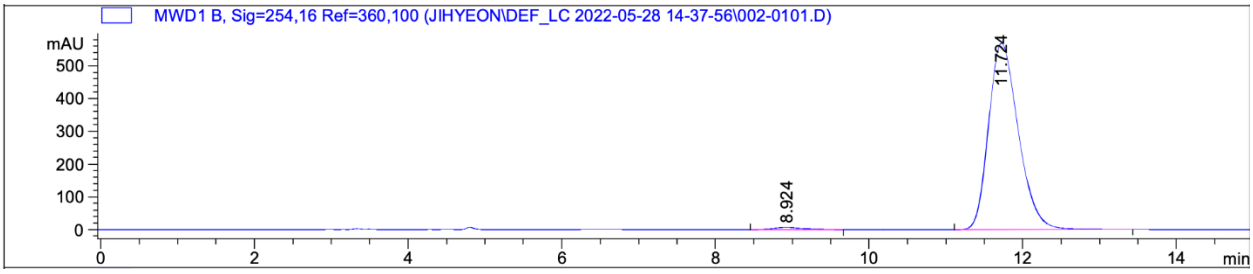
Racemic **7** (Chiralpak OD-H, 90:10 hexanes:isopropanol, 1 mL/min, 254 nm):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

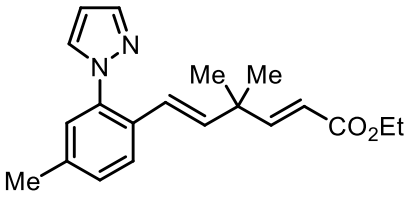
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.855	VB	0.3061	1.52306e4	765.71014	50.3208
2	11.610	VB	0.4070	1.50364e4	571.42316	49.6792
Totals :				3.02671e4	1337.13330	

Enantiomerically enriched **7** (99:1er):

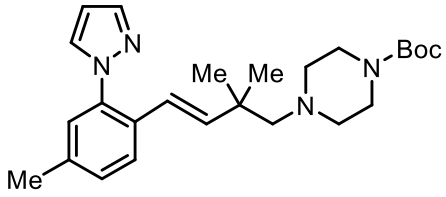


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.924	BB	0.3915	188.82727	6.89492	1.2189
2	11.724	BB	0.4156	1.53022e4	569.18707	98.7811
Totals :				1.54910e4	576.08199	

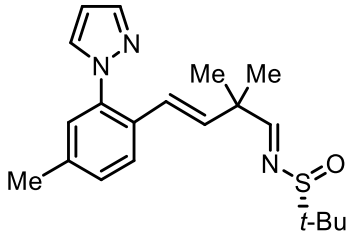


Synthesis of ethyl (2*E*,5*E*)-4,4-dimethyl-6-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hexa-2,5-dienoate (**8**). This procedure was adapted from the literature.[33] NaH (60% dispersion in mineral oil, 6.2 mg, 0.156 mmol, 1.5 equiv) was dissolved in dry Et_2O (1.7 mL) in a 0.5–2.0 mL Biotage® microwave vial. The clear, colourless solution was then cooled to 0 °C under nitrogen. Triethyl phosphonoacetate (50 µL, 0.260 mmol, 2.5 equiv) was then added dropwise via syringe with no apparent change, and the reaction mixture was stirred and refluxed. After 1 h, the solution was cooled to 0 °C again, and the aldehyde **4a** (26.4 mg, 0.104 mmol, 1.0 equiv) diluted in dry Et_2O (0.6 mL) was added dropwise via syringe. The reaction mixture was stirred at room temperature overnight. The next day, LC-MS analysis indicated ~50% conversion. Therefore, in a separate 0.5–2.0 mL Biotage® microwave vial, NaH (60% dispersion in mineral oil, 8.3 mg, 0.208 mmol, 2.0 equiv) was dissolved in dry Et_2O (0.5 mL). The solution was cooled to 0 °C under nitrogen, and triethyl phosphonoacetate (41 µL, 0.207 mmol, 2.0 equiv) was added dropwise via syringe, after which the solution was stirred and refluxed for 1 h. Then, the cooled phosphonoacetate solution was added dropwise via syringe to the original reaction mixture at 0 °C. After 1 h, complete conversion was achieved as evidenced by LC-MS analysis. The reaction mixture was diluted with H_2O (3 mL), transferred to a separatory funnel, and extracted with Et_2O (3 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified via flash column chromatography on silica gel (20% EtOAc in hexanes) affording the title compound as a colorless oil (27.8 mg, 83%). **IR** (neat): 2965, 1714, 1646, 1517, 1458, 1391, 1366, 1308, 1267, 1171, 1098, 1036, 977, 950, 868, 808, 750, 624 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 2.0 Hz, 1H), 7.56 (d, *J* = 2.7 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.23 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 15.9 Hz, 1H), 6.42 (t, *J* = 2.6 Hz, 1H), 6.16 (d, *J* = 16.3 Hz, 1H), 6.02 (d, *J* = 16.1 Hz, 1H), 5.74 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 166.9, 155.8, 140.4, 138.3, 138.20, 138.15, 131.3, 129.9, 129.1, 126.7, 126.6, 123.3, 118.2, 106.3, 60.3, 39.4, 26.4, 20.9, 14.3. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{20}H_{25}N_2O_2^+$, 325.1911; found, 325.1910.

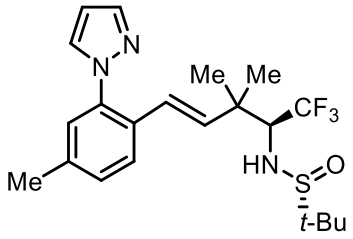


Synthesis of *tert*-butyl (*E*)-4-(2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)piperazine-1-carboxylate (**9**). This procedure was adapted from the literature.[34] An oven-dried 0.5–2.0 mL Biotage® microwave vial containing a magnetic stir bar was charged with aldehyde **4a** (25.2 mg, 0.0991 mmol, 1.0 equiv) and 1-Boc-piperazine (27.7 mg, 0.149 mmol, 1.5 equiv). MeCN (450 µL) was added, affording a clear, colourless solution. Then, $NaBH(OAc)_3$ (42.0 mg, 0.198 mmol, 2.0 equiv) was added all at once as a solid, affording a cloudy, white mixture. The vial was sealed and placed under nitrogen, and the reaction mixture was stirred at room temperature for 1 h, after which TLC analysis (30% EtOAc in hexanes) indicated complete conversion. The vial was uncapped and diluted with saturated aq. $NaHCO_3$ solution (2 mL). The

resulting clear, colourless solution was stirred at room temperature for 10 min, after which time it was transferred to a separatory funnel and extracted with EtOAc (3 x 3 mL). The EtOAc fractions were combined, dried over $MgSO_4$, filtered, and concentrated. The residue was purified via flash chromatography on silica gel (40% Et_2O in hexanes), affording the title compound as a colourless oil (30.0 mg, 69%). **IR** (neat): 2962, 2926, 2805, 1692, 1616, 1516, 1456, 1418, 1364, 1240, 1167, 1121, 1007, 866, 750, 731, 623 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 50 °C): δ 7.70 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.23, (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 6.14 (d, *J* = 16.3 Hz, 1H), 6.09 (d, *J* = 16.3 Hz, 1H), 3.36–3.34 (m, 4H), 2.43–2.41 (m, 4H), 2.37 (s, 3H), 2.22 (s, 2H), 1.45 (s, 9H), 1.01 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 50 °C): δ 155.0, 141.8, 140.5, 138.5, 137.8, 131.4, 131.0, 129.2, 126.9, 126.7, 122.0, 106.2, 79.5, 69.8, 55.3, 44.2, 38.8, 28.6, 25.8, 21.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{25}H_{37}N_4O_2^+$, 425.2911; found, 425.2904.

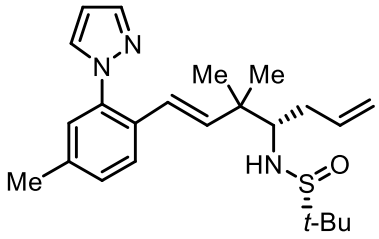


Synthesis of (*R*)-*N*-((3*E*)-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide (**10**). This procedure was adapted from the literature.[35] An oven-dried Biotage® 2.0–5.0 mL microwave vial was charged with aldehyde **4a** (117.0 mg, 0.460 mmol, 1.0 equiv) and (*R*)-2-methyl-2-propane-2-sulfinamide (111.5 mg, 0.920 mmol, 2.0 equiv). The vial was sealed and placed under nitrogen. THF (920 µL) was added, affording a clear, yellow solution. Then, Ti(O*i*-Pr)$_4$ (411 µL, 1.38 mmol, 3.0 equiv) was added via syringe with no apparent change. The reaction mixture was placed in a pre-heated, 50 °C oil bath and stirred at that temperature for 1 h, after which TLC analysis indicated complete conversion. The vial was removed from the bath and allowed to cool to room temperature, after which time it was diluted with EtOAc (7 mL). The solution was then transferred via pipette to a beaker containing a rapidly stirring solution of brine (15 mL). A white solid immediately precipitated, and the mixture was stirred at room temperature for 5 min. Then, the mixture was filtered through Celite, eluting with EtOAc (3 x 10 mL) until the filtrate ran colourless. The filtrate was transferred to a separatory funnel and separated. The aqueous layer was extracted with EtOAc (3 x 10 mL). The EtOAc fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified via flash chromatography on silica gel (50% Et_2O in hexanes), affording the title compound as a colourless oil that solidified to a white solid under reduced pressure (148.5 mg, 90%). **M.p**.: 72–73 °C. **IR** (neat): 3150, 2974, 2955, 2926, 2864, 1620, 1520, 1500, 1458, 1404, 1387, 1364, 1190, 1076, 1049, 1036, 980, 949, 883, 822, 775, 721, 627, 584, 507 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.24 (d, *J* = 16.2 Hz, 1H), 6.11 (d, *J* = 16.2 Hz, 1H), 2.37 (s, 3H), 1.28, (s, 3H), 1.27 (s, 3H), 1.16 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 172.9, 140.6, 138.6, 138.5, 136.0, 131.4, 129.9, 129.3, 126.8, 126.8, 124.9, 106.5, 56.9, 43.8, 24.6, 24.6, 22.5, 21.1. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{20}H_{28}N_3OS^+$, 358.1948; found, 358.1941.



Synthesis of (*R*)-2-methyl-*N*-((*S*,*E*)-1,1,1-trifluoro-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-yl)propane-2-sulfinamide (**11**). This procedure was adapted from the literature.[36] A flame-dried 10 mL Schlenk flask containing a magnetic stir bar was charged with sulfinyl imine **10** (35.7 mg, 0.100 mmol, 1.0 equiv) and tetrabutylammonium difluorotriphenylsilicate (TBAT; 59.4 mg, 0.110 mmol, 1.1 equiv). The flask was sealed with a septum and flushed with nitrogen for ~5 min. THF (1.6 mL) was added via syringe, and the resulting clear, colourless solution was cooled to −55 °C affording a hazy, white suspension. Then, a solution of $TMSCF_3$ (17.7 µL, 0.120 mmol, 1.2 equiv) in THF (400 µL) prepared in a separate, flame-dried 5 mL round-bottom flask was added dropwise via syringe to the cooled sulfinyl imine mixture, affording a hazy white mixture upon complete addition. The mixture was stirred at −55 °C for 1 h, then warmed to −20 °C over 1 h and stirred at −20 °C for 2 h. The reaction mixture was then placed in a 0 °C bath (water/ice) and stirred at 0 °C for 2 h. The mixture was again cooled to −55 °C, after which additional TBAT (108.0 mg, 0.200 mmol, 2.0 equiv) was added quickly as a solid against a positive pressure of nitrogen, followed immediately by additional $TMSCF_3$ (30.0 µL, 0.200 mmol, 2.0 equiv) via syringe once the septum had been replaced, affording a hazy mixture. The mixture was stirred at −55 °C for 2 h, then allowed to warm to −20 °C. After stirring at −20 °C for 1 h, TLC analysis indicated complete conversion. The mixture was cooled to −55 °C and saturated aq. NH_4Cl (1 mL) was added, affording a cloudy white mixture. The mixture was removed from the bath and allowed to warm to room temperature. The colourless biphasic mixture was transferred to a separatory funnel and separated. The aqueous layer was extracted with EtOAc (3 x 3 mL). The organic fractions were combined, dried over Na_2SO_4, filtered, and concentrated. The resulting green oil was purified via preparative thin-layer chromatography (1/2/7, CH_2Cl_2/acetone/hexanes), affording the title compound as a white solid (32.0 mg, 75%, >99:1 dr; single diastereomer). **M.p**.: 69–70 °C. **IR** (neat): 3404, 3142, 3100, 2980, 2928, 2868, 1616, 1518, 1458, 1396, 1352, 1258, 1179, 1148, 1096, 1028, 1016, 899, 845, 816, 766, 704, 590 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.9 Hz, 1H), 7.58 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.21–7.18 (m, 2H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.11 (dd, *J* = 16.2, 1.6 Hz, 1H), 3.55–3.48 (m, 2H), 2.38 (s, 3H), 1.26 (s, 3H), 1.23 (s, 3H), 1.18 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 140.8, 138.8, 138.5, 135.7, 131.2, 129.8, 129.5, 127.1, 126.7, 126.2, 125.7 (q, J_{CF} = 284 Hz), 106.7, 65.1 (q, J_{CF} = 27.0 Hz) 57.1, 39.7, 25.7 (q, J_{CF} = 2.5 Hz), 25.3, 22.6, 21.1. **^{19}F NMR** (471 MHz, $CDCl_3$): δ −68.09 (d, J_{HF} = 7.2 Hz). **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{21}H_{29}F_3N_3OS^+$, 428.1978; found, 428.1970.

The dr was determined via ^{19}F NMR spectroscopic analysis of the crude reaction mixture in $CDCl_3$ prior to chromatography, comparing relevant peaks to an authentic mixture of diastereomers prepared according to the literature.[37] The configuration of the carbon stereocenter in **11** was assigned by analogy to the product of the reaction of (*R*)-*N*-(2,2-dimethylpropylidene)-2-methylpropane-2-sulfinamide and TBAT/$TMSCF_3$, as reported in the literature.[36]



Synthesis of (*R*)-*N*-((*S*,*E*)-3,3-dimethyl-1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hepta-1,6-dien-4-yl)-2-methylpropane-2-sulfinamide (**12**). This procedure was adapted from the literature.[38] A flame-dried 0.5–2.0 mL Bitoage® microwave vial containing a magnetic stir bar was charged with sulfinyl imine **10** (35.8 mg, 0.100 mmol, 1.0 equiv). The vial was sealed and flushed with nitrogen for several minutes. CH_2Cl_2 (625 µL) was added and the resulting clear, colourless solution was cooled to −40 °C (MeCN/dry ice). Then, allylmagnesium bromide solution (200 µL of a 1.0 M solution in Et_2O, 0.200 mmol, 2.0 equiv) was added dropwise via syringe to the cooled solution, affording a clear, pale yellow solution upon complete addition. The solution was stirred at −40 °C for 3 h, after which time additional allylmagnesium bromide solution (100 µL of a 1.0 M solution in Et_2O, 0.100 mmol, 1.0 equiv) was added dropwise via syringe to the cooled solution. The solution was stirred at −40 °C for 1 h (4 h total) after which TLC analysis showed complete conversion. The solution was allowed to warm to 10 °C in the bath over ~3 h, after which time it was diluted with saturated aq. NH_4Cl (1 mL). The reaction mixture was transferred to a separatory funnel and separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 3 mL). The CH_2Cl_2 fractions were combined, dried over $MgSO_4$, filtered and concentrated. The resulting opaque yellow oil was purified via flash chromatography on silica gel (70% Et_2O in hexanes), affording the title compound as a colourless oil (35.0 mg, 88%, 96:4 dr; mixture of diastereomers). **IR** (neat): 3285, 3221, 2959, 2924, 2868, 1639, 1616, 1516, 1456, 1387, 1362, 1329, 1192, 1057, 978, 951, 908, 808, 750, 623, 588 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.21 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 6.02 (d, *J* = 16.2 Hz, 1H), 5.91–5.83 (m, 1H), 5.14–5.07 (m, 2H), 3.20–3.13 (m, 2H), 2.53–2.48 (m, 1H), 2.36 (s, 3H), 2.13–2.06 (m, 1H), 1.19 (s, 9H), 1.04 (s, 3H), 1.01 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 140.5, 139.3, 138.3, 138.1, 135.8, 131.3, 130.5, 129.3, 126.9, 126.8, 123.4, 118.3, 106.4, 63.2, 56.6, 41.9, 36.8, 25.1, 23.9, 23.0, 21.0. **HRMS-ESI (*m/z*)**: $[M+H]^+$ calc'd for $C_{23}H_{34}N_3OS^+$, 400.2417; found, 400.2410.

The dr was determined via ^{1}H NMR spectroscopic analysis of the crude reaction mixture in $CDCl_3$ prior to chromatography, comparing relevant peaks to an authentic mixture of diastereomers prepared according to the literature.[37] The configuration of the carbon stereocenter in **12** was assigned by analogy to the product of the reaction of (*R*)-*N*-(2,2-dimethylpropylidene)-2-methylpropane-2-sulfinamide and allylmagnesium bromide, as reported in the literature.[38]

8. NMR Spectra

Figure S23. ^{1}H NMR spectrum of 3-(1*H*-pyrazol-1-yl)phenol (400 MHz, DMSO-d_6).

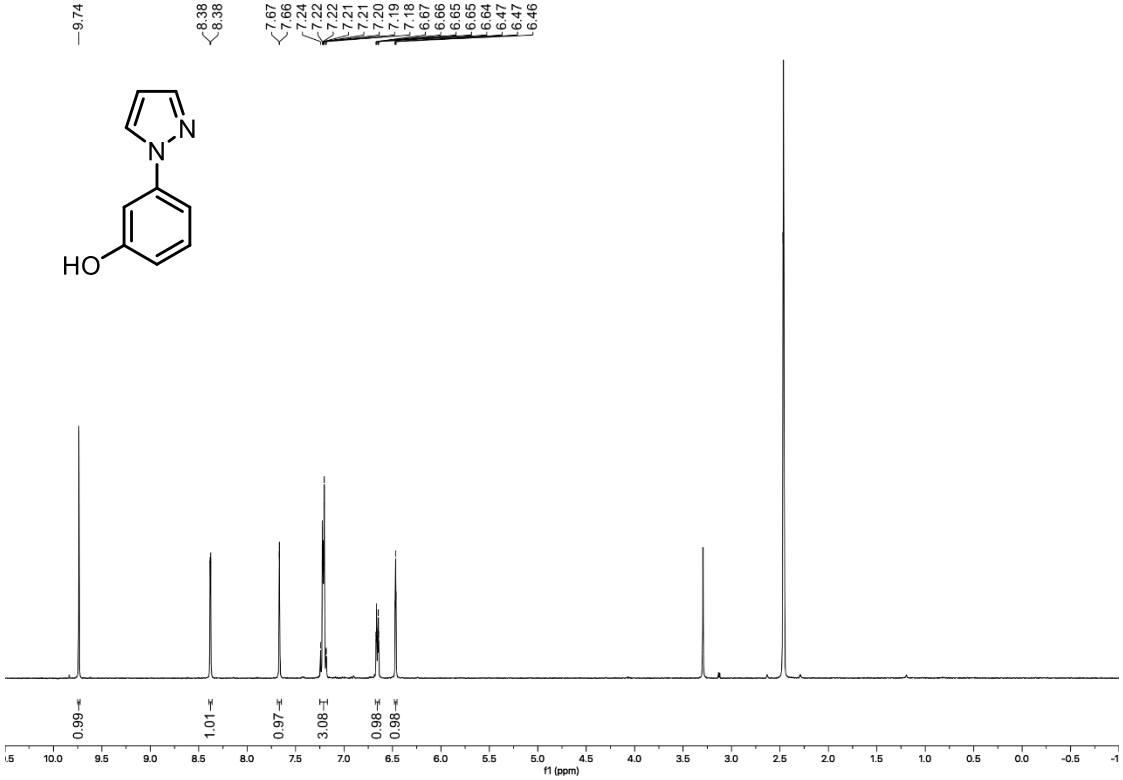


Figure S24. ^{13}C{^{1}H} NMR spectrum of 3-(1*H*-pyrazol-1-yl)phenol (126 MHz, DMSO-d_6).

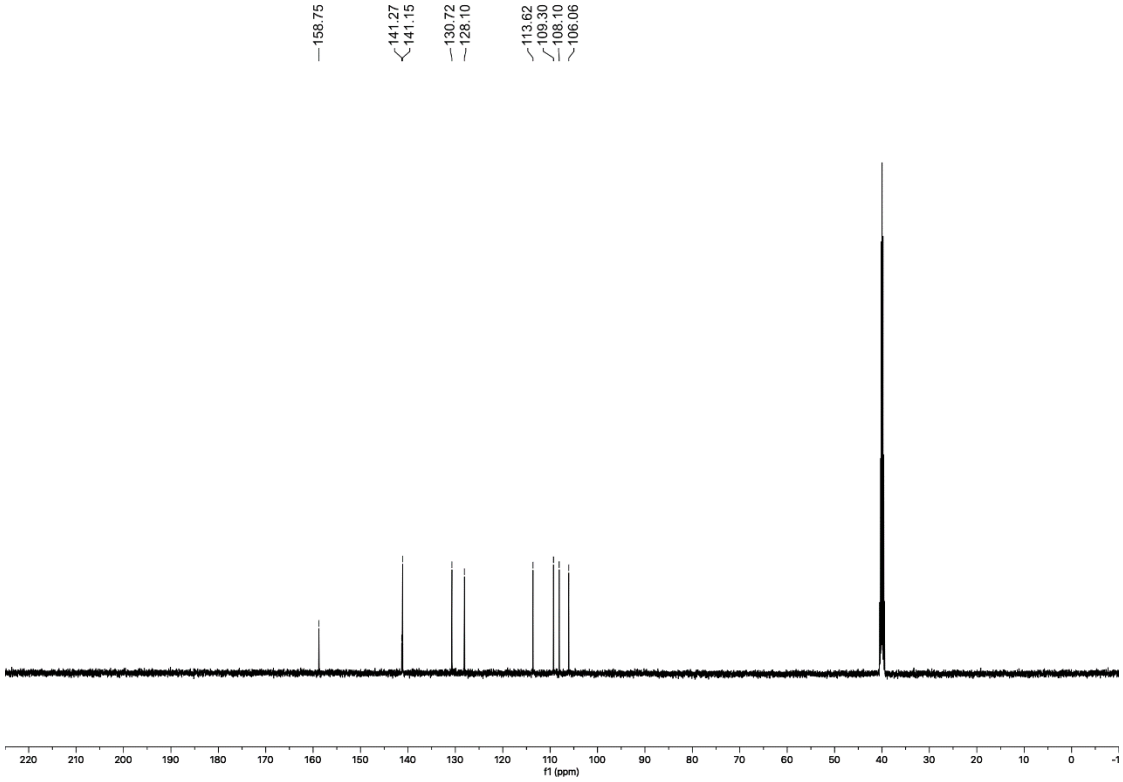


Figure S25. ^{1}H NMR spectrum of 3-(1*H*-pyrazol-1-yl)phenyl pivalate, **1d** (400 MHz, $CDCl_3$).

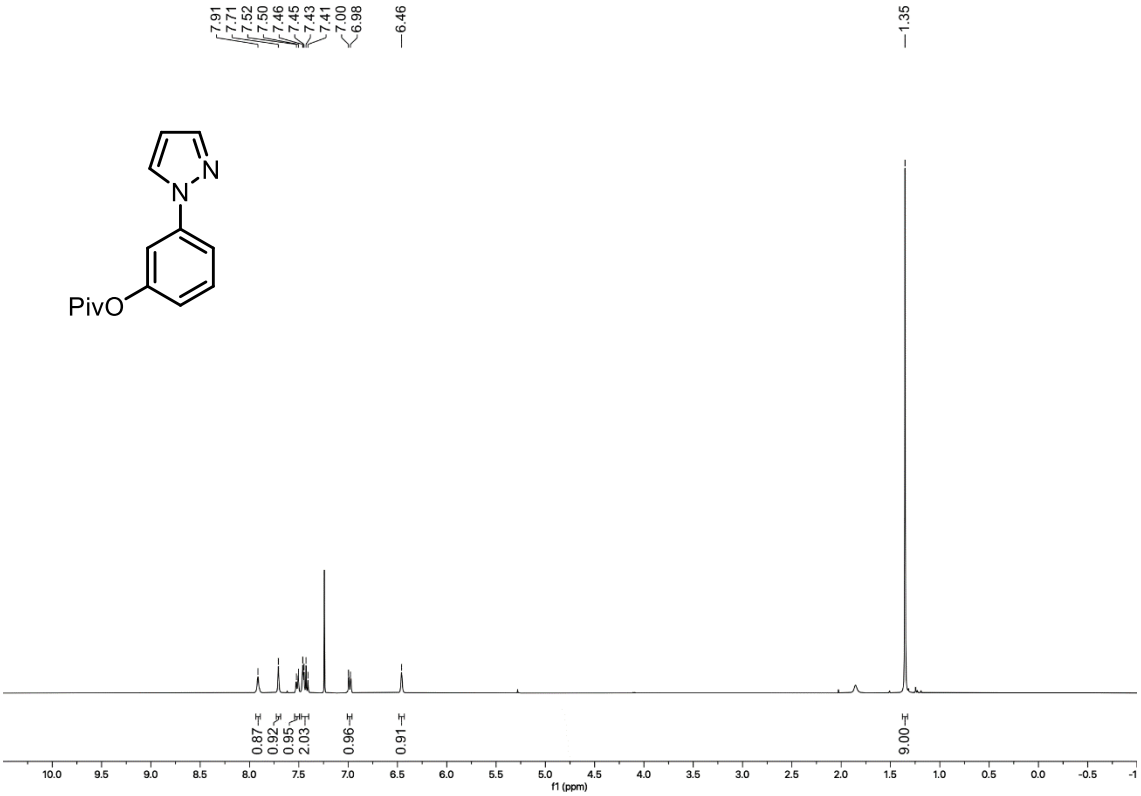


Figure S26. ^{13}C{^{1}H} NMR spectrum of 3-(1*H*-pyrazol-1-yl)phenyl pivalate, **1d** (126 MHz, $CDCl_3$).

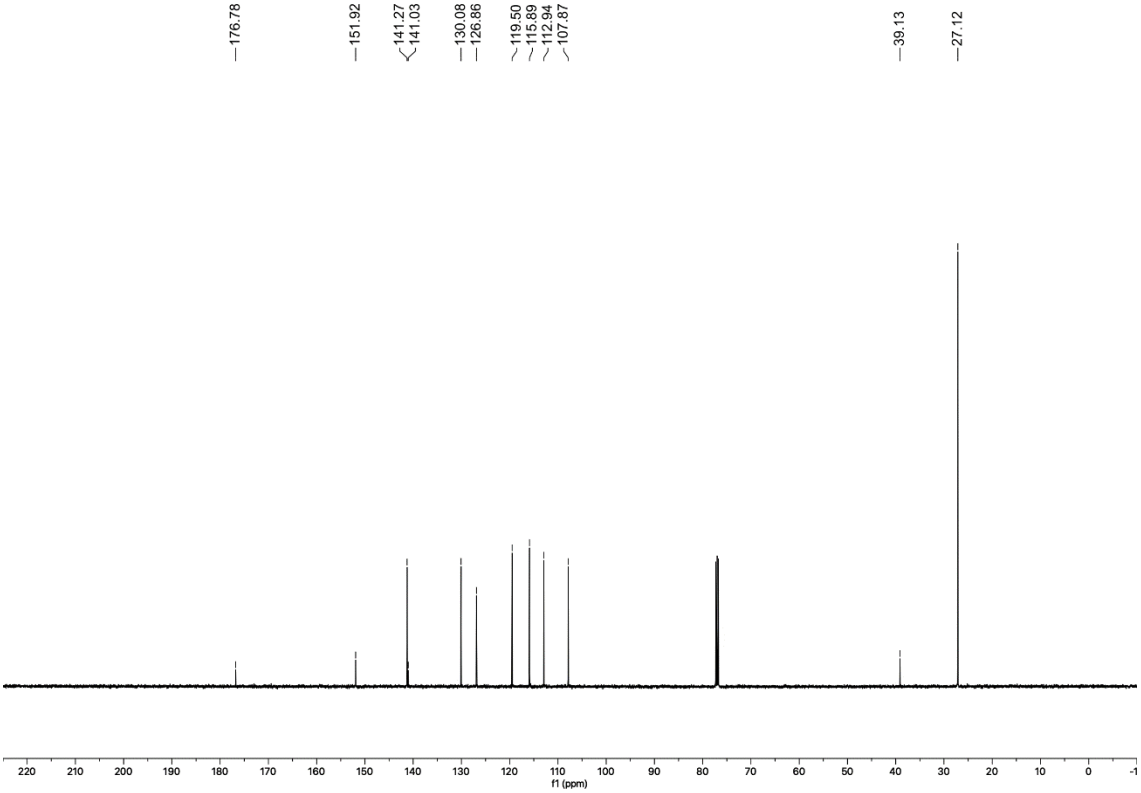


Figure S27. ^{1}H NMR spectrum of (*E*)-1-fluoro-2-(2-methylbuta-1,3-dien-1-yl)benzene, **2i** (400 MHz, $CDCl_3$).

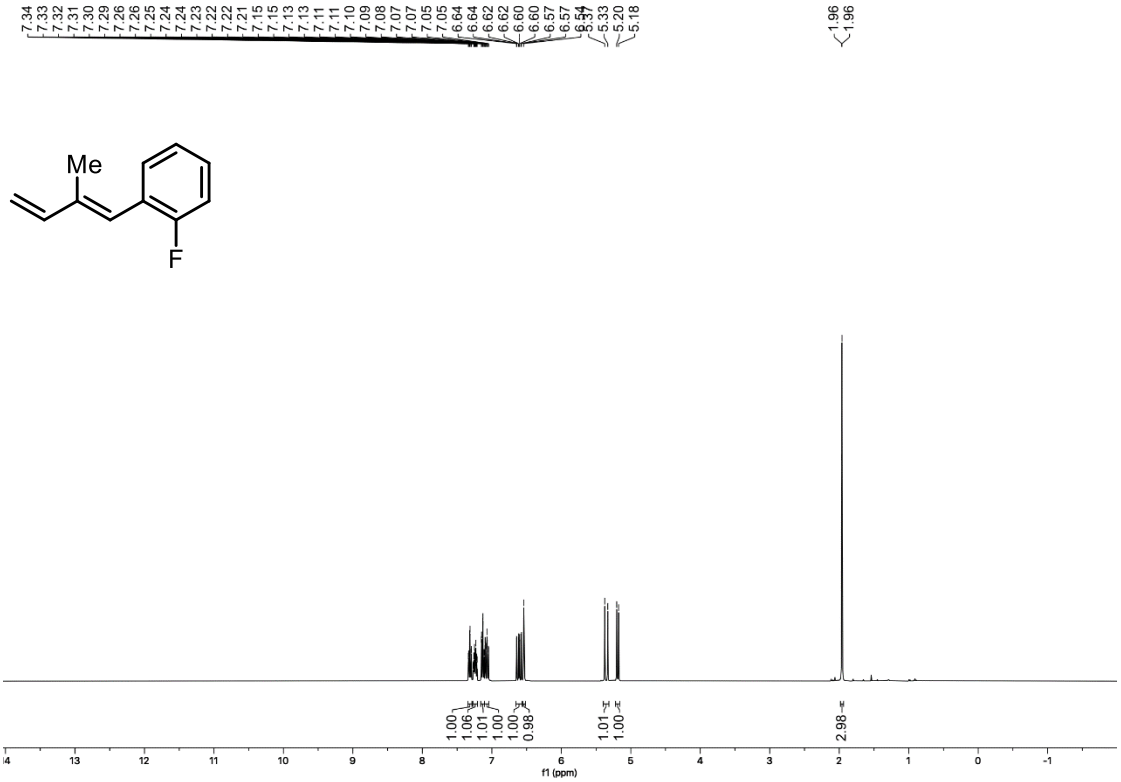


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-fluoro-2-(2-methylbuta-1,3-dien-1-yl)benzene, **2i** (101 MHz, $CDCl_3$).

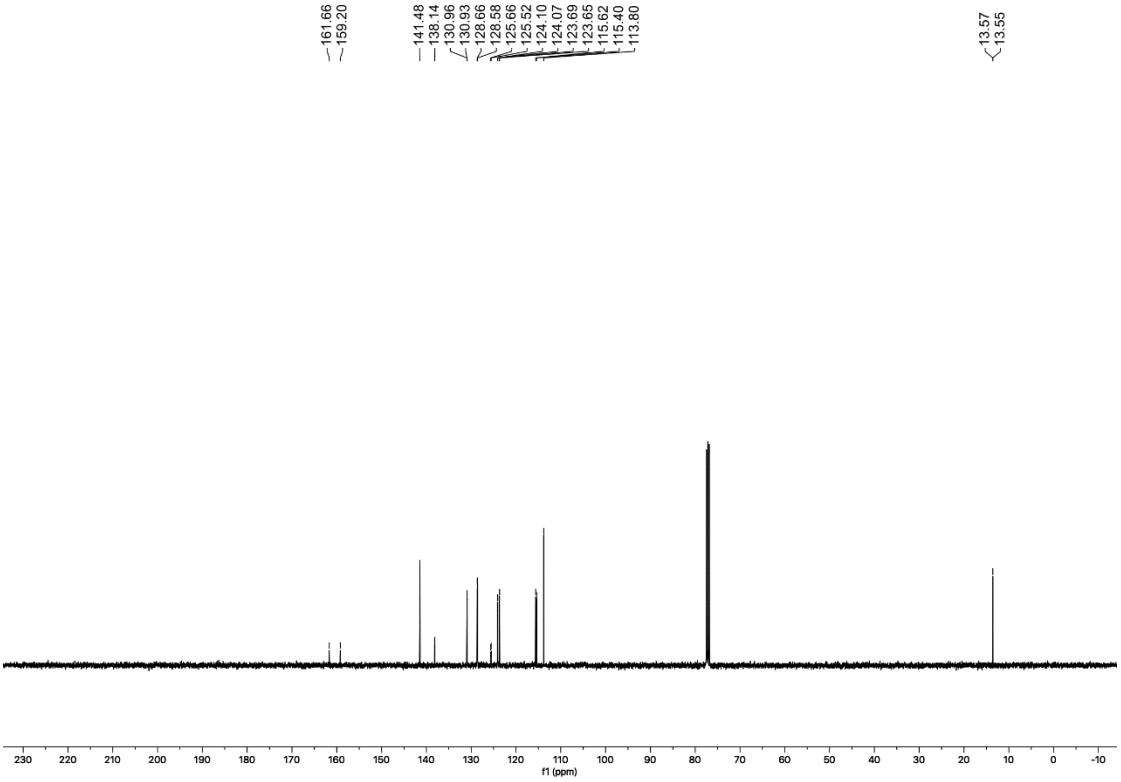


Figure S29. ^{19}F NMR spectrum of (*E*)-1-fluoro-2-(2-methylbuta-1,3-dien-1-yl)benzene, **2i** (101 MHz, $CDCl_3$).

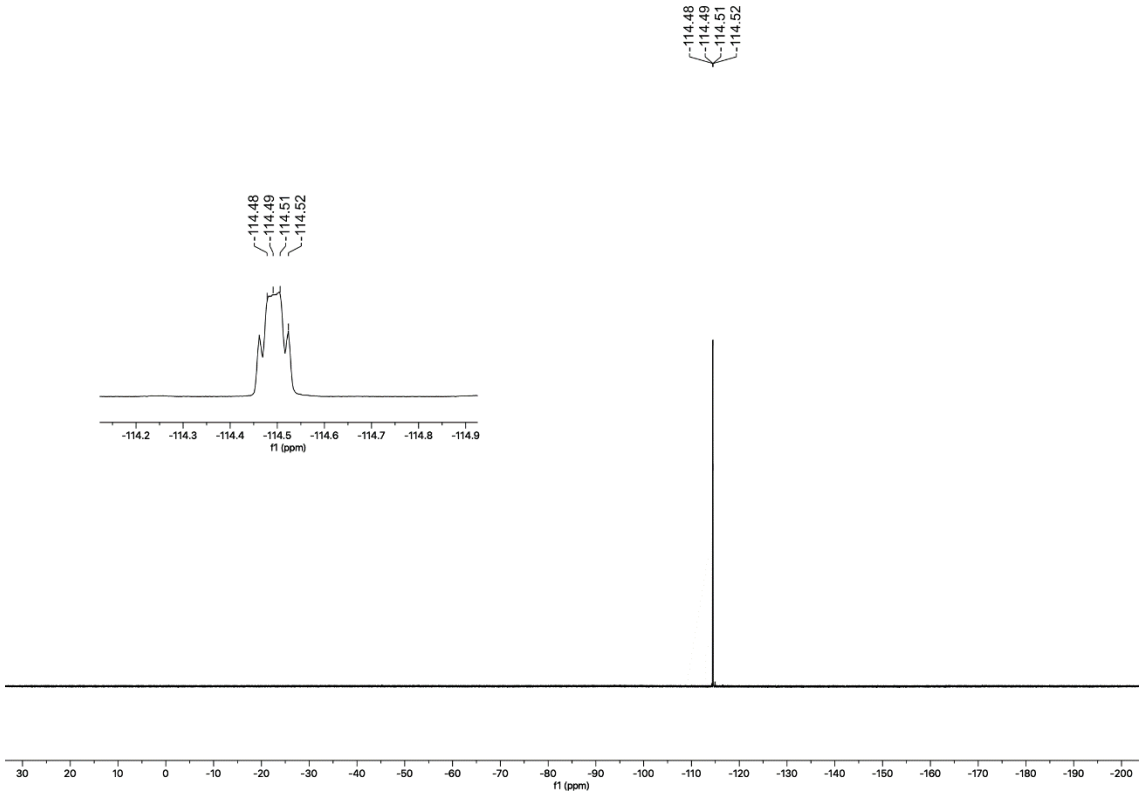


Figure S30. ^{1}H NMR spectrum of (*E*)-1-bromo-4-(2-methylbuta-1,3-dien-1-yl)benzene, **2j** (500 MHz, $CDCl_3$).

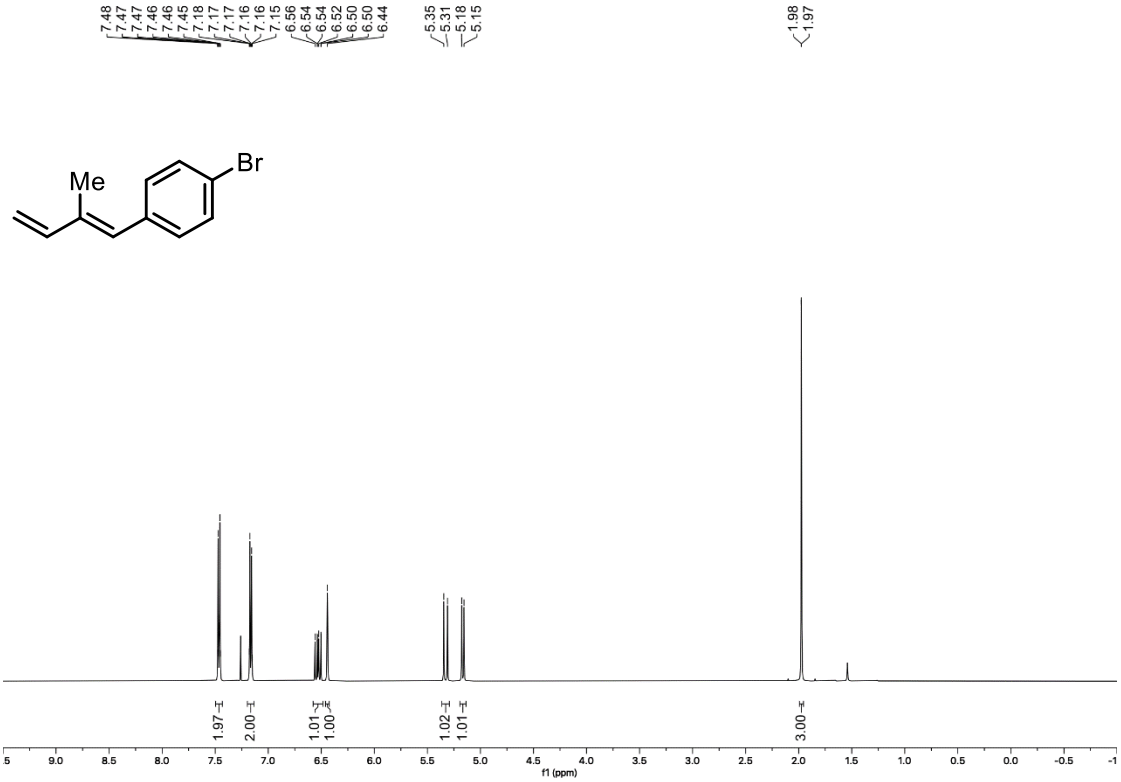


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-bromo-4-(2-methylbuta-1,3-dien-1-yl)benzene, **2j** (126 MHz, $CDCl_3$).

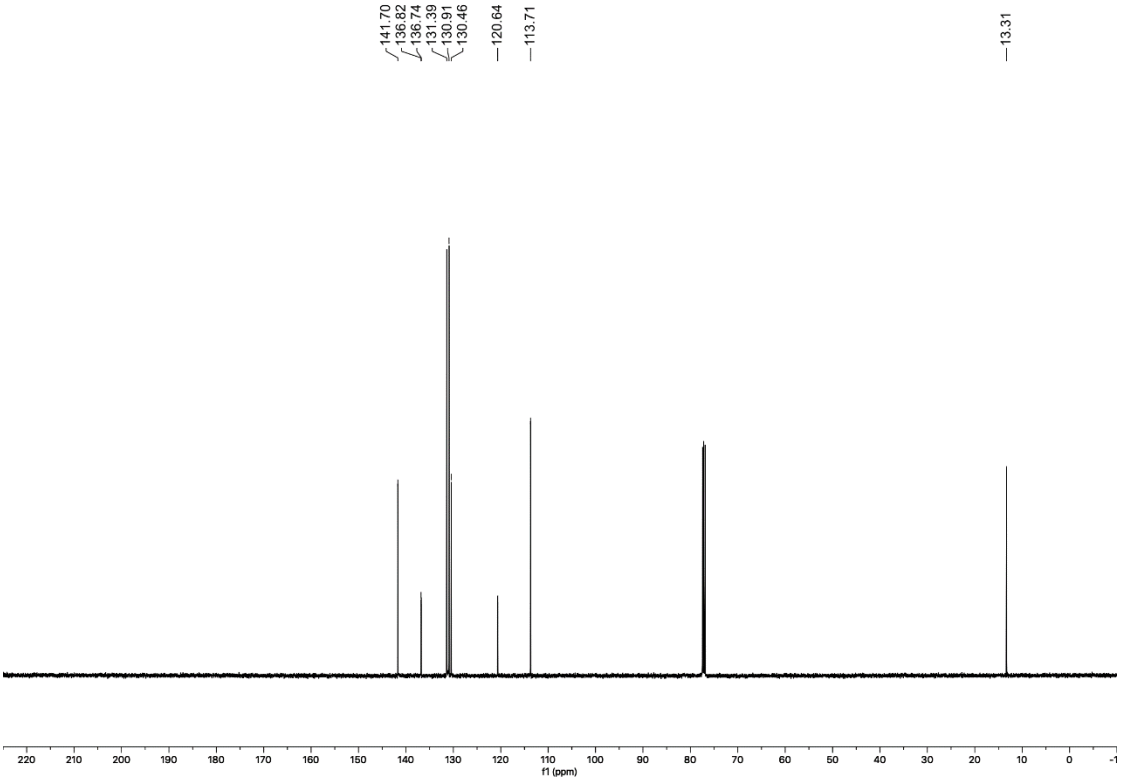


Figure S32. ^{1}H NMR spectrum of (*E*)-2-methyl-3-(3-nitrophenyl)acrylaldehyde (400 MHz, $CDCl_3$).

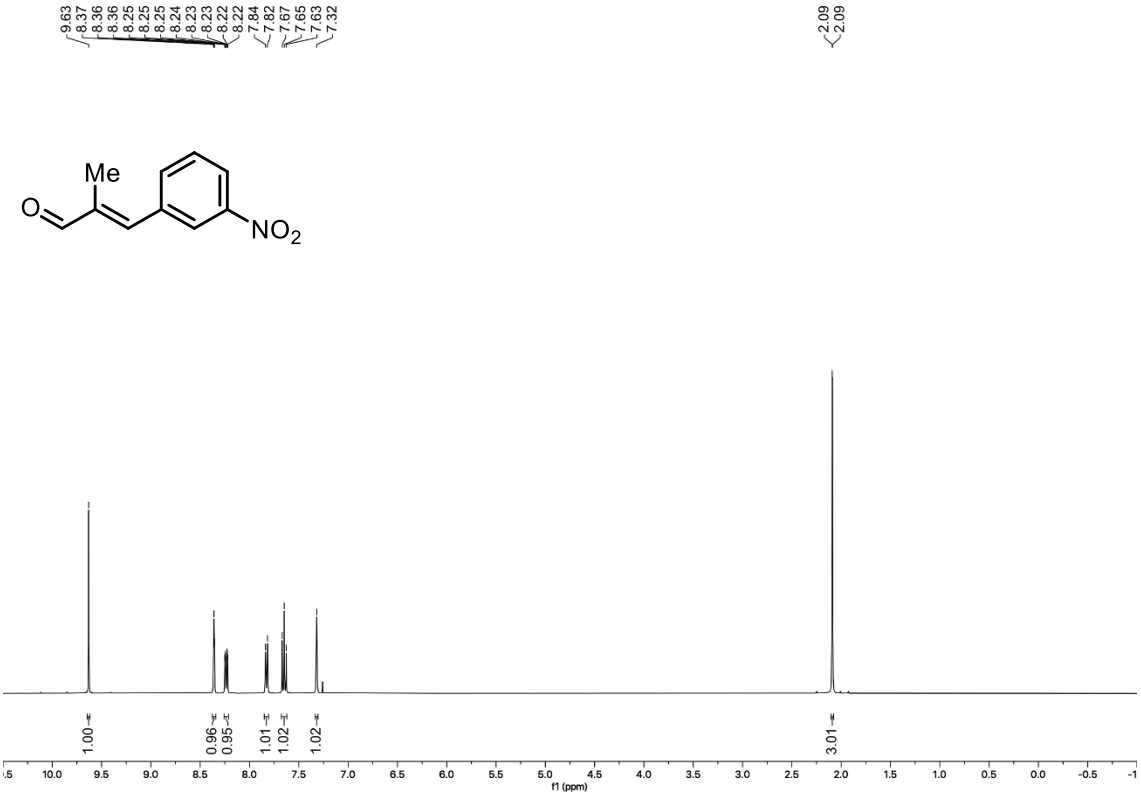


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-methyl-3-(3-nitrophenyl)acrylaldehyde (101 MHz, $CDCl_3$).

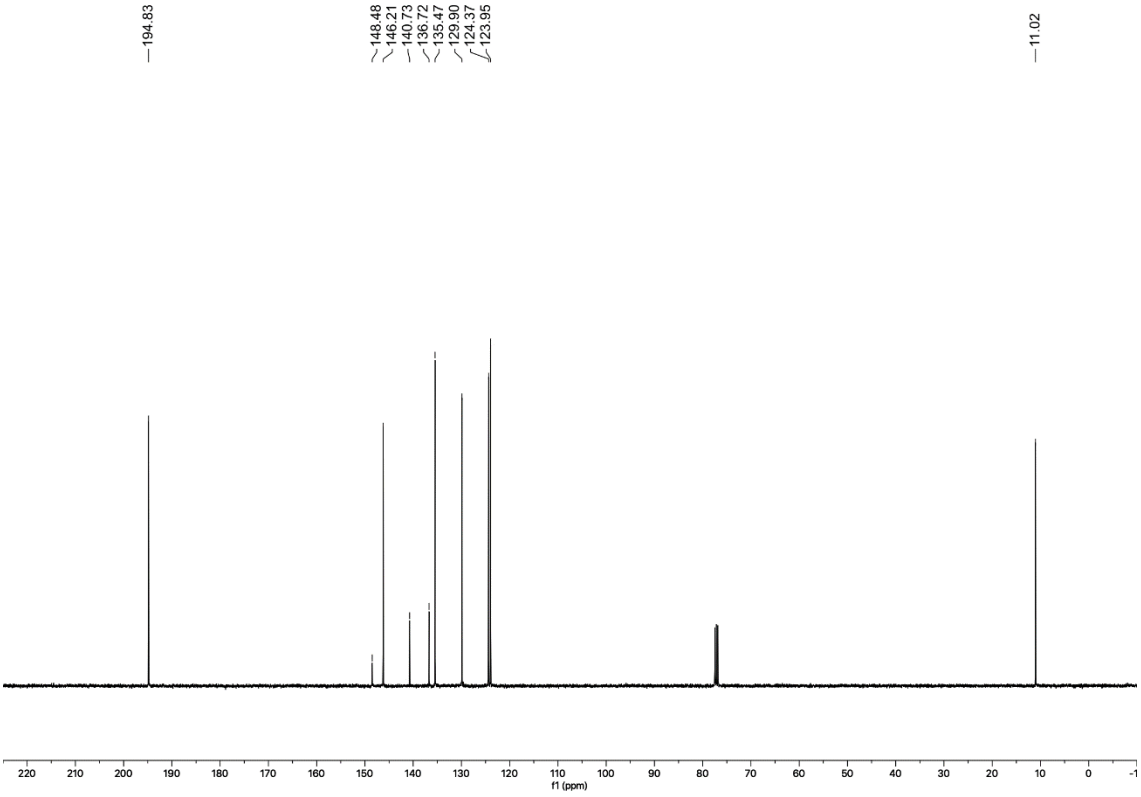


Figure S34. ^{1}H NMR spectrum of (*E*)-1-(2-methylbuta-1,3-dien-1-yl)-3-nitrobenzene, **2l** (400 MHz, $CDCl_3$).

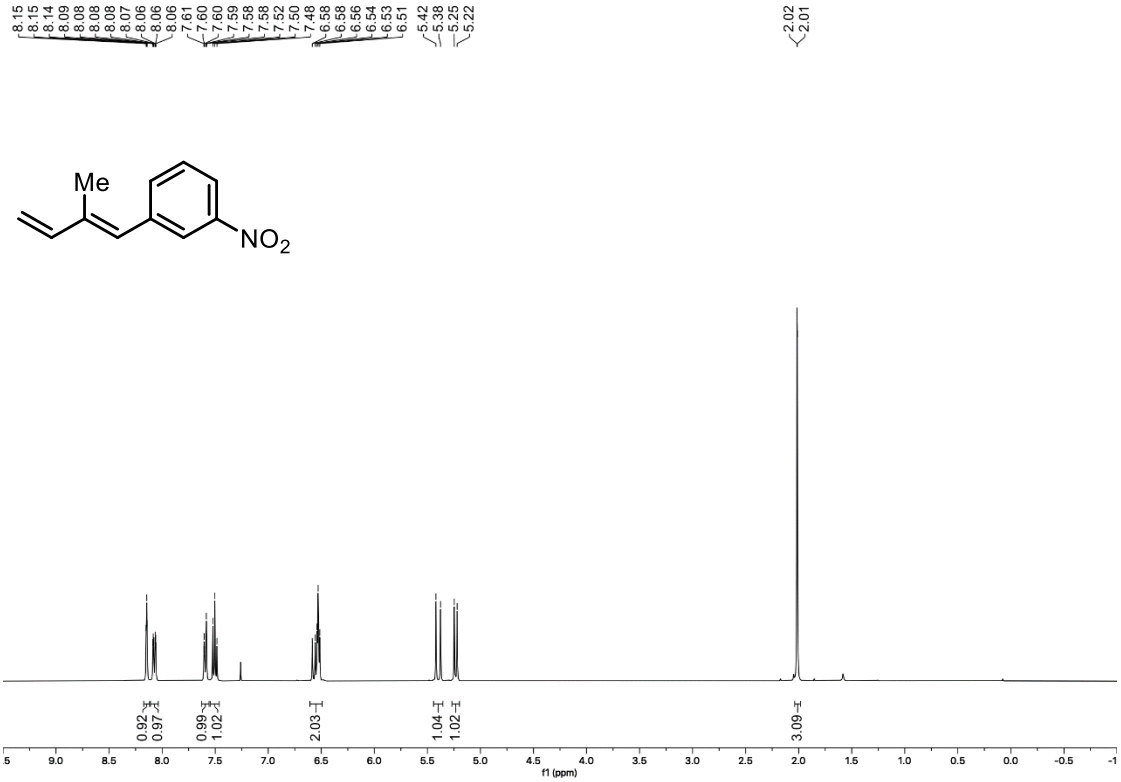


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-(2-methylbuta-1,3-dien-1-yl)-3-nitrobenzene, **2l** (101 MHz, $CDCl_3$).

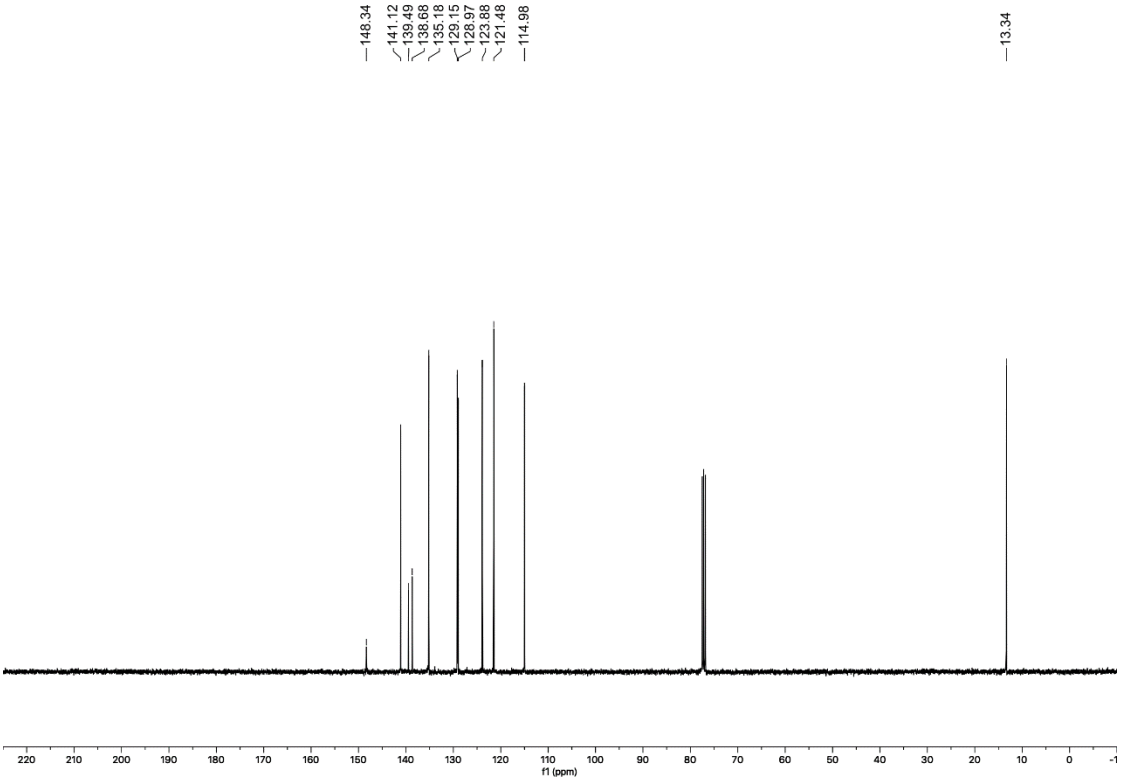


Figure S36. ^{1}H NMR spectrum of methyl (*E*)-3-(2-methyl-3-oxoprop-1-en-1-yl)benzoate (400 MHz, $CDCl_3$).

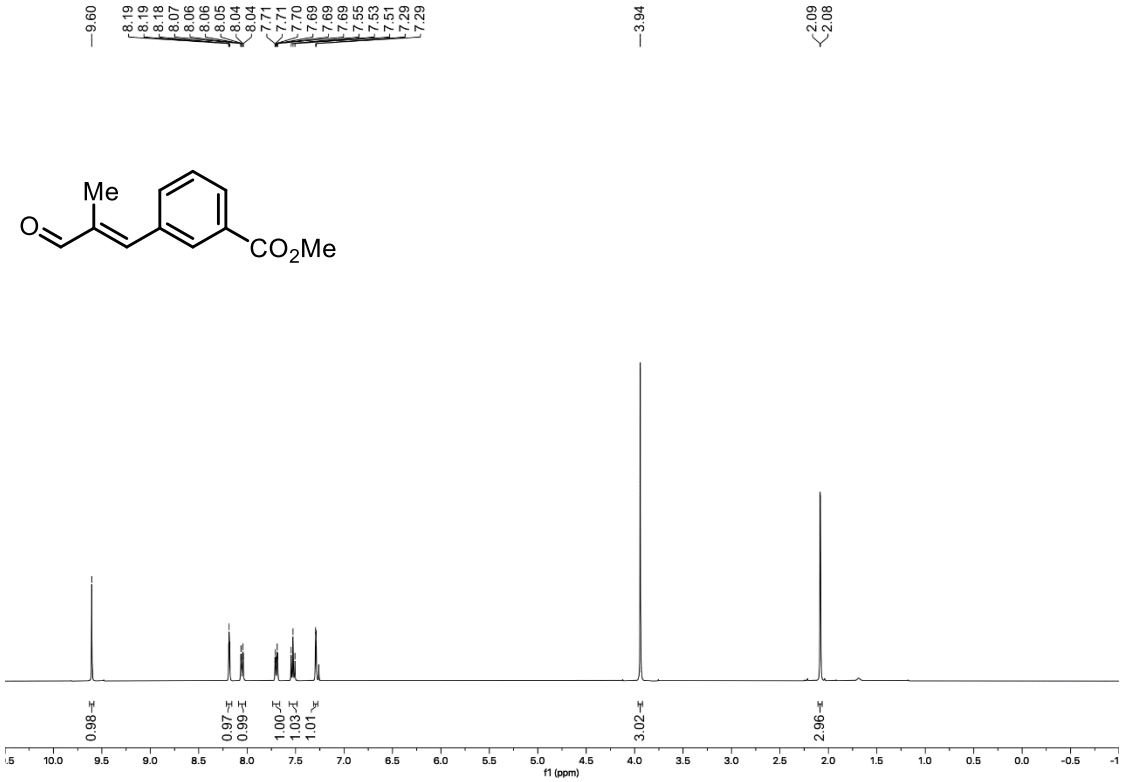


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*E*)-3-(2-methyl-3-oxoprop-1-en-1-yl)benzoate (101 MHz, $CDCl_3$)

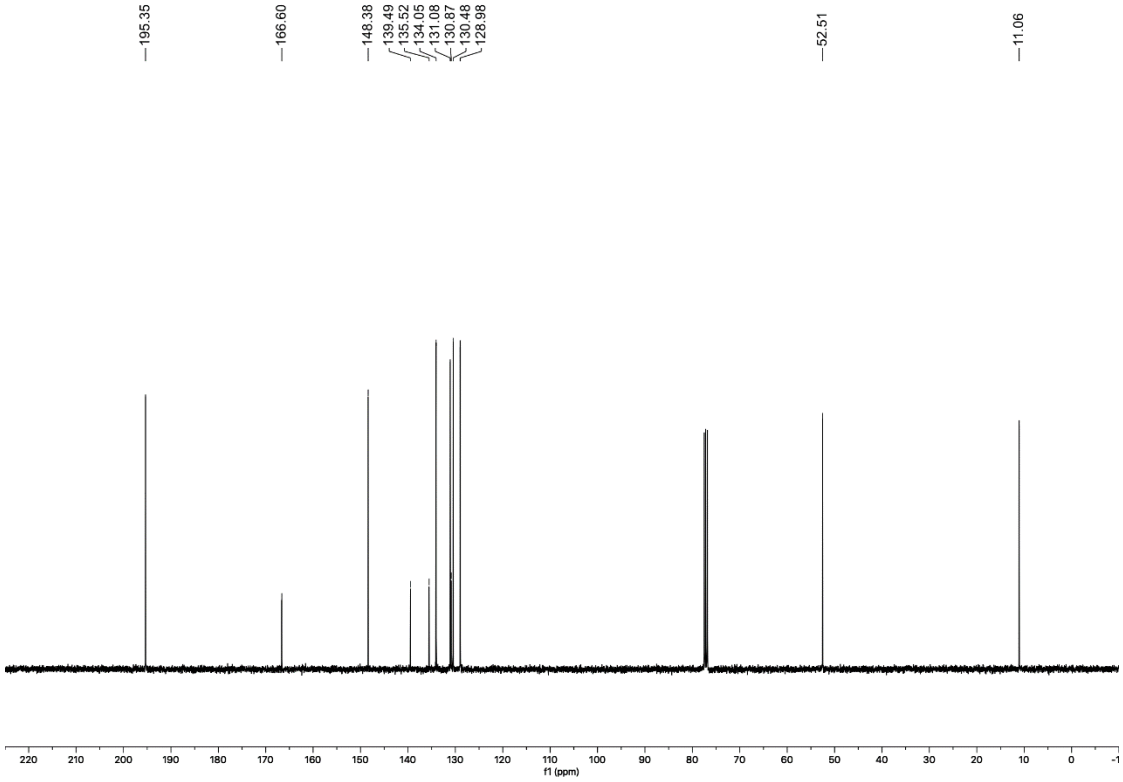


Figure S38. ^{1}H NMR spectrum of methyl (*E*)-3-(2-methylbuta-1,3-dien-1-yl)benzoate, **2n** (500 MHz, $CDCl_3$).

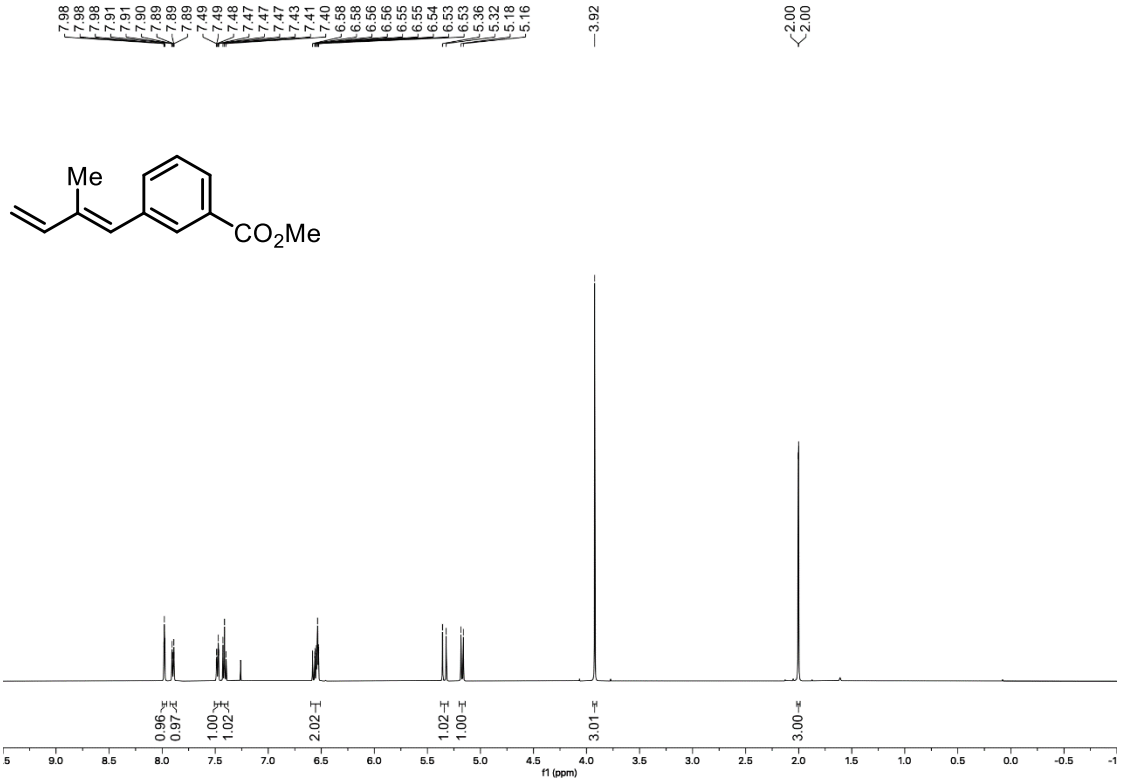


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*E*)-3-(2-methylbuta-1,3-dien-1-yl)benzoate, **2n** (126 MHz, $CDCl_3$).

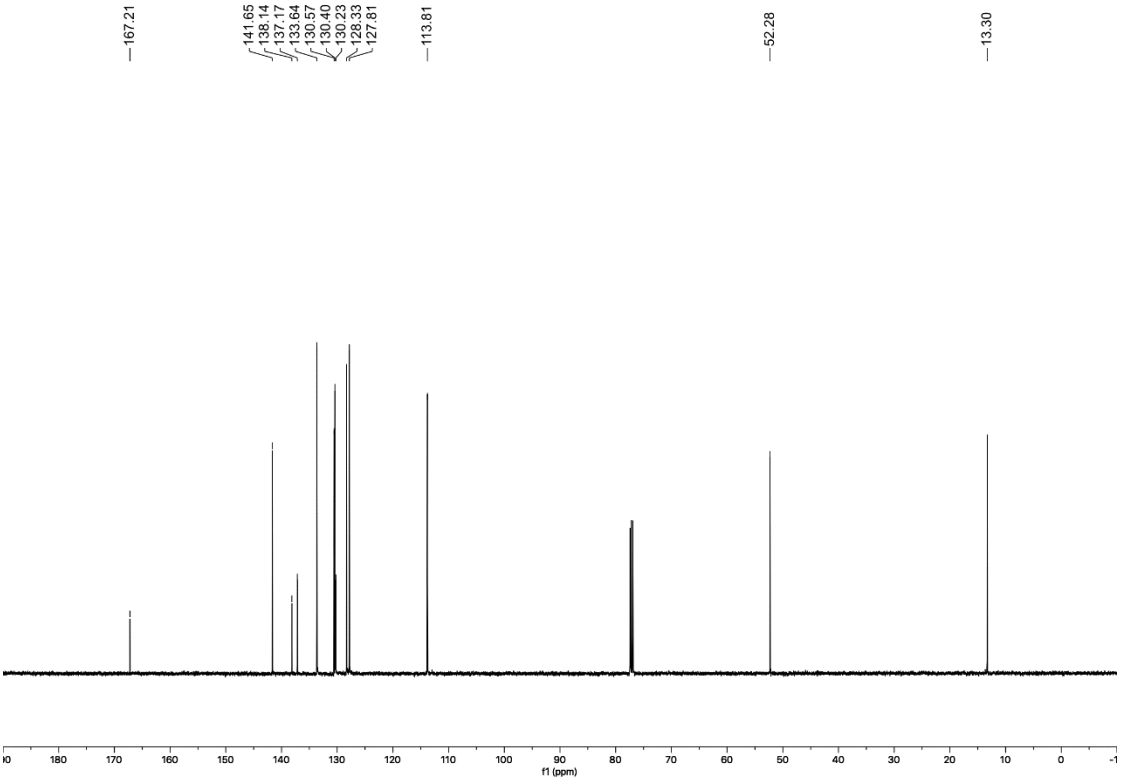


Figure S40. ^{1}H NMR spectrum of (*E*)-1-methyl-3-(2-methylbuta-1,3-dien-1-yl)benzene, **2o** (400 MHz, $CDCl_3$).

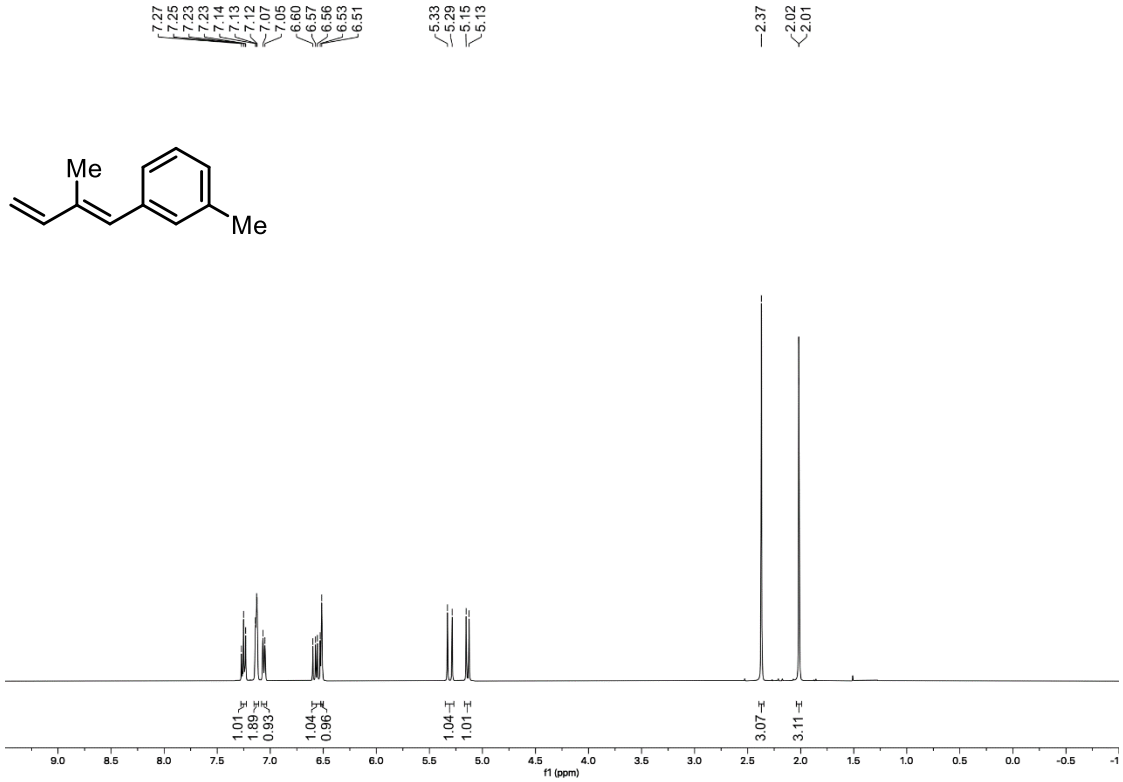


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-methyl-3-(2-methylbuta-1,3-dien-1-yl)benzene, **2o** (126 MHz, $CDCl_3$)

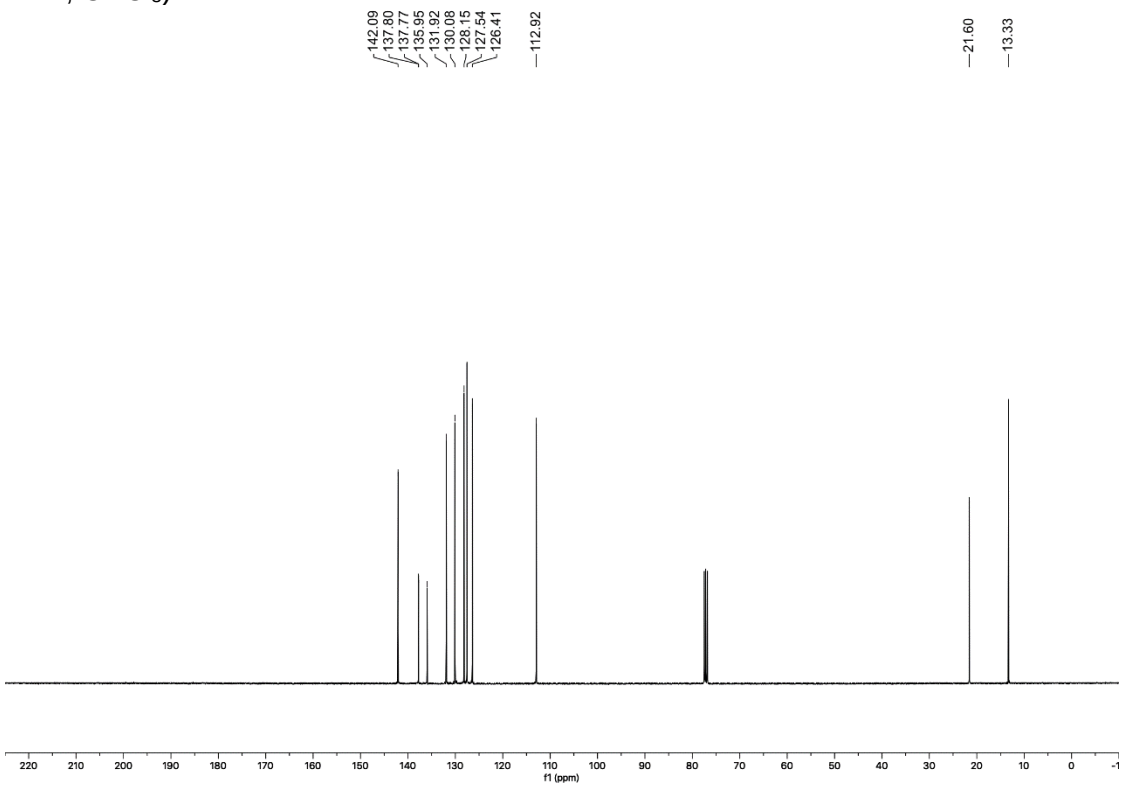


Figure S42. ^{1}H NMR spectrum of (*E*)-1-methoxy-3-(2-methylbuta-1,3-dien-1-yl)benzene, **2p** (400 MHz, $CDCl_3$).

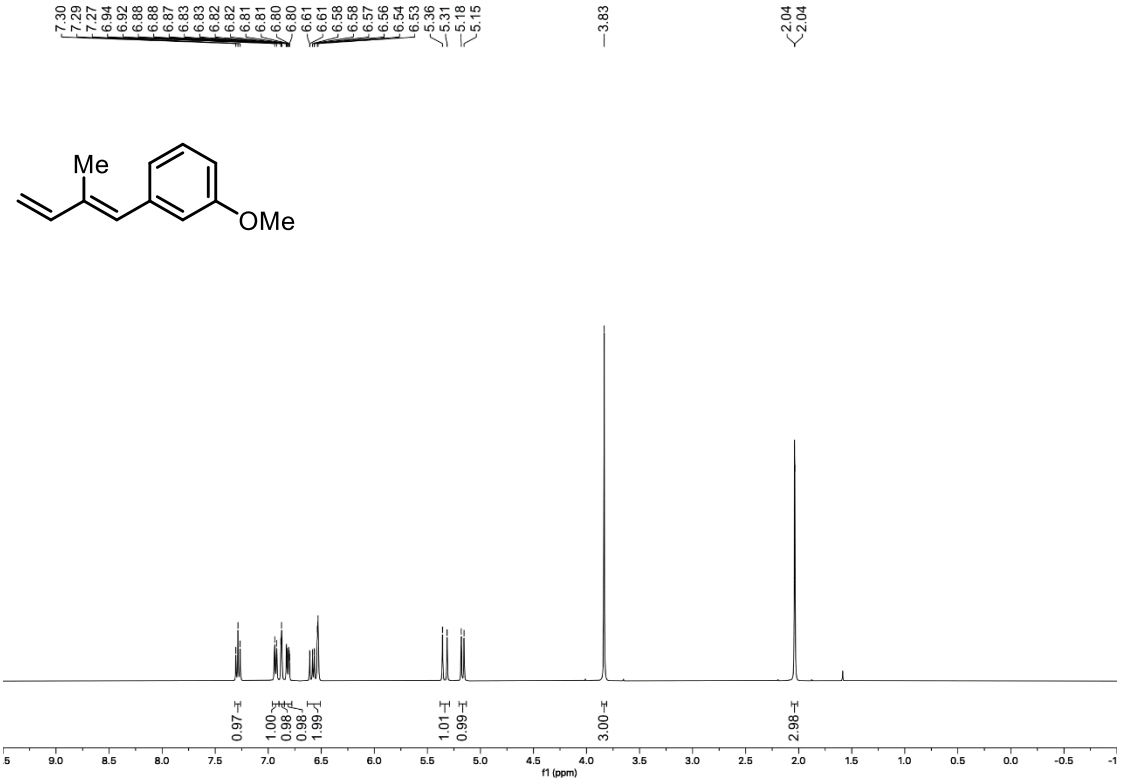


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-methoxy-3-(2-methylbuta-1,3-dien-1-yl)benzene, **2p** (101 MHz, $CDCl_3$).

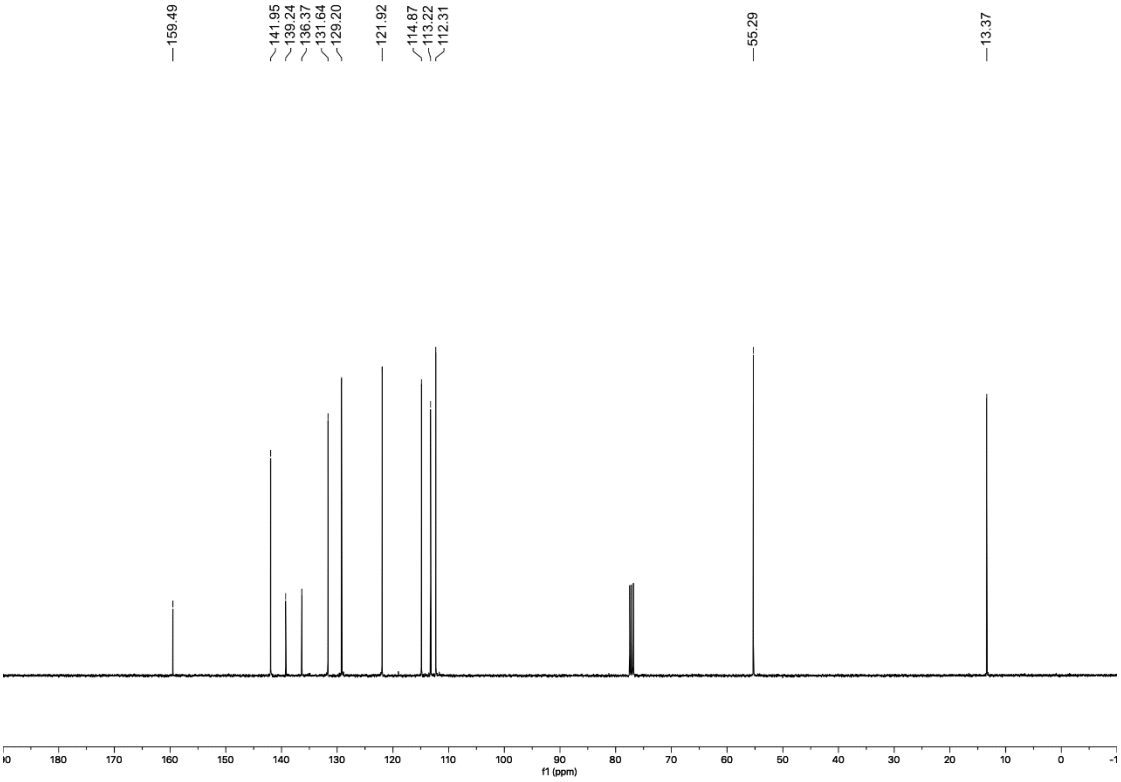


Figure S44. ^{1}H NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4a** (500 MHz, $CDCl_3$).

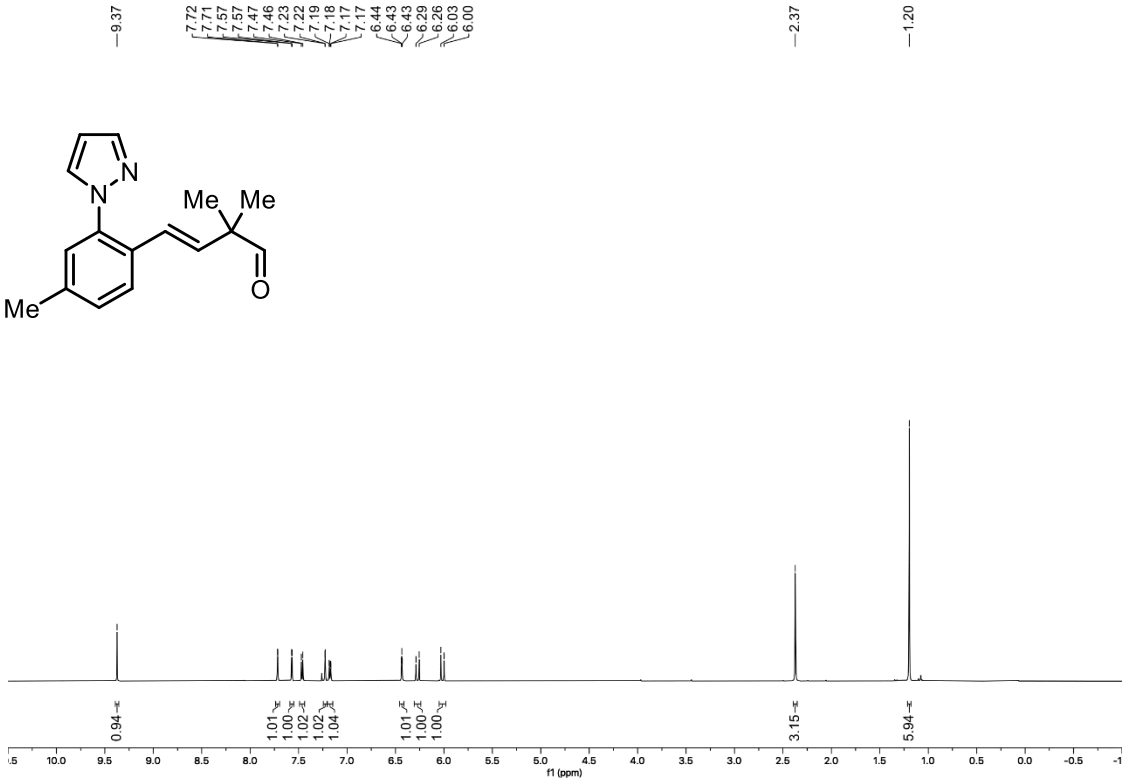


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4a** (126 MHz, $CDCl_3$).

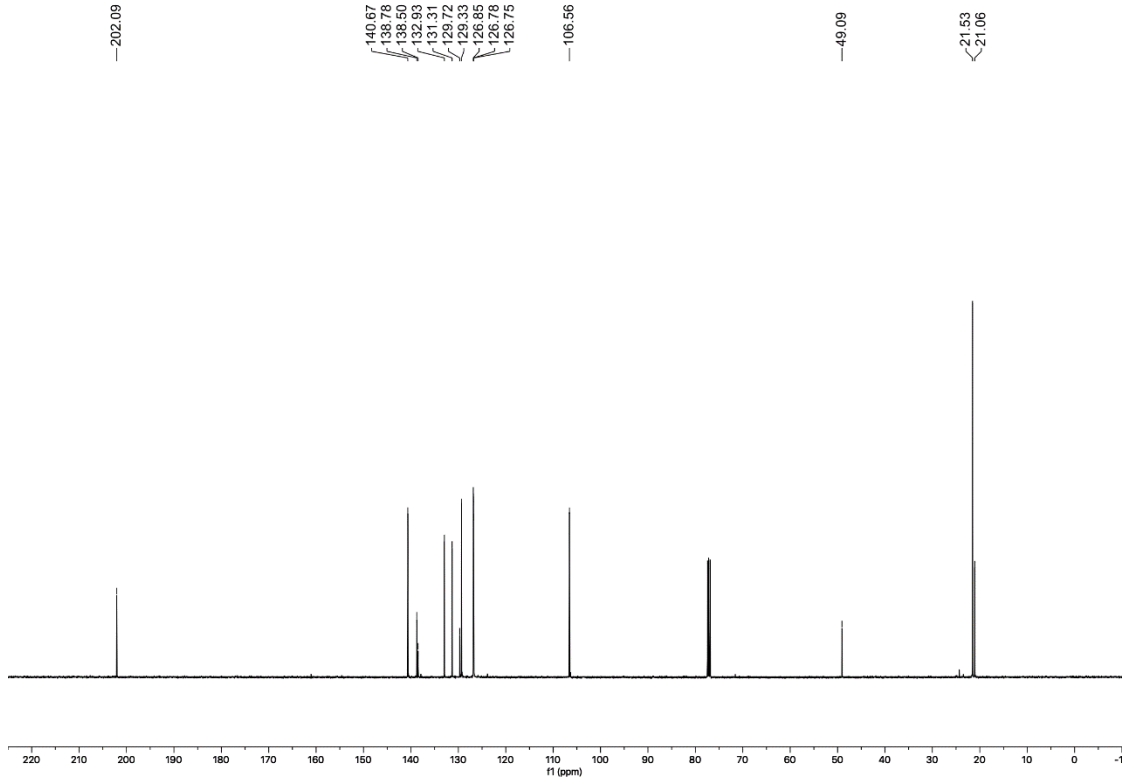


Figure S46. ^{1}H NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-4-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4b** (500 MHz, $CDCl_3$).

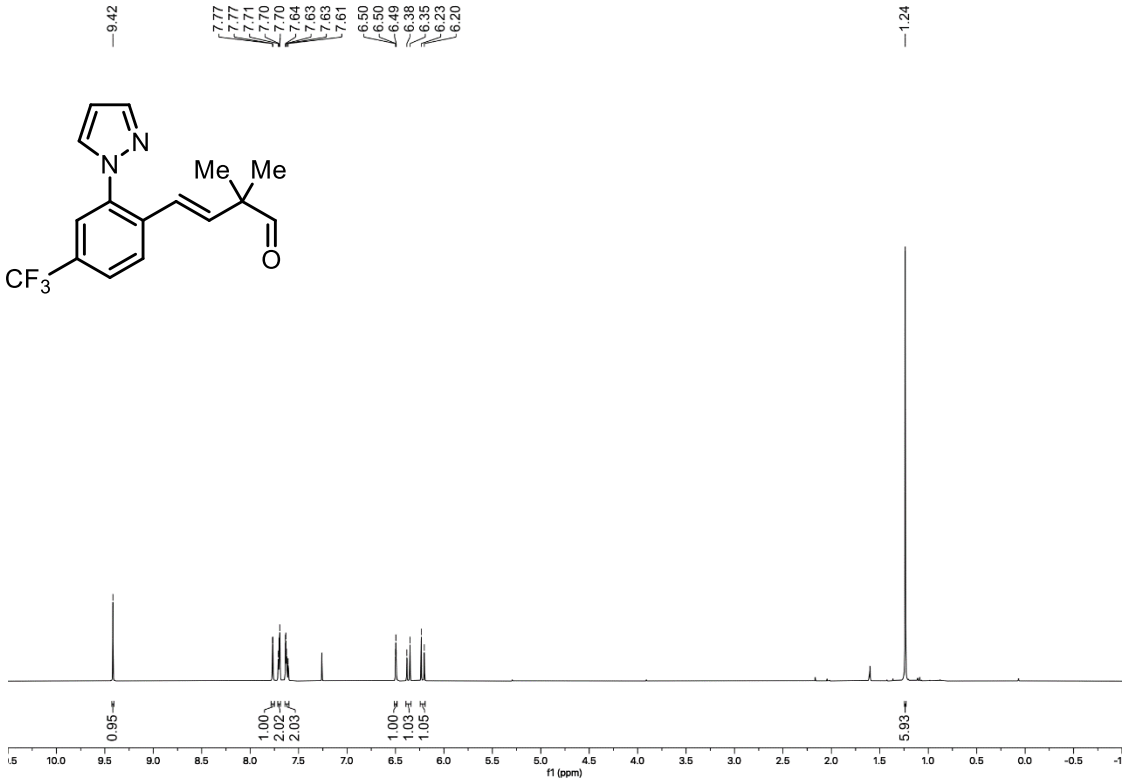


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-4-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4b** (126 MHz, $CDCl_3$).

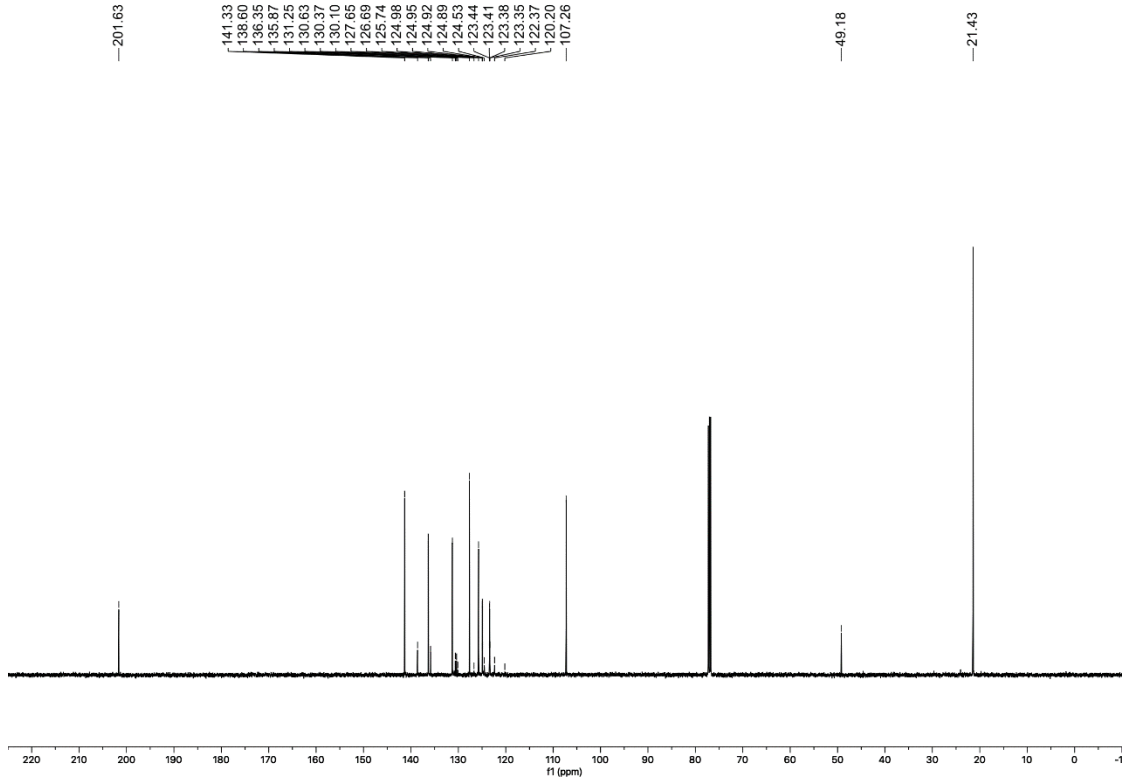


Figure S48. ^{19}F NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-4-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4b** (471 MHz, $CDCl_3$).

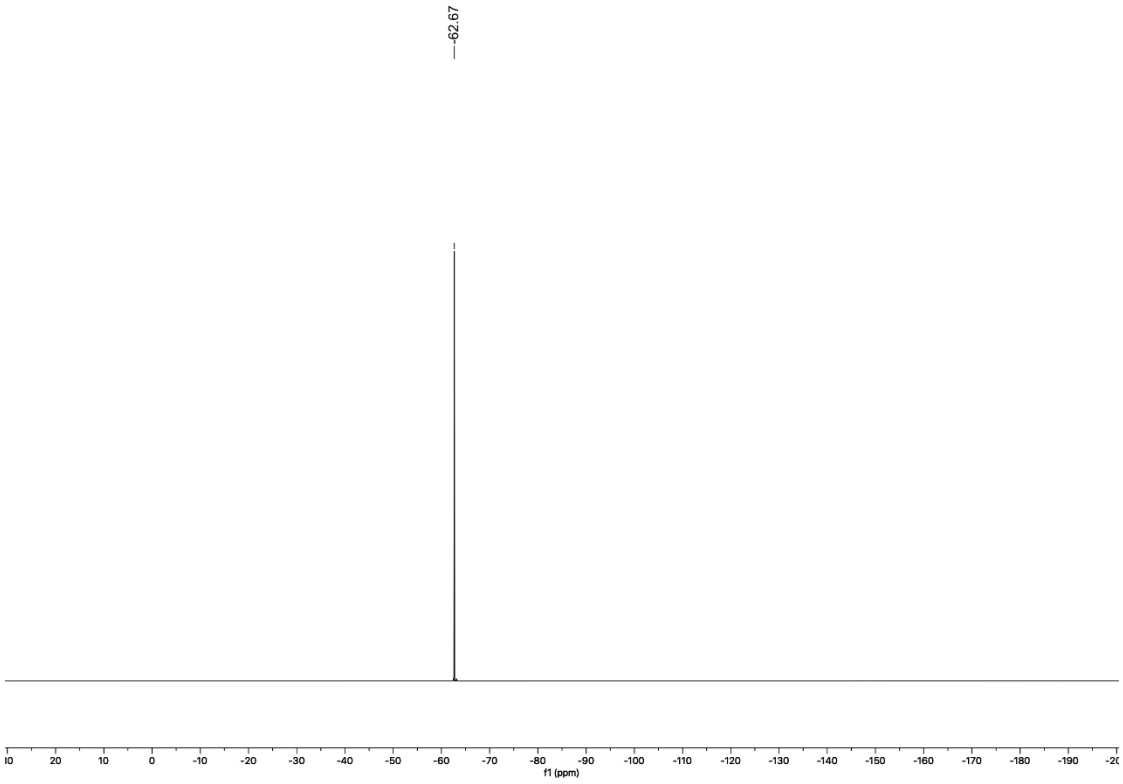


Figure S49. ^{1}H NMR spectrum of (*E*)-4-(4-bromo-2-(1*H*-pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal, **4c** (500 MHz, $CDCl_3$).

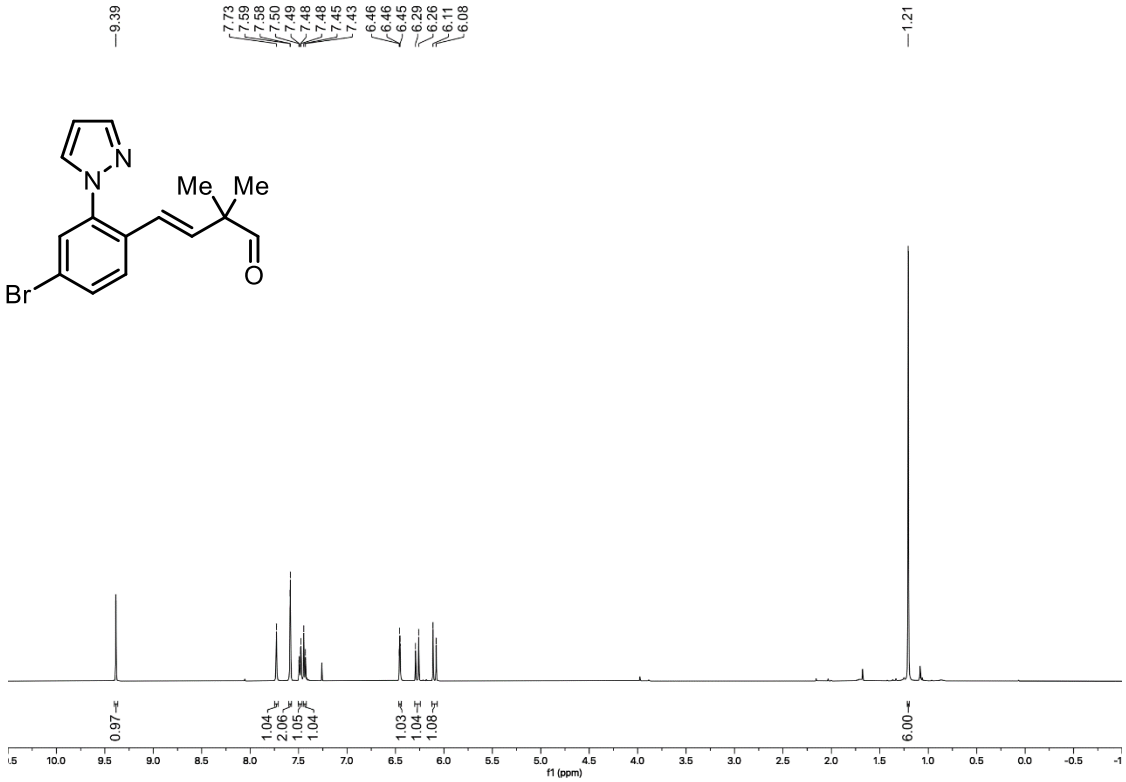


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-4-(4-bromo-2-(1*H*-pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal, **4c** (126 MHz, $CDCl_3$).

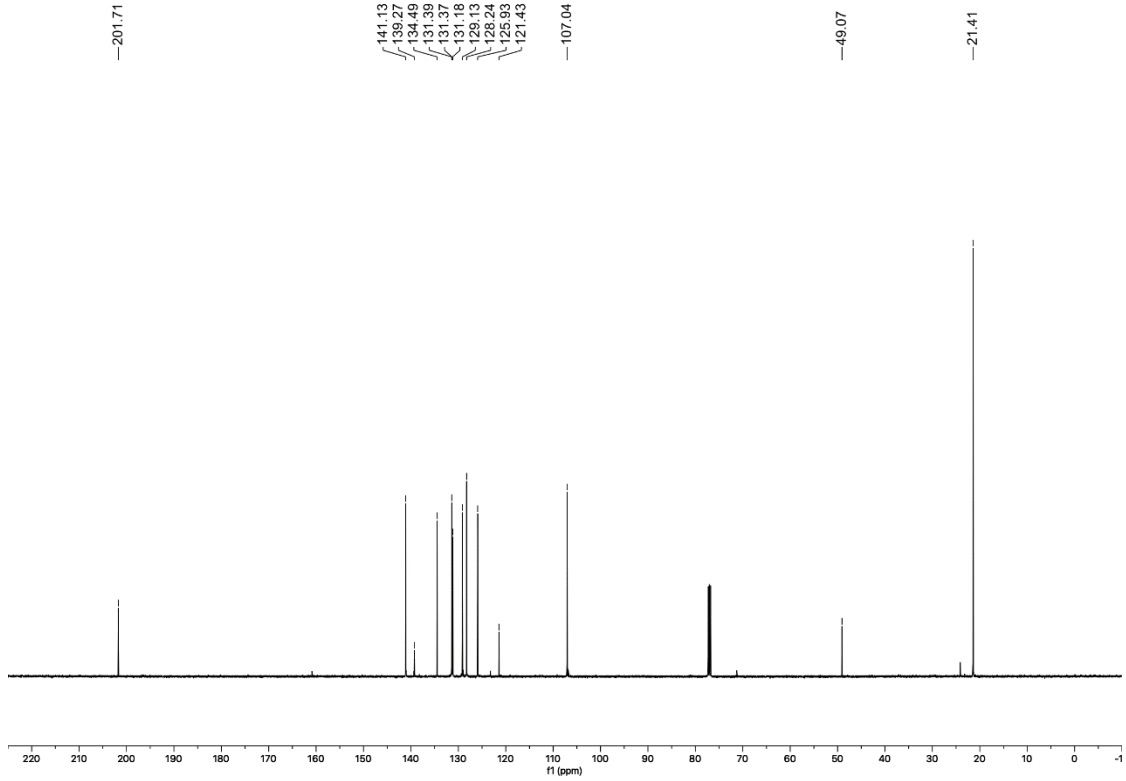


Figure S51. ^{1}H NMR spectrum of (*E*)-4-(3,3-dimethyl-4-oxobut-1-en-1-yl)-3-(1*H*-pyrazol-1-yl)phenyl pivalate, **4d** (500 MHz, $CDCl_3$).

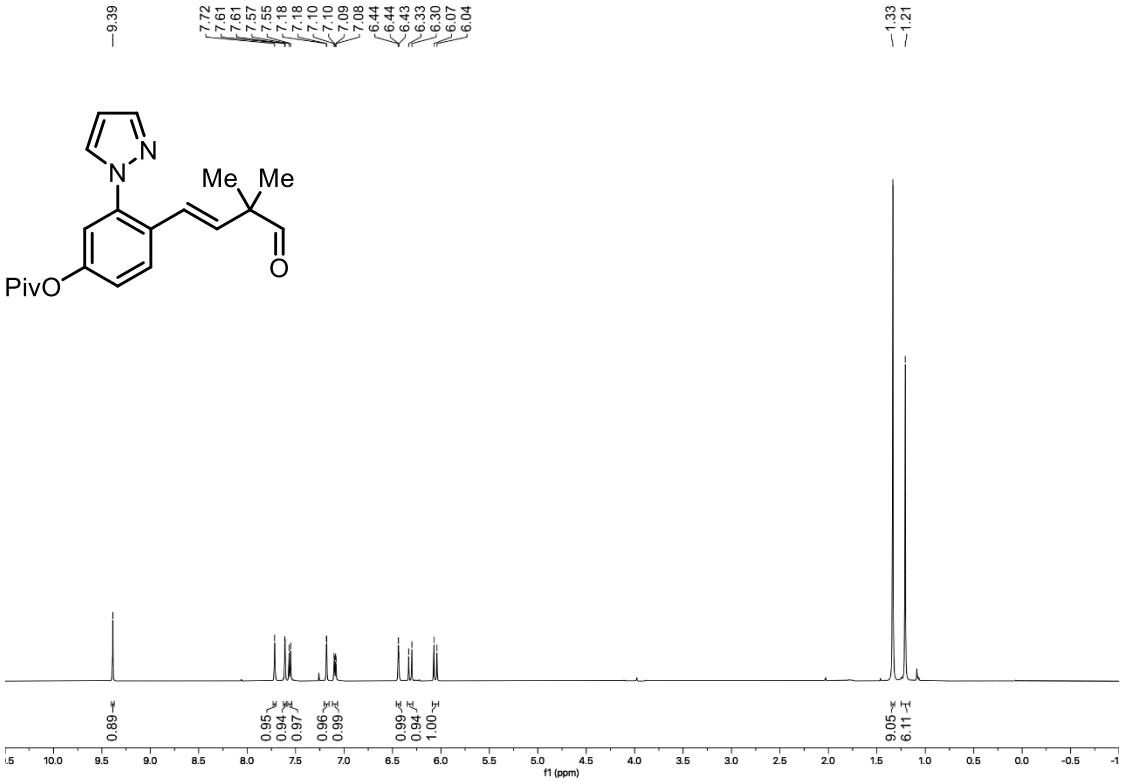


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-4-(3,3-dimethyl-4-oxobut-1-en-1-yl)-3-(1*H*-pyrazol-1-yl)phenyl pivalate, **4d** (126 MHz, $CDCl_3$).

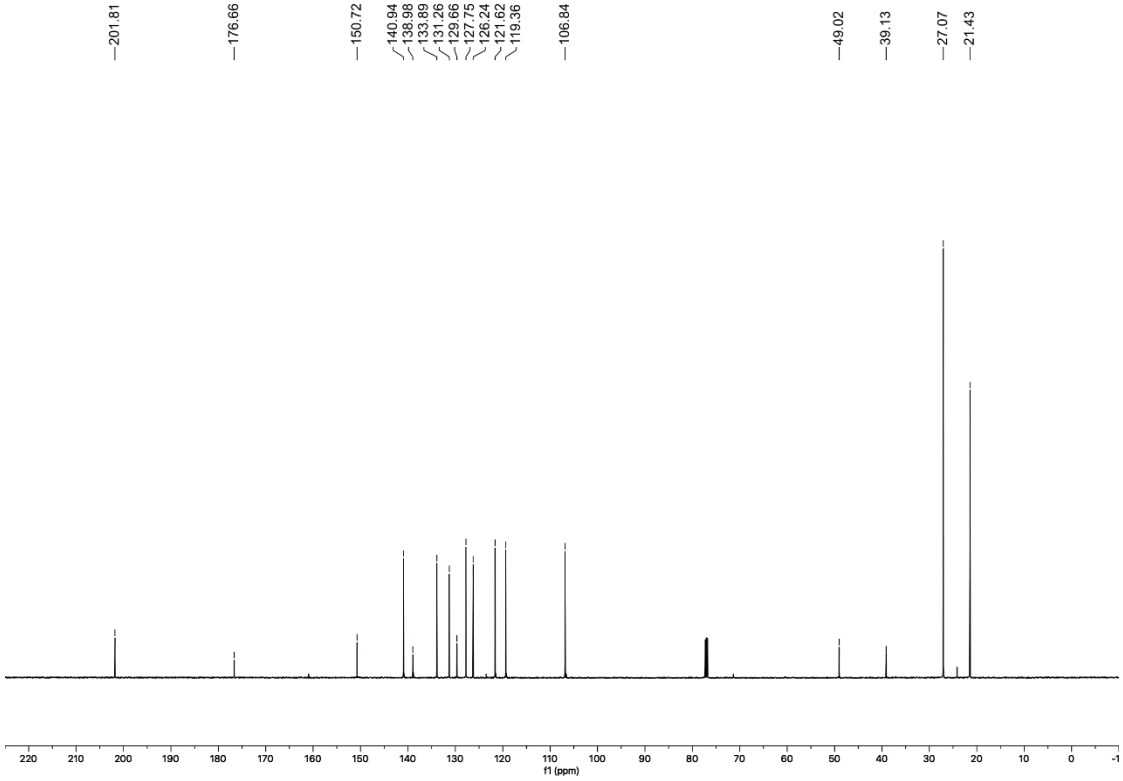


Figure S53. ^{1}H NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-5-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4e** (500 MHz, $CDCl_3$).

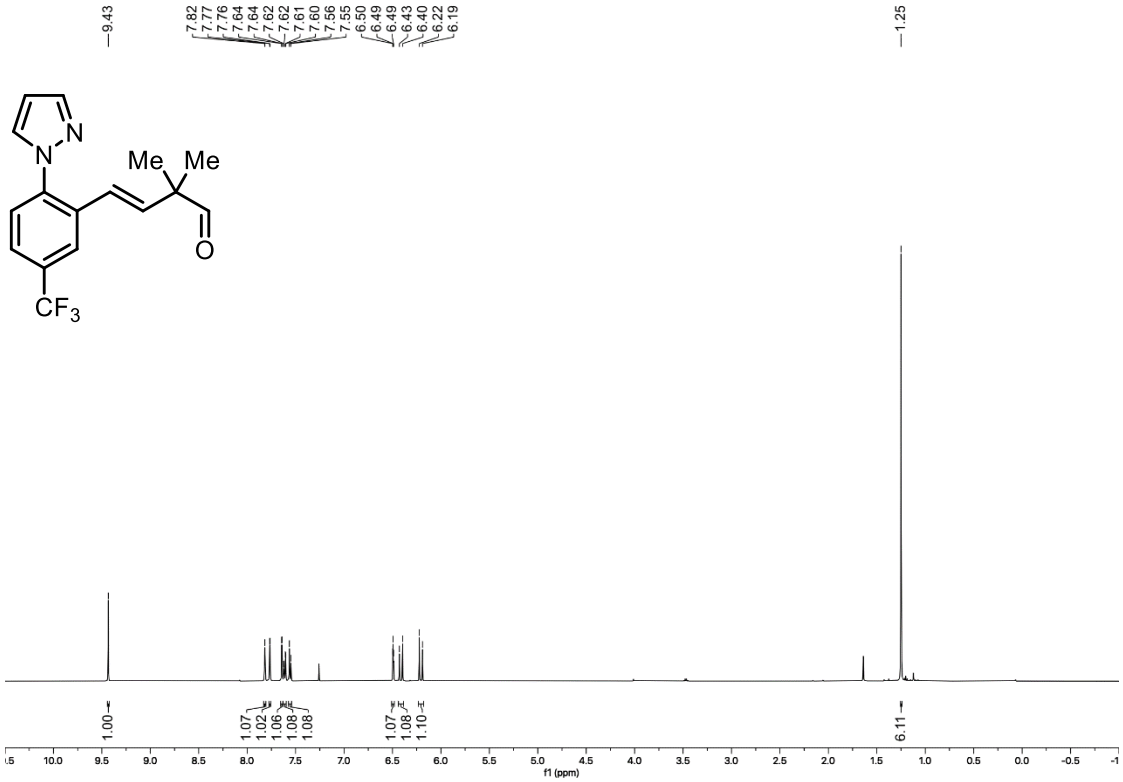


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-5-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4e** (126 MHz, $CDCl_3$).

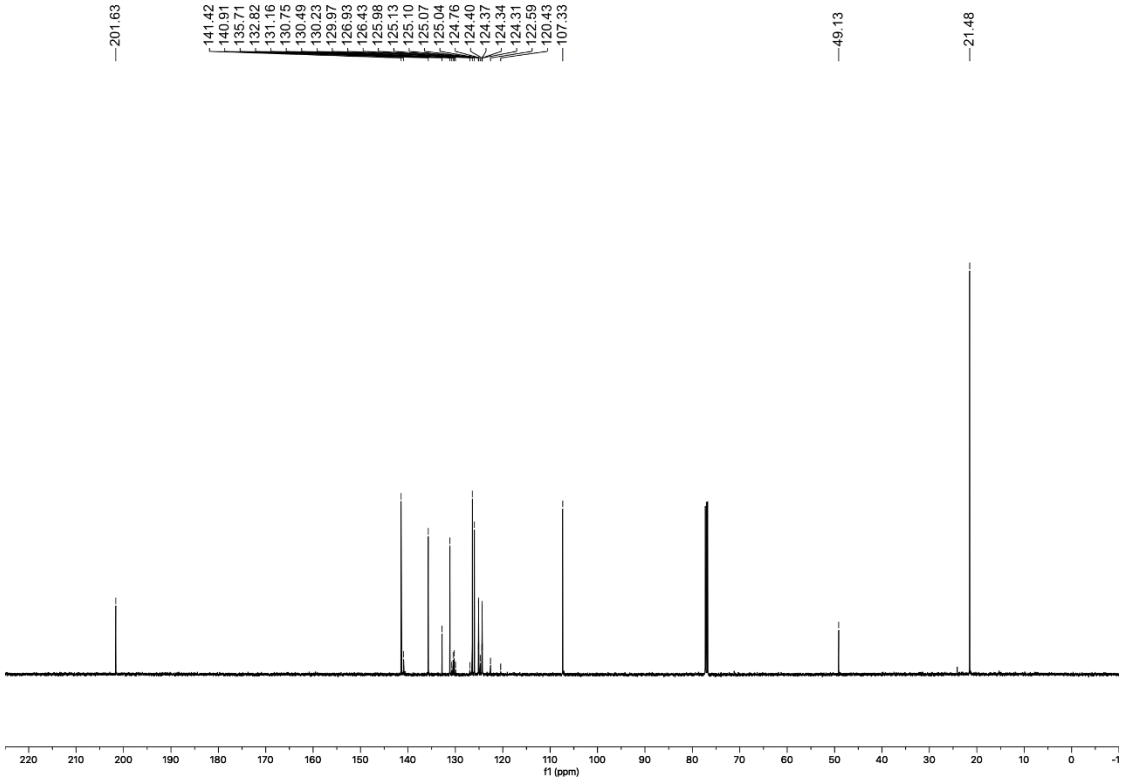


Figure S55. ^{19}F NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)-5-(trifluoromethyl)phenyl)-2,2-dimethylbut-3-enal, **4e** (471 MHz, $CDCl_3$).

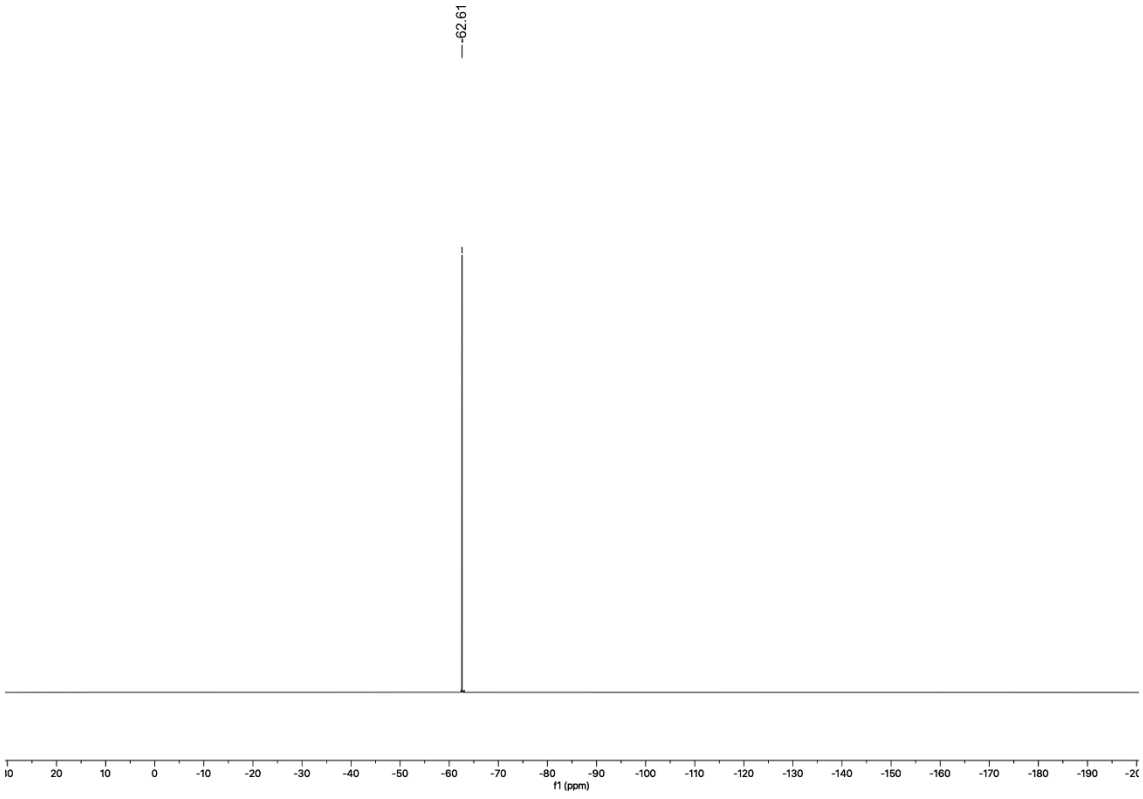


Figure S56. ^{1}H NMR spectrum of *tert*-butyl (*E*)-(3-(3,3-dimethyl-4-oxobut-1-en-1-yl)-4-(1*H*-pyrazol-1-yl)phenyl)carbamate, **4f** (500 MHz, $CDCl_3$, 50 °C).

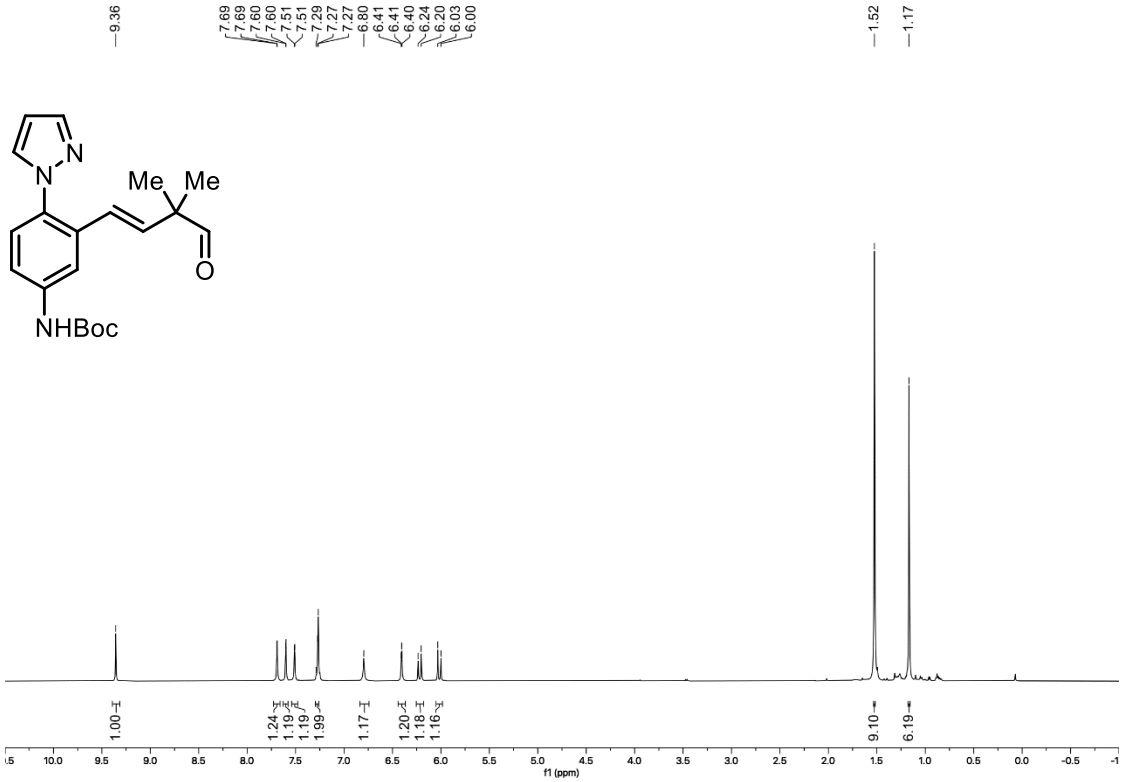


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of *tert*-butyl (*E*)-(3-(3,3-dimethyl-4-oxobut-1-en-1-yl)-4-(1*H*-pyrazol-1-yl)phenyl)carbamate, **4f** (126 MHz, $CDCl_3$).

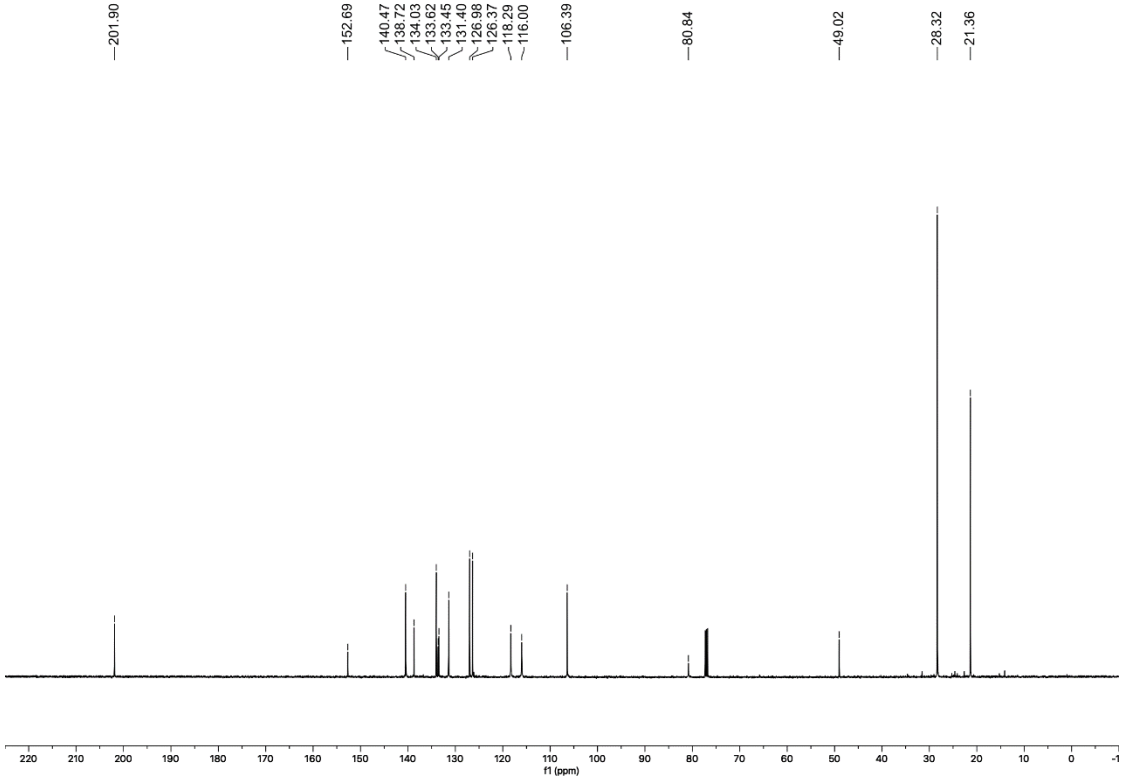


Figure S58. ^{1}H NMR spectrum of (*E*)-4-(5-(1*H*-pyrazol-1-yl)benzo[*d*][1,3]dioxol-4-yl)-2,2-dimethylbut-3-enal, **4g** (500 MHz, $CDCl_3$).

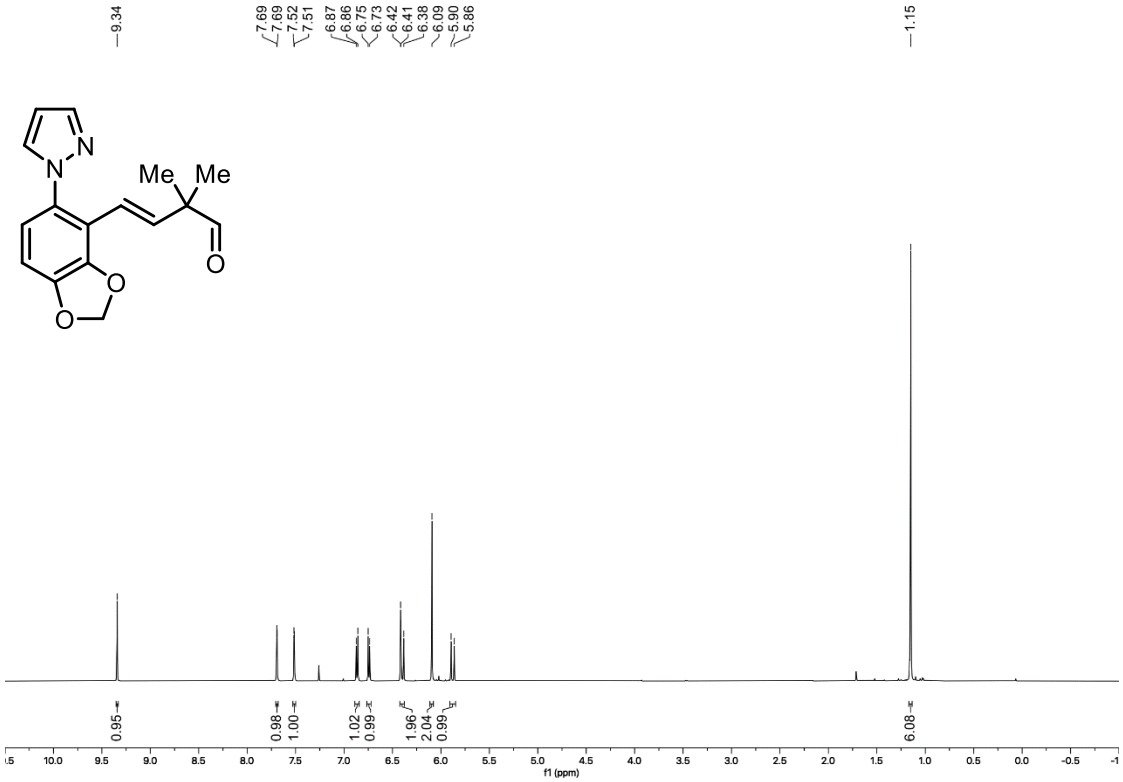


Figure S59. ^{13}C{^{1}H} NMR spectrum of (*E*)-4-(5-(1*H*-pyrazol-1-yl)benzo[*d*][1,3]dioxol-4-yl)-2,2-dimethylbut-3-enal, **4g** (126 MHz, $CDCl_3$).

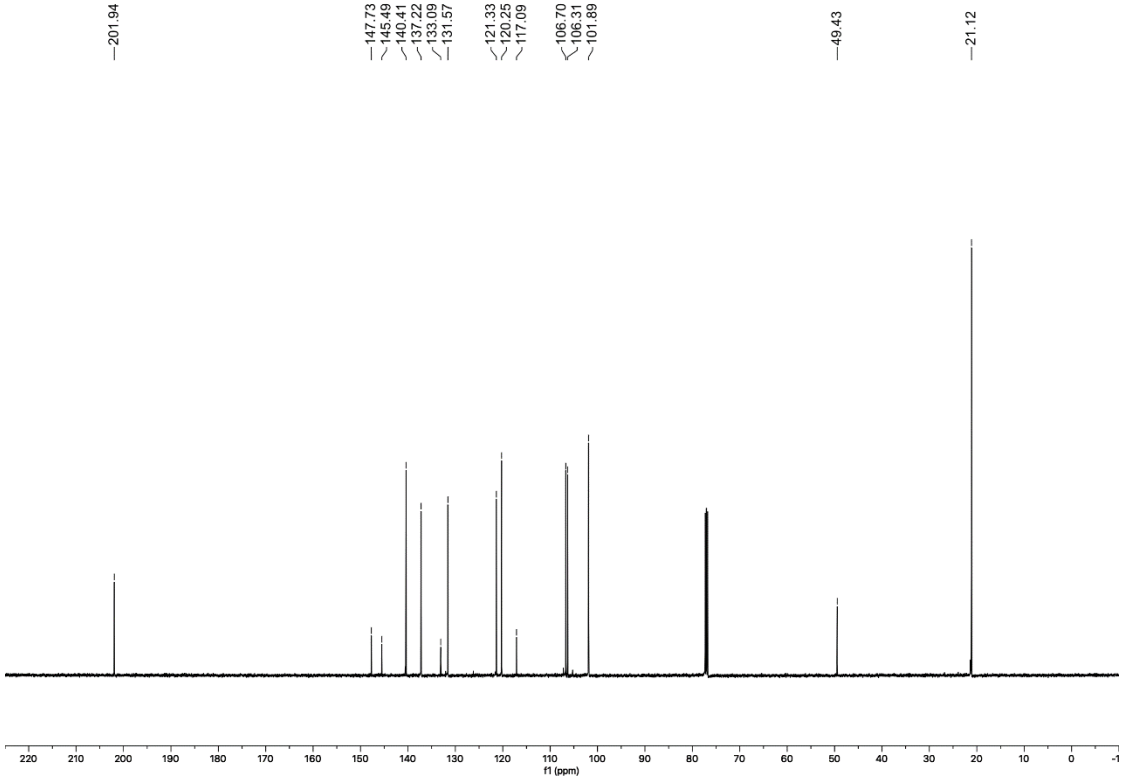


Figure S60. ^{1}H NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal, **4h** (500 MHz, $CDCl_3$).

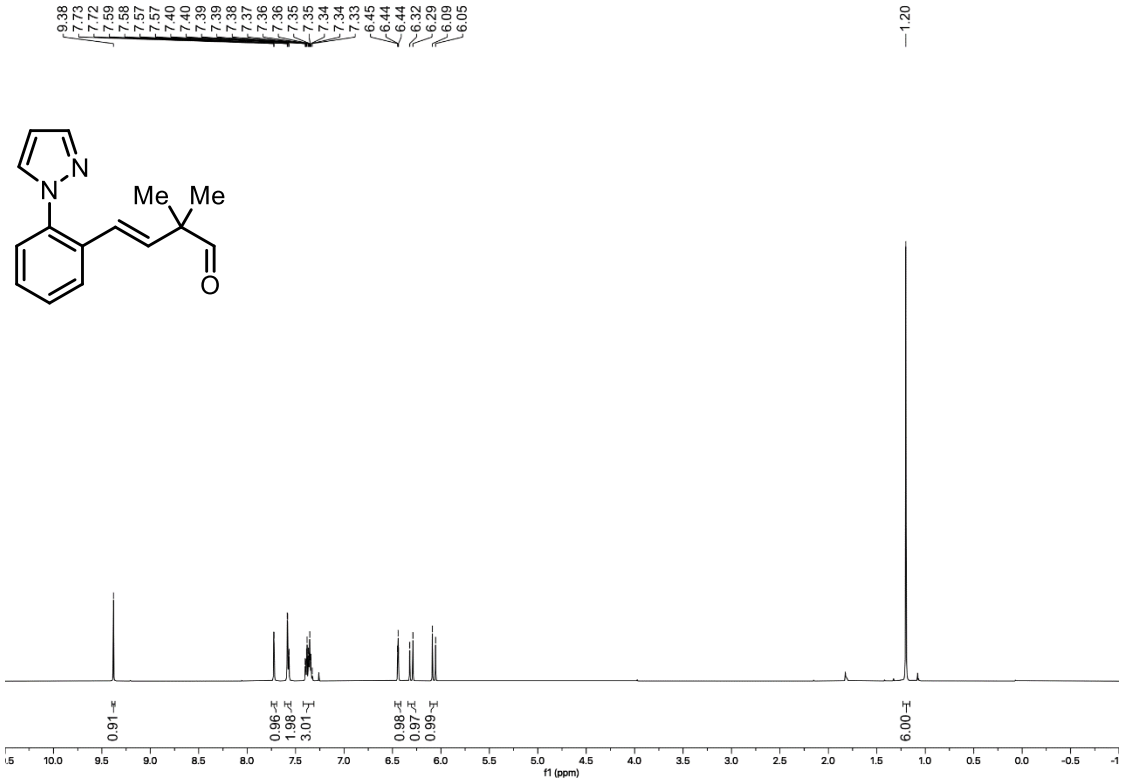


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-4-(2-(1*H*-pyrazol-1-yl)phenyl)-2,2-dimethylbut-3-enal, **4h** (126 MHz, $CDCl_3$).

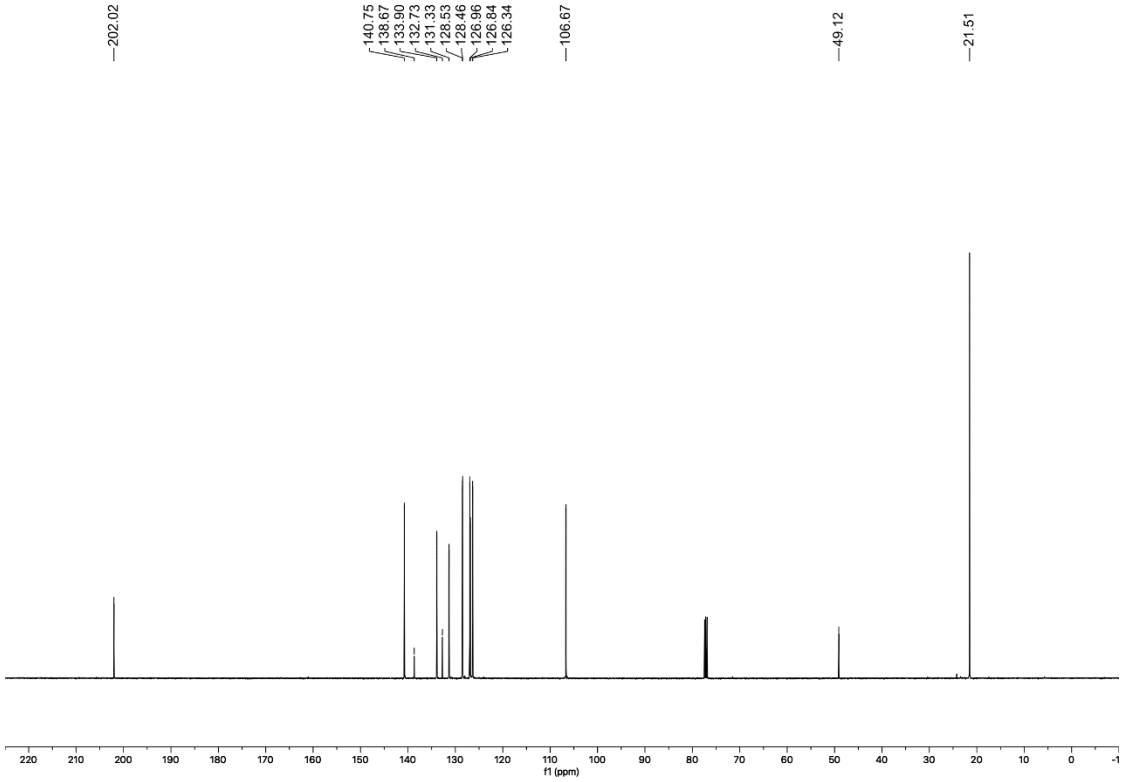


Figure S62. ^{1}H NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)but-3-enal, **4i** (500 MHz, $CDCl_3$).

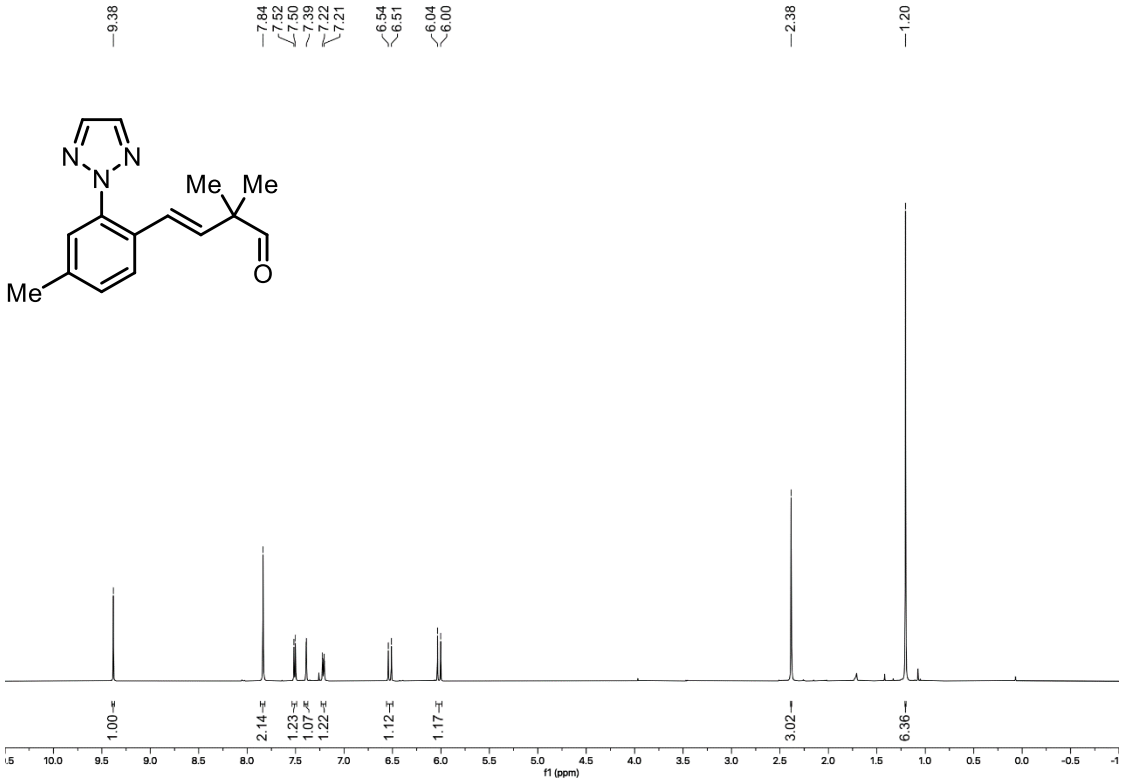


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(2*H*-1,2,3-triazol-2-yl)phenyl)but-3-enal, **4i** (126 MHz, $CDCl_3$).

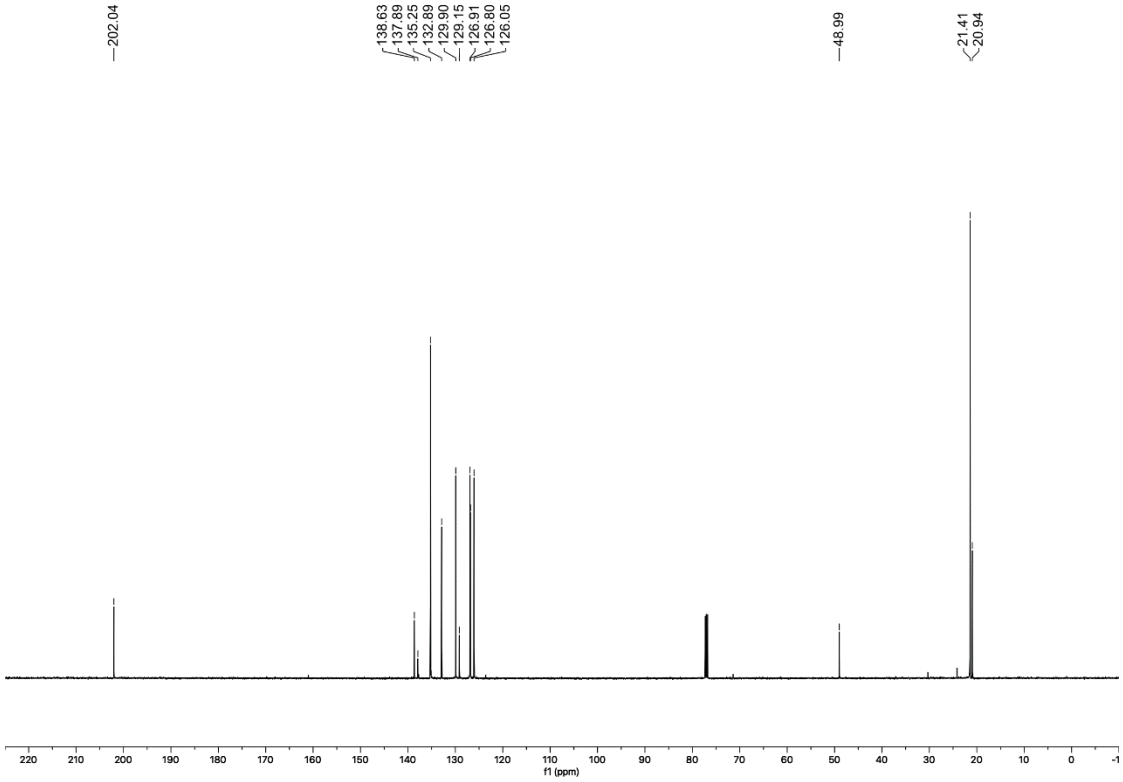


Figure S64. ^{1}H NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(pyrimidin-2-yl)phenyl)but-3-enal, **4j** (600 MHz, $CDCl_3$).

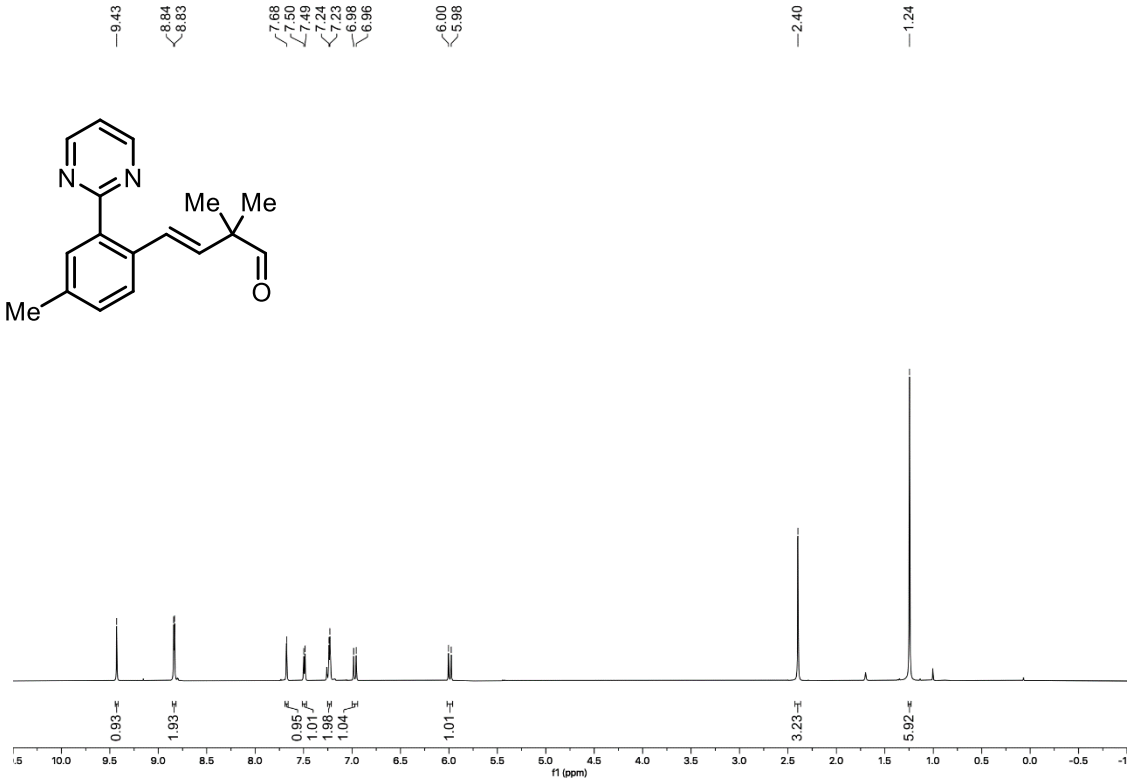


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2,2-dimethyl-4-(4-methyl-2-(pyrimidin-2-yl)phenyl)but-3-enal, **4j** (151 MHz, $CDCl_3$).

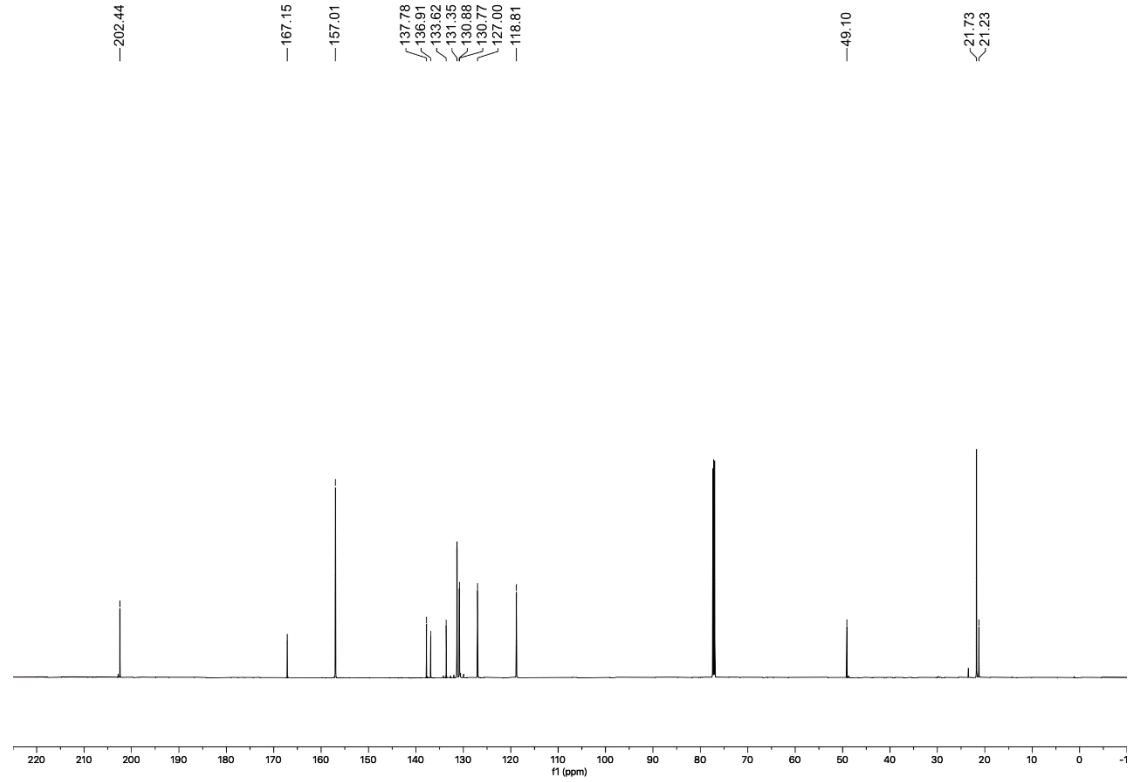


Figure S66. ^{1}H NMR spectrum of (*E*)-2,2-dimethyl-4-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)but-3-enal, **4k** (600 MHz, $CDCl_3$).

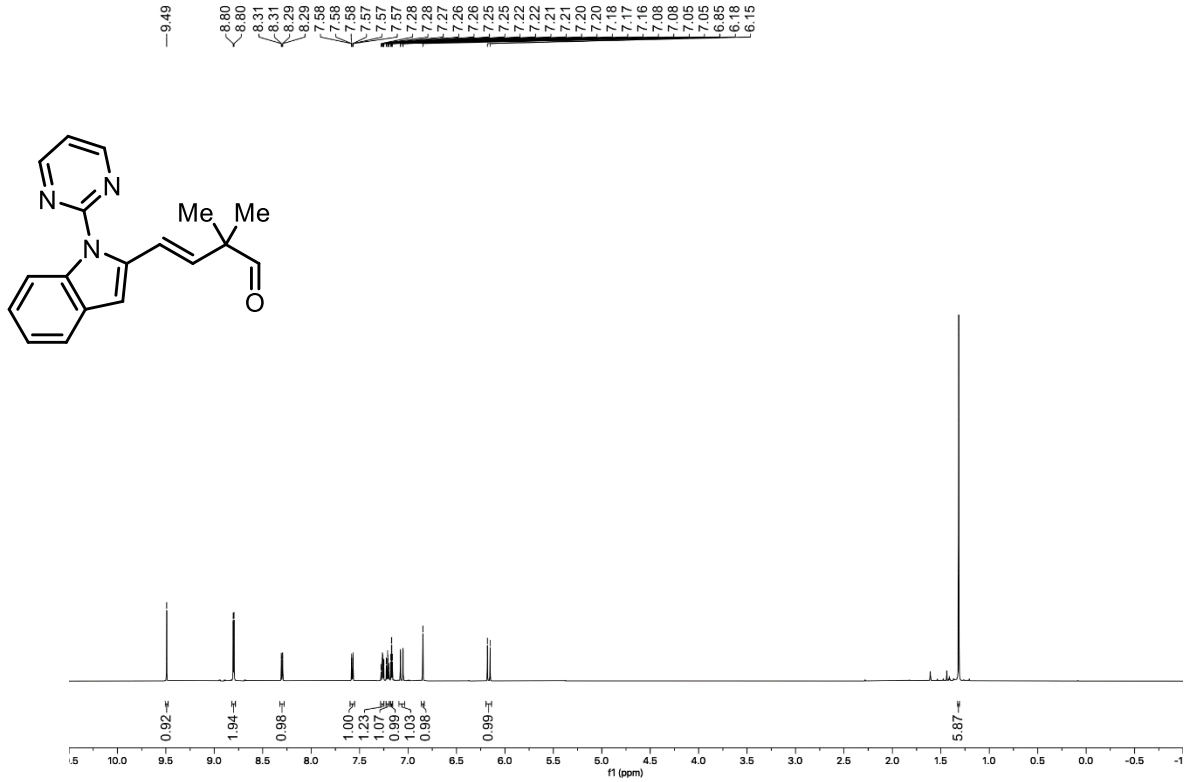


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2,2-dimethyl-4-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)but-3-enal, **4k** (151 MHz, $CDCl_3$).

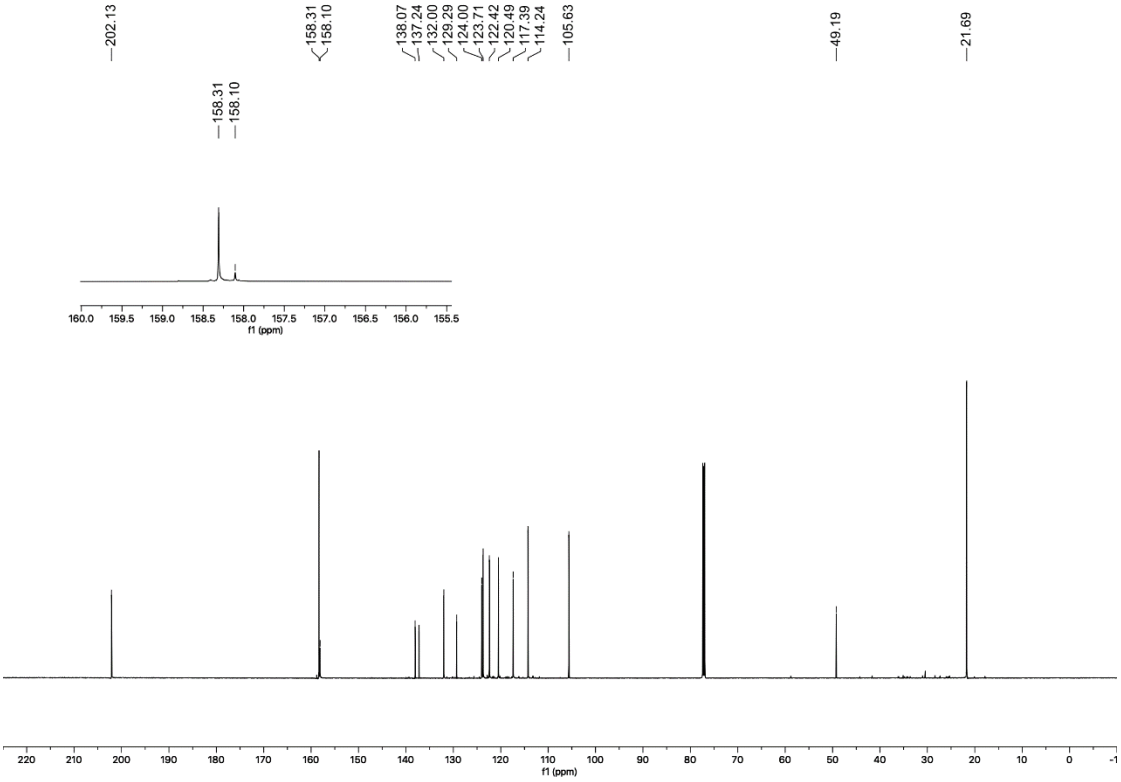


Figure S68. ^{1}H NMR spectrum of (*E*)-2-cyclopentyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4l** (500 MHz, $CDCl_3$).

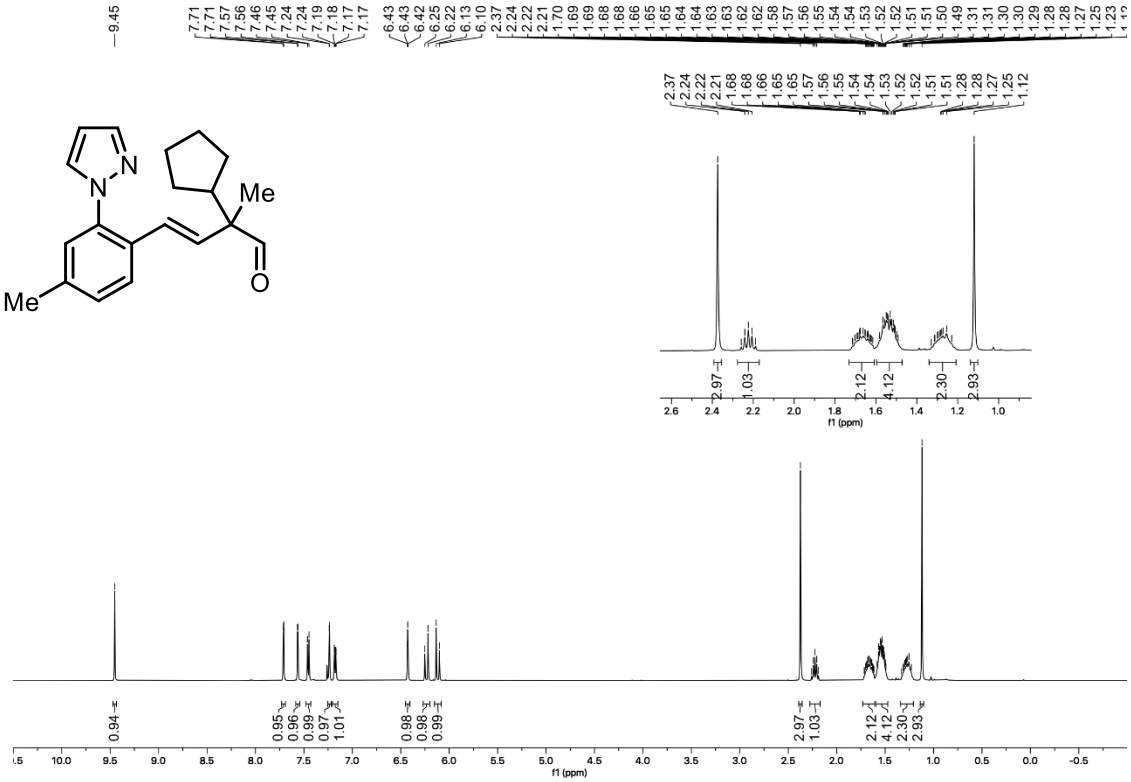


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-cyclopentyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4l** (126 MHz, $CDCl_3$).

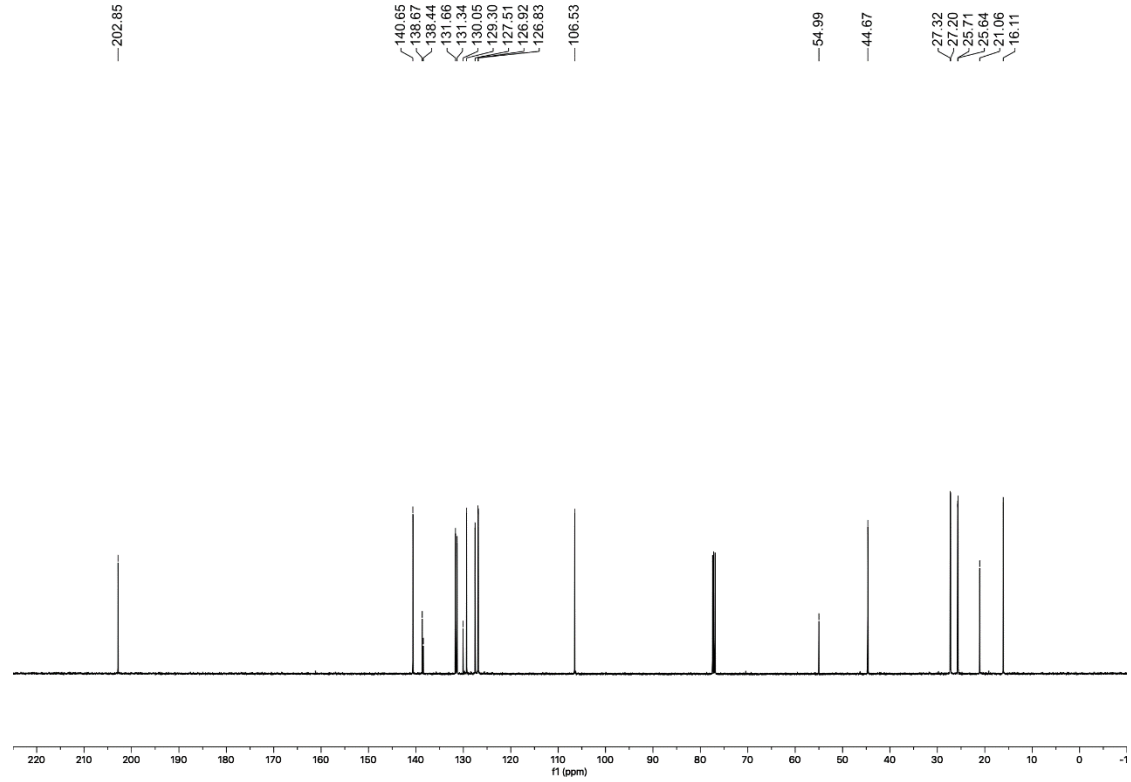


Figure S70. ^{1}H NMR spectrum of (*E*)-2,4-dimethyl-2-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)pentanal, **4m** (600 MHz, $CDCl_3$).

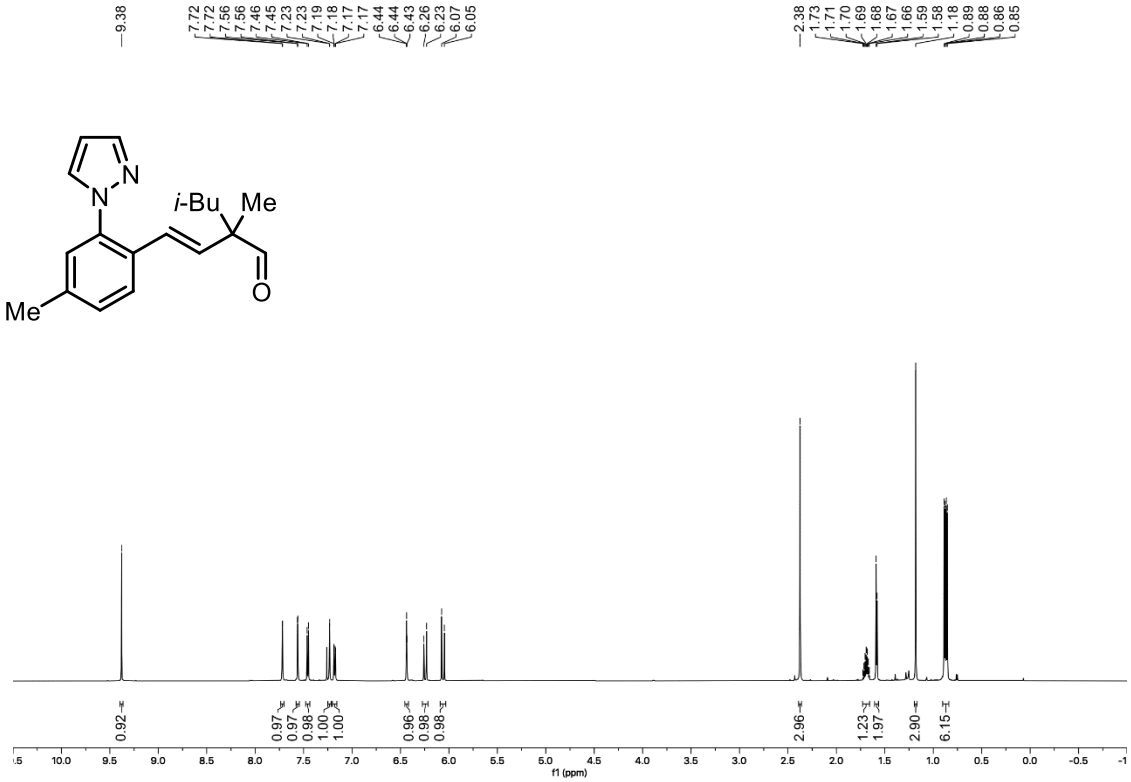


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2,4-dimethyl-2-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)pentanal, **4m** (151 MHz, $CDCl_3$).

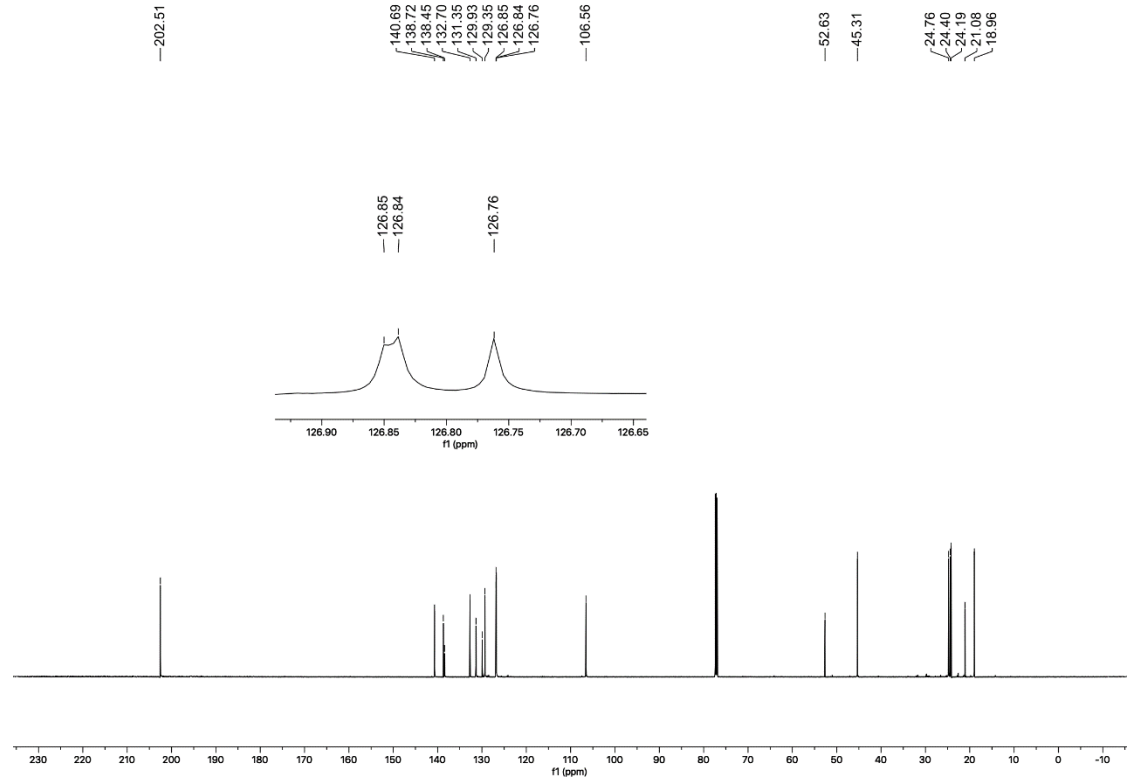


Figure S72. ^{1}H NMR spectrum of (*E*)-2-(cyclohexylmethyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4n** (500 MHz, $CDCl_3$).

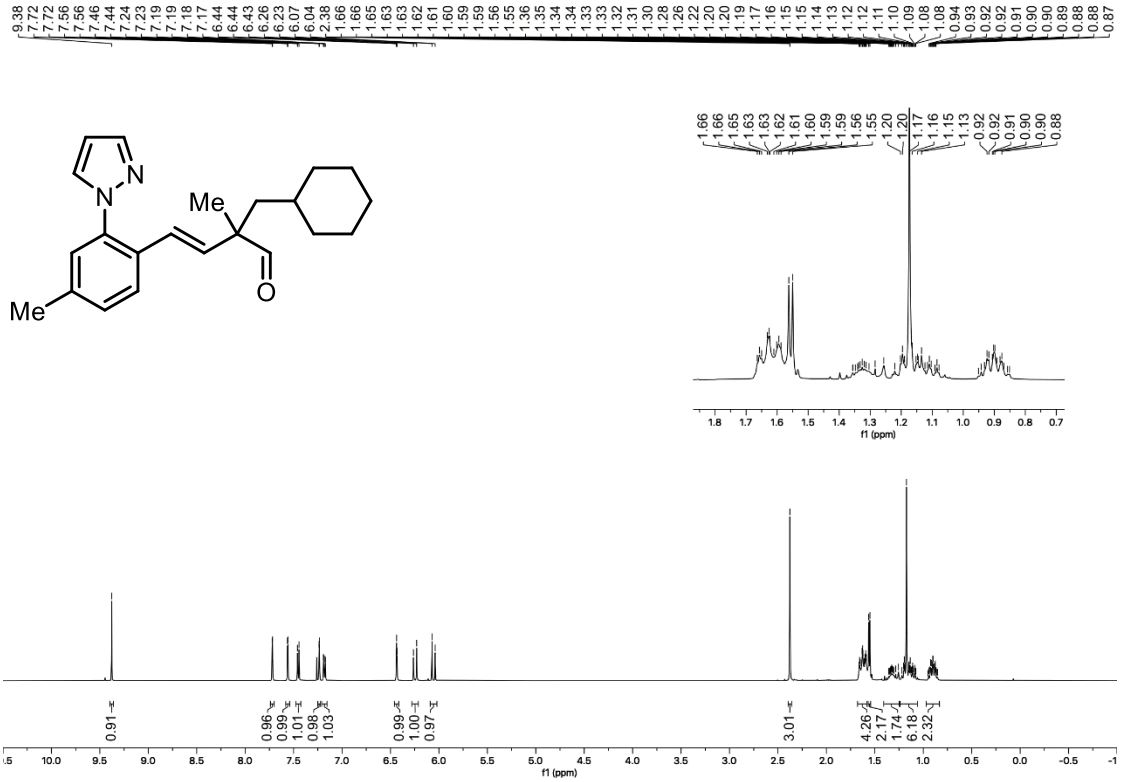


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-(cyclohexylmethyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4n** (126 MHz, $CDCl_3$).

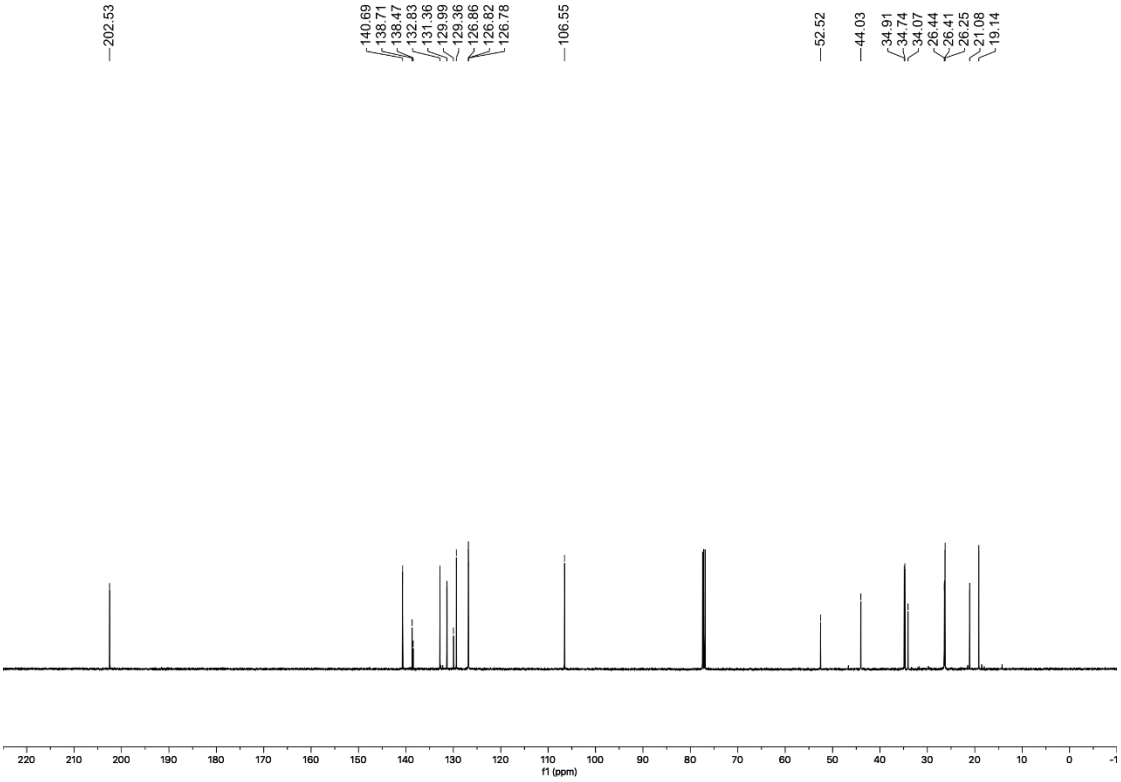


Figure S74. ^{1}H NMR spectrum of (*E*)-1-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde, **4o** (600 MHz, $CDCl_3$).

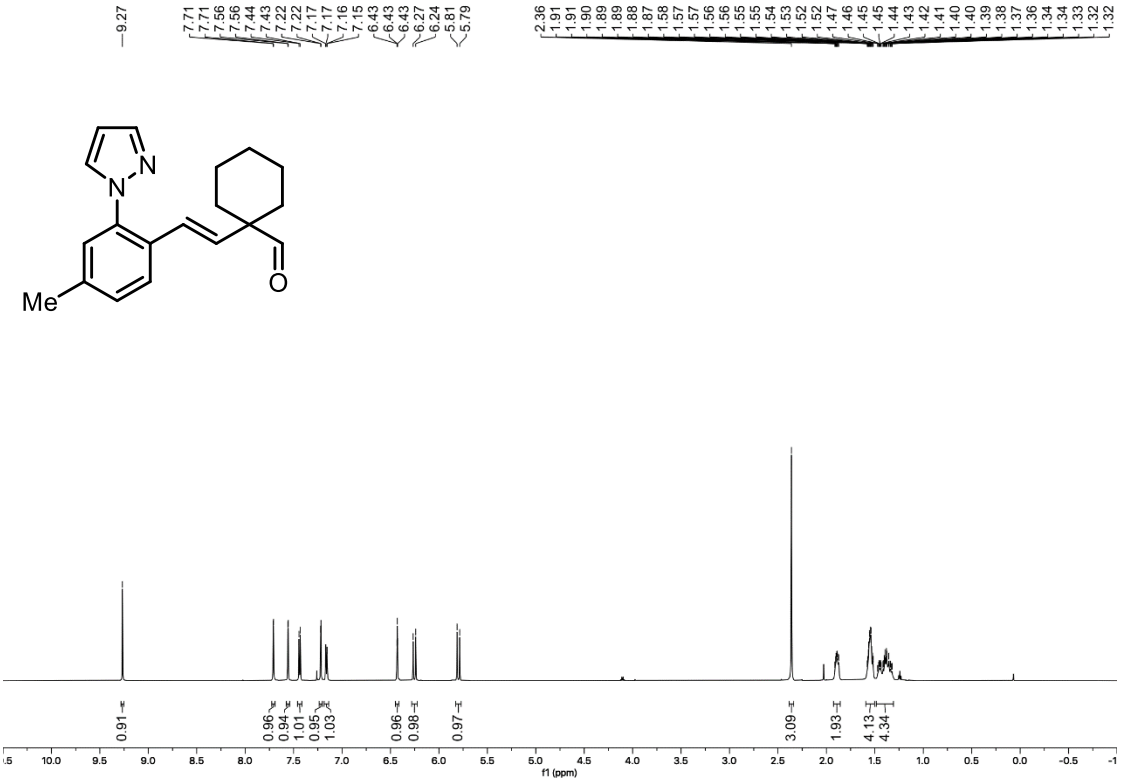


Figure S75. ^{1}H NMR spectrum of (*E*)-1-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde, **4o** (151 MHz, $CDCl_3$).

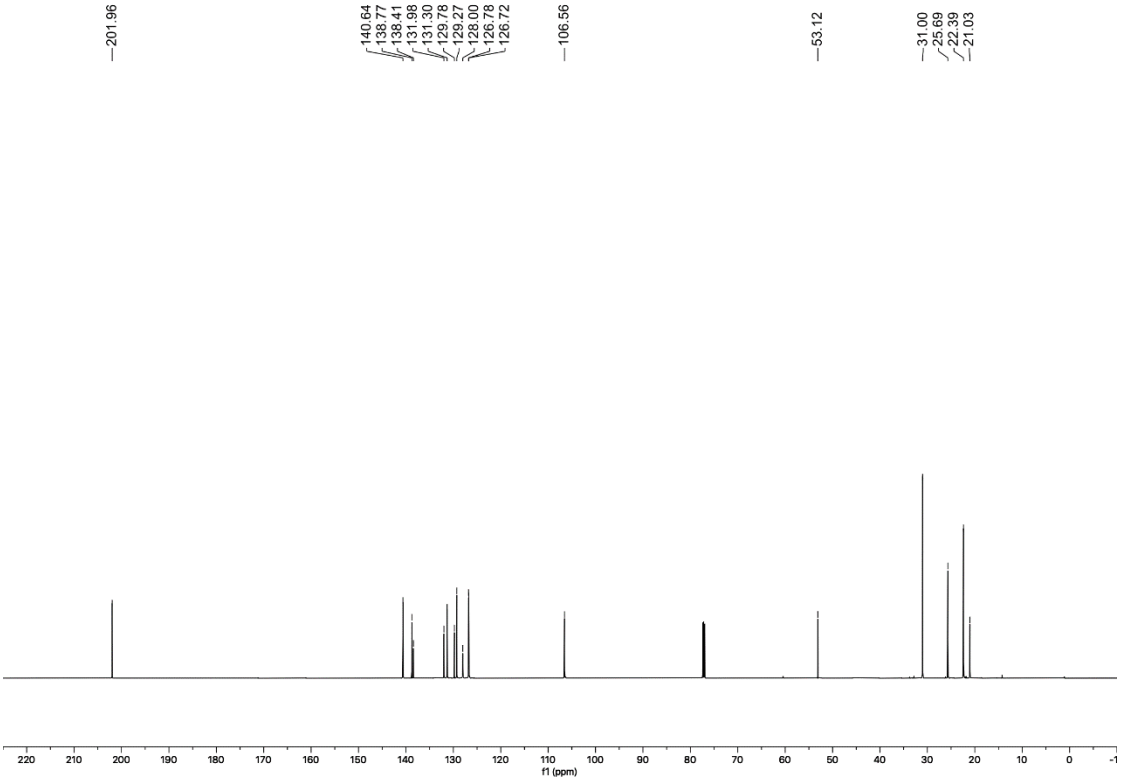


Figure S76. ^{1}H NMR spectrum of (*E*)-1-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde, **4p** (500 MHz, $CDCl_3$).

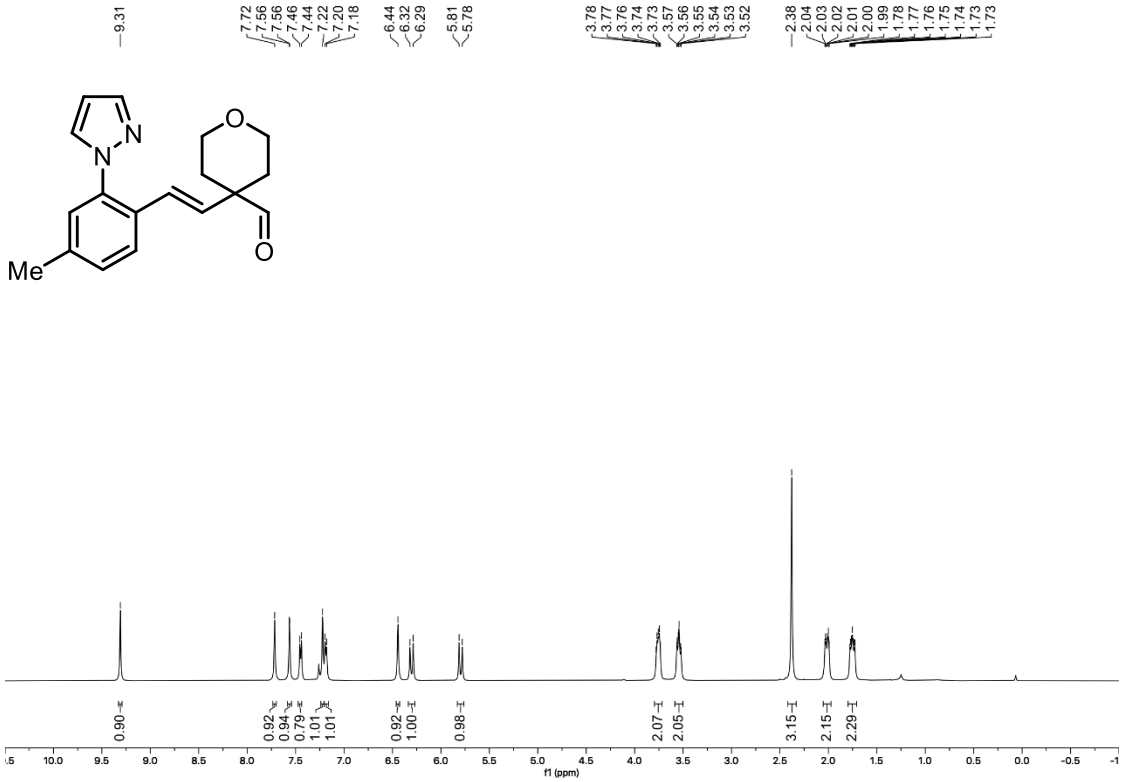


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)cyclohexane-1-carbaldehyde, **4p** (126 MHz, $CDCl_3$).

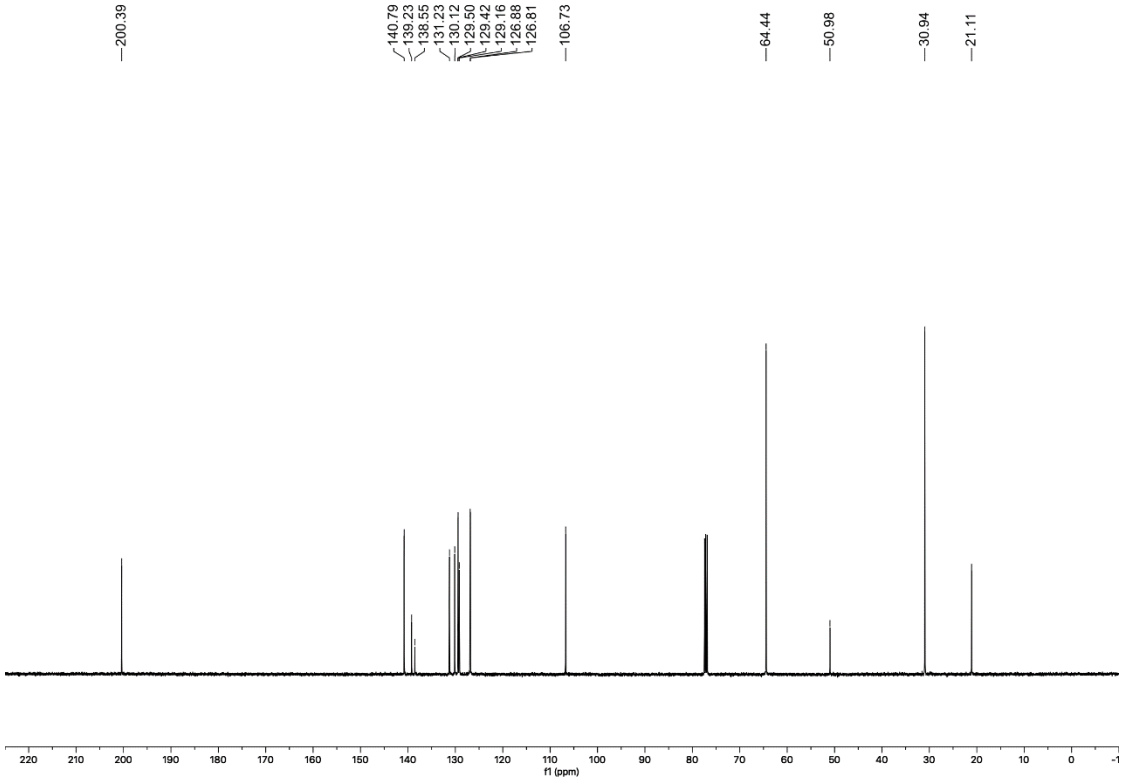


Figure S78. ^{1}H NMR spectrum of benzyl (*E*)-4-formyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)piperidine-1-carboxylate, **4q** (500 MHz, $CDCl_3$, 50 °C).

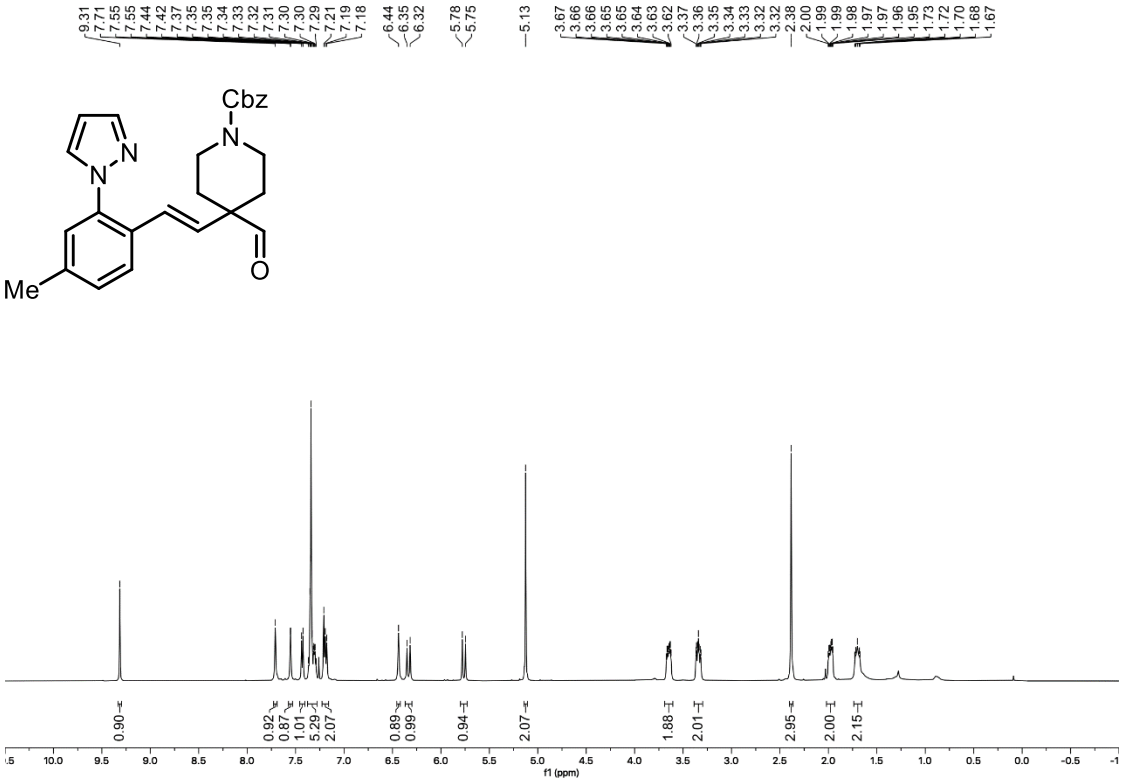


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of benzyl (*E*)-4-formyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)styryl)piperidine-1-carboxylate, **4q** (126 MHz, $CDCl_3$, 50 °C).

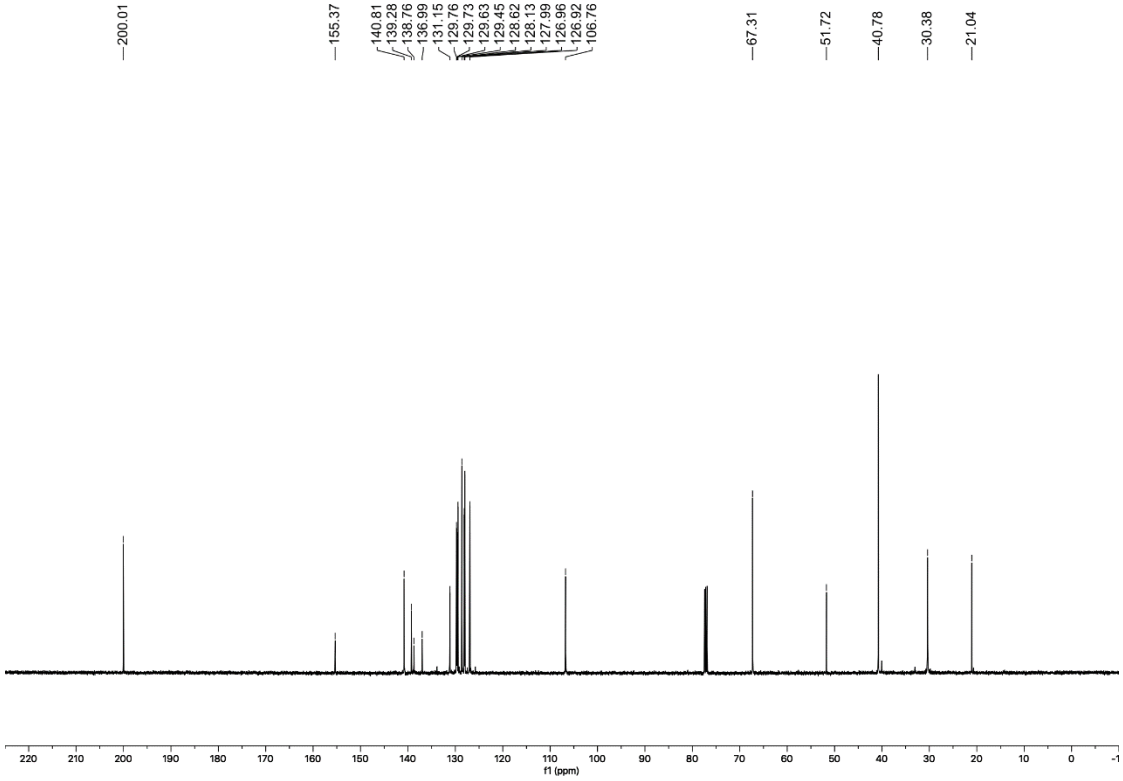


Figure S80. ^{1}H NMR spectrum of (*E*)-2-benzyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4r** (500 MHz, $CDCl_3$).

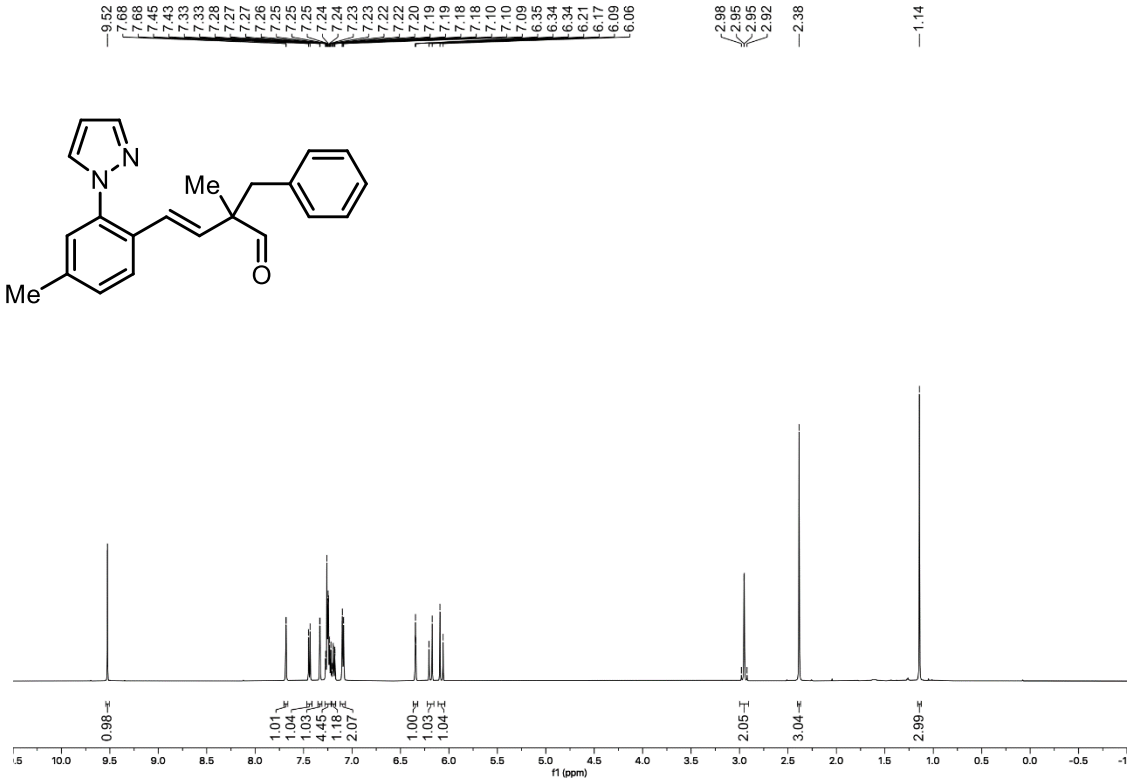


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-benzyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4r** (126 MHz, $CDCl_3$).

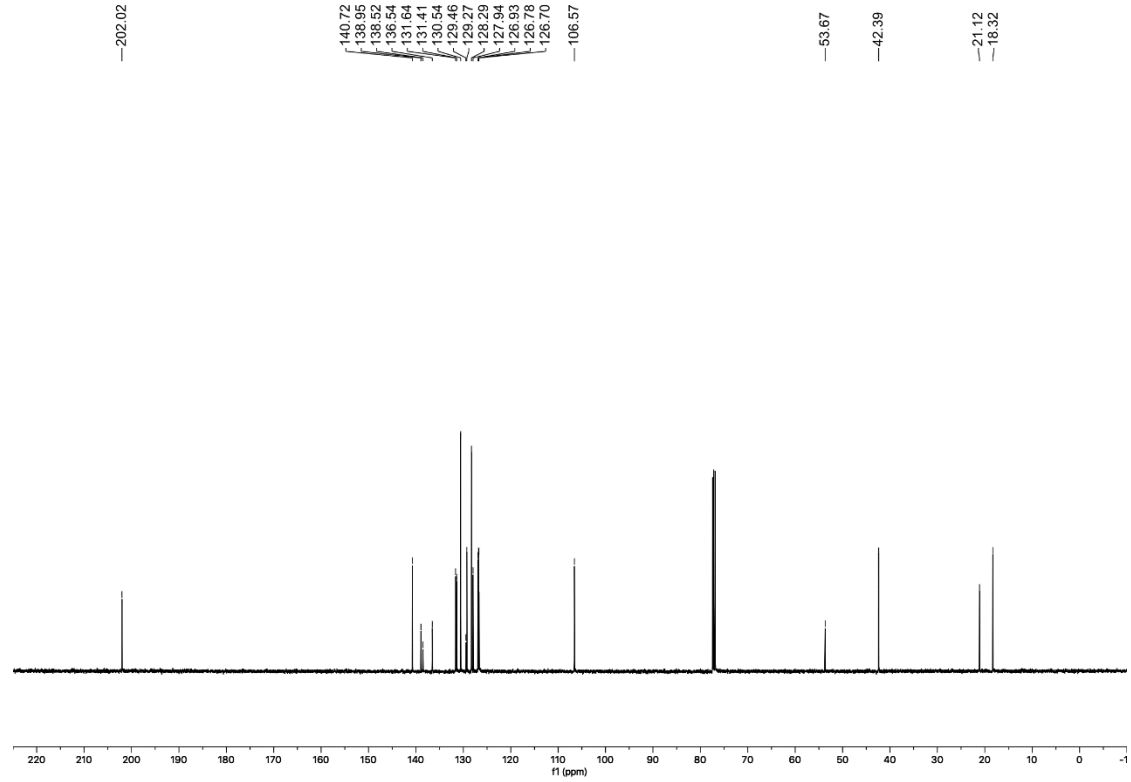


Figure S82. ^{1}H NMR spectrum of (*E*)-2-(2-fluorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4s** (500 MHz, $CDCl_3$).

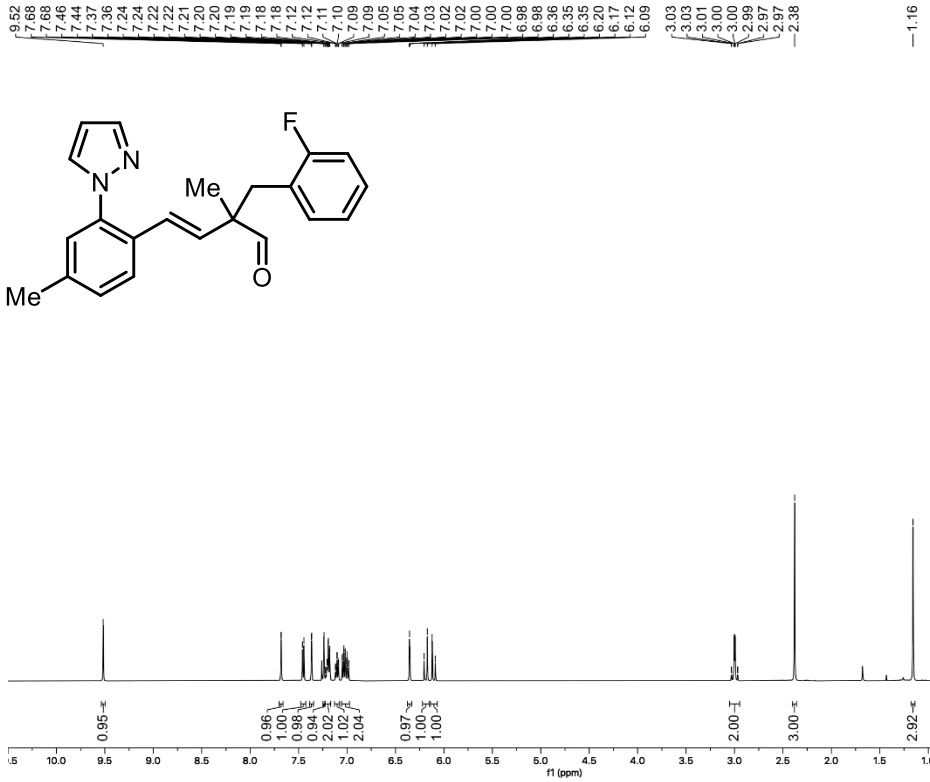


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-(2-fluorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4s** (126 MHz, $CDCl_3$).

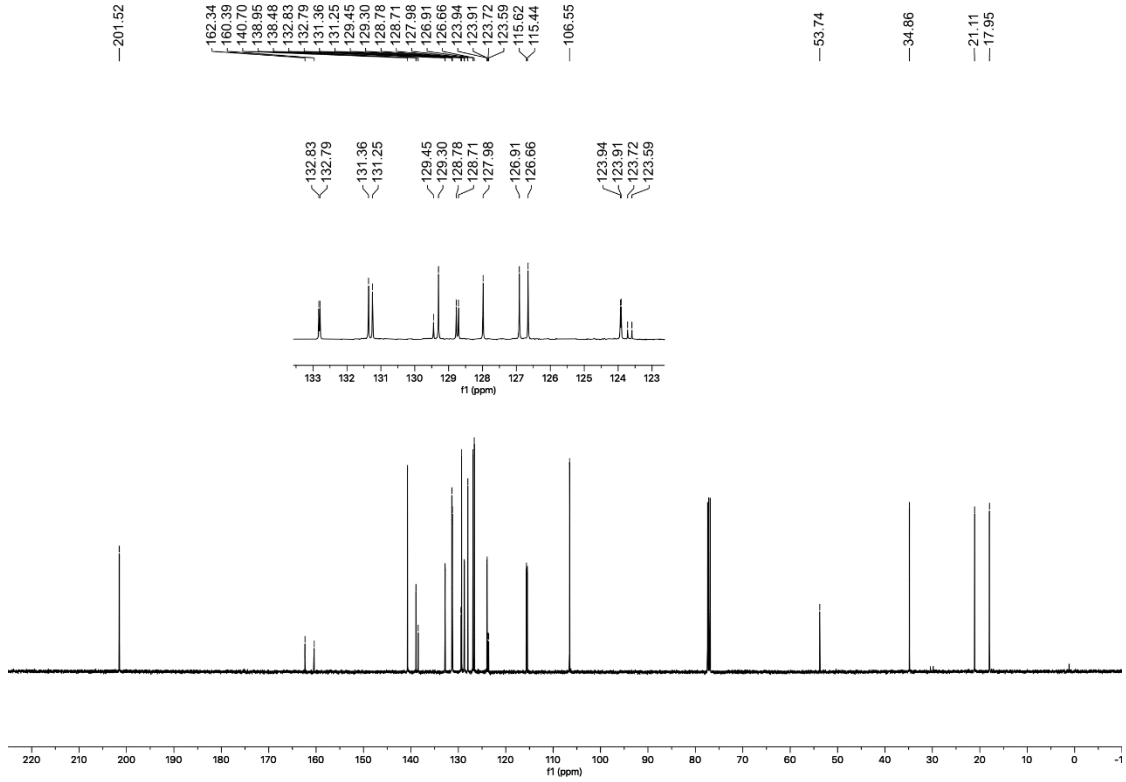


Figure S84. ^{19}F NMR spectrum of (*E*)-2-(2-fluorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4s** (471 MHz, $CDCl_3$).

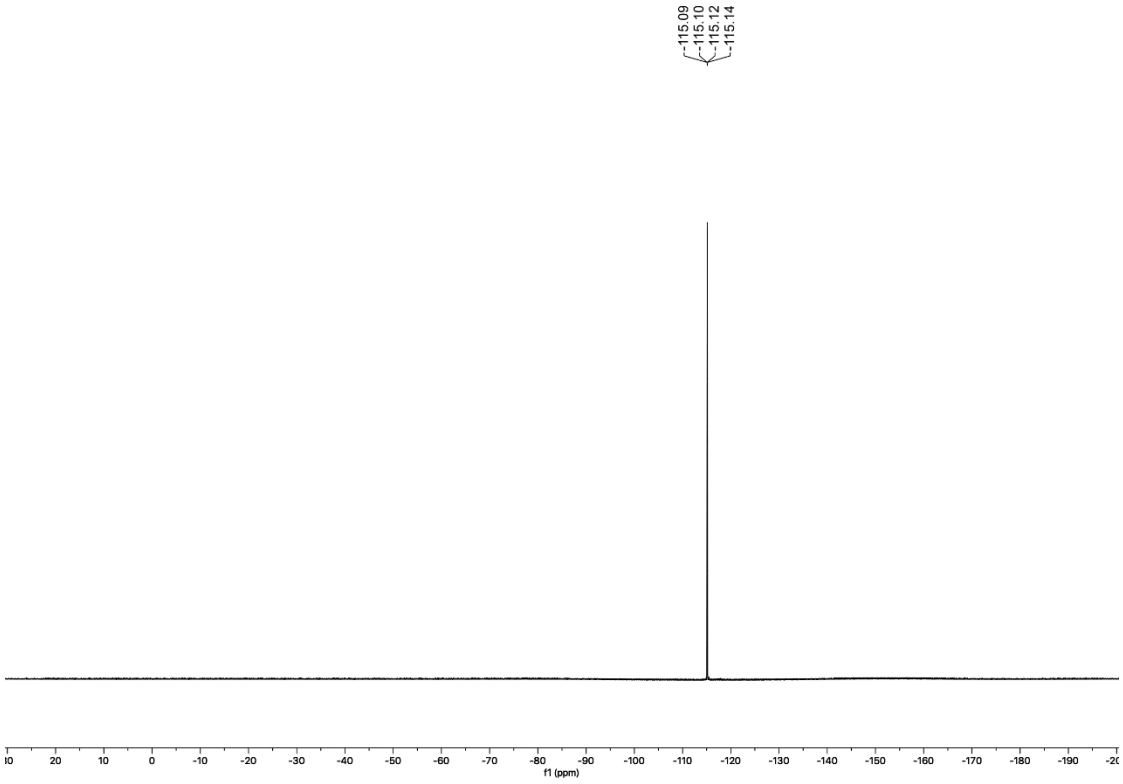


Figure S85. ^{1}H NMR spectrum of (*E*)-2-(4-bromobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4t** (500 MHz, $CDCl_3$).

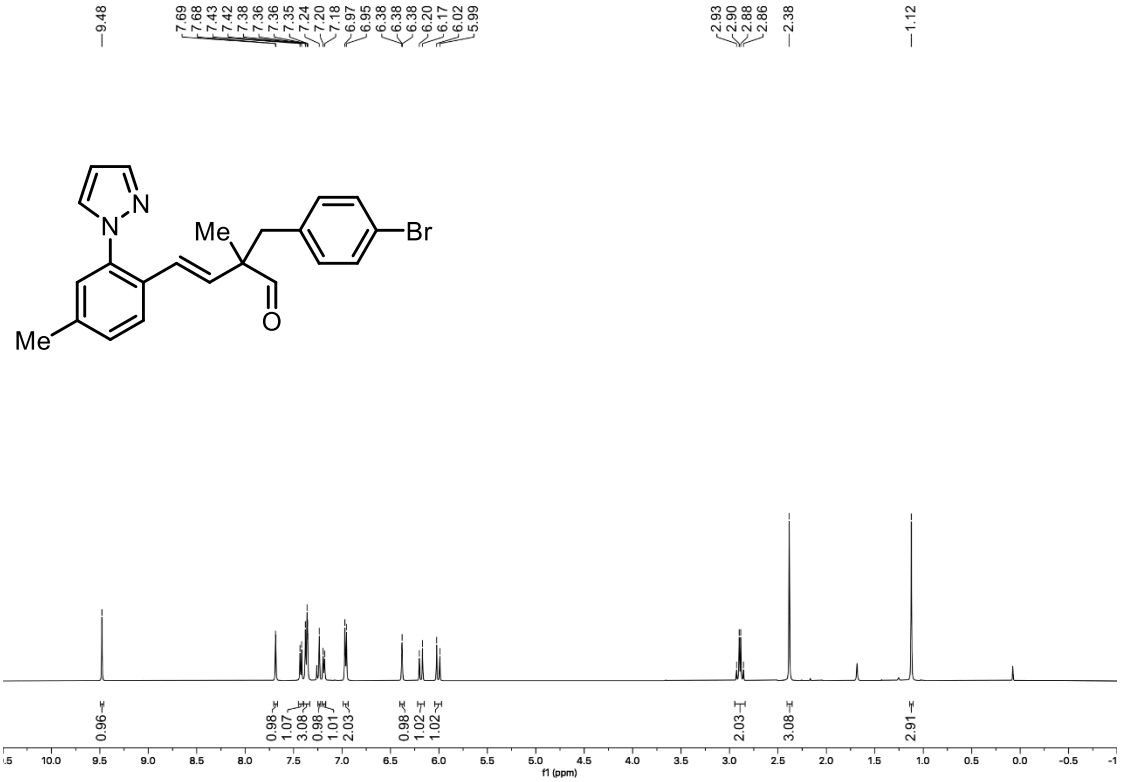


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-(4-bromobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4t** (126 MHz, $CDCl_3$).

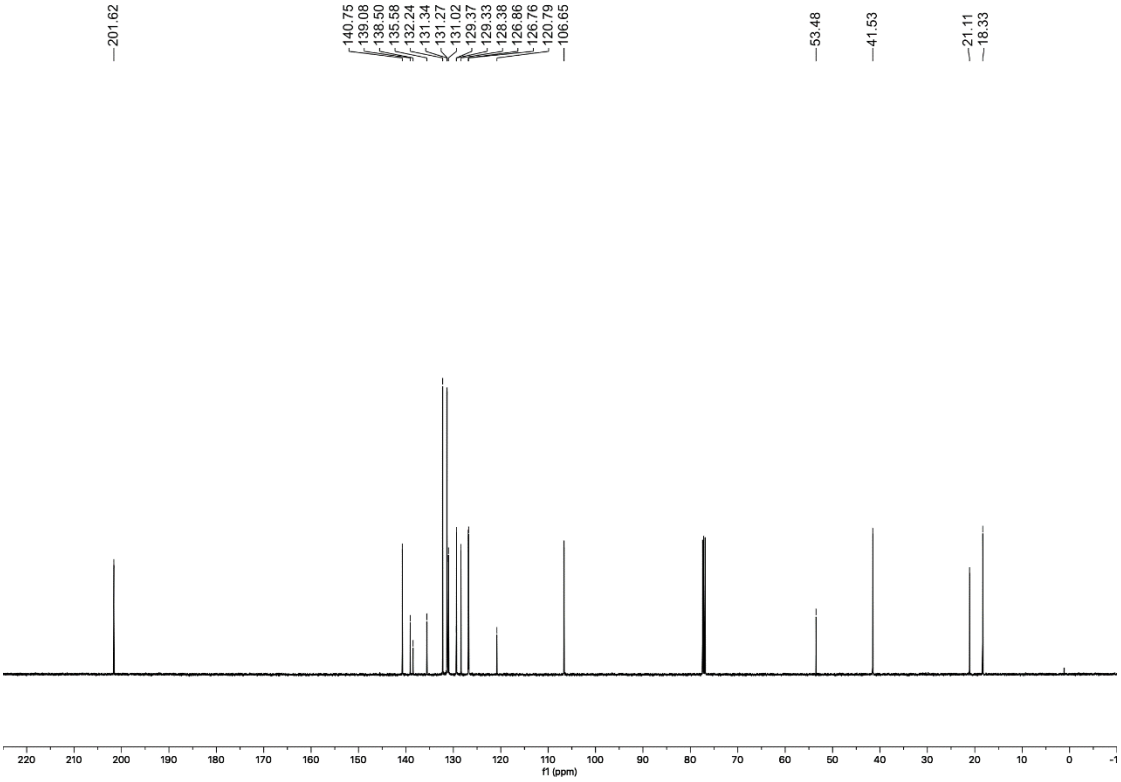


Figure S87. ^{1}H NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(4-(trifluoromethyl)benzyl)but-3-enal, **4u** (500 MHz, $CDCl_3$).

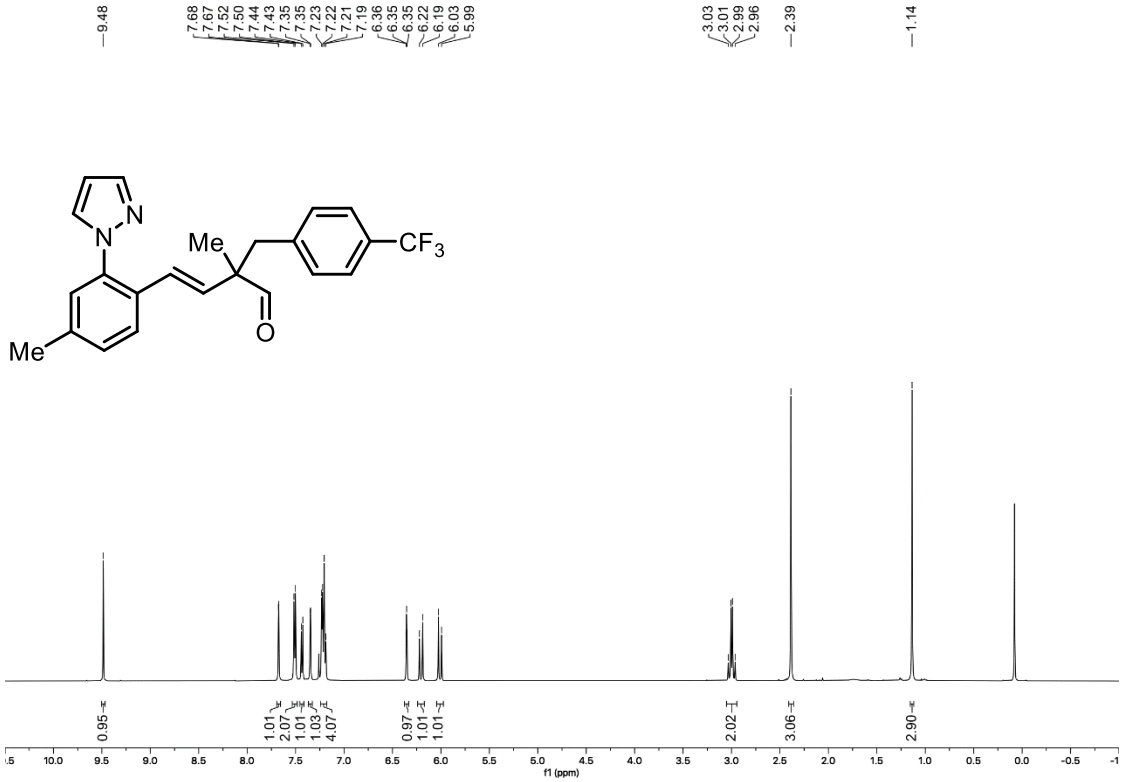


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(4-(trifluoromethyl)benzyl)but-3-enal, **4u** (126 MHz, $CDCl_3$).

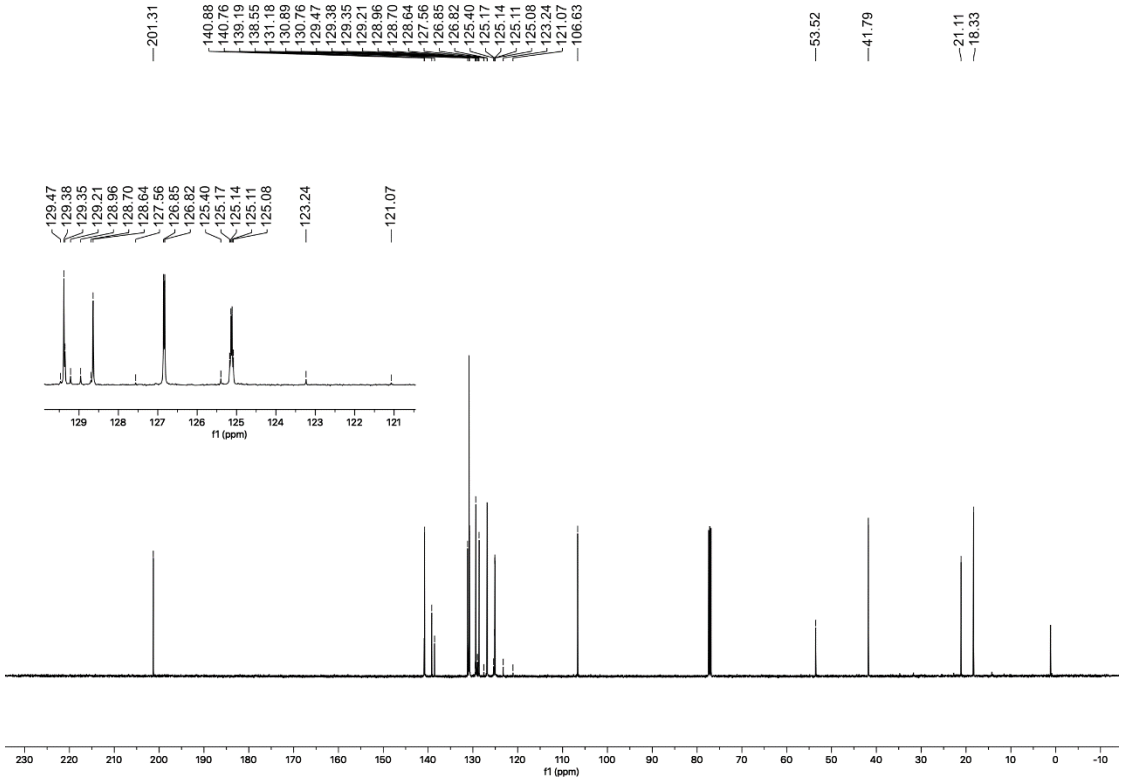


Figure S89. ^{19}F NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(4-(trifluoromethyl)benzyl)but-3-enal, **4u** (471 MHz, $CDCl_3$).

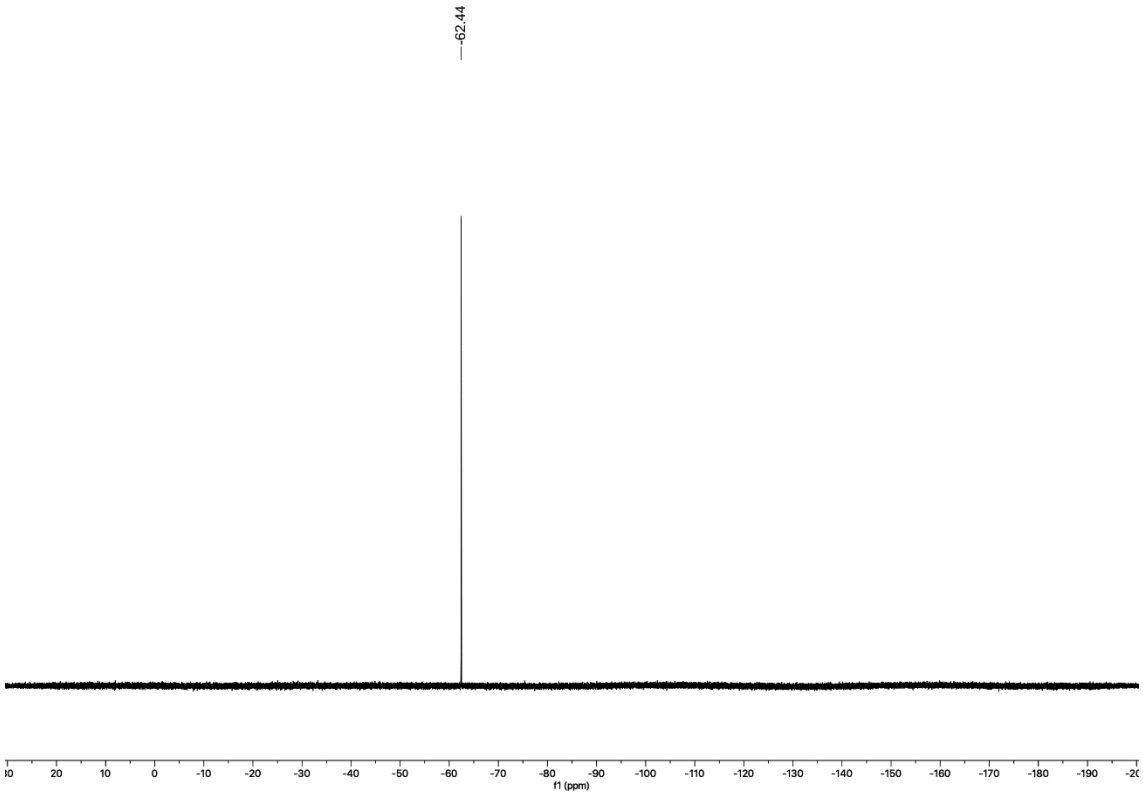
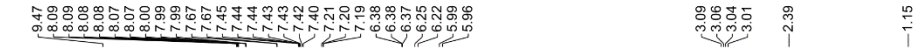
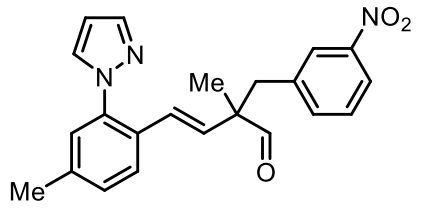


Figure S90. ^{1}H NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-nitrobenzyl)but-3-enal, **4v** (500 MHz, $CDCl_3$).





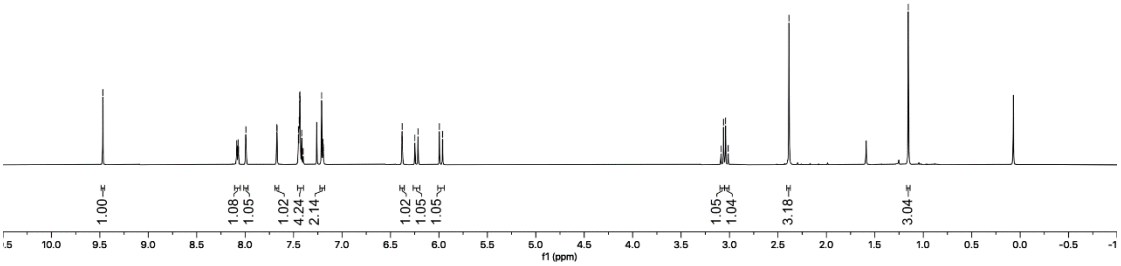
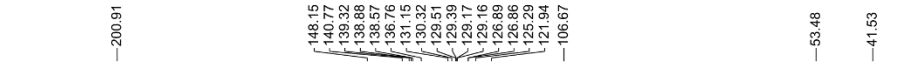


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-nitrobenzyl)but-3-enal, **4v** (126 MHz, $CDCl_3$).



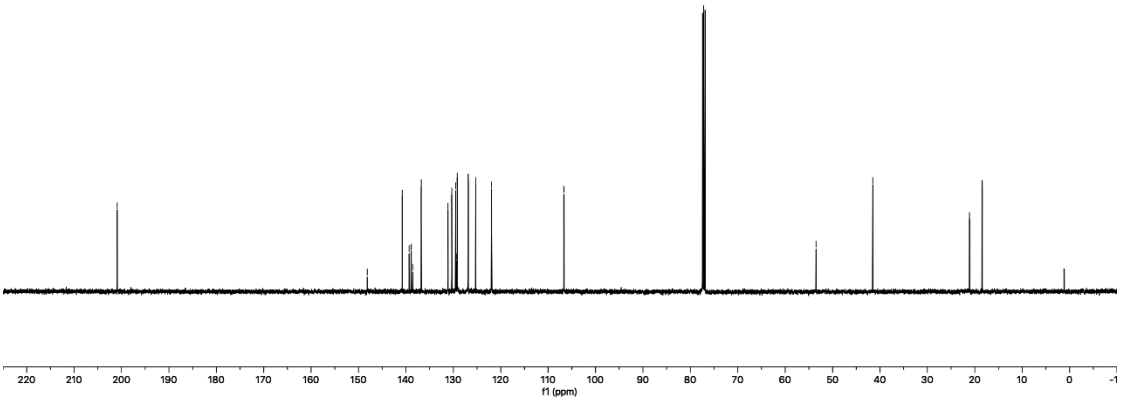


Figure S92. ^{1}H NMR spectrum of (*E*)-2-(3-chlorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4w** (500 MHz, $CDCl_3$).

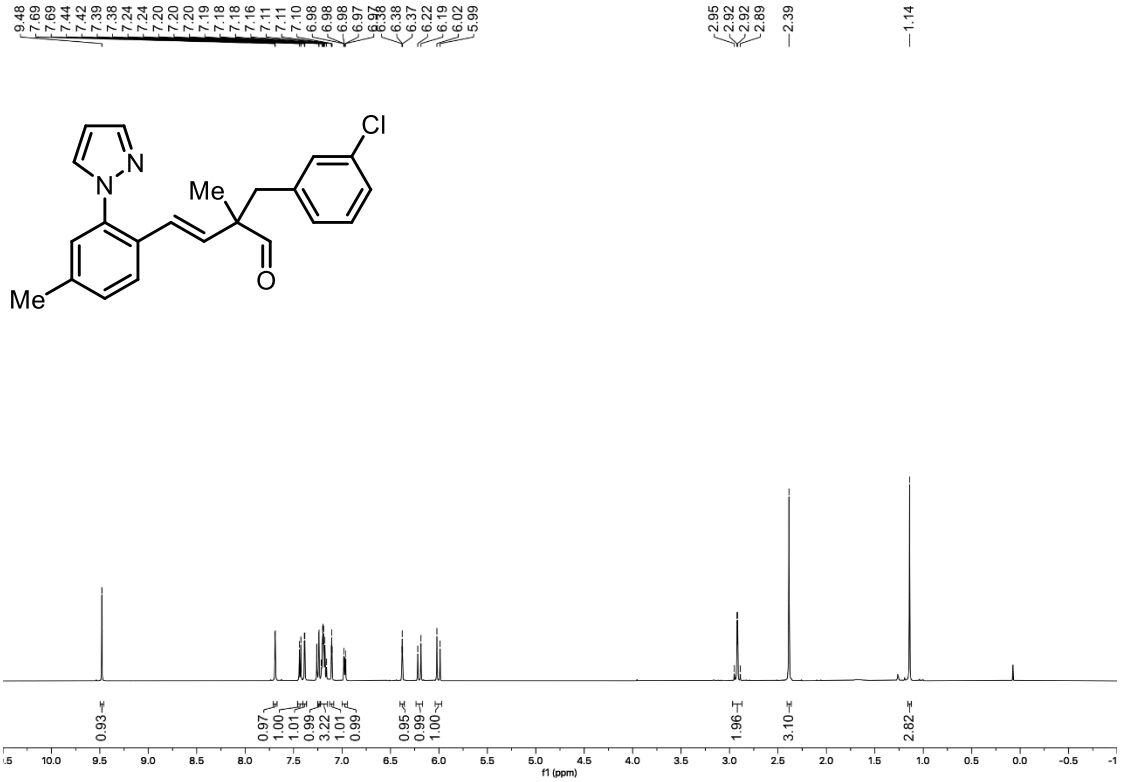


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-(3-chlorobenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4w** (126 MHz, $CDCl_3$)

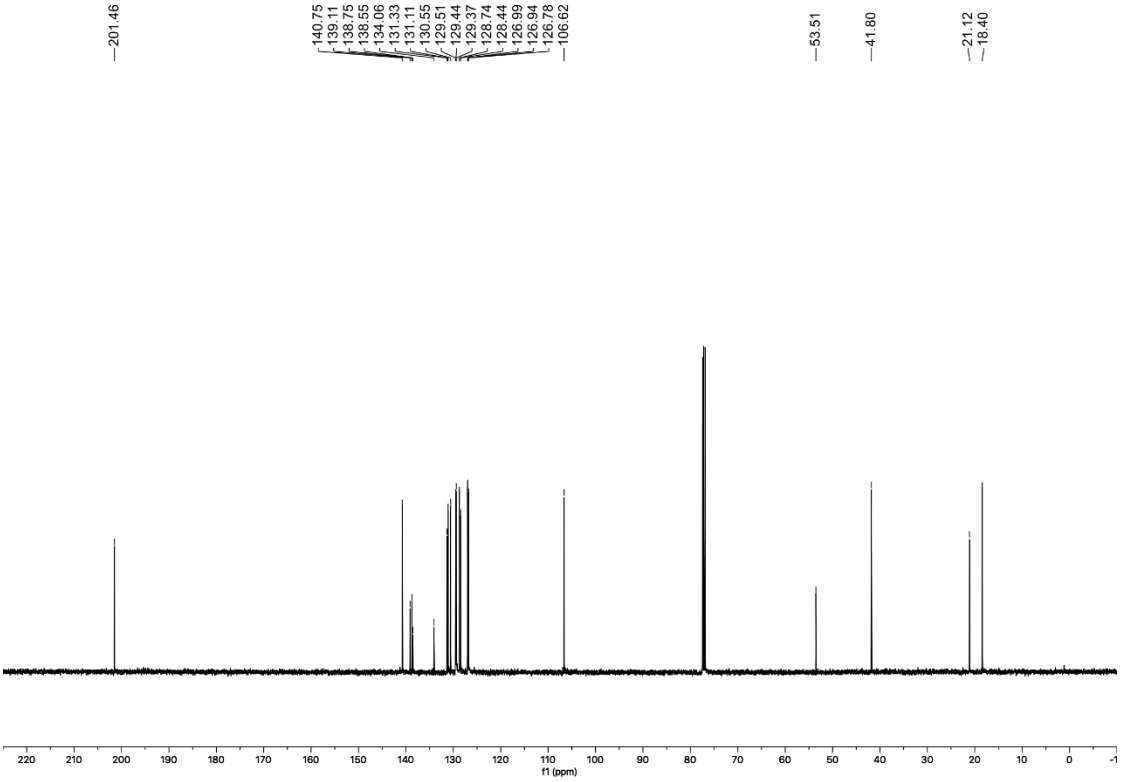


Figure S94. ^{1}H NMR spectrum of methyl (*E*)-3-(2-formyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)benzoate, **4x** (500 MHz, $CDCl_3$).

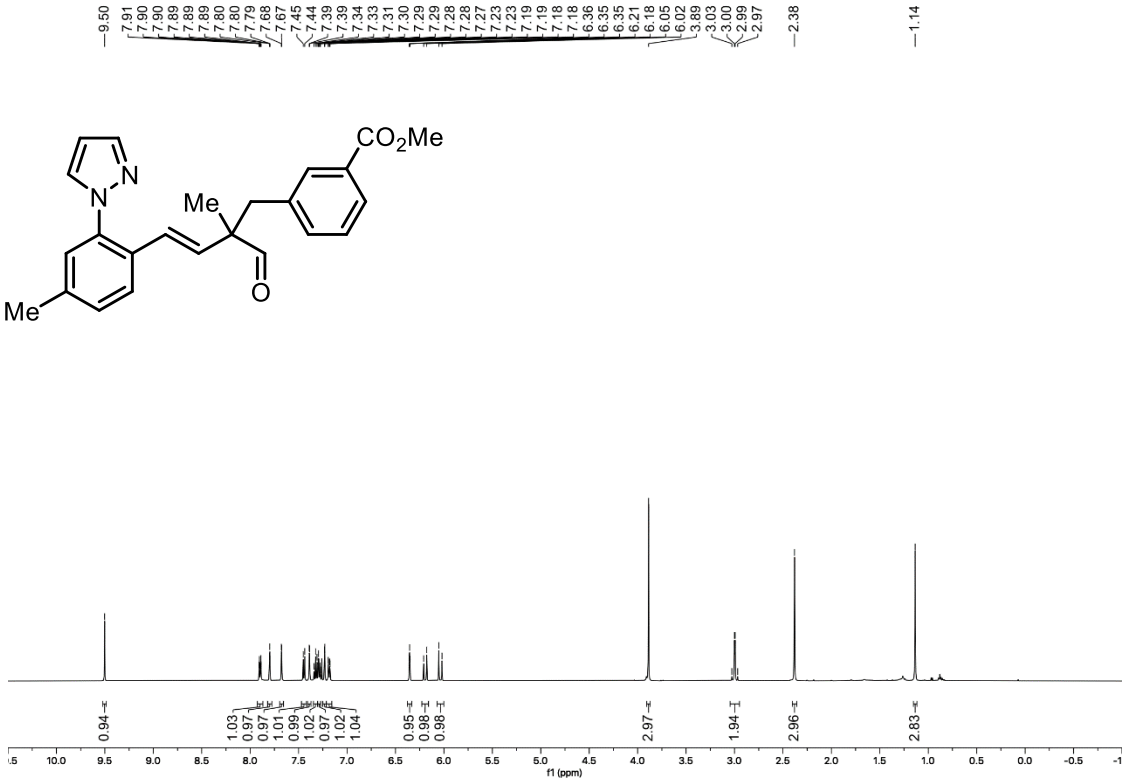


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*E*)-3-(2-formyl-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)benzoate, **4x** (126 MHz, $CDCl_3$).

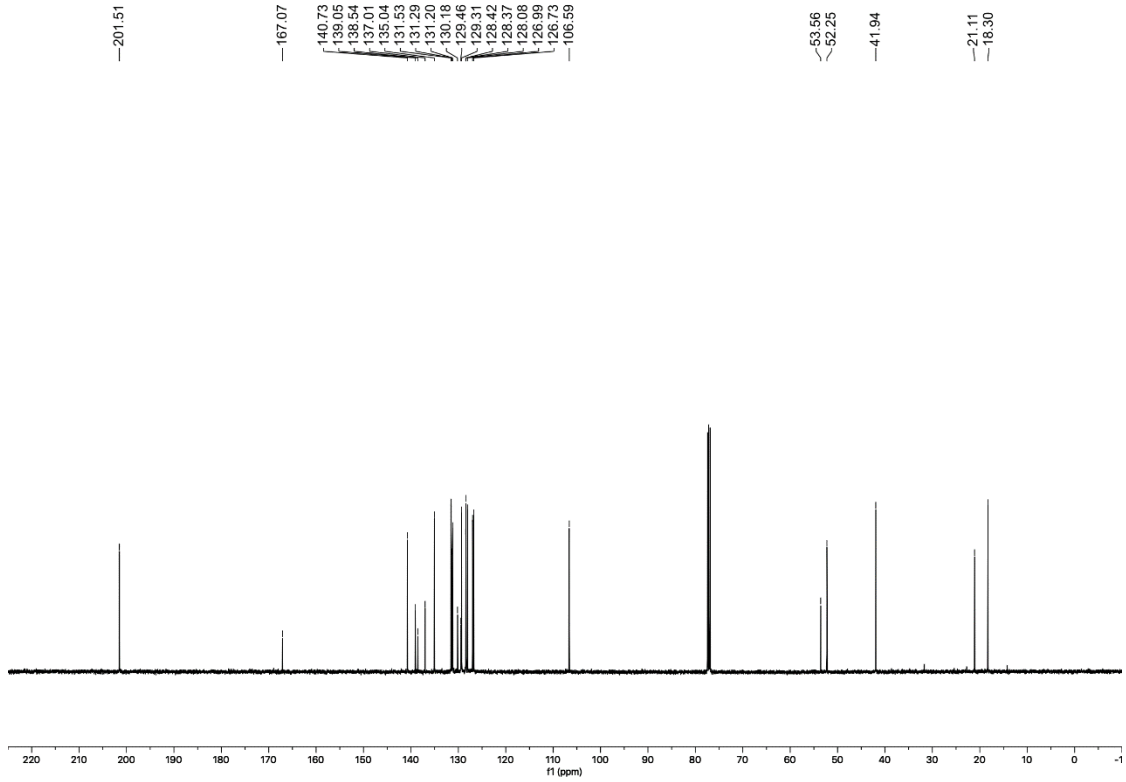


Figure S96. ^{1}H NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-methylbenzyl)but-3-enal, **4y** (500 MHz, $CDCl_3$).

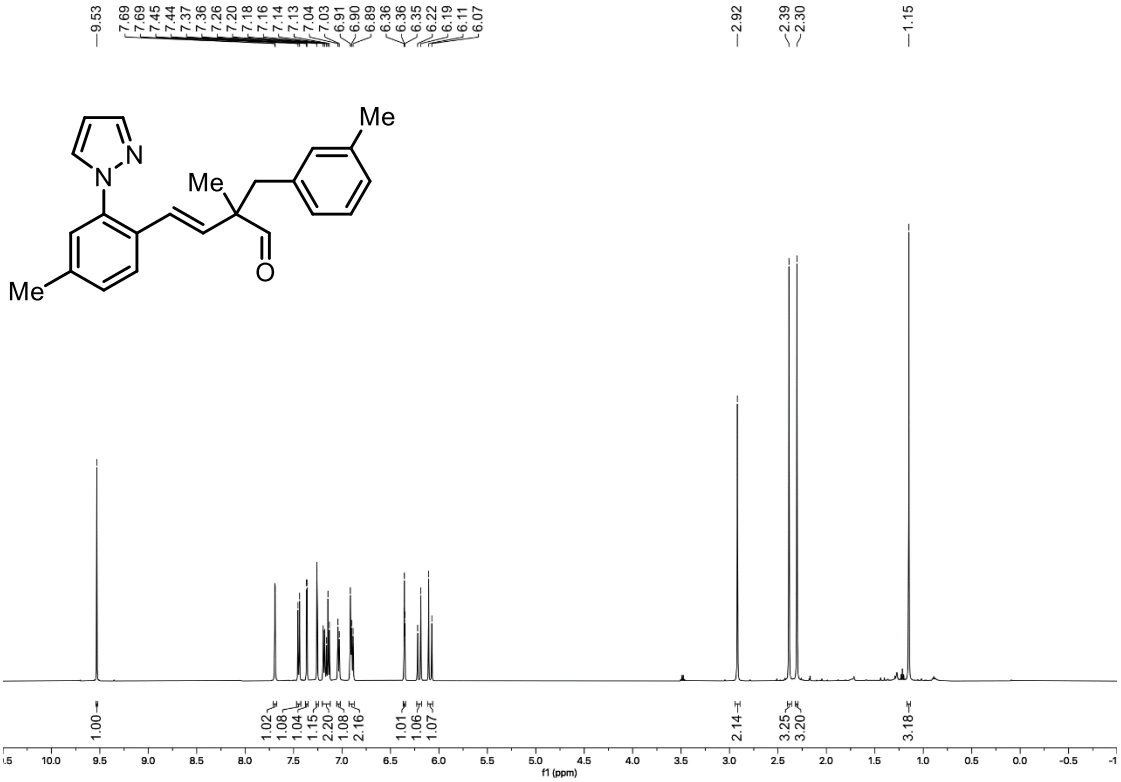


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(3-methylbenzyl)but-3-enal, **4y** (126 MHz, $CDCl_3$).

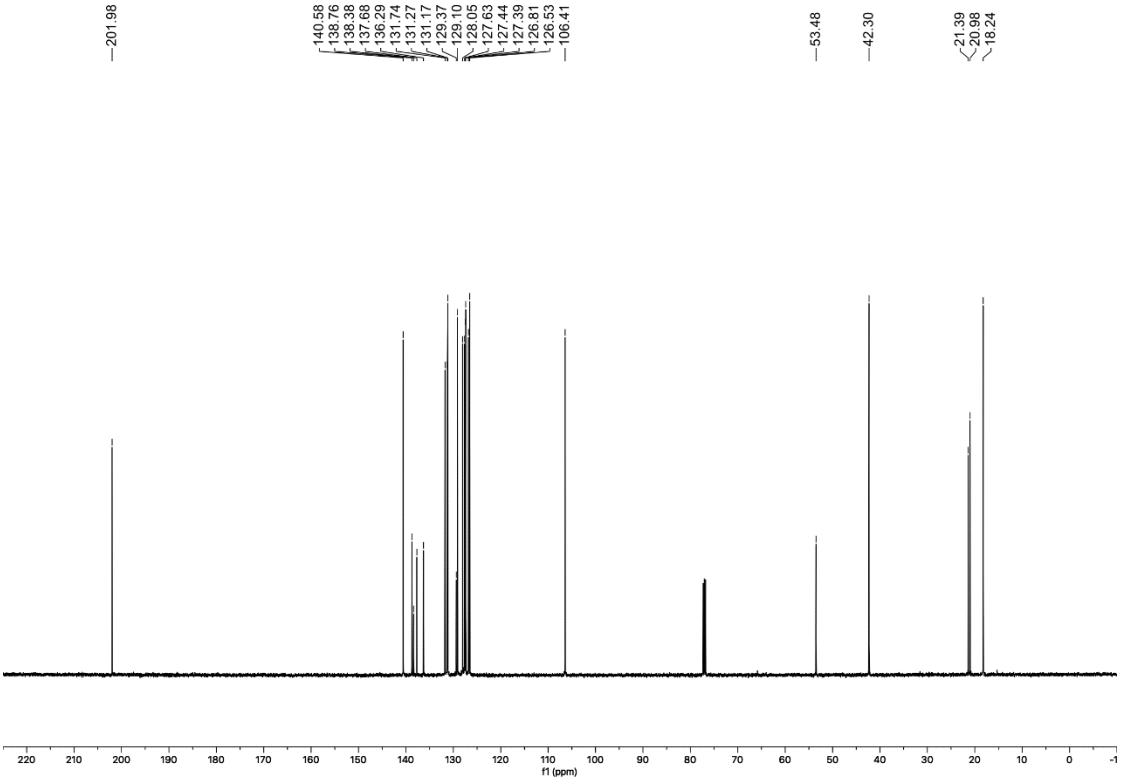


Figure S98. ^{1}H NMR spectrum of (*E*)-2-(3-methoxybenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4z** (500 MHz, $CDCl_3$).

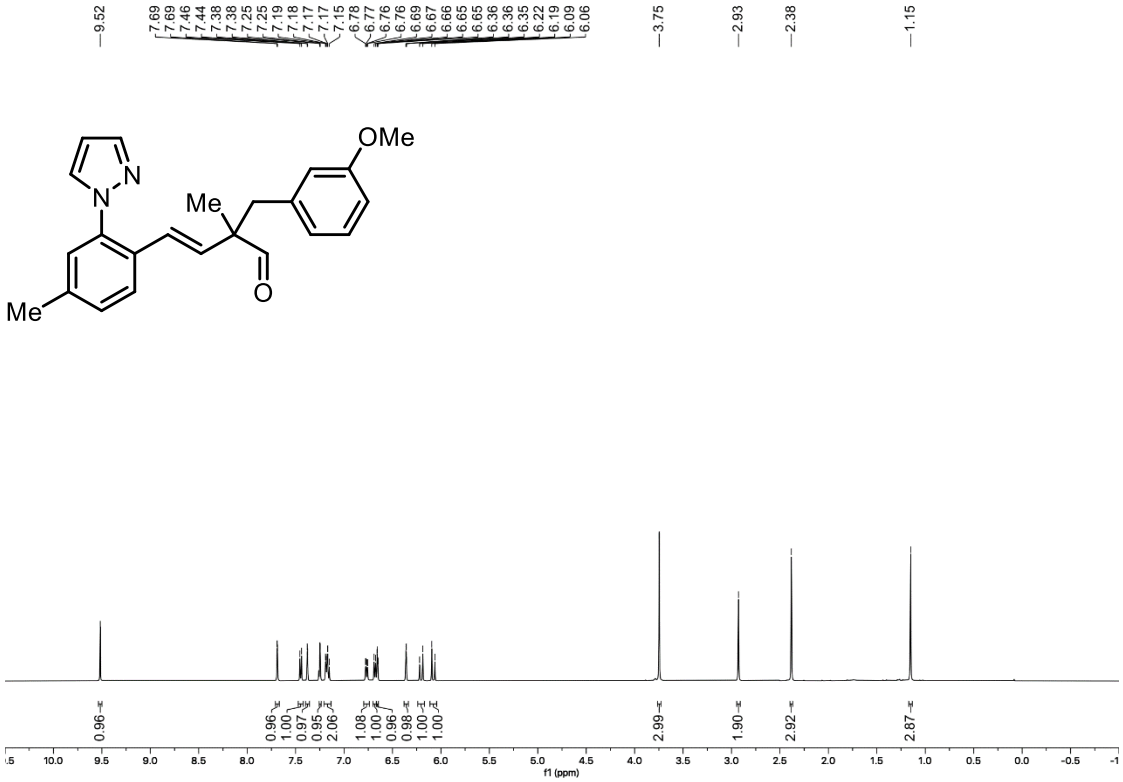


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-(3-methoxybenzyl)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-enal, **4z** (126 MHz, $CDCl_3$).

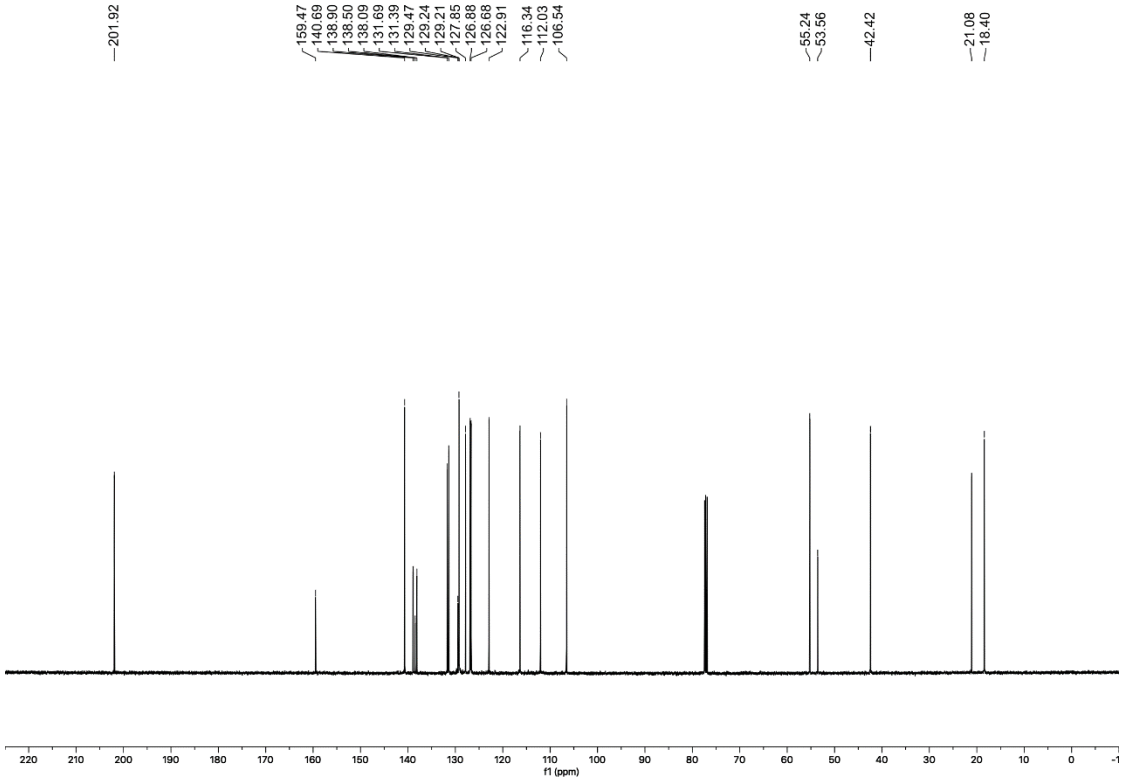


Figure S100. ^{1}H NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(naphthalen-2-ylmethyl)but-3-enal, **4aa** (500 MHz, $CDCl_3$).

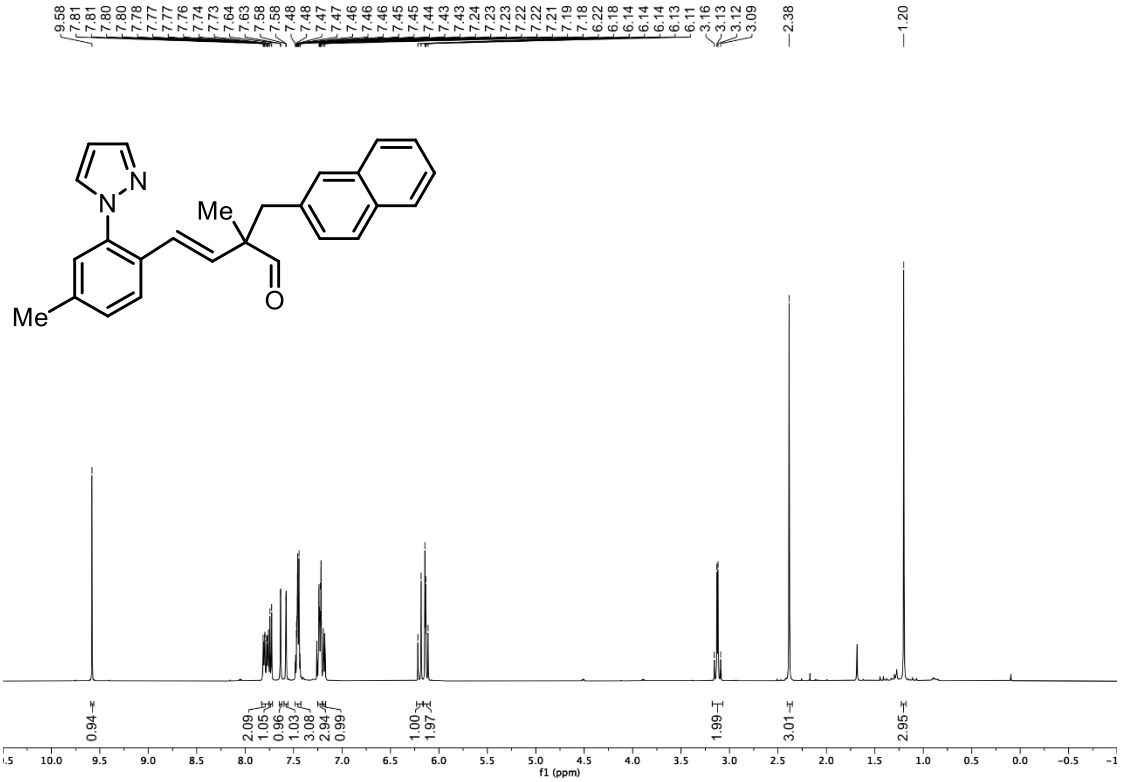


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(naphthalen-2-ylmethyl)but-3-enal, **4aa** (126 MHz, $CDCl_3$).

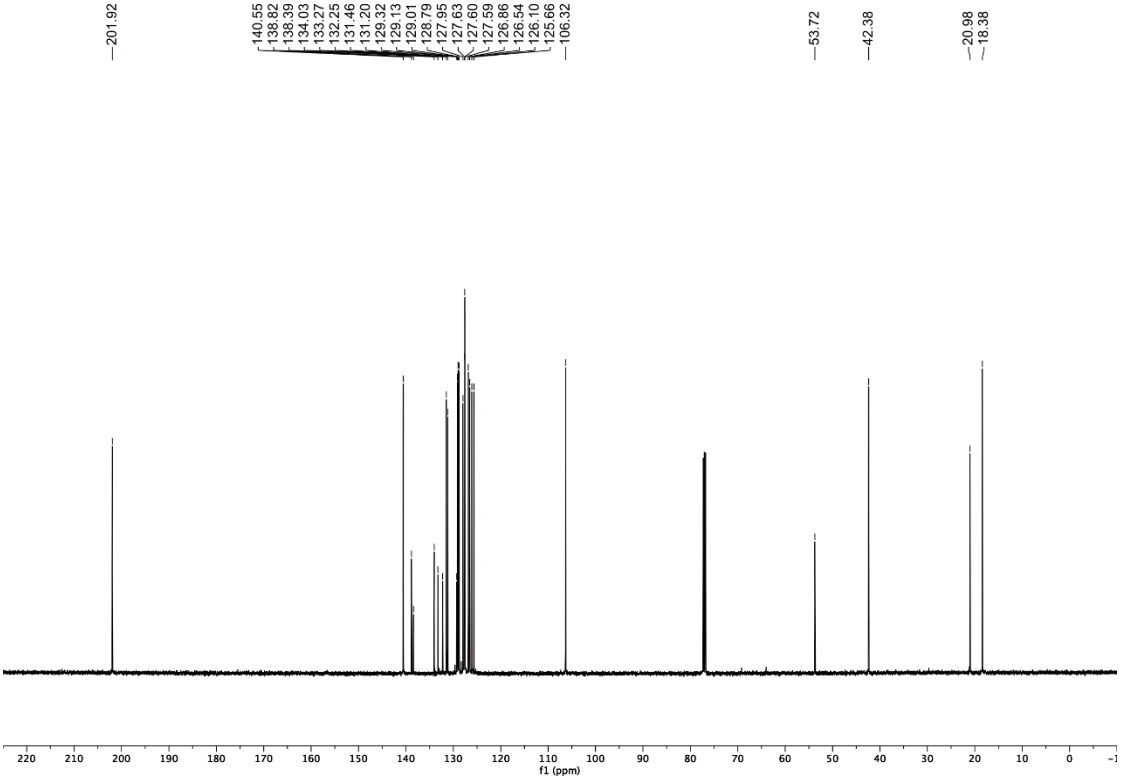


Figure S102. ^{1}H NMR spectrum of (*E*)-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-one, **6** (500 MHz, $CDCl_3$).

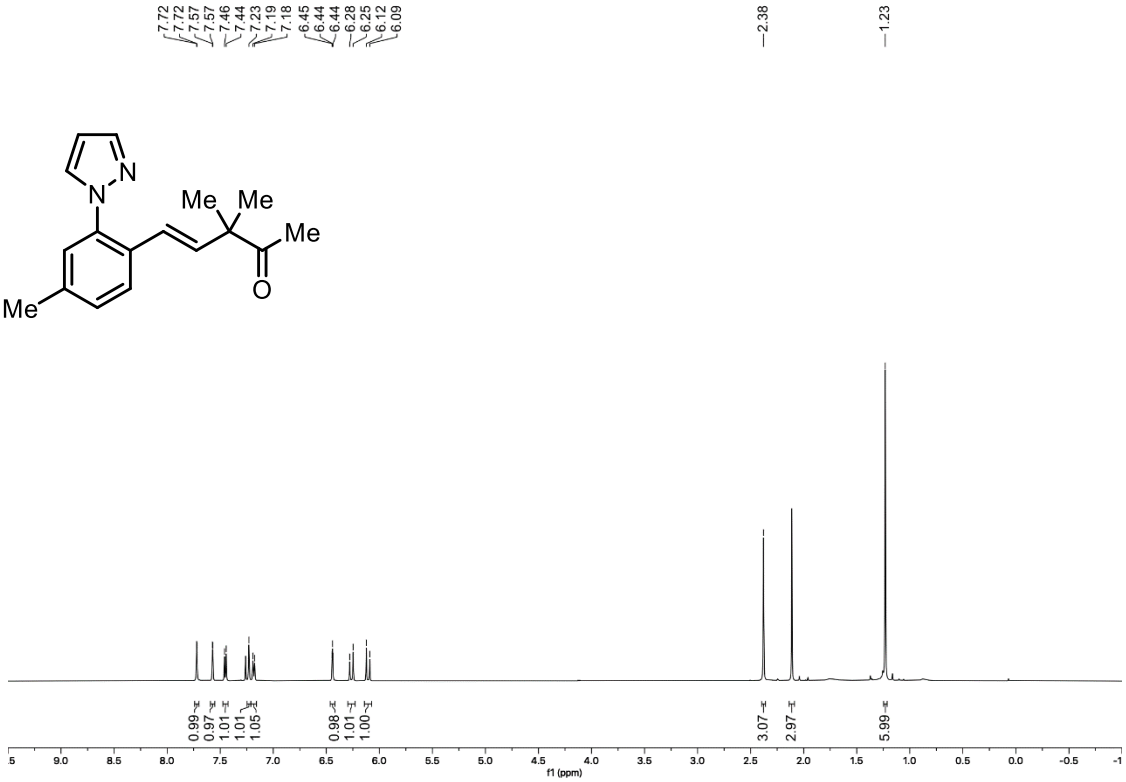


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-one, **6** (126 MHz, $CDCl_3$).

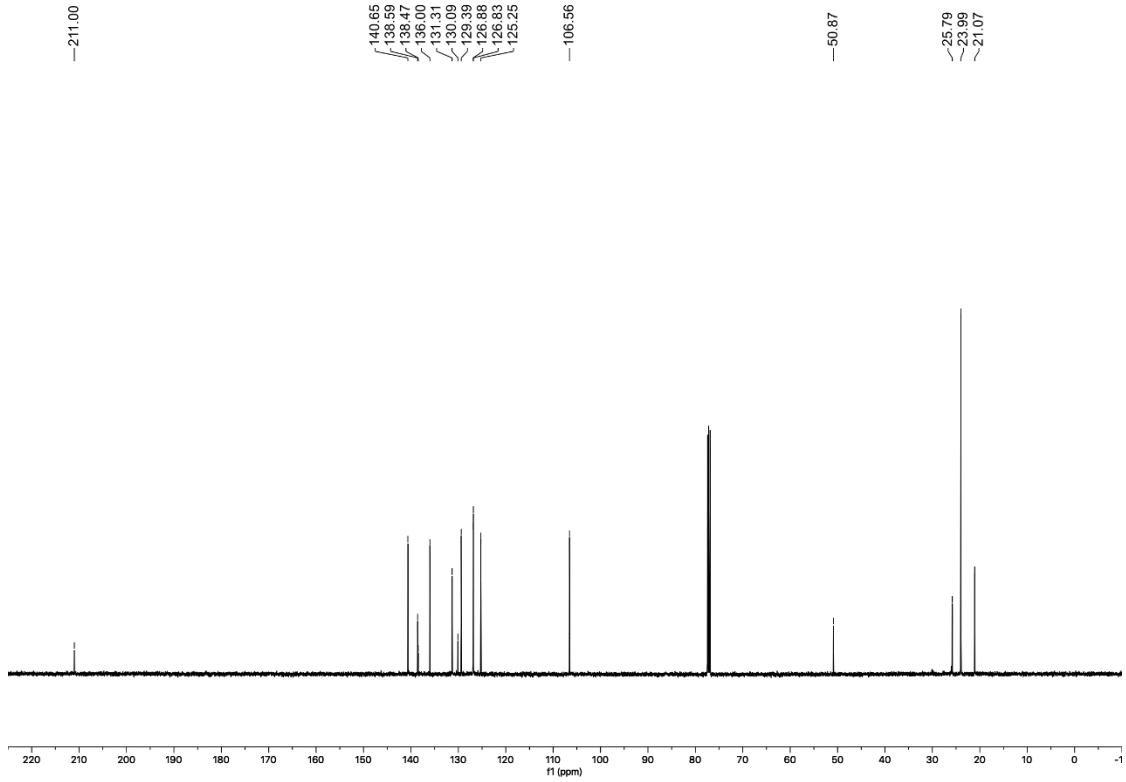


Figure S104. ^{1}H NMR spectrum of (*R*,*E*)-4-hydroxy-5,5-dimethyl-7-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hept-6-en-2-one, **7** (500 MHz, $CDCl_3$).

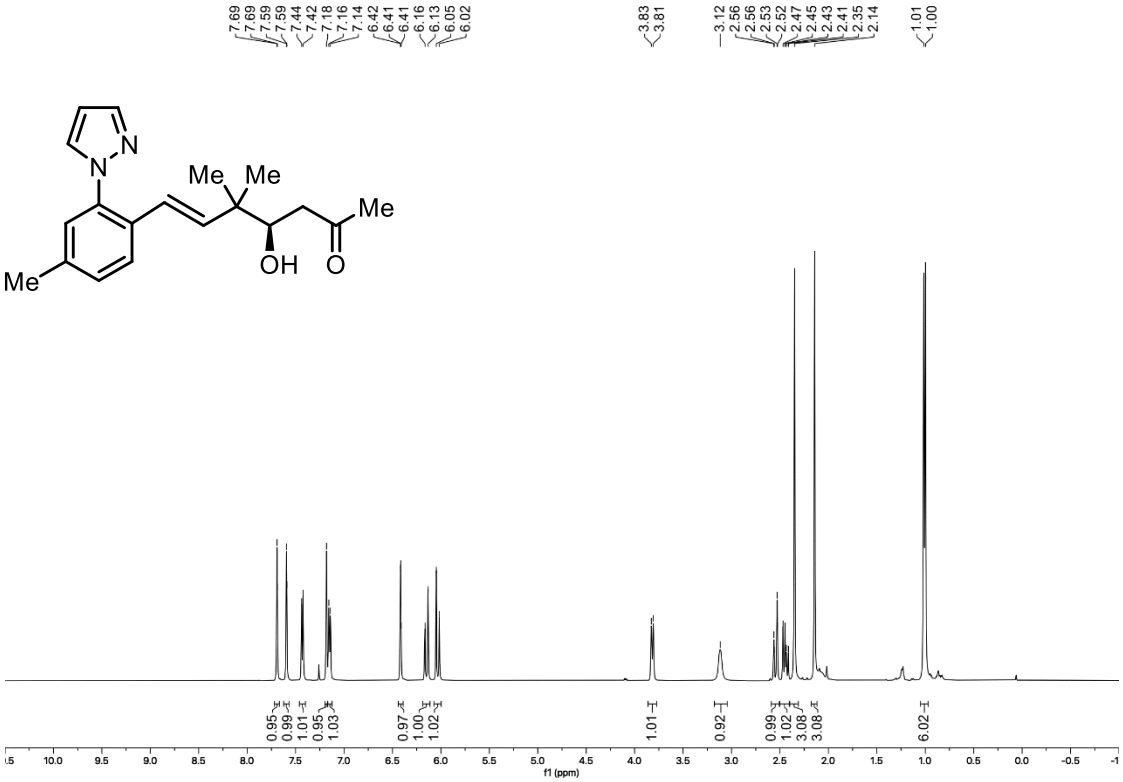


Figure S105. ^{13}C{^{1}H} NMR spectrum of (*R*,*E*)-4-hydroxy-5,5-dimethyl-7-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hept-6-en-2-one, **7** (500 MHz, $CDCl_3$).

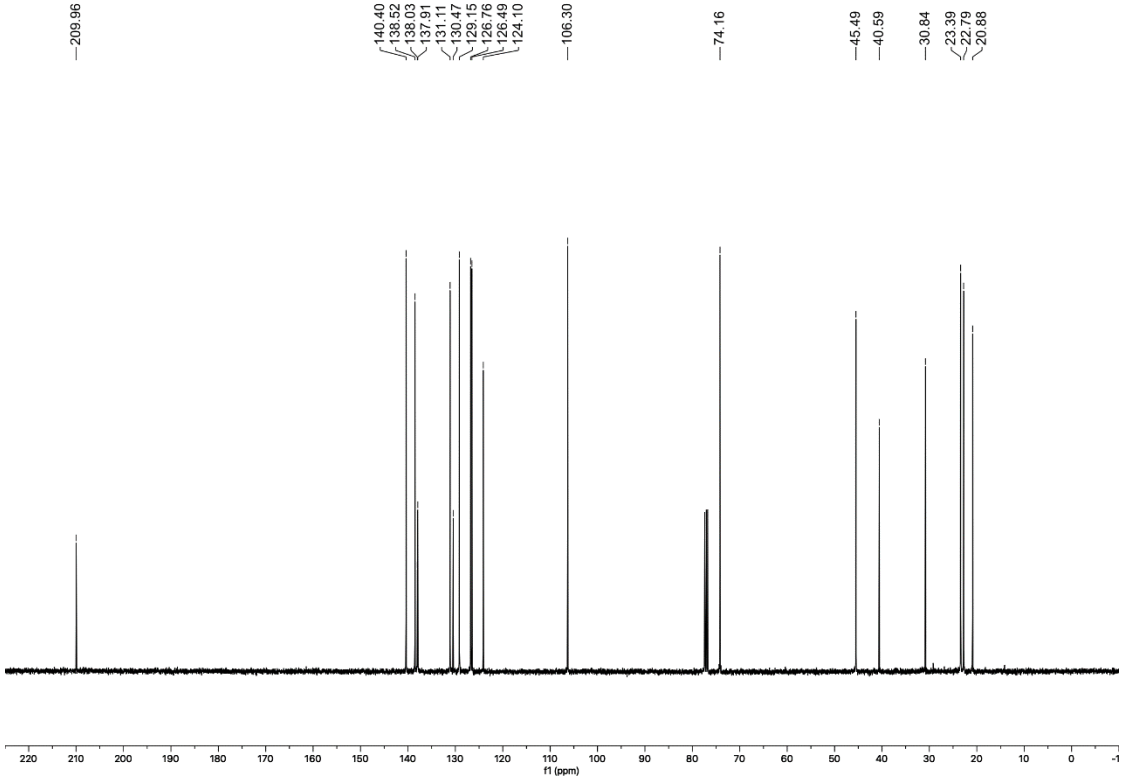


Figure S106. ^{1}H NMR spectrum of ethyl (2*E*,5*E*)-4,4-dimethyl-6-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hexa-2,5-dienoate, **8** (500 MHz, $CDCl_3$).

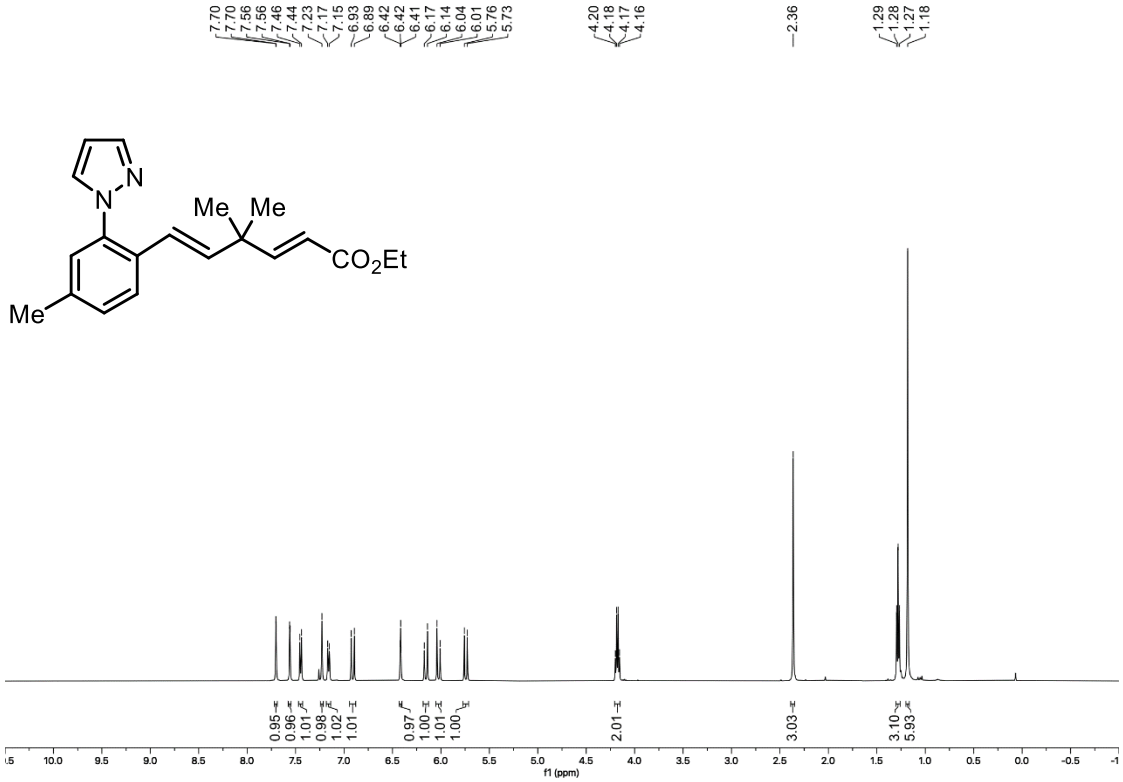


Figure S107. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl (2*E*,5*E*)-4,4-dimethyl-6-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hexa-2,5-dienoate, **8** (126 MHz, $CDCl_3$).

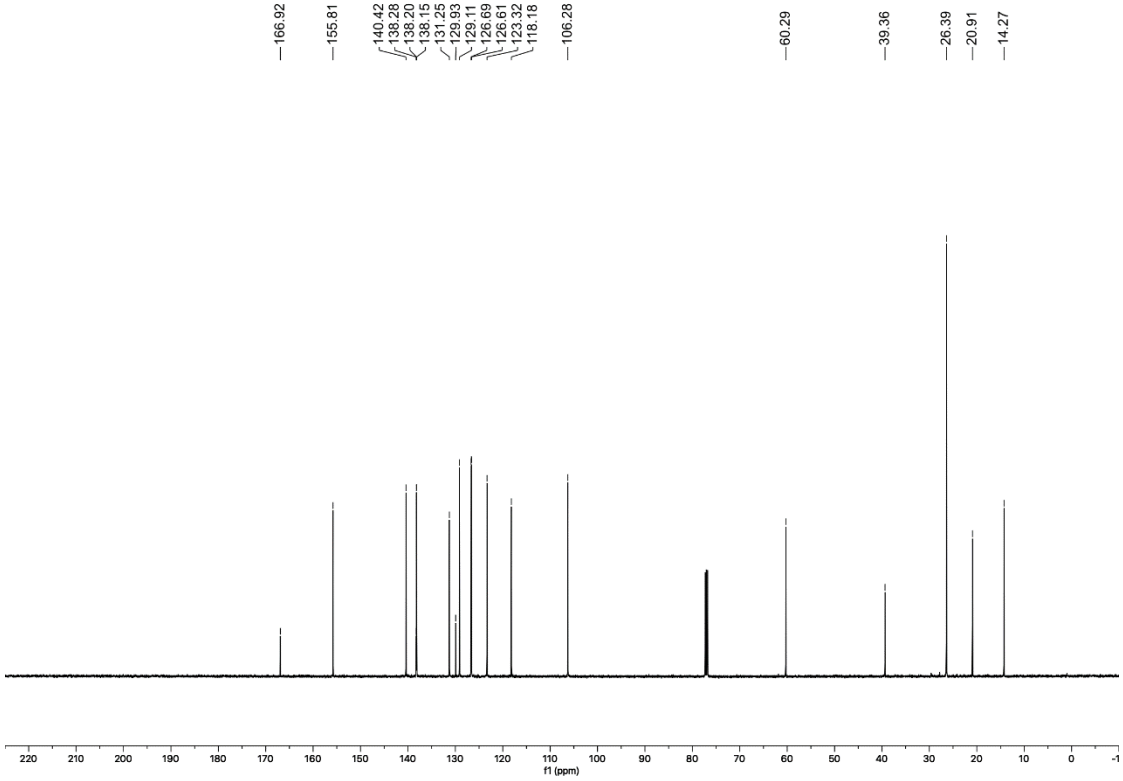


Figure S108. ^{1}H NMR spectrum of *tert*-butyl (*E*)-4-(2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)piperazine-1-carboxylate, **9** (500 MHz, $CDCl_3$, 50 °C).

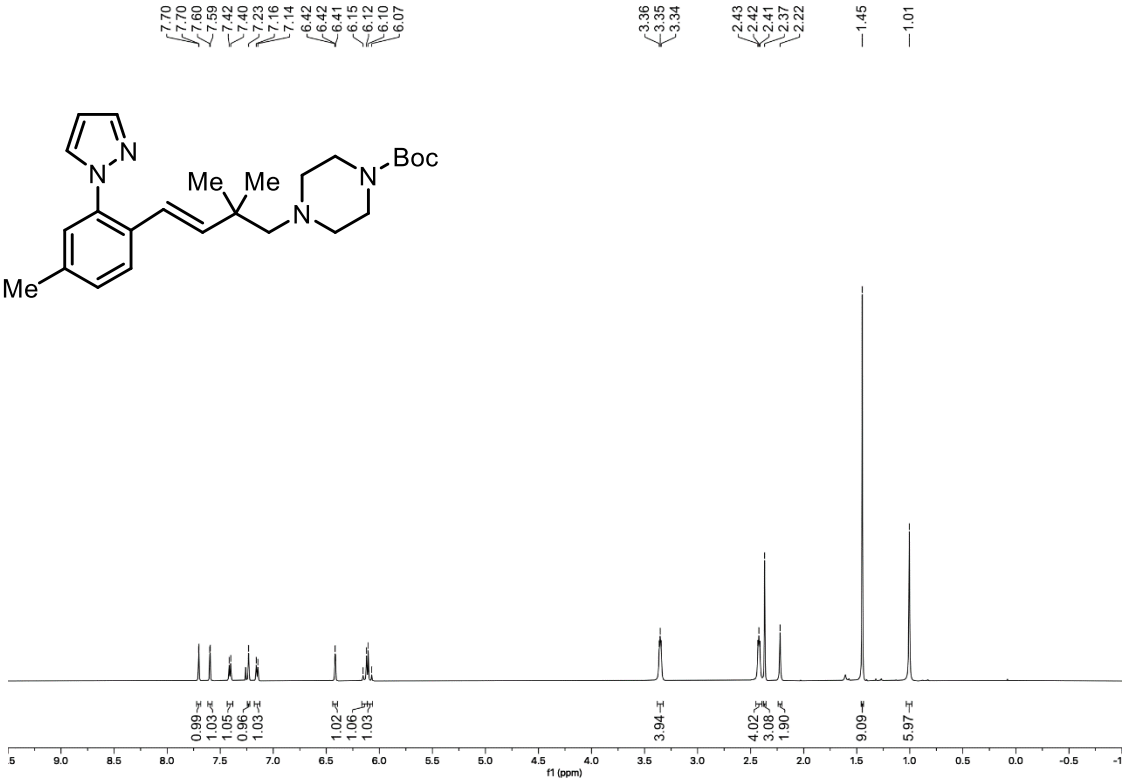


Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum of *tert*-butyl (*E*)-4-(2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)piperazine-1-carboxylate, **9** (126 MHz, $CDCl_3$, 50 °C).

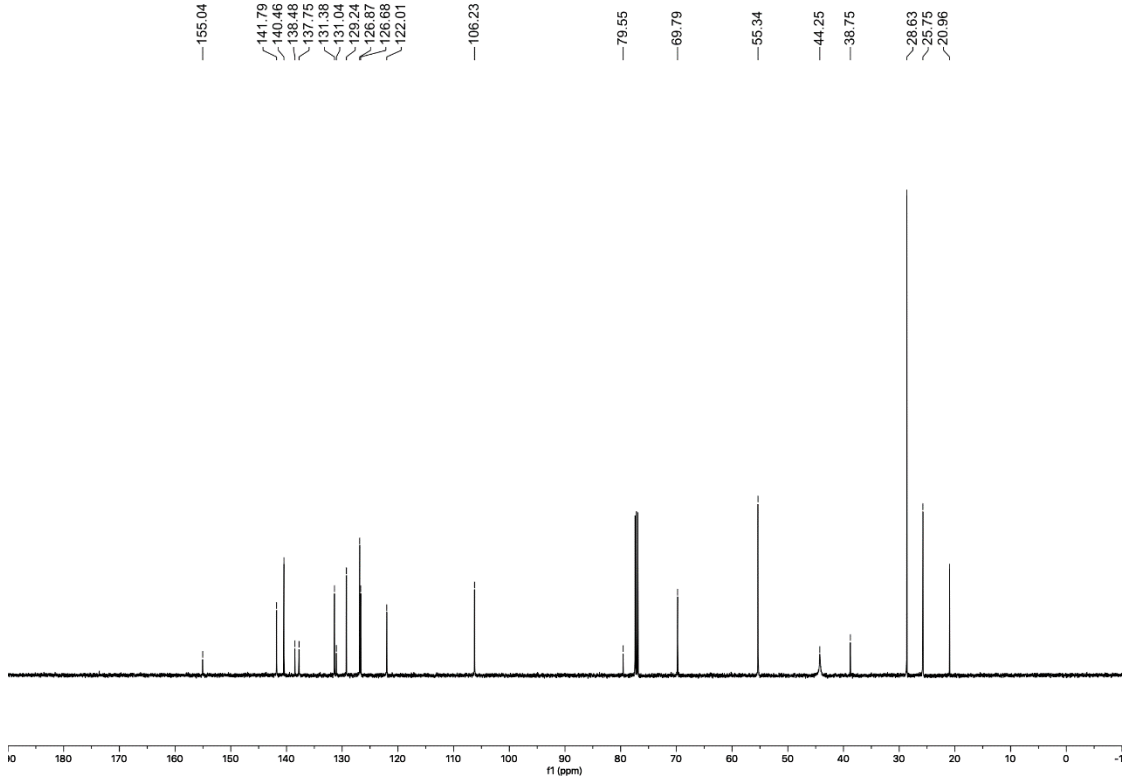


Figure S110. ^{1}H NMR spectrum of (*R*)-*N*-((3*E*)-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide, **10** (500 MHz, $CDCl_3$).

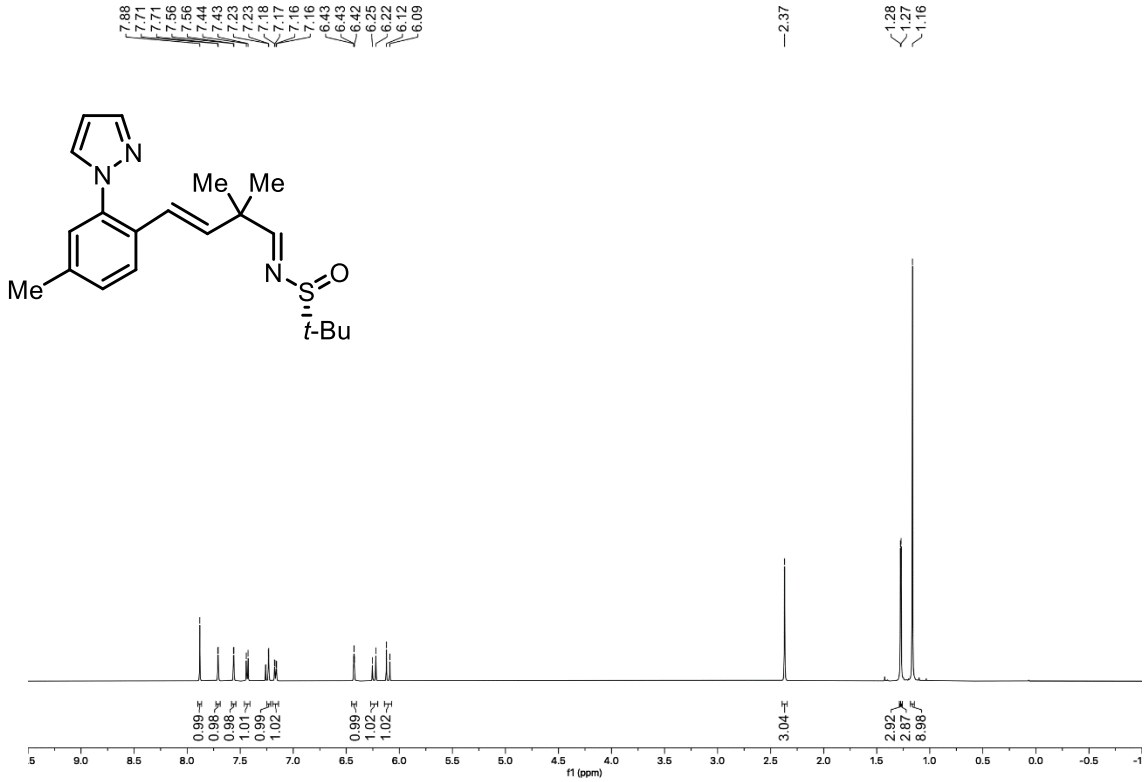


Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum of (*R*)-*N*-((3*E*)-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ylidene)-2-methylpropane-2-sulfinamide, **10** (126 MHz, $CDCl_3$).

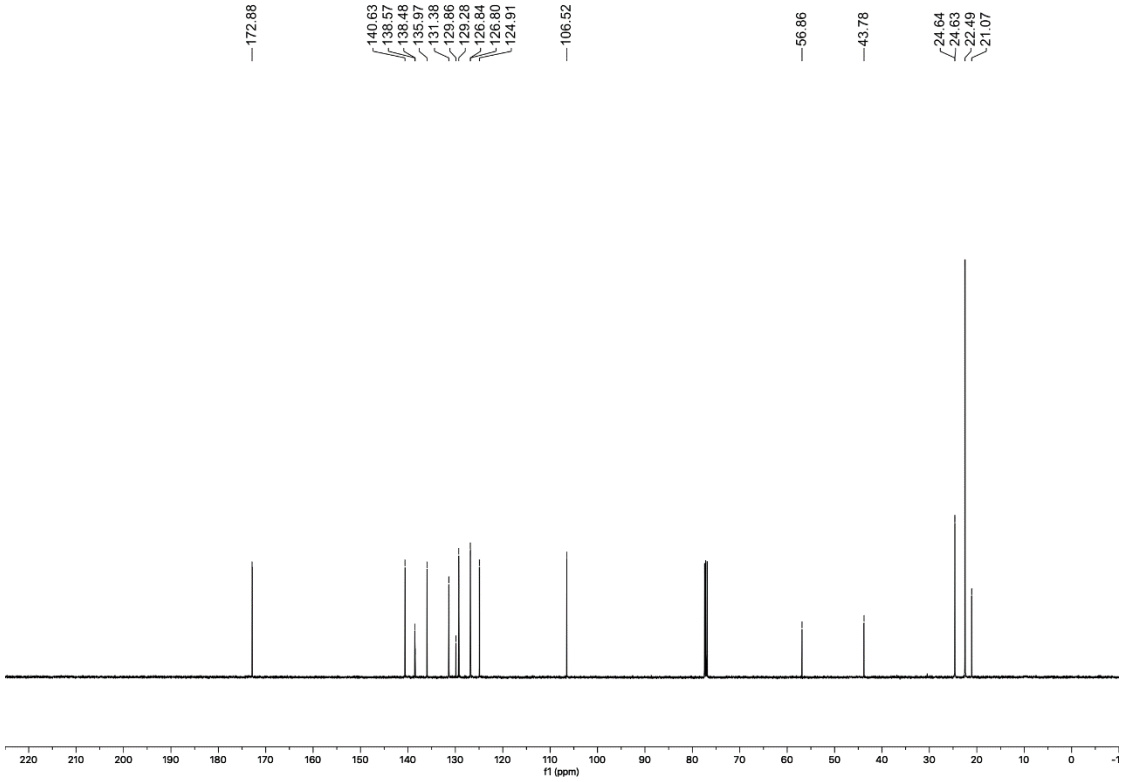


Figure S112. ^{1}H NMR spectrum of (*R*)-2-methyl-*N*-((*S*,*E*)-1,1,1-trifluoro-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-yl)propane-2-sulfinamide, **11** (500 MHz, $CDCl_3$).

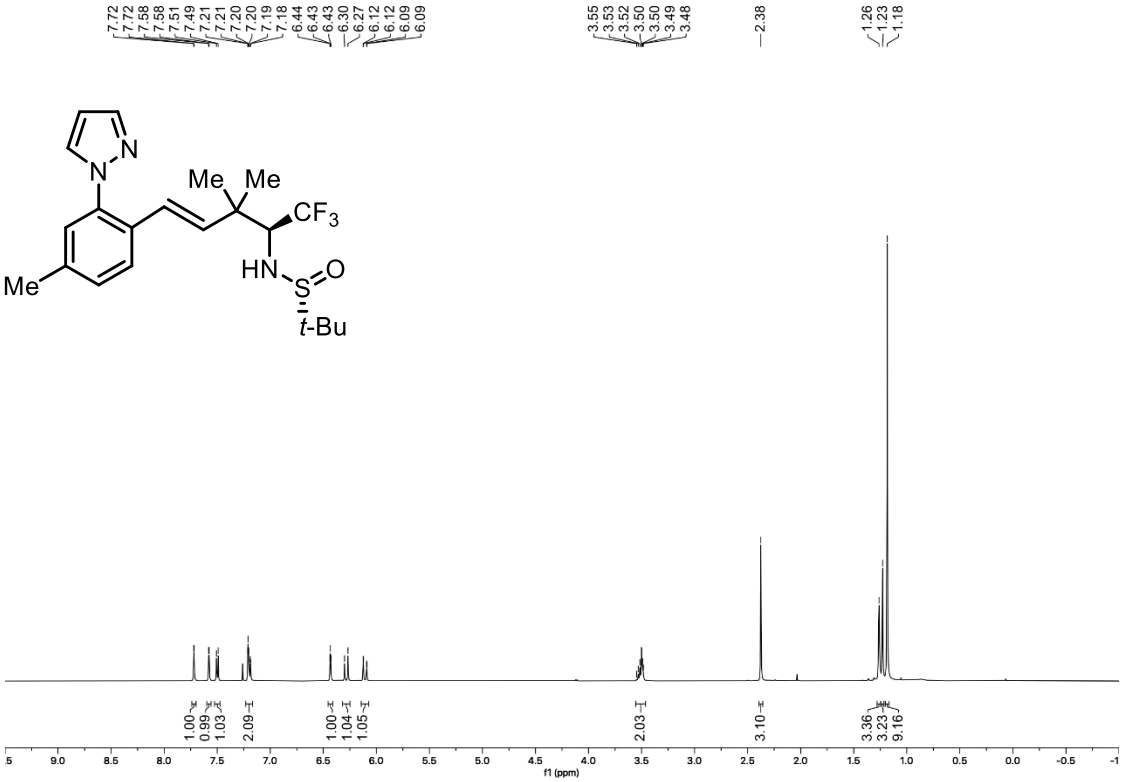


Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum of (*R*)-2-methyl-*N*-((*S*,*E*)-1,1,1-trifluoro-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-yl)propane-2-sulfinamide, **11** (126 MHz, $CDCl_3$).

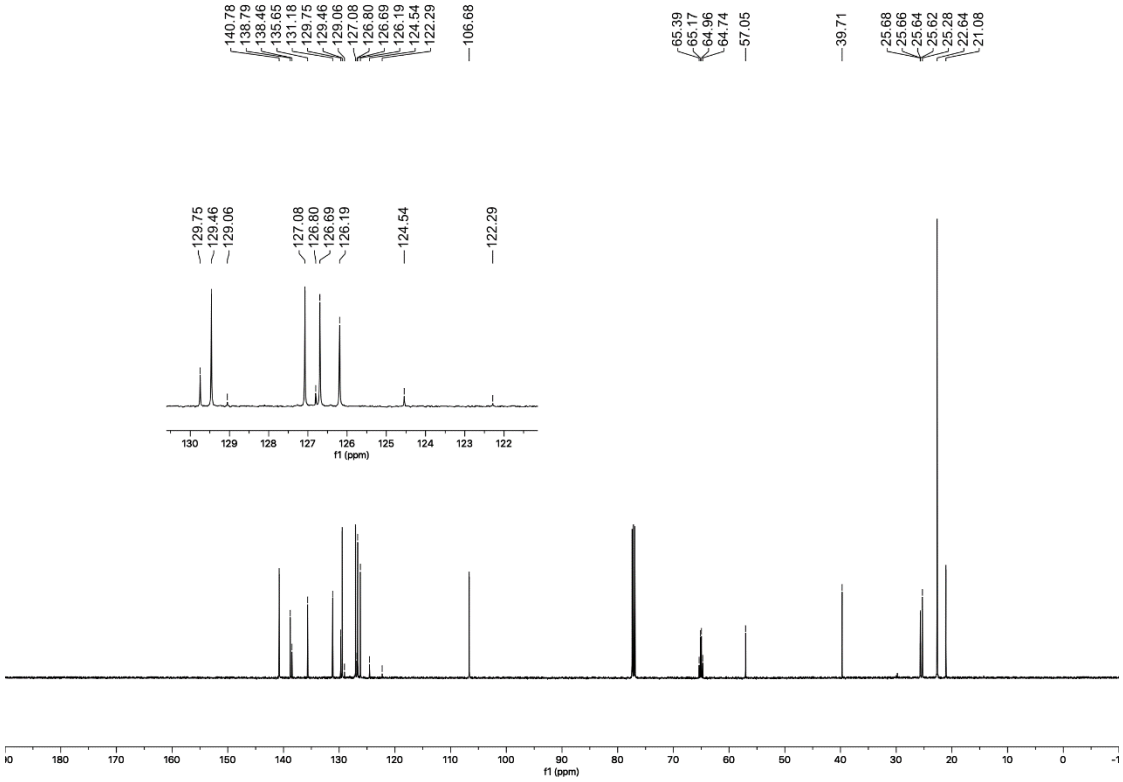


Figure S114. ^{19}F NMR spectrum of (*R*)-2-methyl-*N*-((*S*,*E*)-1,1,1-trifluoro-3,3-dimethyl-5-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-yl)propane-2-sulfinamide, **11** (471 MHz, $CDCl_3$).

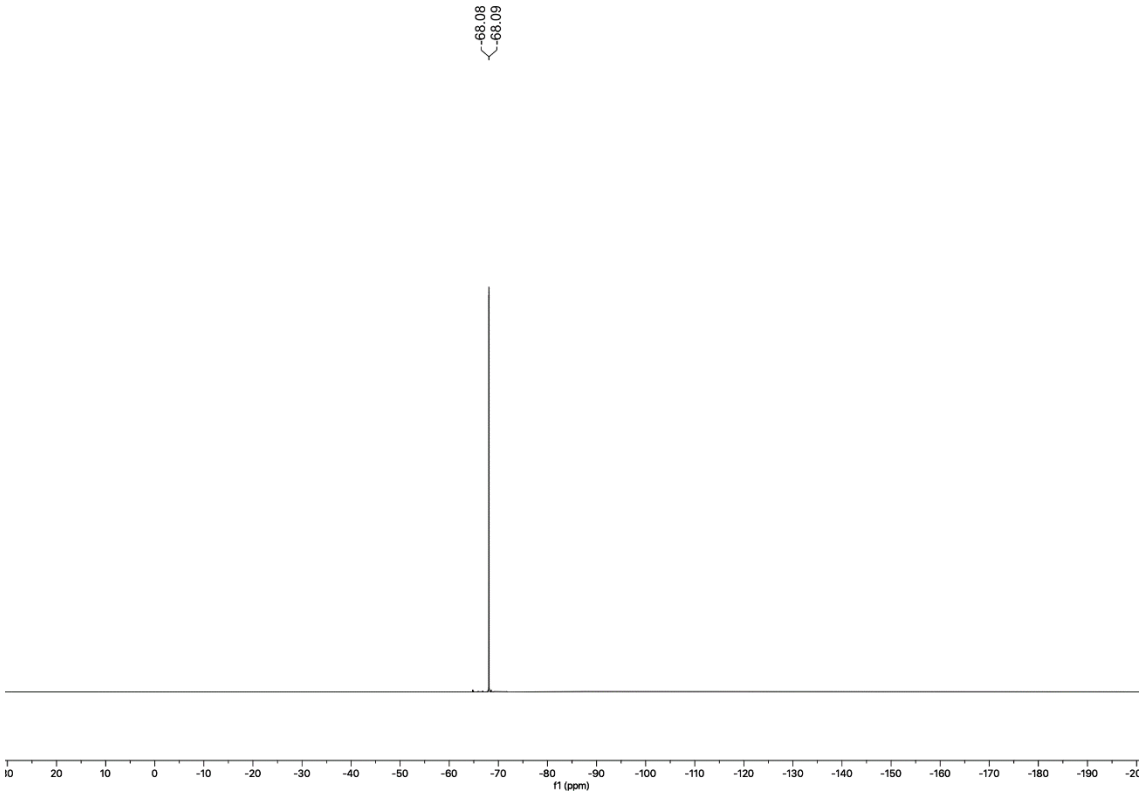


Figure S115. ^{1}H NMR spectrum of (*R*)-*N*-((*S*,*E*)-3,3-dimethyl-1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hepta-1,6-dien-4-yl)-2-methylpropane-2-sulfinamide, **12** (500 MHz, $CDCl_3$).

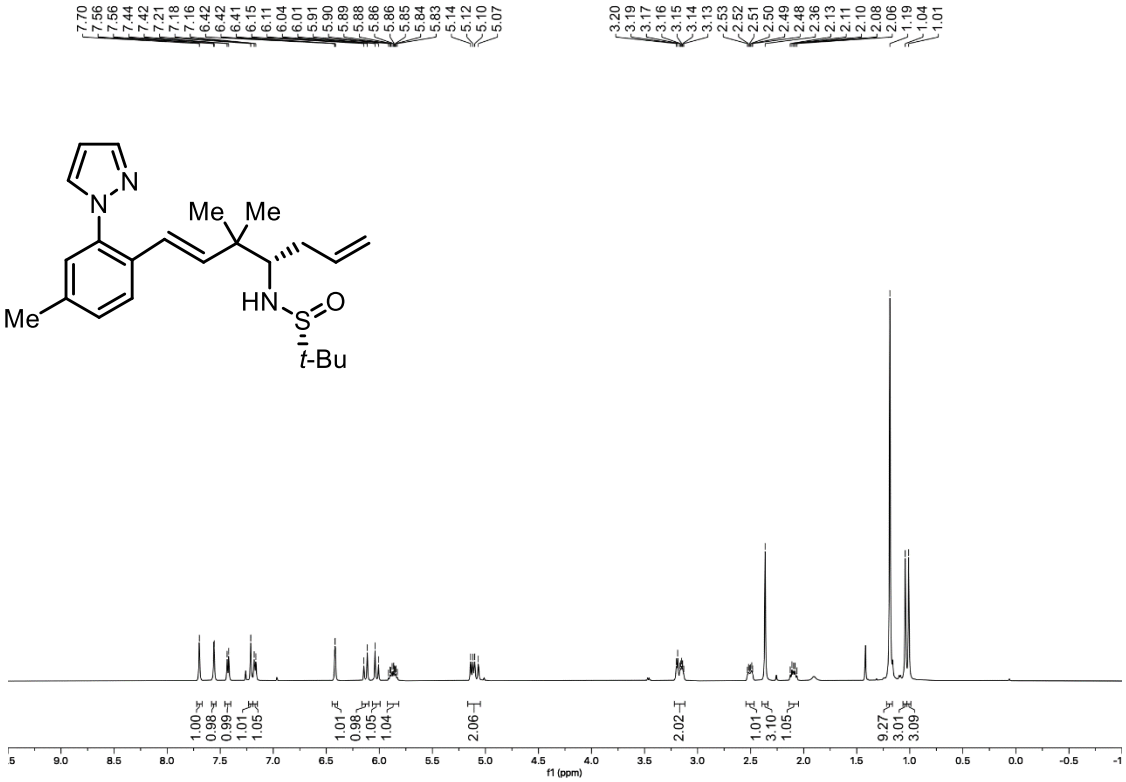
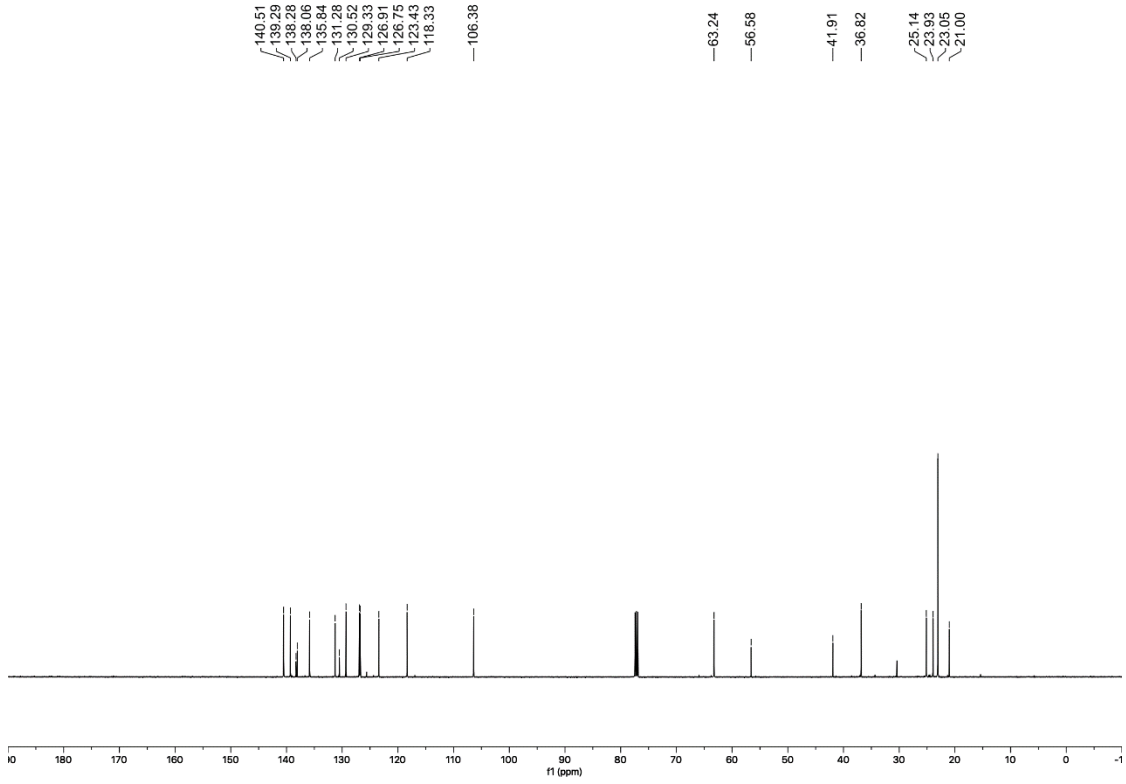


Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum of (*R*)-*N*-((*S*,*E*)-3,3-dimethyl-1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hepta-1,6-dien-4-yl)-2-methylpropane-2-sulfinamide, **12** (126 MHz, $CDCl_3$).



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