Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Belonging to the paper

Catalytic *1,2*-Dihydronaphthalene and *E*-Aryl-Diene Synthesis via Co^{III}-Carbene Radical and o-Quinodimethane Intermediates

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Contents

Experimental data.

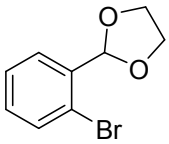
General Considerations

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents used for catalysis were dried over and distilled from sodium (toluene) or CaH_2 (dichloromethane, hexane, ethyl acetate, methanol). All chemicals were purchased from commercial suppliers (either from Sigma-Aldrich or Fluorochem) and used without further purification. NMR spectra (^1H, ^{13}C and ^{19}F) were measured on a Bruker DRX 500, Bruker AMX 400, Bruker DRX 300 or on a Varian Mercury 300 spectrometer at r.t. unless noted otherwise. Individual peaks are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant in Hz. Mass spectra of the newly synthesized compounds were recorded on an Agilent-5973 GC-MS spectrometer, and the corresponding HRMS data were recorded on a JEOL AccuTOF 4G via direct injection probe using CSI (Cold Spray Ionization). EPR spectra were recorded on a Bruker EMXplus spectrometer at room temperature (298 K).

General Procedure A, aldehyde protection.

2-bromobenzaldehyde (1 eq), ethylene glycol (5 eq) and *p*-toluene sulfonic acid (0.03 eq) were combined in toluene (0.5 M) and refluxed for 24h. After cooling down the solution was extracted with water and EtOAc, after which the organic layers were dried over $MgSO_4$. The solvent was evaporated and column chromatography yielded the pure product.

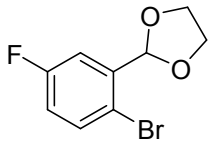
2-(2-bromophenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (hexanes → 20:1 hexanes:EtOAc) as a colorless liquid (90%).

^1H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 2H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.25 (td, *J* = 7.6, 1.8 Hz, 1H), 6.13 (s, 1H), 4.24 – 4.03 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.62, 133.00, 130.64, 127.83, 127.45, 122.96, 102.64, 65.51.

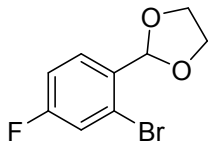
2-(2-bromo-5-fluorophenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (40:1 hexanes:EtOAc) as a colorless liquid (95%, 97% based on recovery of starting material).

^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, J = 8.7, 5.1 Hz, 1H), 7.35 (dd, J = 9.3, 3.1 Hz, 1H), 6.98 (ddd, J = 8.7, 7.7, 3.1 Hz, 1H), 6.07 (d, J = 1.4 Hz, 1H), 4.26 – 4.01 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.99 (d, J = 247.3 Hz), 138.93 (d, J = 6.9 Hz), 134.27 (d, J = 7.7 Hz), 117.75 (d, J = 22.7 Hz), 116.82 (d, J = 3.3 Hz), 115.13 (d, J = 24.3 Hz), 102.02 (d, J = 1.3 Hz), 65.56 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.93 (s).

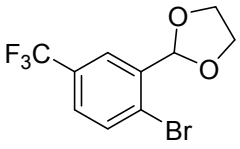
2-(2-bromo-4-fluorophenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (9:1 hexanes:EtOAc) as a yellow oil (71%).

^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.7, 6.1 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.05 (td, *J* = 8.3, 2.6 Hz, 1H), 6.04 (s, 1H), 4.29 – 3.94 (m, 4H).

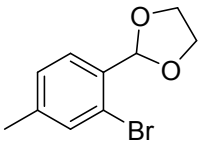
2-(2-bromo-5-(trifluoromethyl)phenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (20:1 hexanes:EtOAc) as a colorless liquid (84%, 93% based on recovery of starting material).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.10 (s, 1H), 4.14 (ddt, *J* = 19.4, 9.0, 6.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.03 (s), 133.75 (s), 130.16 (q, *J* = 33.0 Hz, ArC-CF_3), 127.32 (q, *J* = 3.7 Hz), 126.94 (s), 125.06 (q, *J* = 3.7 Hz), 123.83 (q, *J* = 272.7 Hz, CF_3), 102.03 (s, Ar-*C*H-O), 65.78 (s, O-*C*H_2*C*H_2-O). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.73.

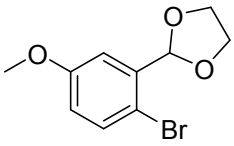
2-(2-bromo-4-methylphenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (20:1 hexanes:EtOAc) as a colorless liquid (89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.20 – 7.09 (m, 1H), 6.09 (s, 1H), 4.41 – 3.92 (m, 4H), 2.35 (s, 3H).

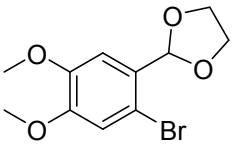
2-(2-bromo-5-methoxyphenyl)-1,3-dioxolane



The reaction was performed according to general procedure A. The product was isolated after column chromatography (1:0 → 20:1 hexanes:EtOAc) as a colorless liquid (66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 3.1 Hz, 1H), 6.81 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.06 (s, 1H), 4.23 – 4.03 (m, 4H), 3.82 (s, 3H).

2-(2-bromo-4,5-dimethoxyphenyl)-1,3-dioxolane



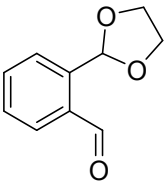
The reaction was performed according to general procedure A. The product was isolated after column chromatography (4:1 hexanes:EtOAc) as a white solid (56%, 83% based on recovery of starting material).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.01 (s, 1H), 5.99 (s, 1H), 4.26 – 3.98 (m, 4H), 3.89 (s, 3H), 3.88 (s, 3H).

General Procedure B, aldehyde introduction.

2-(2-bromophenyl)-1,3-dioxolane (1 eq) in THF (0.5 M) was cooled down to -78°C. Then n-BuLi (1.5 eq) was added dropwise and stirred for 20 min. Next N,N-DMF (2 eq) was added dropwise and the mixture was allowed to warm to 0°C. The reaction was then quenched by addition of sat. NH_4Cl and water. This was extracted with EtOAc, the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The product was purified by column chromatography.

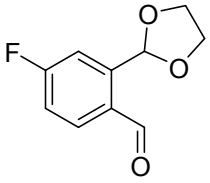
2-(1,3-dioxolane-2-yl)benzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (9:1 H:Et) and obtained as a yellow liquid (87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.76 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.64 (td, *J* = 7.5, 1.5 Hz, 1H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 6.43 (s, 1H), 4.29 – 4.03 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.82, 139.06, 134.46, 133.66, 130.20, 129.48, 127.01, 101.12, 65.39.

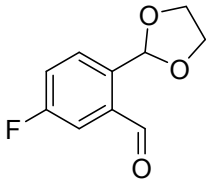
2-(1,3-dioxolan-2-yl)-4-fluorobenzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (4:1 H:Et) and obtained as a yellow oil (97%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.99 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.47 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.20 (td, *J* = 8.2, 2.6 Hz, 1H), 6.46 (s, 1H), 4.27 – 4.02 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.01 (s), 165.83 (d, *J* = 256.6 Hz), 142.89 (d, *J* = 8.2 Hz), 133.16 (d, *J* = 9.5 Hz), 130.81 (d, *J* = 2.9 Hz), 116.39 (d, *J* = 21.9 Hz), 114.20 (d, *J* = 24.0 Hz), 99.87 (d, *J* = 1.4 Hz), 65.50 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -102.70 (s). IR (neat) ν 2960, 2892, 1693, 1604, 1588, 1236, 1160, 1112, 1065, 825 cm^{-1}. HRMS(FD^{+}) calcd. for $C_{10}H_9FO_3$ $[M]^{+}$ 196.05357, found 196.05364.

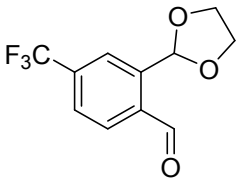
2-(1,3-dioxolan-2-yl)-5-fluorobenzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (20:1 → 9:1 hexanes:EtOAc) as a yellow oil (51%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.40 (d, *J* = 2.5 Hz, 1H), 7.70 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.28 (td, *J* = 8.2, 2.8 Hz, 1H), 6.29 (s, 1H), 4.23 – 3.97 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.10.

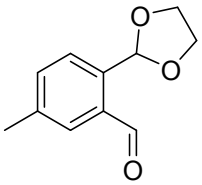
2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)benzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (4:1 hexanes:EtOAc) as a yellow oil (64%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.10 – 7.96 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 6.41 (s, 1H), 4.29 – 3.97 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.21.

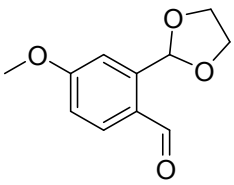
2-(1,3-dioxolan-2-yl)-5-methylbenzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (3:1 hexanes:EtOAc) as a yellow liquid (75%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.35 (s, 1H), 4.30 – 3.87 (m, 4H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.17, 139.71, 136.35, 134.48, 134.43, 130.75, 127.31, 101.37, 65.44, 21.17. IR (neat) ν 2957, 2923, 2890, 1691, 1072, 823 cm^{-1}. HRMS(EI^{+}) calcd. for $C_{11}H_{12}O_3$ $[M]^{+}$ 192.0786, found 192.0782.

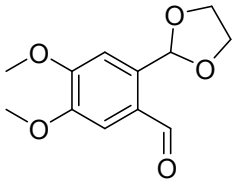
2-(1,3-dioxolan-2-yl)-4-methoxybenzaldehyde



The reaction was performed according to general procedure B. The product was isolated after column chromatography (7:3 hexanes:EtOAc) and obtained as a yellow oil (94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.00 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.47 (s, 1H), 4.22 – 4.03 (m, 4H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.20, 163.79, 141.57, 133.25, 127.56, 114.21, 112.07, 100.30, 65.28, 55.53.

2-(1,3-dioxolan-2-yl)-4,5-dimethoxybenzaldehyde



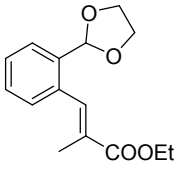
The reaction was performed according to general procedure B. The product was isolated after column chromatography (1:1 hexanes:EtOAc) as a white solid (88%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.47 (s, 1H), 7.21 (s, 1H), 6.36 (s, 1H), 4.28 – 4.04 (m, 4H), 3.98 (s, 3H), 3.95 (s, 3H).

General Procedure C, Horner-Wadsworth-Emmons reaction.

A Schlenk was charged with NaH (60% in oil, 1.2 eq) and THF was added. After cooling to 0°C the phosphonate was slowly added and the mixture was stirred for 30 min. 2-(1,3-dioxolane-2-yl)benzaldehyde (1 eq) was then slowly added and the mixture was stirred for another 30 min. Then the mixture was extracted with Et_2O and sat. $NaHCO_3$, washed with brine and dried over $MgSO_4$. The product was used without further purification.

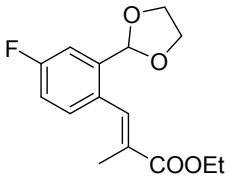
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)phenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a colorless liquid and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.59 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.22 (dd, *J* = 6.9, 2.1 Hz, 1H), 5.85 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.19 – 3.90 (m, 4H), 1.93 (d, *J* = 1.5 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

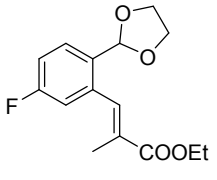
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-4-fluorophenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a yellow oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 1H), 7.32 (dd, *J* = 9.5, 2.8 Hz, 1H), 7.21 (dd, *J* = 5.6, 0.8 Hz, 1H), 7.19 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.06 (td, *J* = 8.3, 2.8 Hz, 1H), 5.83 (d, *J* = 1.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.19 – 3.98 (m, 4H), 1.92 (d, *J* = 1.5 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.81 (s).

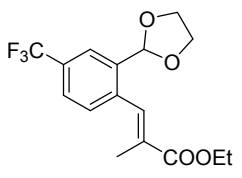
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-5-fluorophenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a yellow oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.57 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.03 (td, *J* = 8.3, 2.5 Hz, 1H), 6.92 (dd, *J* = 9.5, 2.6 Hz, 1H), 5.80 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.20 – 3.89 (m, 4H), 1.93 (d, *J* = 1.6 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.40.

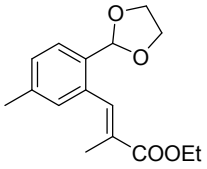
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-4-(trifluoromethyl)phenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a yellowish oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.67 (m, 2H), 7.50 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.10 – 3.95 (m, 4H), 1.78 (d, *J* = 1.6 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.67.

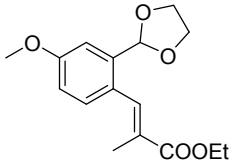
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-5-methylphenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a yellowish oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.02 (s, 1H), 5.81 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.19 – 3.96 (m, 4H), 2.36 (s, 3H, C*H*$_3$Ar), 1.93 (d, *J* = 1.5 Hz, 3H, *CH*$_3$-allyl), 1.34 (t, *J* = 7.1 Hz, 3H).

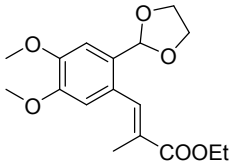
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-4-methoxyphenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a yellowish oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.6 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 6.93 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.87 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22 – 4.02 (m, 4H), 3.86 (s, 3H, O*Me*), 1.99 (d, *J* = 1.5 Hz, 3H, allyl), 1.37 (t, *J* = 7.1 Hz, 3H).

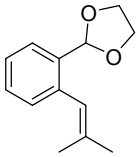
ethyl (E)-3-(2-(1,3-dioxolan-2-yl)-4,5-dimethoxyphenyl)-2-methylacrylate



The reaction was performed according to general procedure C. The product was obtained as a light green oil and used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (br s, 1H, allyl), 7.16 (s, 1H), 6.92 (s, 1H), 6.03 (s, 1H), 3.98 (q, *J* = 7.0 Hz, 2H), 3.90 – 3.83 (m, 4H, O*CH*$_2$*CH*$_2$O), 3.68 (s, 3H, OMe), 3.63 (s, 3H, OMe), 1.70 (d, *J* = 1.7 Hz, 3H, *CH*$_3$-allyl), 1.06 (t, *J* = 7.1, 3H).

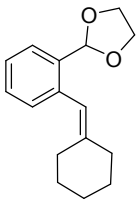
2-(2-(2-methylprop-1-en-1-yl)phenyl)-1,3-dioxolane



Under Schlenk conditions isopropyltriphenylphosphonium iodide was dissolved in THF and cooled down to -78 °C. Next BuLi was added dropwise and the solution was stirred for 1h at -78 °C and 1h at room temperature. Then the aldehyde was added and the solution was stirred for another 2h after which the reaction was quenched with water and extracted with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The mixture was then purified by column chromatography (40:1 hexanes:EtOAc) to give the product as a colorless liquid (40%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.37 – 7.19 (m, 2H), 7.14 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.40 (s, 1H), 5.92 (s, 1H), 4.26 – 3.85 (m, 4H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.69 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.17, 136.70, 135.37, 130.11, 128.78, 126.60, 125.83, 122.57, 101.79, 65.51, 26.23, 19.52.

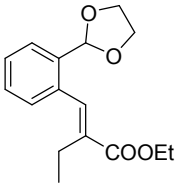
2-(2-(cyclohexylidenemethyl)phenyl)-1,3-dioxolane



Under Schlenk conditions at 10°C cyclohexyltriphenylphosphonium bromide (1 eq) in Et_2O (0.4M) was treated with n-BuLi (2.5M, 1.1 eq), The salt gradually dissolved to give a blood red solution. This was stirred for another 1.5h. Then a solution of 2-(1,3-dioxolane-2-yl)benzaldehyde (1.01 eq) in Et_2O (1.5M) was added slowly and the mixture was stirred over night at room temperature. The mixture was then concentrated, hexanes was added and a filtration was done to remove triphenylphosphine oxide. The filtrate was concentrated and extracted with Et_2O, washed with brine, dried over $MgSO_4$ and concentrated again to give the product as a white oil which was used without further purification

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.36 – 7.20 (m, 2H), 7.17 – 7.08 (m, 1H), 6.34 (s, 1H), 5.94 (s, 1H), 4.22 – 3.95 (m, 4H), 2.33 – 2.22 (m, 2H), 2.19 – 2.10 (m, 2H), 1.73 – 1.45 (m, 6H).

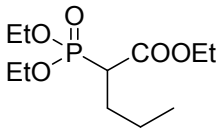
ethyl (E)-2-(2-(1,3-dioxolan-2-yl)benzylidene)butanoate



The reaction was performed according to general procedure C. The product was obtained as a yellow oil and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.60 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.21 (dd, *J* = 6.5, 2.3 Hz, 1H), 5.85 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.19 – 3.98 (m, 4H), 2.36 (q, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.00 (td, *J* = 7.4, 1.0 Hz, 3H).

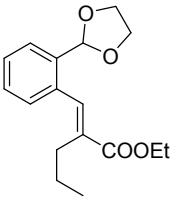
ethyl 2-(diethoxyphosphoryl)pentanoate



Under Schlenk conditions KO^{t}Bu (1,1 eq) was added at 0°C to a solution of ethyl 2-(diethoxyphosphoryl)acetate (1 eq) in DMSO (1.0 M). This mixture was stirred at room temperature until the KO^{t}Bu was dissolved. Then 1-bromopropane (1,1 eq) was added. Next the solution was stirred for 1 hour at 60°C. Finally the mixture was poured into a saturated ammonium chloride solution and extracted with ether. The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated to yield the product as a colorless liquid (93%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.32 – 4.06 (m, 6H), 3.07 – 2.83 (m, 1H), 2.08 – 1.69 (m, 2H), 1.56 – 1.22 (m, 11H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.96. HRMS(EI$^+$) calcd. for $C_9H_{18}O_5P$ [M-Et]$^+$ 237.08918, found 237.08902.

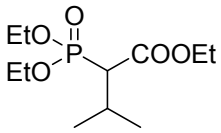
ethyl (E)-2-(2-(1,3-dioxolan-2-yl)benzylidene)pentanoate



The reaction was performed according to general procedure C. The product was obtained as a yellow oil and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.61 – 7.55 (m, 1H), 7.43 – 7.30 (m, 2H), 7.22 – 7.14 (m, 1H), 5.83 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.19 – 3.97 (m, 4H), 2.35 – 2.23 (m, 2H), 1.51 – 1.40 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H).

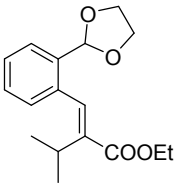
ethyl 2-(diethoxyphosphoryl)-3-methylbutanoate



Under Schlenk conditions KO^{t}Bu (1,1 eq) was added at 0°C to a solution of ethyl 2-(diethoxyphosphoryl)acetate (1 eq) in DMSO (1.0 M). This mixture was stirred at room temperature until the KO^{t}Bu was dissolved. Then 2-iodopropane (1,1 eq) was added. Next the solution was stirred for 1 hour at 60°C. Finally the mixture was poured into a saturated ammonium chloride solution and extracted with ether. The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated to yield the product as a yellow oil (95%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.32 – 4.02 (m, 6H), 2.69 (dd, *J* = 20.2, 9.4 Hz, 1H), 2.36 (dq, *J* = 17.8, 8.1, 7.5 Hz, 1H), 1.28 (dt, *J* = 10.2, 6.7 Hz, 9H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H). ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.60.

ethyl (E)-2-(2-(1,3-dioxolan-2-yl)benzylidene)-3-methylbutanoate

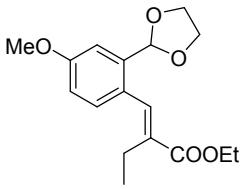


The reaction was performed according to general procedure C. The product was obtained as a mixture of E and Z isomers in a 2:1 ratio and as a colorless oil and used without further purification.

Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.61 – 7.50 (m, 1H), 7.37 – 7.31 (m, 1H), 7.31 – 7.22 (m, 1H), 7.15 – 7.09 (m, 1H), 5.90 (s, 1H), 4.18 – 3.97 (m, 4H), 3.94 (q, *J* = 7.1 Hz, 2H), 2.94 – 2.72 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 6H), 0.87 (t, *J* = 7.1 Hz, 3H).

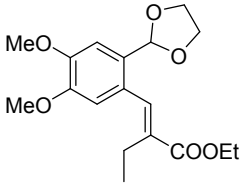
E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 1H), 7.37 – 7.31 (m, 1H), 7.31 – 7.22 (m, 1H), 7.15 – 7.09 (m, 1H), 6.90 (d, *J* = 1.3 Hz, 1H), 5.81 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.18 – 3.97 (m, 4H), 2.94 – 2.72 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 6H).

ethyl (E)-2-(2-(1,3-dioxolan-2-yl)-4-methoxybenzylidene)butanoate



The reaction was performed according to general procedure C. The product was obtained as a light yellow oil and used without further purification.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.15 (s, 1H), 6.90 (dd, *J* = 8.4, 2.7 Hz, 2H), 5.83 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.18 – 3.96 (m, 4H), 3.84 (s, 3H), 2.37 (q, *J* = 7.4 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H).

ethyl (E)-2-(2-(1,3-dioxolan-2-yl)-4,5-dimethoxybenzylidene)butanoate



The reaction was performed according to general procedure C. The product was obtained as a yellow oil and used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.11 (s, 1H), 6.72 (s, 1H), 5.78 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.92 (s, 3H), 3.87 (s, 3H), 2.39 (q, *J* = 7.8 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H).

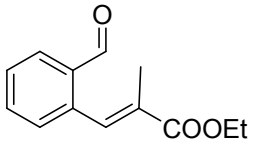
General Procedure D, aldehyde deprotection.

To a solution of ethyl (E)-3-(2-(1,3-dioxolan-2-yl)phenyl)-2-methylacrylate (1 eq) in acetone (0.15 M) $FeCl_3$ (0.2 eq) was added. The reaction was stirred overnight. Then it was filtered over a plug of silica and eluted with EtOAc followed by removal of the solvent in vacuo. The residue was purified by column chromatography.

General Procedure E, Heck coupling.

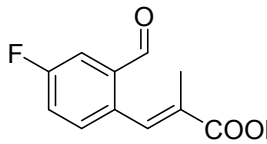
The alkene was filtered over basic alumina before the reaction. Under Schlenk conditions bromobenzaldehyde (1 eq) was dissolved in toluene (0.5M). Then $Pd(OAc)_2$ (0.02 eq), $P(o\text{-}tol)_3$ (0.04 eq), α-methylstyrene (1.5 eq) and triethylamine (2.5M) were added and the reaction was heated to reflux for 48h. The reaction was then cooled down to room temperature, diluted with water and extracted with DCM. The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography.

ethyl (E)-3-(2-formylphenyl)-2-methylacrylate



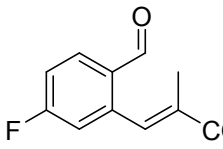
The reaction was performed according to general procedure D. The residue was purified by column chromatography (9:1 hexanes:EtOAc) and the product was obtained as yellow oil (62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.06 (s, 1H), 7.94 (dd, J = 7.7, 1.4 Hz, 1H), 7.62 (td, J = 7.6, 1.5 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.90 (d, J = 1.5 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H).

ethyl (E)-3-(4-fluoro-2-formylphenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as yellow oil (42%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (d, *J* = 2.5 Hz, 1H), 7.98 (t, *J* = 1.6 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.35 – 7.29 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.89 (d, *J* = 1.6 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.09 (d, *J* = 1.9 Hz), 167.43 (s), 162.40 (d, *J* = 250.8 Hz), 135.42 (d, *J* = 6.2 Hz), 134.94 (d, *J* = 3.3 Hz), 134.50 (s), 132.83 (s), 131.94 (d, *J* = 7.2 Hz), 121.03 (d, *J* = 22.0 Hz), 115.43 (d, *J* = 22.4 Hz), 61.24 (s), 14.29 (s), 14.05 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.80 (s). IR (neat) ν 2982, 2931, 2854, 1695, 1488, 1250, 1112 cm^{-1}. HRMS(EI^+) calcd. for $C_{10}H_8FO$ [M-$COOEt^+$] 163.05592, found 163.05557.

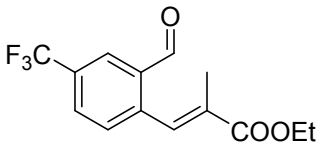
ethyl (E)-3-(5-fluoro-2-formylphenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 → 4:1 hexanes:EtOAc) and obtained as a yellow oil (59%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.99 (s, 1H), 7.96 (dd, *J* = 5.9, 2.8 Hz, 1H), 7.17 (td, *J* = 8.3, 2.5 Hz, 1H), 7.00 (dd, *J* = 9.2, 2.5 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.91 (d, *J* = 1.6 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.97 (d, *J* = 7.2 Hz), 167.44 (s), 165.71 (d, *J* = 257.5 Hz), 141.86 (d, *J* = 9.2 Hz), 134.60 (s), 133.14 (s), 132.75 (d, *J* = 9.9 Hz), 130.51 (d, *J* = 2.5 Hz), 117.02 (d, *J* = 22.6 Hz), 115.92 (d, *J* = 22.0 Hz), 61.42 (s), 14.40 (s), 14.18 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -102.85. IR (neat) ν 2983, 2932, 2852, 1698, 1575, 1257, 1233, 1114 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{11}H_8FO_3$ $[M\text{-}Et]^+$ 207.0457, found 207.0466.

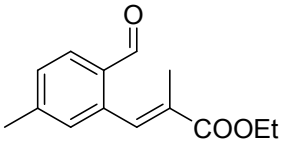
ethyl (E)-3-(2-formyl-4-(trifluoromethyl)phenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The residue was purified by column chromatography (9:1 hexanes:EtOAc) and the product was obtained as a 7:1 mixture of E:Z isomers as a yellow oil (32%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.18 (br s, 1H), 8.01 (s, 1H), 7.84 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.88 (d, *J* = 1.5 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.15, 167.29, 142.29, 134.32, 134.10, 133.88, 131.08 (d, *J* = 33.7 Hz), 130.85, 130.13 (q, *J* = 3.4 Hz), 126.63 (q, *J* = 3.6 Hz), 123.53 (d, *J* = 272.4 Hz), 61.54, 14.41, 14.26. ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.00. IR (neat) ν 2985, 2854, 1702, 1330, 1253, 1169, 1127 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{14}H_{13}F_3O_3$ $[M]^+$ 286.0817 found 286.0823.

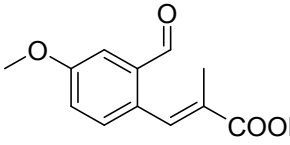
ethyl (E)-3-(2-formyl-5-methylphenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as an orange oil (56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.03 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.90 (d, *J* = 1.6 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.41, 167.87, 144.90, 139.02, 136.34, 131.90, 131.65, 130.54, 130.21, 129.37, 61.22, 22.00, 14.45, 14.22. IR (neat) ν 2982, 2850, 2746, 1695, 1602, 1257, 1229, 1112, 821 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{12}H_{11}O_3$ $[M\text{-}Et]^+$ 203.0708, found 203.0751.

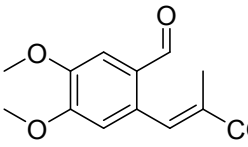
ethyl (E)-3-(2-formyl-4-methoxyphenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The product was purified by column chromatography (4:1 hexanes:EtOAc) and obtained as an orange oil (74%, 80% based on recovery of starting material).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.17 – 7.93 (m, 1H), 7.45 (d, *J* = 2.7 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H, O*Me*), 1.93 (d, *J* = 1.5 Hz, 3H, allyl), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.22, 167.79, 159.62, 135.33, 134.83, 131.66, 131.57, 131.37, 120.87, 112.26, 61.07, 55.61, 14.32, 14.09.

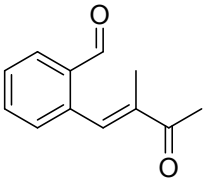
ethyl (E)-3-(2-formyl-4,5-dimethoxyphenyl)-2-methylacrylate



The reaction was performed according to general procedure D. The product was purified by column chromatography (4:1 hexanes:EtOAc) and obtained as a white solid (22%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.08 – 7.94 (m, 1H), 7.45 (s, 1H), 6.72 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H, OMe), 3.95 (s, 3H, OMe), 1.91 (d, *J* = 1.5 Hz, 3H, allyl), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.91, 167.70, 153.69, 149.22, 135.32, 134.42, 132.67, 127.25, 111.54, 109.61, 61.29, 56.37, 56.24, 14.37, 13.92. IR (neat) ν 2978, 2938, 2850, 1680, 1510, 1275, 1250, 1217, 1108 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_5$ $[M]^+$ 278.1154, found 278.1146.

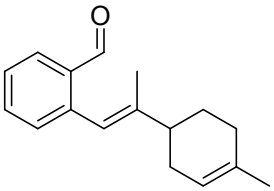
(E)-2-(2-methyl-3-oxobut-1-en-1-yl)benzaldehyde



The reaction was performed according to general procedure E. The product was purified by column chromatography (3:1 hexanes:EtOAc) and obtained as a red brown oil (27%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.00 (br s, 1H), 7.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.65 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 2.52 (s, 3H, C(O)*Me*), 1.85 (d, *J* = 1.4 Hz, 3H allyl *Me*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.22, 192.30, 139.69, 138.04, 137.79, 133.77, 133.75, 132.41, 130.29, 128.80, 26.13, 13.06. IR (neat) ν 2924, 2849, 2745, 1696, 1668, 1246, 754 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{12}H_{12}O_2$ $[M]^+$ 188.0837, found 188.0823.

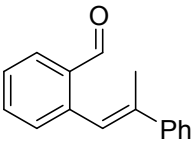
(E)-2-(2-(4-methylcyclohex-3-en-1-yl)prop-1-en-1-yl)benzaldehyde



The reaction was performed according to general procedure E. The product was purified by column chromatography (40:1 hexanes:EtOAc) and obtained as a 2:1 mixture of the E and Z isomers as a yellow liquid (47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H, C*H*O, Z), 10.21 (s, 1H, C*H*O, E), 7.93 – 7.84 (m, 1H+1H, E+Z), 7.58 – 7.48 (m, 1H+1H, E+Z), 7.43 – 7.31 (m, 1H+1H, E+Z), 7.30 – 7.19 (m, 1H+1H, E+Z), 6.60 (s, 1H, allyl CH, E), 6.53 (s, 1H, allyl CH, Z), 5.48 – 5.43 (m, 1H, CH alkene cyclohexyl, E), 5.43 – 5.38 (m, 1H, CH alkene cyclohexyl, Z), 1.88 (d, *J* = 1.5 Hz, 1H, allyl Me, Z), 1.71 – 1.67 (s, 3H, Me cyclohexyl, E), 1.65 (s, 3H, Me cyclohexyl, Z), 1.63 (d, *J* = 1.3 Hz, 3H, allyl Me, E), 2.26 – 0.95 (m, 7H+7H, cyclohexyl, E+Z). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.86, 192.22, 154.19, 147.27, 142.74, 142.45, 134.06, 133.96, 133.71, 132.04, 131.63, 130.89, 130.74, 130.45, 129.16, 127.94, 127.08, 127.03, 126.94, 120.58, 120.52, 119.65, 43.07, 40.37, 37.58, 31.48, 31.00, 30.74, 30.63, 28.37, 28.01, 23.65, 23.59, 16.17. IR (neat) ν 2961, 2919, 2834, 1693, 1643, 1596, 1449, 1208, 1192, 815, 795, 754 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{17}H_{20}O$ $[M]^+$ 240.15141, found 240.15088.

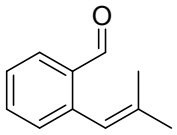
(E)-2-(2-phenylprop-1-en-1-yl)benzaldehyde



The reaction was performed according to general procedure E. The product was purified by column chromatography (40:1 hexanes:EtOAc) and obtained as a 3:1 mixture of the E and Z isomers as an orange liquid (40%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.28 (s, 1H, C*H*O, E), 10.24 (s, 1H, C*H*O, Z), 7.98-6.90 (m, 10H+10H, E+Z), 2.32 (d, *J* = 1.5 Hz, 3H, Me, Z), 2.09 (d, *J* = 1.3 Hz, 3H, Me, E). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.58, 142.61, 141.83, 140.64, 134.14, 133.78, 130.80, 129.04, 128.62, 127.94, 127.46, 126.10, 123.90, 17.48. IR (neat) ν 3058, 2917, 2850, 2742, 1692, 1595, 755, 696 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{16}H_{14}O$ $[M]^+$ 222.10446, found 222.10323.

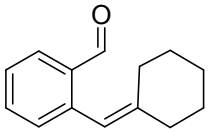
2-(2-methylprop-1-en-1-yl)benzaldehyde



The reaction was performed according to general procedure E. The product was purified by column chromatography (20:1 hexanes:EtOAc) and obtained as a yellow liquid (63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 6.58 (br s, 1H), 1.96 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.1 Hz, 3H).

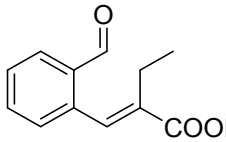
2-(cyclohexylidenemethyl)benzaldehyde



The reaction was performed according to general procedure D. The product was purified by column chromatography (hexanes) and obtained as yellow oil (59%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.28 (d, *J* = 0.8 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (dddd, *J* = 7.9, 7.2, 1.3, 0.7 Hz, 1H), 7.24 (ddt, *J* = 7.7, 1.3, 0.6 Hz, 1H), 6.53 (s, 1H), 2.41 – 2.30 (m, 2H), 2.12 (td, *J* = 5.9, 1.1 Hz, 2H), 1.79 – 1.46 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.84, 147.10, 141.97, 133.92, 133.58, 130.91, 127.72, 126.79, 117.75, 37.25, 29.82, 28.57, 27.66, 26.48.

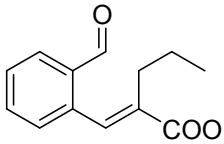
ethyl (E)-2-(2-formylbenzylidene)butanoate



The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as a yellow oil (58%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.00 (s, 1H), 7.93 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.62 (td, *J* = 7.5, 1.4 Hz, 1H), 7.55 – 7.42 (m, 1H), 7.29 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.31 (qd, *J* = 7.4, 0.6 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.72, 167.43, 139.07, 138.15, 135.75, 133.92, 133.78, 129.93, 129.69, 128.53, 61.10, 21.21, 14.43, 13.89.

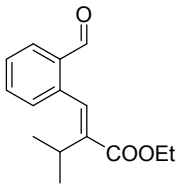
ethyl (E)-2-(2-formylbenzylidene)pentanoate



The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as a yellow oil (43%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.01 (s, 1H), 7.93 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.39 – 2.17 (m, 2H), 1.49 – 1.39 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.61, 167.49, 139.08, 136.76, 136.05, 133.78, 133.64, 129.71, 129.61, 128.36, 60.98, 29.66, 22.39, 14.29, 14.02. IR (neat) ν 2962, 1699, 1225, 1094, 756 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_3$ $[M]^+$ 246.1256, found 246.1257.

ethyl (E)-2-(2-formylbenzylidene)-3-methylbutanoate

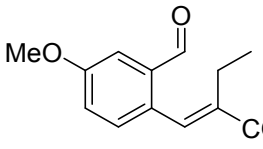


The reaction was performed according to general procedure D. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as a yellow oil (27%).

E-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.89 – 7.82 (m, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 – 7.33 (m, 1H), 7.30 – 7.17 (m, 1H), 7.06 (s, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.89 (pd, *J* = 6.8, 1.4 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 6H), 0.87 (t, *J* = 7.1 Hz, 3H).

Z-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.93 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.86 (s, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 – 7.17 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.73 (p, *J* = 6.9 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.06, 168.92, 144.77, 140.70, 135.19, 133.95, 133.51, 129.62, 128.15, 127.85, 60.56, 32.44, 21.66, 13.72. IR (neat) ν 2966, 1699, 1233, 1056, 756 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{15}H_{18}O_3$ $[M]^+$ 246.1256, found 246.1270.

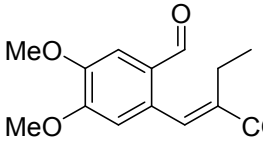
ethyl (E)-2-(2-formyl-4-methoxybenzylidene)butanoate



The reaction was performed according to general procedure D. The product was purified by column chromatography (5:1 pet ether 40-60:EtOAc) and obtained as a light yellow oil (57%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.98 (s, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.23 (s, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 2.35 (q, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.34, 167.53, 159.72, 138.01, 135.07, 134.82, 131.84, 131.04, 121.11, 112.31, 61.03, 55.71, 21.17, 14.42, 13.87. IR (neat) ν 2975, 2938, 1694, 1602, 1493, 1229, 1125, 708, 565 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_4$ [M]$^+$ 262.12051, found 262.12059.

ethyl (E)-2-(2-formyl-4,5-dimethoxybenzylidene)butanoate



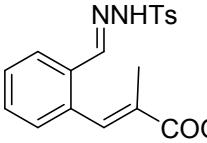
The reaction was performed according to general procedure D. The product was purified by column chromatography (5:1 pet ether 40-60:EtOAc) and obtained as a white solid (50%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.95 (s, 1H), 7.44 (s, 1H), 6.72 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H+3H), 2.34 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.92, 167.34, 153.74, 149.17, 138.73, 134.94, 134.52, 127.14, 111.34, 109.60, 61.15, 56.35, 56.25, 21.42, 14.44, 13.88. IR (neat) ν 2974, 2937, 1707, 1682, 1593, 1510, 1278, 1236, 1219, 1071, 1021, 747, 582 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{16}H_{20}O_5$ [M]$^+$ 292.1311, found 292.1316.

General Procedure F, tosylhydrazone introduction.

To benzaldehyde (1 eq) in dry MeOH (1M) *p*-toluenesulfonyl hydrazide (1.11 eq) was added under rapid stirring. If the substrate doesn't dissolve within 15 min. the reaction was heated to 60°C for 1h, during which the substrate should dissolve quickly followed by precipitation of the product. Next the reaction was concentrated and triturated with Et_2O. The product was obtained by concentration of the ether solution.

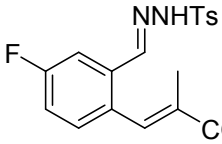
ethyl (E)-2-methyl-3-(2-((E)-(2-tosylhydrazineylidene)methyl)phenyl)acrylate (1*a*)



The reaction was performed according to general procedure F. The product was isolated as an off white solid (81%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 1H), 7.94 (s, 1H), 7.78 – 7.65 (m, 4H), 7.46 – 7.34 (m, 4H), 7.26 (dd, *J* = 6.9, 1.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H, COO*CH*$_2$CH$_3$), 2.35 (s, 3H, Ts Me), 1.69 (d, *J* = 1.5 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (126 MHz, DMSO) δ 166.97, 145.12, 143.40, 136.46, 136.02, 134.76, 131.32, 130.32, 129.55, 129.52, 129.39, 128.39, 127.11, 126.05, 60.55, 20.92, 14.08, 13.69. IR (neat) ν 3180, 2982, 2926, 1704, 1165 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{20}H_{22}N_2O_4S$ [M]$^+$ 386.13003, found 386.12849.

ethyl (E)-3-(4-fluoro-2-((E)-(2-tosylhydrazono)methyl)phenyl)-2-methylacrylate (1*b*)

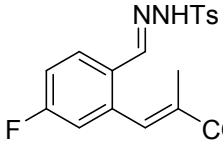


The reaction was performed according to general procedure F. The product was isolated by trituration and obtained as a white powder (73%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.60 (s, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.67 (s, 1H), 7.48 – 7.37 (m, 3H), 7.39 – 7.25 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H, COO*CH*$_2$CH$_3$), 2.36 (s, 3H, Ts Me), 1.68 (d, *J* = 1.4 Hz, 3H, *CH*$_3$-allyl), 1.28 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.97 (s, C=O), 161.70 (d, *J* = 249.4 Hz, CF), 143.85 (s), 143.66 (s), 135.91 (s), 135.54 (s), 133.79 (d, *J* = 7.8 Hz), 132.04 (d, *J* = 8.5 Hz), 131.24 (d, *J* = 3.2 Hz), 130.81 (s), 129.72 (s), 127.22 (s), 116.85 (d, *J* = 20.3 Hz), 111.83 (d, *J* = 22.8 Hz), 60.73 (s, COO*CH*$_2$CH$_3$), 21.04 (s, Ts Me), 14.18 (s, COOCH$_2$*CH*$_3$), 13.80 (s, allyl-Me). ^{19}F NMR (282 MHz, DMSO-d_6) δ -112.74. IR

(neat) ν 3165, 2986, 2921, 1674, 1443, 1271, 1184, 1125, 1090 cm^{-1}. HRMS(FD^+) calcd. for $C_{20}H_{21}FN_2O_4S$ $[M]^+$ 404.1206, found 404.1210.

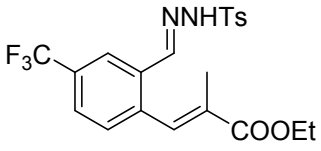
ethyl (E)-3-(5-fluoro-2-((E)-(2-tosylhydrazineylidene)methyl)phenyl)-2-methylacrylate (1*c*)



The reaction was performed according to general procedure F. The product was isolated as a white solid (78%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.45 (s, 1H), 7.89 (s, 1H, alkene), 7.81 – 7.58 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 2H, Ar Ts), 7.24 (td, *J* = 8.6, 2.7 Hz, 1H), 7.13 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H, COO*CH*$_2$CH$_3$), 2.35 (s, 3H, Ts Me), 1.69 (d, *J* = 1.5 Hz, 3H, C*H*$_3$-allyl), 1.29 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.80, 162.33 (d, *J* = 248.7 Hz), 144.23, 143.49, 137.19 (d, *J* = 8.5 Hz), 136.00, 135.25, 131.34, 129.61, 128.51 (d, *J* = 9.1 Hz), 128.03 (d, *J* = 3.1 Hz), 127.16, 116.03 (d, *J* = 22.4 Hz), 115.78 (d, *J* = 22.1 Hz), 60.75, 20.99, 14.13, 13.75. ^{19}F NMR (282 MHz, DMSO-d_6) δ -110.81. IR (neat) ν 3204, 2982, 2927, 1706, 1597, 1240, 1162, 1118, 1088 cm^{-1}. HRMS(FD^+) calcd. for $C_{20}H_{21}FN_2O_4S$ $[M]^+$ 404.1206, found 404.1216.

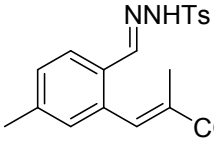
ethyl (E)-2-methyl-3-(2-((E)-(2-tosylhydrazineylidene)methyl)-4-(trifluoromethyl)phenyl)acrylate (1*d*)



The reaction was performed according to general procedure F. The product was isolated by trituration and obtained as a 7:1 mixture of E:Z isomers a yellow solid (97%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.68 (s, 1H), 7.98 (s, 1H), 7.93 (d, *J* = 1.9 Hz, 1H), 7.75 (ddd, *J* = 11.0, 7.0, 2.1 Hz, 4H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.68 (d, *J* = 1.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.75, 143.70, 138.75, 135.91, 135.28, 132.41, 131.77, 130.86, 130.04, 129.68, 128.80 (q, *J* = 32.2 Hz), 127.15, 125.82 (q, *J* = 4.0 Hz), 123.78 (q, *J* = 272.3 Hz), 122.37 (q, *J* = 3.6 Hz), 60.85, 30.67, 14.14, 13.80. ^{19}F NMR (282 MHz, DMSO) δ -61.49. IR (neat) ν 3186, 2984, 1710, 1327, 1270, 1256, 1165, 1126, 1078, 813, 667 cm^{-1}. HRMS(FD^+) calcd. for $C_{21}H_{21}F_3N_2O_4S$ $[M]^+$ 454.1174, found 454.1168.

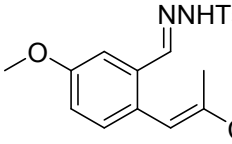
ethyl (E)-2-methyl-3-(5-methyl-2-((E)-(2-tosylhydrazineylidene)methyl)phenyl)acrylate (1*e*)



The reaction was performed according to general procedure F. The product was isolated as an off white solid (91%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.89 (s, 1H), 7.72 (dd, *J* = 8.5, 1.9 Hz, 3H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.06 (s, 1H), 4.21 (qd, *J* = 7.1, 1.8 Hz, 2H, COO*CH*$_2$CH$_3$), 2.35 (s, 3H, Ts Me), 2.31 (s, 3H, Ar Me), 1.68 (d, *J* = 1.6 Hz, 3H, C*H*$_3$-allyl), 1.29 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.11, 145.42, 143.50, 139.60, 136.70, 136.05, 134.82, 130.26, 129.79, 129.63, 129.29, 128.70, 127.22, 126.20, 60.68, 21.04, 20.91, 14.20, 13.85. IR (neat) ν 3189, 2923, 2853, 1704, 1165, 813 cm^{-1}. HRMS(FD^+) calcd. for $C_{21}H_{24}N_2O_4S$ $[M]^+$ 400.14568, found 400.14412.

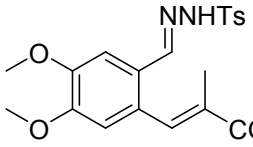
ethyl (E)-3-(4-methoxy-2-((E)-(2-tosylhydrazineylidene)methyl)phenyl)-2-methylacrylate (1*f*)



The reaction was performed according to general procedure F. The product was isolated as a white solid (quantitative yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.45 (s, 1H), 7.92 (s, 1H), 7.80 – 7.71 (m, 2H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 2.7 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H, COO*CH*$_2$CH$_3$), 3.79 (s, 3H, Ar O*Me*), 2.36 (s, 3H, Ts *Me*), 1.72 (d, *J* = 1.5 Hz, 3H, *CH*$_3$-allyl), 1.28 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (75 MHz, DMSO) δ 167.22, 159.03, 144.98, 143.58, 136.23, 135.93, 132.88, 131.22, 131.20, 129.63, 129.35, 127.24, 115.85, 110.43, 60.56, 55.30, 21.02, 14.19, 13.85. IR (neat) ν 3188, 2925, 1705, 1251, 1167, 813 cm^{-1}. HRMS(FD^+) calcd. for $C_{21}H_{24}N_2O_5S$ $[M]^+$ 416.14059, found 416.13968.

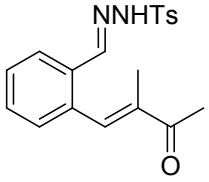
ethyl (E)-3-(4,5-dimethoxy-2-((E)-(2-tosylhydrazineylidene)methyl)phenyl)-2-methylacrylate (1*g*)



The reaction was performed according to general procedure F. The product was isolated as a yellow solid (79%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.23 (s, 1H), 7.85 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 1H), 6.81 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H, OMe), 3.77 (s, 3H, OMe), 2.35 (s, 3H, Ts Me), 1.71 (d, *J* = 1.4 Hz, 3H, allyl), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 167.69, 167.18, 149.74, 148.20, 145.52, 143.47, 135.98, 131.18, 129.61, 128.34, 127.32, 124.20, 111.60, 107.81, 60.01, 55.74, 55.50, 21.05, 14.24, 13.60. IR (neat) ν 3185, 2927, 1703, 1508, 1247, 1163, 1109, 1033, 547 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{22}H_{26}N_2O_6S$ [M]$^+$ 446.1512, found 446.1492.

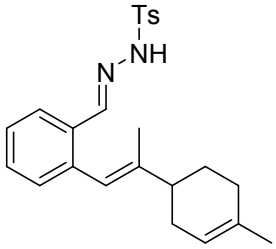
4-methyl-N'-((E)-2-((E)-2-methyl-3-oxobut-1-en-1-yl)benzylidene)benzenesulfonohydrazide (1*h*)



The reaction was performed according to general procedure F and purified by column chromatography (2:1 hexanes:EtOAc). The product was isolated as a green powder (61%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.46 (s, 1H), 8.00 (s, 1H), 7.81 (s, 1H), 7.74 – 7.62 (m, 3H), 7.52 – 7.31 (m, 4H), 7.27 (dd, *J* = 7.1, 1.9 Hz, 1H), 2.44 (s, 3H, C(O)Me), 2.34 (s, 3H, Ts Me), 1.60 (d, *J* = 1.3 Hz, 3H, allyl Me). ^{13}C NMR (126 MHz, DMSO) δ 199.59, 145.85, 143.48, 138.52, 137.95, 136.02, 135.01, 131.22, 129.60, 129.54, 129.45, 128.44, 127.05, 126.83, 25.86, 20.96, 12.48. IR (neat) ν 3185, 2923, 2853, 1664, 1366, 1328, 1165, 813, 667 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{19}H_{20}N_2O_3S$ [M]$^+$ 356.11946, found 356.11987.

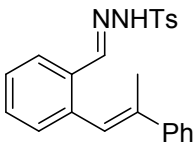
4-methyl-N'-((E)-2-((E)-2-(4-methylcyclohex-3-en-1-yl)prop-1-en-1-yl)benzylidene) benzenesulfonohydrazide (1*i*)



The reaction was performed according to general procedure F and purified by column chromatography (1:2 Et_2O:hexanes). The product was isolated as a white solid (20%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.44 (s, 1H), 7.99 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 2H, tosyl), 7.66 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H, tosyl), 7.32 (d, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.29 (s, 1H, allyl C*H*), 5.43 (s, 1H, alkene cyclohexyl), 2.72 (s, 1H), 2.36 (s, 3H, Ts Me), 2.30 – 1.87 (m, 4H), 1.84 (d, *J* = 12.3 Hz, 1H), 1.65 (s, 3H, allyl Me), 1.46 (s, 3H, cyclohexyl Me), 1.23 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 145.75, 145.09, 143.42, 137.99, 136.16, 133.18, 131.22, 129.95, 129.67, 129.51, 127.14, 126.73, 124.76, 120.45, 120.12, 42.23, 30.35, 30.12, 27.35, 23.32, 20.99, 15.61. IR (neat) ν 3192, 2919, 1165, 758 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{24}H_{28}N_2O_2S$ [M]$^+$ 408.1871, found 408.1881.

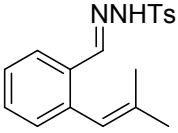
4-methyl-N'-((E)-2-((E)-2-phenylprop-1-en-1-yl)benzylidene)benzenesulfonohydrazide (1*j*)



The reaction was performed according to general procedure F. The product was isolated as brown solid (quantitative yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.39 (s, 1H), 8.11 (s, 1H), 7.73 (dd, J = 8.4, 2.0 Hz, 4H), 7.63 – 7.58 (m, 2H), 7.49 – 7.23 (m, 7H), 6.98 (s, 1H), 2.36 (s, 3H, Ts Me), 1.90 (d, J = 1.4 Hz, 3H, Me).

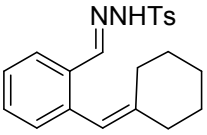
(E)-4-methyl-N'-(2-(2-methylprop-1-en-1-yl)benzylidene)benzenesulfonohydrazide (1*k*)



The reaction was performed according to general procedure F. The product was isolated as an off white solid (74%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 8.01 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.29 (br s, 1H), 2.36 (s, 3H), 1.86 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.96, 143.40, 137.84, 137.31, 136.13, 131.19, 129.97, 129.62, 129.51, 127.17, 126.74, 124.86, 121.86, 25.64, 20.99, 19.00. IR (neat) ν 3194, 2925, 1166, 669, 549 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{18}H_{20}N_2O_2S$ [M]$^+$ 328.1245, found 328.1233.

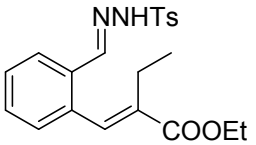
(E)-N'-(2-(cyclohexylidenemethyl)benzylidene)-4-methylbenzenesulfonohydrazide (1*l*)



The reaction was performed according to general procedure F. The product was isolated as a white solid (96%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.39 (s, 1H), 8.02 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 2.35 (s, 3H, Ts Me), 2.23 (t, *J* = 5.9 Hz, 2H), 1.86 (t, *J* = 6.0 Hz, 2H), 1.66 – 1.45 (m, 4H), 1.35 (q, *J* = 6.4, 5.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.94, 144.89, 143.40, 137.52, 136.16, 131.41, 130.00, 129.64, 129.55, 127.17, 126.76, 124.82, 118.61, 36.39, 29.18, 27.96, 26.93, 25.95, 21.00. IR (neat) ν 3205, 3183, 2926, 2851, 2361, 2342, 1167 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{21}H_{24}N_2O_2S$ [M]$^+$ 368.1558, found 368.1574.

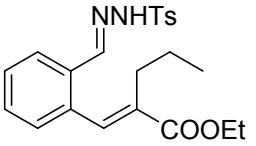
ethyl 2-((E)-2-((E)-(2-tosylhydrazineylidene)methyl)benzylidene)butanoate (1*m*)



The reaction was performed according to general procedure F. The product was obtained as a 6:1 mixture of E:Z isomers and as an off white solid (96%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.45 (s, 1H), 7.96 (s, 1H), 7.77 – 7.62 (m, 4H), 7.46 – 7.32 (m, 4H), 7.20 (d, *J* = 7.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.67, 145.10, 143.48, 136.52, 136.26, 136.04, 134.88, 131.22, 129.77, 129.61, 128.95, 128.43, 127.17, 126.21, 60.54, 21.00, 20.57, 14.14, 13.32. IR (neat) ν 3186, 2978, 2935, 1707, 1448, 1242, 1168, 1048, 668, 548 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{21}H_{24}N_2O_4S$ [M]$^+$ 400.1457, found 400.1426.

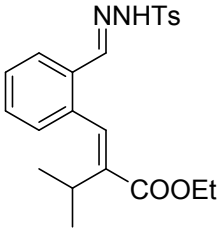
ethyl 2-((E)-2-((E)-(2-tosylhydrazono)methyl)benzylidene)pentanoate (1*n*)



The reaction was performed according to general procedure F. The product was obtained as a 6:1 mixture of E:Z isomers and as an off white solid (quantitative).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.46 (s, 1H), 7.95 (s, 1H), 7.81 – 7.56 (m, 4H), 7.49 – 7.34 (m, 4H), 7.19 (dd, *J* = 7.1, 1.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.42 – 3.34 (m, 2H), 2.35 (s, 3H), 2.12 – 2.04 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.63 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.84, 145.09, 143.44, 137.03, 136.07, 135.01, 134.93, 131.21, 129.73, 129.60, 128.98, 128.36, 127.16, 126.13, 60.53, 29.06, 21.55, 21.00, 14.13, 13.71. IR (neat) ν 3194, 2962, 2364, 1708, 1227, 1168, 668, 548 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{22}H_{26}N_2O_4S$ [M]$^+$ 414.1613, found 414.1598.

ethyl 3-methyl-2-((E)-2-((E)-(2-tosylhydrazineylidene)methyl)benzylidene)butanoate (1*o*)

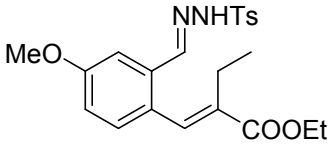


The reaction was performed according to general procedure F. The product was obtained as a 2:1 mixture of E:Z isomers and as a white solid (quantitative).

E-isomer: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 8.02 (s, 1H), 7.75 (dd, *J* = 10.2, 8.1 Hz, 2H), 7.66 – 7.58 (m, 1H), 7.40 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.08 – 6.98 (m, 1H), 6.85 (s, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.81 – 2.66 (m, 1H), 2.37 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 6H), 0.79 (t, *J* = 7.1 Hz, 3H). Z-isomer: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (s, 1H), 7.97 (s, 1H), 7.75 (dd, *J* = 10.2, 8.1 Hz, 2H), 7.71 –

7.67 (m, 1H), 7.57 (s, 1H), 7.40 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.81 – 2.66 (m, 1H), 2.40 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 168.31, 145.37, 143.44, 143.02, 136.58, 136.20, 130.87, 129.65, 129.38, 128.13, 127.77, 127.60, 127.13, 125.57, 59.88, 31.95, 21.20, 14.11, 13.41. IR (neat) ν 3193, 2964, 2932, 2874, 1710, 1239, 1166, 1053, 668, 589, 549 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{22}H_{26}N_2O_4S$ [M]$^+$ 414.1613, found 414.1618.

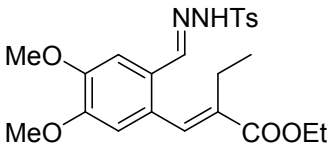
ethyl 2-((E)-4-methoxy-2-((E)-(2-tosylhydrazineylidene)methyl)benzylidene)butanoate (1*p*)



The reaction was performed according to general procedure F. The product was obtained as a 8:1 mixture of E:Z isomers and as a white solid (65%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.76 (m, 4H), 7.63 (s, 1H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.93 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 167.31, 159.46, 145.36, 144.01, 136.62, 136.42, 135.96, 133.17, 131.01, 130.08, 127.70, 127.68, 116.38, 111.11, 60.92, 55.73, 21.47, 21.00, 14.62, 13.87. IR (neat) ν 3187, 2977, 2937, 1705, 1597, 1562, 1494, 1456, 1236, 1166, 1131, 1046, 907, 667, 548 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{22}H_{26}N_2O_5S$ [M]$^+$ 430.1562, found 430.1549.

ethyl 2-((E)-4,5-dimethoxy-2-((E)-(2-tosylhydrazineylidene)methyl)benzylidene)butanoate (1*q*)



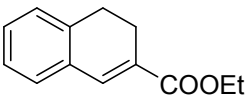
The reaction was performed according to general procedure F. The product was obtained as a 7.5:1 mixture of E:Z isomers and as a yellow solid (96%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.23 (s, 1H), 7.88 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.63 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 1H), 6.74 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 2.35 (s, 3H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 166.73, 149.98, 148.64, 145.07, 143.41, 136.05, 136.00, 129.52, 128.25, 128.23, 127.25, 123.99, 111.63, 108.02, 60.44, 55.59, 55.44, 20.97, 20.68, 14.14, 13.24. IR (neat) ν 3194, 2963, 2930, 2360, 2342, 1707, 1595, 1510, 1463, 1343, 1278, 1239, 1168, 1117, 1046, 668, 549 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{23}H_{28}N_2O_6S$ [M]$^+$ 460.1668, found 460.1669.

General Procedure G, catalytic reaction.

Under Schlenk conditions the tosyl hydrazone (1 eq), LiOtBu (1.2 eq) and [Co(TPP)] (0.05 eq) were put together after which the tube was evacuated for 15 min. and then refilled with N_2. Next benzene (2 mL) was added and the mixture was heated to 60 °C over night in a dark fumehood. The mixture was then filtered over a silica plug and eluted with EtOAc. After concentration the product was purified by column chromatography.

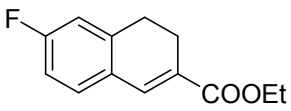
ethyl 3,4-dihydronaphthalene-2-carboxylate (2*a*)



The reaction was performed according to general procedure G. The product was isolated by column chromatography (20:1 hexanes:EtOAc) and obtained as red oil (89%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.7 Hz, 1H), 7.34 – 7.11 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.89 (dd, *J* = 9.2, 7.3 Hz, 2H), 2.64 (td, *J* = 8.1, 7.6, 1.5 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.46, 136.98, 136.30, 132.62, 129.59, 129.40, 128.41, 127.64, 126.71, 60.62, 27.64, 22.26, 14.38.

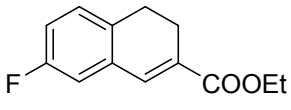
ethyl 6-fluoro-3,4-dihydronaphthalene-2-carboxylate (2*b*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as an yellow oil (76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.17 (dd, *J* = 9.1, 5.6 Hz, 1H), 6.89 (ddd, *J* = 8.9, 5.9, 2.6 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H, COO*CH*$_2$CH$_3$), 2.85 (t, *J* = 8.3 Hz, 2H, Ar-*CH*$_2$-CH2), 2.59 (t, *J* = 8.3 Hz, 2H, Ar-CH$_2$-*CH*$_2$), 1.35 (t, *J* = 7.1 Hz, 3H, COOCH$_2$*CH*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.43 (s, C=O), 163.35 (d, *J* = 249.8 Hz, CF), 139.80 (d, *J* = 7.8 Hz, CF-CH-*C*-C-CH-CH), 135.36 (s), 130.10 (d, *J* = 8.6 Hz, CF-CH-C-C-*CH*-CH), 129.03 (d, *J* = 3.0 Hz, CF-CH-C-*C*-CH-CH), 128.97 (s), 115.11 (d, *J* = 21.9 Hz, CF-CH-C-C-CH-*CH*), 113.59 (d, *J* = 21.7 Hz, CF-*CH*-C-C-CH-CH), 60.77 (s, COO*CH*$_2$CH$_3$), 28.02 (s, Ar-*CH*$_2$-CH$_2$), 21.98 (s, Ar-CH$_2$-*CH*$_2$), 14.49 (s, COOCH$_2$*CH*$_3$). IR (neat) ν 2979, 2903, 1703, 1494, 1299, 1237 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{13}H_{13}FO_2$ [M$^+$] 220.0900, found 220.0909.

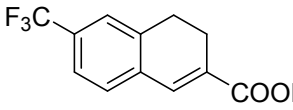
ethyl 7-fluoro-3,4-dihydronaphthalene-2-carboxylate (2*c*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (19:1 hexanes:EtOAc) and obtained as a yellow oil (74%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.11 (dd, *J* = 8.3, 5.8 Hz, 1H), 7.02 – 6.84 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 8.3 Hz, 2H), 2.70 – 2.49 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.26 (s), 161.74 (d, *J* = 243.8 Hz), 135.36 (d, *J* = 2.8 Hz), 134.35 (d, *J* = 8.1 Hz), 132.50 (d, *J* = 3.2 Hz), 131.18 (s), 128.90 (d, *J* = 7.9 Hz), 115.78 (d, *J* = 21.3 Hz), 114.92 (d, *J* = 21.6 Hz), 60.90 (s), 27.04 (s), 22.61 (s), 14.46 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.67. IR (neat) ν 2980, 2896, 1706, 1493, 1277, 1232 cm^{-1}. HRMS (EI$^+$) calcd. for $C_{13}H_{13}FO_2$ [M]$^+$ 220.0900, found 220.0905.

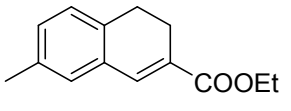
ethyl 6-(trifluoromethyl)-3,4-dihydronaphthalene-2-carboxylate (2*d*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as an red oil (65%)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.41 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 8.3 Hz, 2H), 2.65 (td, *J* = 8.5, 1.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.05 (s), 137.61 (s), 135.98 (s), 134.81 (s), 132.36 (s), 130.99 (q, *J* = 32.2 Hz), 128.45 (s), 124.55 (q, *J* = 3.9 Hz), 124.16 (q, *J* = 272.1 Hz), 123.83 (q, *J* = 4.1 Hz), 61.03 (s), 27.64 (s), 22.24 (s), 14.46 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.72. IR (neat) ν 2982, 1704, 1317, 1272, 1162, 1117, 1068, 831, 738 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{14}H_{13}F_3O_2$ [M$^+$] 270.0868, found 270.0882.

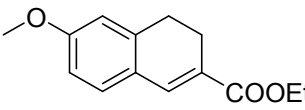
ethyl 7-methyl-3,4-dihydronaphthalene-2-carboxylate (2*e*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as an red oil (40%)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.6 Hz, 1H), 7.10 – 6.97 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.82 (t, *J* = 8.2 Hz, 2H), 2.59 (t, *J* = 8.2 Hz, 2H), 2.32 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.65, 136.60, 136.32, 134.10, 132.63, 130.16, 129.64, 129.24, 127.60, 60.69, 27.35, 22.58, 21.09, 14.49. IR (neat) ν 2929, 1700, 1275, 1227, 1198, 1170, 1070 cm^{-1}. HRMS(FD$^+$) calcld. for $C_{14}H_{16}O_2$ [M]$^+$ 216.11503, found 216.11524.

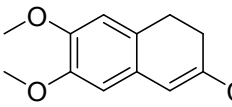
ethyl 6-methoxy-3,4-dihydronaphthalene-2-carboxylate (2*f*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (6:1 hexanes:EtOAc) and obtained as an red oil (75%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.4 Hz, 1H), 7.19 – 7.08 (m, 1H), 6.78 – 6.68 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H, OMe), 2.84 (t, *J* = 8.3 Hz, 2H), 2.59 (ddd, *J* = 9.5, 7.6, 1.5 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.76, 160.73, 139.18, 136.22, 129.96, 126.90, 125.90, 113.88, 111.69, 60.55, 55.43, 28.33, 22.21, 14.52. IR (neat) ν 2901, 2836, 1695, 1604, 1272, 1247, 1196, 1069, 1032, 808 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{14}H_{16}O_3$ [M$^+$] 232.10994, found 232.10916.

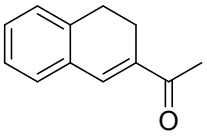
ethyl 6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate (2*g*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (4:1 hexanes:EtOAc) and obtained as a red oil (71%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 6.75 (s, 1H), 6.71 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 2.81 (t, *J* = 8.4 Hz, 2H), 2.58 (t, *J* = 8.4 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.69, 150.04, 147.70, 136.32, 130.47, 127.33, 125.43, 111.94, 111.30, 60.56, 56.26, 56.15, 27.66, 22.46, 14.53. IR (neat) ν 2956, 2834, 1699, 1464, 1240, 1200 cm^{-1}. HRMS (EI$^+$) calcd. for $C_{15}H_{18}O_4$ [M]$^+$ 262.1205, found 262.1216.

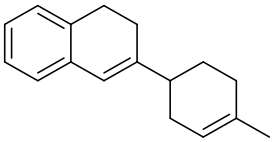
1-(3,4-dihydronaphthalen-2-yl)ethan-1-one (2*h*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (4:1 hexanes:EtOAc) and obtained as a red oil (35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.31 – 7.19 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 1H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.59 (t, *J* = 8.2 Hz, 2H), 2.45 (s, 3H).

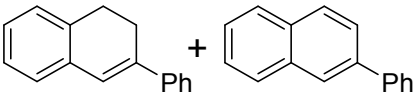
3-(4-methylcyclohex-3-en-1-yl)-1,2-dihydronaphthalene (2*i*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (hexanes) and obtained as a light yellow oil (44%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.04 (m, 3H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.24 (s, 1H), 5.44 (d, *J* = 5.0 Hz, 1H), 2.79 (t, *J* = 8.1 Hz, 2H), 2.38 – 2.27 (m, 1H), 2.27 (t, *J* = 8.1 Hz, 2H), 2.20 – 1.93 (m, 4H), 1.88 (ddq, *J* = 12.6, 4.6, 2.2 Hz, 1H), 1.68 (s, 3H), 1.59 (ddt, *J* = 17.1, 11.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.61, 135.17, 134.88, 134.02, 127.22, 126.54, 126.16, 125.66, 120.73, 120.62, 41.13, 30.56, 30.53, 28.56, 27.68, 26.02, 23.69. IR (neat) ν 3042, 2922, 2885, 2853, 2831, 1486, 1452, 1436, 747 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{17}H_{20}$ [M]$^+$ 224.15650, found 224.15937.

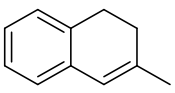
3-phenyl-1,2-dihydronaphthalene with 2-phenylnaphthalene (2*j*)



The reaction was performed according to general procedure G. The product was isolated as a white solid in a 2:1 mixture of the dihydronaphthalene and naphthalene after column chromatography in hexanes (50% 2*H*-naphthalene and 28% naphthalene).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 1.8 Hz, 1H, naphthalene), 7.97 – 7.81 (m, 3H, naphthalene), 7.75 (ddd, J = 8.1, 6.8, 1.4 Hz, 3H, naphthalene), 7.59 – 7.54 (m, 2H, *2H*-naphthalene), 7.50 (m, 4H, naphthalene), 7.43 – 7.35 (m, 2H *2H*-naphthalene + 1H naphthalene), 7.32 – 7.28 (m, 1H, *2H*-naphthalene), 7.23 – 7.10 (m, 4H, *2H*-naphthalene), 6.86 (d, J = 1.4 Hz, 1H, *2H*-naphthalene alkene), 2.97 (dd, J = 9.2, 6.9 Hz, 2H, *2H*-naphthalene), 2.77 (dd, J = 9.1, 6.9 Hz, 2H, *2H*-naphthalene).

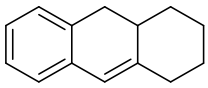
3-methyl-1,2-dihydronaphthalene (2*k*)



The reaction was performed according to general procedure G. The product was purified by column chromatography (hexane) and obtained as a colorless liquid (21%, 68% based on NMR with standard).

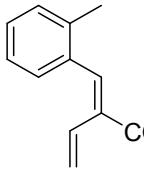
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.01 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.22 (q, *J* = 1.6 Hz, 1H), 2.82 (t, *J* = 8.2 Hz, 2H), 2.32 – 2.14 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.41, 135.17, 134.17, 127.28, 126.49, 126.06, 125.20, 122.82, 28.99, 28.21, 23.66.

1,2,3,4,4a,10-hexahydroanthracene (2*l*)



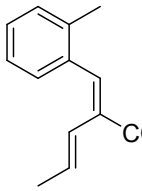
The reaction was performed according to general procedure G. The product was purified by column chromatography (PE) and obtained as a white solid (17%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 1H), 7.09 – 7.04 (m, 2H), 6.97 (d, *J* = 7.1 Hz, 1H), 6.16 (d, *J* = 2.3 Hz, 1H), 2.93 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.59 (dd, *J* = 15.4, 12.5 Hz, 1H), 2.52 – 2.32 (m, 2H), 2.25 – 1.98 (m, 2H), 1.93 – 1.80 (m, 2H), 1.49 – 1.20 (m, 3H).

ethyl (E)-2-(2-methylbenzylidene)but-3-enoate (3*m*)



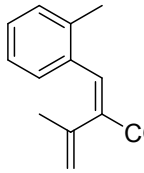
The reaction was performed according to general procedure G. The product was purified by column chromatography (20:1 hexanes:EtOAc) and obtained as a red liquid (85%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.37 – 7.16 (m, 4H), 6.51 (dd, *J* = 17.7, 11.6 Hz, 1H), 5.87 (dd, *J* = 17.8, 1.8 Hz, 1H), 5.38 (dt, *J* = 11.6, 1.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 138.54, 136.87, 134.39, 130.83, 129.96, 129.58, 129.50, 128.41, 125.37, 120.19, 60.83, 19.86, 14.18. IR (neat) ν 3019, 1714, 1242, 1139, 1063, 923, 794, 748 cm^{-1}. HRMS(FD$^+$) calcd. for $C_{14}H_{16}O_2$ [M]$^+$ 216.1150, found 216.1145.

ethyl (E)-2-((E)-2-methylbenzylidene)pent-3-enoate (3*n*)



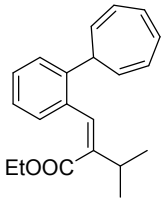
The reaction was performed according to general procedure G. The product was purified by column chromatography (100:1 hexanes:EtOAc) and obtained as a colorless liquid (95%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34 – 7.16 (m, 4H), 6.32 (dq, *J* = 15.9, 6.4 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.79 (d, *J* = 6.2 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.97, 136.93, 135.70, 134.92, 132.25, 131.09, 130.04, 129.64, 128.17, 125.44, 123.95, 60.89, 20.00, 19.24, 14.32. IR (neat) ν 2929, 1713, 1446, 1373, 1296, 1238, 1130, 744 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_2$ [M]$^+$ 230.1307, found 230.1315.

ethyl (E)-3-methyl-2-(2-methylbenzylidene)but-3-enoate (3*o*)



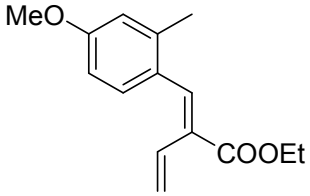
The reaction was performed according to general procedure G. The product was purified by column chromatography (40:1 hexanes:EtOAc) and isolated containing 10% cycloheptatriene (*vide infra*) obtained as a yellow oil (83%). This compound was obtained as a mixture of ~90% **3o** and ~10% **4**. It proved difficult to isolate compound **3o**, free from **4**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.12 (td, *J* = 7.1, 2.3 Hz, 1H), 5.07 (t, *J* = 1.7 Hz, 1H), 4.85 – 4.71 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.91 (d, *J* = 1.2 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, proton coupled) δ 167.39, 138.87 (d, *J* = 239.2 Hz), 137.41, 137.03, 135.79, 134.73, 129.93 (d, *J* = 57.8 Hz), 128.72 (d, *J* = 12.3 Hz), 128.25 (d, *J* = 11.6 Hz), 125.50 (d, *J* = 57.2 Hz), 117.90 (t, *J* = 18.6 Hz), 60.98 (t, *J* = 5.2 Hz), 22.88 (q, *J* = 29.8 Hz), 20.02 (q, *J* = 23.7 Hz), 14.27 (q, *J* = 39.1, 38.1 Hz). HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_2$ [M]$^+$ 230.1307, found 230.1315.

ethyl (Z)-2-(2-(cyclohepta-2,4,6-trien-1-yl)benzylidene)-3-methylbutanoate (4)



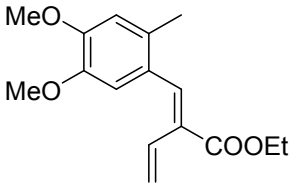
This compound was characterized from a mixture of ~90% **3o** and ~10% **4**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.24 – 7.07 (m, 3H), 6.72 (t, *J* = 3.2 Hz, 2H), 6.61 (s, 1H), 6.25 (d, *J* = 8.9 Hz, 2H), 5.43 (dd, *J* = 9.2, 5.5 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 2.80 – 2.71 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H), 0.90 (t, *J* = 7.1 Hz, 3H). HRMS(EI$^+$) calcd. for $C_{19}H_{18}O$ [M-EtOH]$^+$ 262.1358, found 262.1338.

ethyl (E)-2-(4-methoxy-2-methylbenzylidene)but-3-enoate (3*p*)



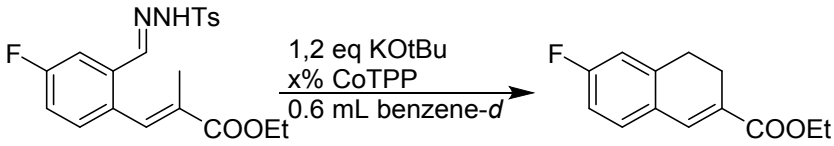
The reaction was performed according to general procedure G. The product was purified by column chromatography (9:1 hexanes:EtOAc) and obtained as a red oil (89%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.69 (m, 2H), 6.50 (dd, *J* = 17.7, 11.6 Hz, 1H), 5.83 (d, *J* = 17.7 Hz, 1H), 5.34 (d, *J* = 11.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.30 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 160.00, 139.28, 138.42, 131.52, 130.08, 129.73, 127.04, 119.99, 115.82, 110.90, 60.95, 55.35, 20.41, 14.44. IR (neat) ν 2959, 2934, 2360, 1712, 1604, 1495, 1302, 1249, 1139, 1037, 819, 569 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{15}H_{18}O_3$ [M]$^+$ 246.1256, found 246.1255.

ethyl (E)-2-(4,5-dimethoxy-2-methylbenzylidene)but-3-enoate (3*q*)

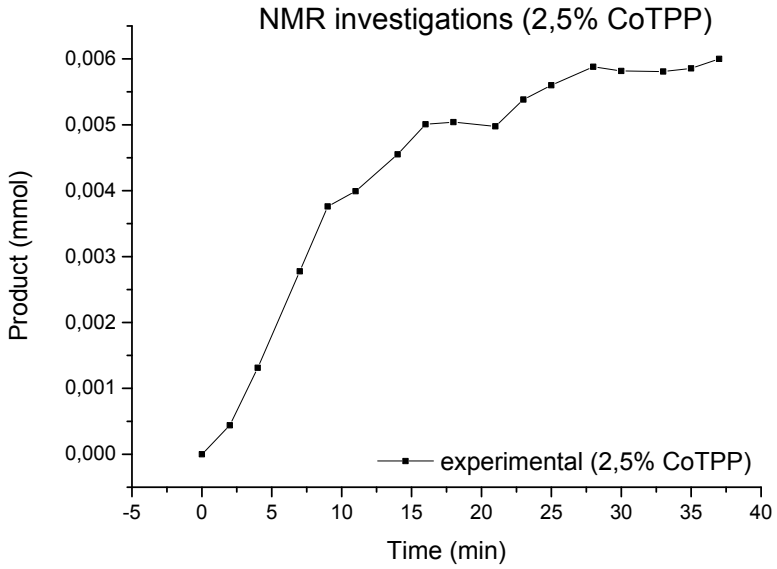


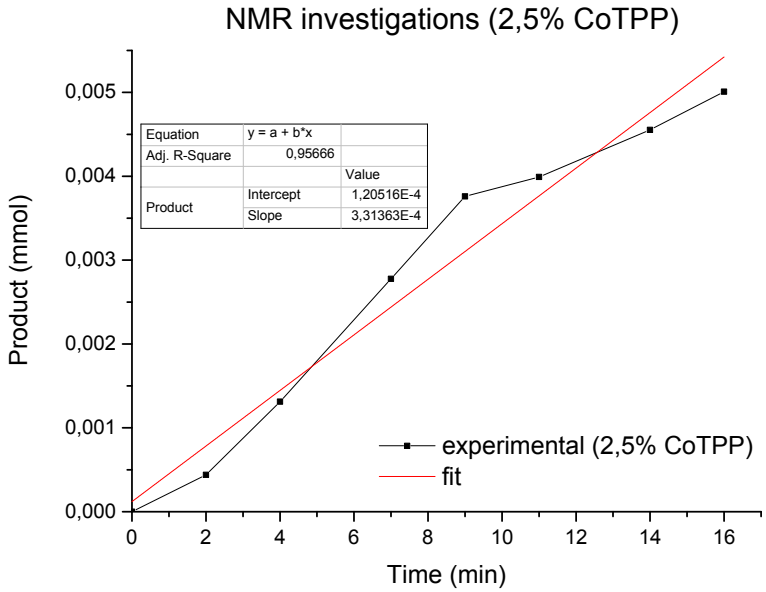
The reaction was performed according to general procedure G. The product was purified by column chromatography (6:1 hexanes:EtOAc) and obtained as a red oil (90%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 6.85 (s, 1H), 6.71 (s, 1H), 6.60 – 6.42 (m, 2H), 5.82 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.36 (dt, *J* = 11.6, 1.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 2.26 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.62, 149.30, 146.53, 138.61, 130.50, 130.13, 129.78, 126.38, 120.17, 113.30, 113.26, 60.98, 56.18, 55.98, 19.62, 14.43. IR (neat) ν 2934, 2361, 2342, 1714, 1605, 1512, 1465, 1275, 1250, 1215, 1172, 1109, 1035, 1004, 868 cm^{-1}. HRMS(EI$^+$) calcd. for $C_{16}H_{20}O_4$ [M]$^+$ 276.1362, found 276.1363.

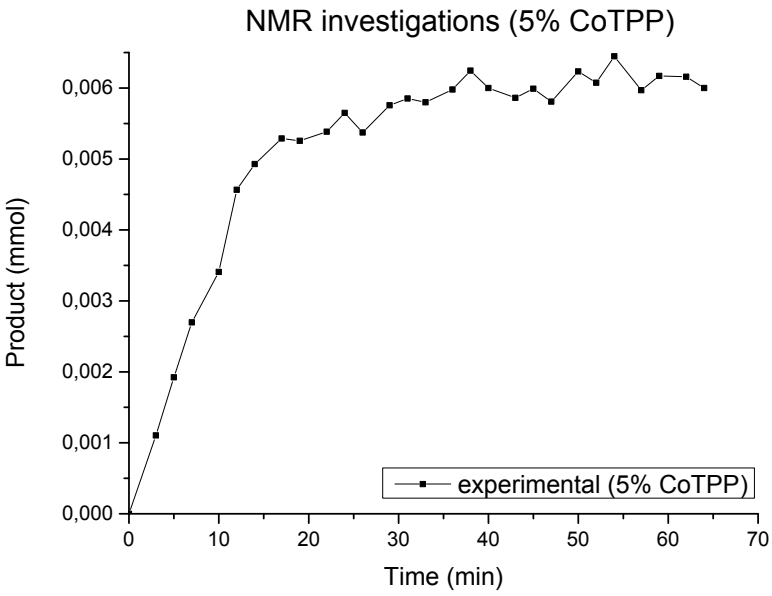
NMR kinetic investigations.

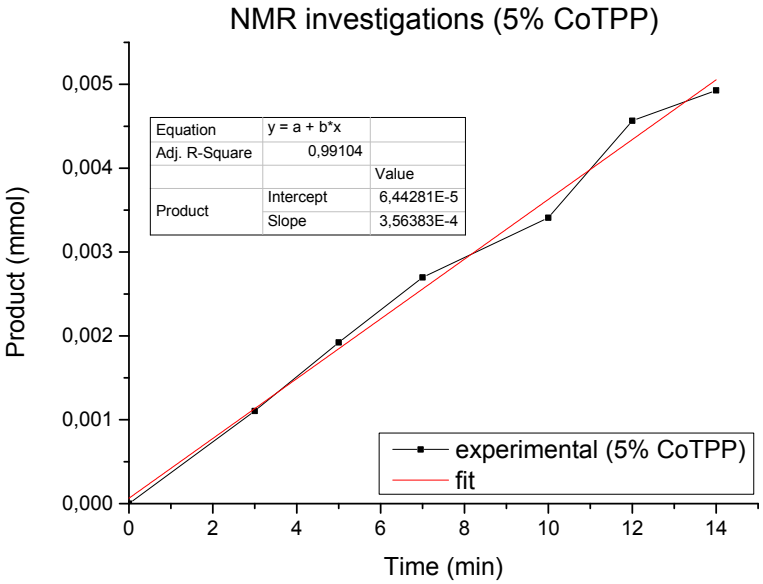


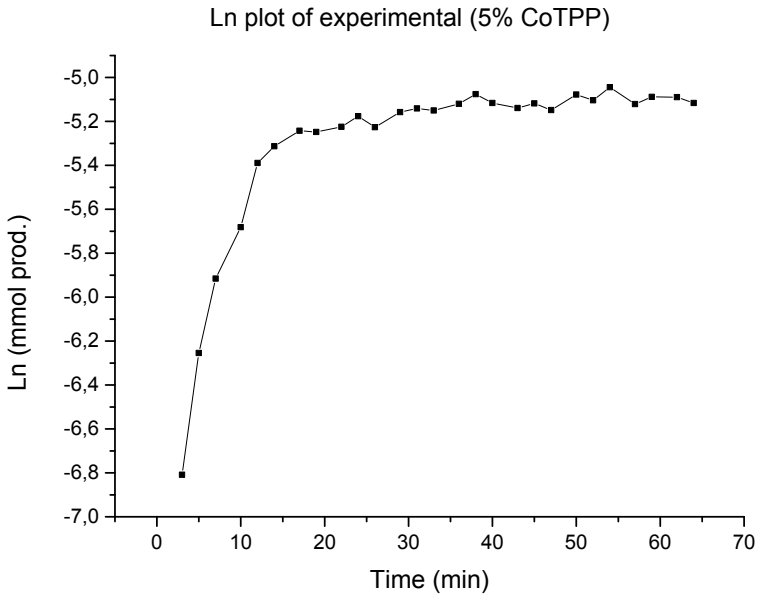
[Co(TPP)] (x eq, 671.65 g/mol), ethyl (E)-3-(4-fluoro-2-((E)-(2-tosylhydrazono)methyl)phenyl)-2-methylacrylate (1 eq, 0.006 mmol, 2.4 mg) and 1,3,5-trimethoxybenzene (0.1 eq, 0.0006 mg, 0.10 mg) were combined in a pressure NMR tube which was then evacuated. LiO^{t}Bu (1.2 eq, 0.0072 mmol, 0.6 mg) was dissolved in benzene-*d* (0.6 mL) and added to the pressure NMR tube. The resulting mixture was dissolved as much as possible by tilting and using a vortex. The tube was next entered in the preheated NMR machine (346K) with spinning and immediately spectra were measured with 16 scans.

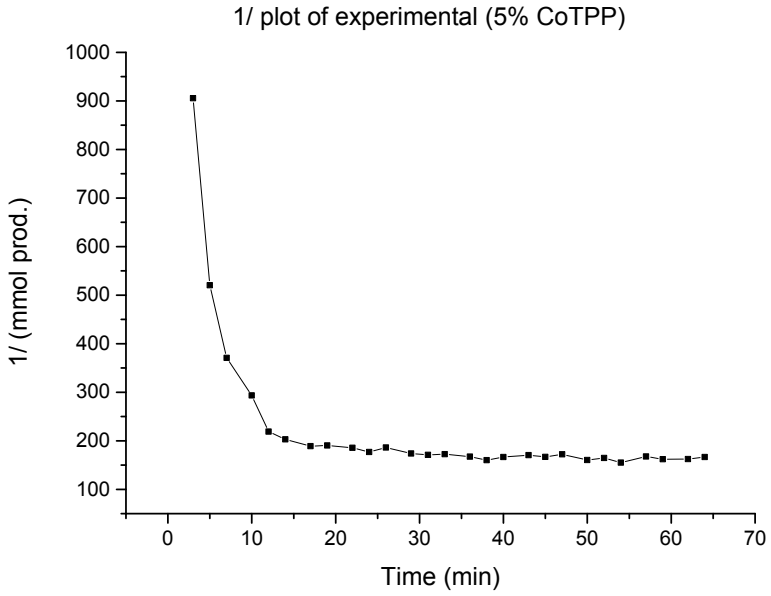





NMR investigations (5% CoTPP)
Product (mmol)
0,000
0,001
0,002
0,003
0,004
0,005
0,006
0
10
20
30
40
50
60
70
Time (min)
experimental (5% CoTPP)

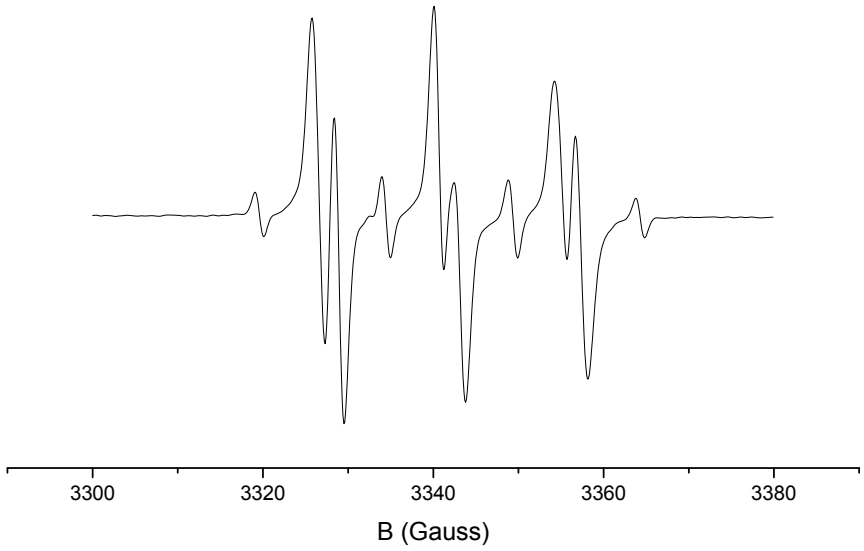

NMR investigations (5% CoTPP)
Product (mmol)
0,000
0,001
0,002
0,003
0,004
0,005
0
2
4
6
8
10
12
14
Time (min)
Equation
y = a + b*x
Adj. R-Square
0,99104
Value
Product
Intercept
6,44281E-5
Slope
3,56383E-4
experimental (5% CoTPP)
fit

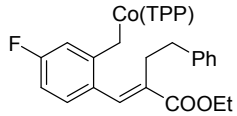

Ln plot of experimental (5% CoTPP)
Ln (mmol prod.)
-5,0
-5,2
-5,4
-5,6
-5,8
-6,0
-6,2
-6,4
-6,6
-6,8
-7,0
0
10
20
30
40
50
60
70
Time (min)


1/ plot of experimental (5% CoTPP)
1/ (mmol prod.)
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
Time (min)

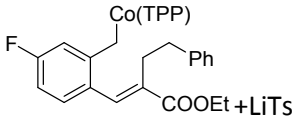
Spin trapping

Under Schlenk conditions ethyl (E)-3-(4-fluoro-2-((E)-(2-tosylhydrazono)methyl)phenyl)-2-methylacrylate (1 eq, 0.05 mmol) and LiOtBu (1.2 eq, 0.06 mmol) in dry benzene (1 mL) were heated to 60°C for 20 min. After cooling down a mixture of [Co(TPP)] (0.05 eq, 0.0025 mmol) and PBN (2 eq, 0.10 mmol) in dry benzene was added. This was stirred and a sample was transferred to an EPR tube and sealed with parafilm. The same solution was also investigated using ESI^+. Note that the PBN (fragment) is drawn attached to the allylic carbon, but this could also be at the carbene carbon.

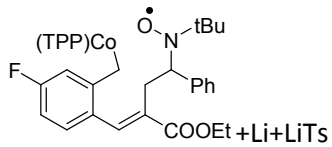




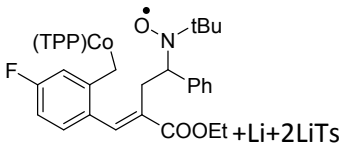
$C_{64}H_{48}CoFLiN_4O_2$
Calcd. mass 989.3255
Found. 989.2945



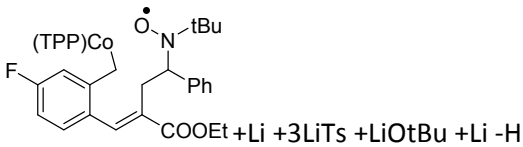
$C_{71}H_{55}CoFLi_2N_4O_4S$
Calcd. mass 1151.3583
Found. 1151.3042



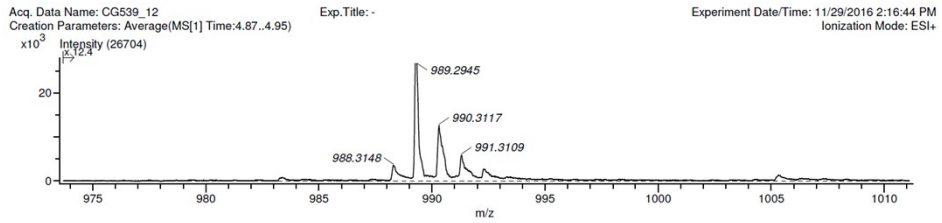
$C_{75}H_{63}CoFLi_2N_5O_5S$
Calcd. mass 1237.4189
Found 1237.4507

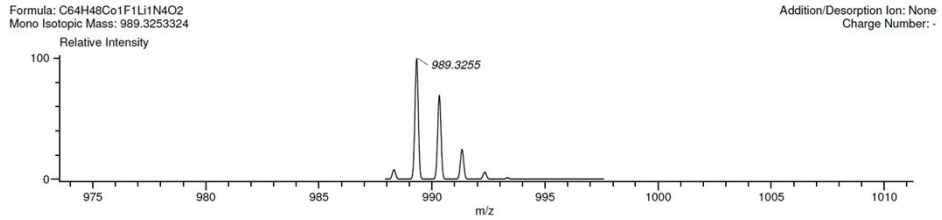


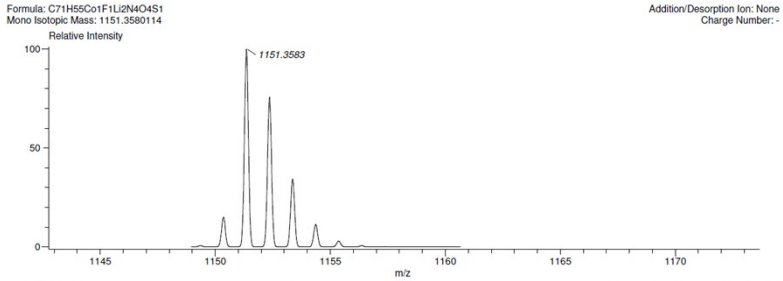
$C_{82}H_{70}CoFLi_3N_5O_7S_2$
Calcd. mass 1399.4517
Found 1399.4035

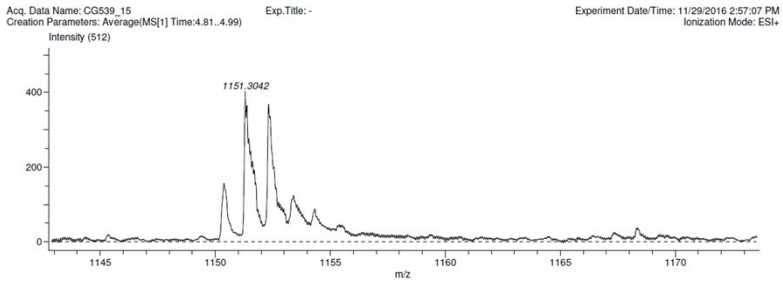


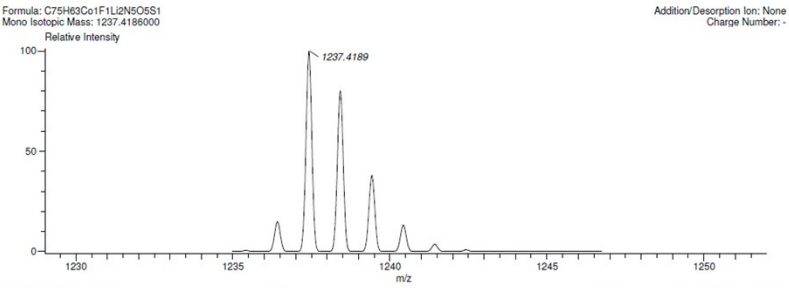
$C_{93}H_{85}CoFLi_6N_5O_{10}S_3$
Calcd. mass 1647.5744
Found 1647.5247


Acq. Data Name: CG539_12
Exp.Title: -
Experiment Date/Time: 11/29/2016 2:16:44 PM
Creation Parameters: Average(MS[1] Time:4.87..4.95)
Ionization Mode: ESI+
x10^3
Intensity (26704)
989.2945
990.3117
991.3109
988.3148
m/z


Formula: C64H48Co1F1Li1N4O2
Addition/Desorption Ion: None
Mono Isotopic Mass: 989.3253324
Charge Number: -
Relative Intensity
989.3255
m/z


Formula: C71H55Co1F1Li2N4O4S1
Addition/Desorption Ion: None
Mono Isotopic Mass: 1151.3580114
Charge Number: -
Relative Intensity
1151.3583
m/z


Acq. Data Name: CG539_15
Exp.Title: -
Experiment Date/Time: 11/29/2016 2:57:07 PM
Creation Parameters: Average(MS[1] Time:4.81..4.99)
Ionization Mode: ESI+
Intensity (512)
1151.3042
m/z


Formula: C75H63Co1F1Li2N5O5S1
Addition/Desorption Ion: None
Mono Isotopic Mass: 1237.4186000
Charge Number: -
Relative Intensity
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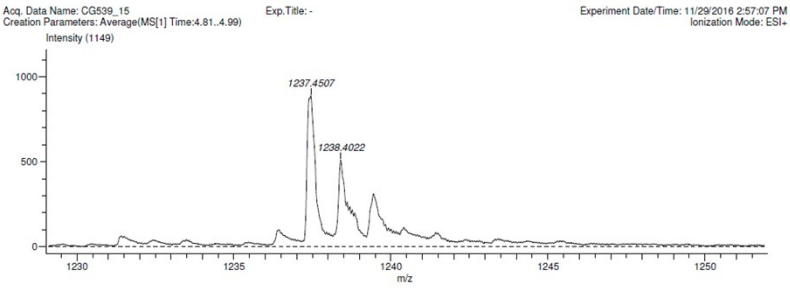
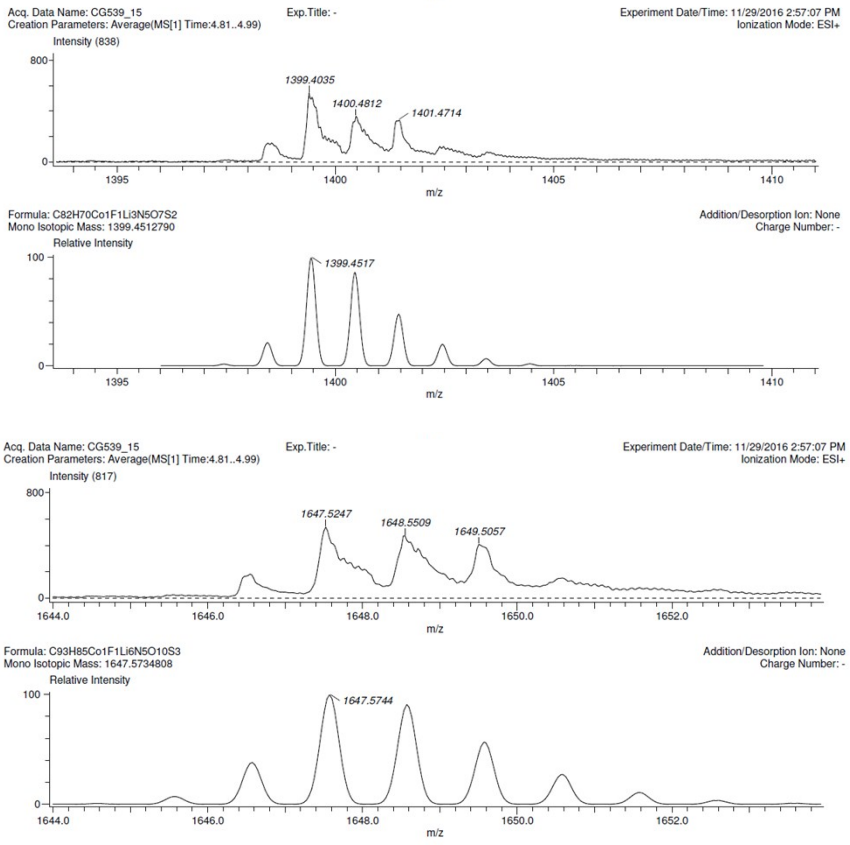
m/z

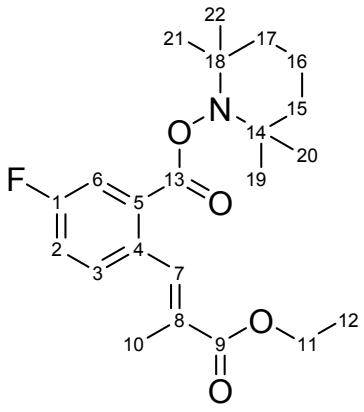

Acq. Data Name: CG539_15
Exp.Title: -
Experiment Date/Time: 11/29/2016 2:57:07 PM
Creation Parameters: Average(MS[1] Time:4.81..4.99)
Ionization Mode: ESI+
Intensity (1149)
1237.4507
1238.4022
m/z


Acq. Data Name: CG539_15
Creation Parameters: Average(MS[1] Time:4.81..4.99)
Exp.Title: -
Experiment Date/Time: 11/29/2016 2:57:07 PM
Ionization Mode: ESI+
Intensity (838)
800
0
1399.4035
1400.4812
1401.4714
1395
1400
1405
1410
m/z
Formula: C82H70Co1F1Li3N5O7S2
Mono Isotopic Mass: 1399.4512790
Addition/Desorption Ion: None
Charge Number: -
Relative Intensity
100
0
1399.4517
1395
1400
1405
1410
m/z

Acq. Data Name: CG539_15
Creation Parameters: Average(MS[1] Time:4.81..4.99)
Exp.Title: -
Experiment Date/Time: 11/29/2016 2:57:07 PM
Ionization Mode: ESI+
Intensity (817)
800
0
1647.5247
1648.5509
1649.5057
1644.0
1646.0
1648.0
1650.0
1652.0
m/z
Formula: C93H85Co1F1Li6N5O10S3
Mono Isotopic Mass: 1647.5734808
Addition/Desorption Ion: None
Charge Number: -
Relative Intensity
100
0
1647.5744
1644.0
1646.0
1648.0
1650.0
1652.0
m/z

Radical trapping

Under Schlenk conditions, ethyl (E)-3-(4-fluoro-2-((E)-(2-tosylhydrazono)methyl)phenyl)-2-methylacrylate (1 eq, 0.10 mmol), LiOtBu (1.2 eq, 0.12 mmol), TEMPO (2 eq, 0.20 mmol) and [Co(TPP)] (0.05 eq, 0.005 mmol) were put together after which the tube was evacuated for 15 min. and then refilled with N_2. Next benzene (2 mL) was added and the mixture was heated to 60 °C over night in a dark fumehood. The mixture was then filtered over a silica plug and eluted with EtOAc. After concentration the product was purified by column chromatography (9:1 hexanes:EtOAc) to yield the product as a red oil (59%).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.74 – 7.65 (m, 1H), 7.31 – 7.21 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.90 (d, *J* = 1.6 Hz, 3H, allyl Me), 1.79 – 1.65 (m, 4H, C_{15}/C_{17}), 1.66 – 1.51 (m, 2H, C_{16}), 1.32 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 6H, TEMPO), 1.10 (s, 6H, TEMPO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.18 (s, C_9), 165.85 (d, *J* = 2.7 Hz, C_{13}), 161.81 (d, *J* = 248.9 Hz, C_1), 138.34 (s, C_7), 133.65 (d, *J* = 3.6 Hz, C_4), 132.28 (d, *J* = 7.7 Hz, C_3), 131.27 (d, *J* = 7.2 Hz, C_5), 129.13 (s, C_8), 119.04 (d, *J* = 21.3 Hz, C_6), 117.36 (d, *J* = 23.4 Hz, C_2), 61.00 (s, C_{14}/C_{18}), 60.57 (s, C_{11}), 39.28 (s, C_{15}/C_{17}), 32.04 (s, C_{19}/C_{21}), 21.17 (s, C_{20}/C_{22}), 17.09 (s, C_{16}), 14.40 (s, C_{12}), 14.04 (s, C_{10}). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.74 (s). IR (neat) ν 2978, 2933, 1752, 1712, 1489, 1262, 1174, 1112, 1041 cm^{-1}. HRMS (EI^+) calcd. for $C_{22}H_{30}FNO_4$ $[M]^+$ 391.21589, found 391.21530.

List of Abreviations

M	molar
EtOAc	ethyl acetate
h	hour(s)
min	minutes
eq	equivalents
N,N-DMF	N,N-dimethylformamide
NMR	nuclear magnetic resonance
IR	infrared
THF	tetrahydrofuran
sat.	saturated
br s	broad singlet
MHz	mega hertz
calcd.	calculated
PE	petroleum ether 40-60°C
mL	milliliter
DCM	dichloromethane
PBN	N-*tert*-butyl-α-phenylnitrone
TEMPO	…

Computational details

The mechanism of the [Co(por)]-catalyzed *1,2*-dihydronaphthalene and E-aryl-diene formation reactions were explored computationally, using DFT. A simplified model porphyrin without *meso*-substituents was used to reduce computation time. Geometry optimizations were carried out with the Turbomole program package[1] coupled to the PQS Baker optimizer[2] via the BOpt package.[3] We used unrestricted ri-DFT-D3 calculations at the BP86 level,[4] in combination with the def2-TZVP basis set,[5] and a small (m4) grid size. Grimme's dispersion corrections[6] (version 3, disp3, 'zero damping') were used to include Van der Waals interactions. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by following the intrinsic reaction coordinate. The relative free energies ($\Delta G°_{333K}$ in kcal mol^{-1}) obtained from these calculations are reported in the main text. A separate archive file containing an excel sheet containing the energies and entropies (ΔG_{333K}, ΔG_{298K}, ΔH, ΔS, SCF+ZPE, SCF) and negative eigenvalues of the transition states and all optimized geometries (.pdb and .xyz format) is provided.

DFT calculations without dispersion corrections strongly underestimate the metal-ligand interactions, as was clear from a series of test calculations. We therefore employed Grimme's version 3 (disp3) dispersion corrections. Used as such, the computed dispersion corrected metal-ligand association/dissociation energies to/from the *non-solvated* [Co(por)] catalyst **A** are overestimated though. This is due to neglected dispersion interactions between the metal binding site of the catalyst and a solvent molecule in solution. We therefore used the Van der Waals π-complex between [Co(por)] catalyst **A** and a discrete toluene solvent molecule (interacting with catalyst at the metal binding site) as the energetic reference point in our calculations to prevent overestimation of the metal-ligand interactions as a result of such uncompensated dispersion forces. However, this approach also leads to an erroneous cancelation of all translational entropy contributions to the computed free energies. This is because the translational entropy contributions to substrate/product association/dissociation are fully counterbalanced by the translational entropy contributions resulting from dissociation/association of the involved solvent molecule in the DFT calculated thermodynamics (A-solv + L $\rightleftarrows$ A-L + solv). This is not realistic in comparison to actual solution phase chemistry, for which the translational entropy contributions associated with substrate/product association/dissociation steps can of course not be neglected.[7] Therefore we applied a translational entropy contribution of 20 cal mol^{-1} K^{-1} to the computed free energies of all substrate/product binding/dissociation steps in the catalytic cycle. See also the excel sheet in the separate archive file.

Energy Tables

Table S1. Free Energies, Enthalpies and Entropies.

BP86, def2-TZVP, disp3, m4		ΔG_333K	ΔG_298K	ΔH_298K	ΔS
		kcal/mol	kcal/mol	kcal/mol	cal/mol/K
A		1.0	2.6	16.7	47.2
A_toluene_adduct	-	0.0	0.0	0.0	0.0
toluene					
diazo_substrate		0.0			0.0
N2					
B		0.4	-0.5	-8.1	-25.6
TS1		10.8	9.9	2.2	-26.1
C (+ N2)		-12.3	-11.7	-7.4	14.5
C_rotated (+ N2)		-11.2	-10.7	-6.8	13.1
TS2 (+ N2)		-6.7	-6.5	-4.9	5.3
D (+ N2)		-22.1	-21.7	-18.7	10.3
TS3 (+ N2)		-6.9	-6.6	-4.5	7.1
F + A_toluene_adduct (+ N2)		-60.3	-59.3	-50.9	28.1
D (+ N2)		-22.1	-21.7	-18.7	10.3
E + A_toluene_adduct (+ N2)		-11.1	-9.8	1.2	36.9
TS4 + A_toluene_adduct (+ N2)		-7.2	-6.1	3.1	30.9
F + A_toluene_adduct (+ N2)		-60.3	-59.3	-50.9	28.1
D'		0.0	0.0	0.0	0.0
TS5		15.3	15.1	13.8	-4.4
TS5' (Me other side)		15.9	15.8	15.0	-2.9
F' + A_toluene_adduct (+ N2)		-36.2	-35.7	-30.9	16.1
E'		7.0	7.8	14.3	21.9
TS8		9.0	9.6	14.5	16.6
G		-14.3	-13.4	-5.5	26.6

BP86, def2-TZVP, m4, disp3					
		ΔG_333K	ΔG_298K	ΔH_298K	ΔS
		kcal/mol	kcal/mol	kcal/mol	cal/mol/K
E'	trans	0.0	0.0	0.0	0.0
E''	cis	2.6	2.8	4.6	6.1
TS8		2.0	1.8	0.3	-5.3
G		-21.3	-21.1	-19.7	4.7
TS6	cis	7.2	9.7	9.4	-1.2
TS7	trans	12.4	9.6	6.8	-9.3
F'		-43.2	-43.4	-45.2	-5.7

Table S2. Free Energy Barriers 333K.

BP86, def2-TZVP, disp3, m4, 333 K		neg. eigenv.		kcal/mol	barriers
A	-2371.75642	-	-2643.34648	**1.0**	
A_toluene_adduct -	-2643.34805	-	-2643.34805	**0.0**	
toluene	-271.59006	-	-2914.93811		
diazo_substrate	-724.58595	-	-3367.934	**0.0**	
N2	-109.5968	-			
B	-3096.35393	-	-3367.94399	**0.4**	
TS1	-3096.33727	-405.05 cm-1	-3367.92733	**10.8**	**10.8**
C (+ N2)	-2986.77731	-	-3367.96417	**-12.3**	
C_rotated (+ N2)	-2986.77555	-	-3367.96241	**-11.2**	
TS2 (+ N2)	-2986.76845	-1291.11 cm-1	-3367.95531	**-6.7**	**5.6**
D (+ N2)	-2986.79299	-	-3367.97985	**-22.1**	
TS3 (+ N2)	-2986.76874	-704.62 cm-1	-3367.9556	**-6.9**	**15.2**
F + A_toluene_adduct (+ N2)	-615.08522	-	-3368.03007	**-60.3**	
D (+ N2)	-2986.79299	-	-3367.97985	**-22.1**	
E + A_toluene_adduct (+ N2)	-615.00678	-	-3367.95163	**-11.1**	
TS4 + A_toluene_adduct (+ N2)	-615.00067	-273.84 cm-1	-3367.94552	**-7.2**	**14.9**
F + A_toluene_adduct (+ N2)	-615.08522	-	-3368.03007	**-60.3**	
D'	-3026.10368	-	-3407.29054	**0.0**	
TS5	-3026.0793	-672.19 cm-1	-3407.26616	**15.3**	**15.3**
TS5' (Me other side)	-3026.07828	-704.62 cm-1	-3407.26514	**15.9**	**15.9**
F' + A_toluene_adduct (+ N2)	-654.39283	-	-3407.33768	**-36.2**	
E'	-654.32392	-	-3407.26877	**7.0**	
TS8	-654.32068	-617.70 cm-1	-3407.26553	**9.0**	**9.0**
G	-654.35784	-	-3407.30269	**-14.3**	

BP86, def2-TZVP, m4, disp3, free energies 333 K			
			ΔG_333K
		G	**kcal/mol**
E'	trans	-654.32392	**0.0**
E''	cis	-654.31983	**2.6**
TS8		-654.32068	**2.0**
G		-654.35784	**-21.3**
TS6	cis	-654.30833	**7.2**
TS7	trans	-654.30408	**12.4**
F'		-654.39283	**-43.2**

Table S3. Free Energy Barriers 298K.

BP86, def2-TZVP, disp3, m4, 298 K		neg. eigenv.		kcal/mol	barriers
A	-2371.74867	-	-2643.3341	**2.6**	
A_toluene_adduct -	-2643.33832	-	-2643.33832	**0.0**	
toluene	-271.58543	-	-2914.92375		
diazo_substrate	-724.57855	-	-3367.91687	**0.0**	
N2	-109.59415	-			
B	-3096.34171	-	-3367.92714	**-0.5**	
TS1	-3096.32509	-405.05 cm-1	-3367.91052	**9.9**	**10.4**
C (+ N2)	-2986.76551	-	-3367.94509	**-11.7**	
C_rotated (+ N2)	-2986.76383	-	-3367.94341	**-10.7**	
TS2 (+ N2)	-2986.75717	-1291.11 cm-1	-3367.93675	**-6.5**	**5.2**
D (+ N2)	-2986.78143	-	-3367.96101	**-21.7**	
TS3 (+ N2)	-2986.75735	-704.62 cm-1	-3367.93693	**-6.6**	**15.1**
F + A_toluene_adduct (+ N2)	-615.07892	-	-3368.01139	**-59.3**	
D (+ N2)	-2986.78143	-	-3367.96101	**-21.7**	
E + A_toluene_adduct (+ N2)	-614.99997	-	-3367.93244	**-9.8**	
TS4 + A_toluene_adduct (+ N2)	-614.9942	-273.84 cm-1	-3367.92667	**-6.1**	**15.6**
F + A_toluene_adduct (+ N2)	-615.07892	-	-3368.01139	**-59.3**	
D'	-3026.09166	-	-3407.27124	**0.0**	
TS5	-3026.06753	-672.19 cm-1	-3407.24711	**15.1**	**15.1**
TS5' (Me other side)	-3026.06642	-704.62 cm-1	-3407.246	**15.8**	**15.8**
F' + A_toluene_adduct (+ N2)	-654.38616	-	-3407.31863	**-35.7**	
E'	-654.31692	-	-3407.24939	**7.8**	
TS8	-654.31399	-617.70 cm-1	-3407.24646	**9.6**	**9.6**
G	-654.35058	-	-3407.28305	**-13.4**	

BP86, def2-TZVP, m4, disp3, free energies 298 K			
			ΔG_298K
		G	**kcal/mol**
E'	trans	-654.31692	**0.0**
E''	cis	-654.31249	**2.8**
TS8		-654.31399	**1.8**
G		-654.35058	**-21.1**
TS6	cis	-654.30141	**7.0**
TS7	trans	-654.29726	**12.3**
F'		-654.38616	**-43.4**

Table S4. Enthalpy Barriers 298K.

BP86, def2-TZVP, disp3, m4	H_298		SCF	ZPE_corr	H_corr	kcal/mol	barriers
A	-2371.68485	-2643.23157	-2371.97065	0.26715	0.2858	**16.7**	
A_toluene_adduct -	-2643.25822	-2643.25822	-2643.67769	0.39317	0.41947	**0.0**	
toluene	-271.54672	-2914.80494	-271.67806	0.12398	0.13134		
diazo_substrate	-724.5172	-3367.77542	-724.74601	0.21199	0.22881	**0.0**	
N2	-109.57176		-109.58042	0.00535	0.00866		
B	-3096.24162	-3367.78834	-3096.75714	0.47994	0.51552	**-8.1**	
TS1	-3096.22524	-3367.77196	-3096.73979	0.47918	0.51455	**2.2**	**10.3**
C (+ N2)	-2986.66876	-3367.78724	-2987.17331	0.4711	0.50455	**-7.4**	
C_rotated (+ N2)	-2986.66774	-3367.78622	-2987.17146	0.4703	0.50372	**-6.8**	
TS2 (+ N2)	-2986.6648	-3367.78328	-2987.16368	0.46666	0.49888	**-4.9**	**2.5**
D (+ N2)	-2986.68667	-3367.80515	-2987.19086	0.47119	0.50419	**-18.7**	
TS3 (+ N2)	-2986.66411	-3367.78259	-2987.16682	0.47018	0.50271	**-4.5**	**14.2**
F + A_toluene_adduct (+ N2)	-615.0266	-3367.85658	-615.24626	0.2064	0.21966	**-50.9**	
D (+ N2)	-2986.68667	-3367.80515	-2987.19086	0.47119	0.50419	**-18.7**	
E + A_toluene_adduct (+ N2)	-614.94347	-3367.77345	-615.16006	0.202	0.21659	**1.2**	
TS4 + A_toluene_adduct (+ N2)	-614.94056	-3367.77054	-615.15628	0.20204	0.21572	**3.1**	**21.7**
F + A_toluene_adduct (+ N2)	-615.0266	-3367.85658	-615.24626	0.2064	0.21966	**-50.9**	
D'	-3025.9932	-3407.11168	-3026.52627	0.49841	0.53307	**0.0**	
TS5	-3025.97116	-3407.08964	-3026.50277	0.49758	0.53161	**13.8**	**13.8**
TS5' (Me other side)	-3025.96935	-3407.08783	-3026.50088	0.49728	0.53153	**15.0**	**15.0**
F' + A_toluene_adduct (+ N2)	-654.33093	-3407.16091	-654.57937	0.23374	0.24844	**-30.9**	
E'	-654.25896	-3407.08894	-654.50408	0.22932	0.24512	**14.3**	
TS8	-654.25855	-3407.08853	-654.50009	0.22687	0.24154	**14.5**	**14.5**
G	-654.29039	-3407.12037	-654.53665	0.22994	0.24626	**-5.5**	

BP86, def2-TZVP, m4, disp3						
		H	SCF	ZPE_cor	H_corr	kcal/mol
E'	trans	-654.259	-654.50408	0.22932	0.24512	**0.0**
E''	cis	-654.2516	-654.4967	0.22864	0.24508	**4.6**
TS8		-654.2586	-654.50009	0.22687	0.24154	**0.3**
G		-654.2904	-654.53665	0.22994	0.24626	**-19.7**
TS6	cis	-654.244	-654.4885	0.22919	0.24447	**9.4**
TS7	trans	-654.2408	-654.48507	0.22918	0.24428	**6.8**
F'		-654.3309	-654.57937	0.23374	0.24844	**-45.2**

Table S5. SCF+ZPE Barriers.

BP86, def2-TZVP, disp3, m4	SCF+ZPE		SCF	ZPE_corr	H_corr	kcal/mol	barriers
A	-2371.7035	-2643.25758	-2371.97065	0.26715	0.2858	**16.9**	
A_toluene_adduct -	-2643.28452	-2643.28452	-2643.67769	0.39317	0.41947	**0.0**	
toluene	-271.55408	-2914.8386	-271.67806	0.12398	0.13134		
diazo_substrate	-724.53402	-3367.81854	-724.74601	0.21199	0.22881	**0.0**	
N2	-109.57507		-109.58042	0.00535	0.00866		
B	-3096.2772	-3367.83128	-3096.75714	0.47994	0.51552	**-8.0**	
TS1	-3096.26061	-3367.81469	-3096.73979	0.47918	0.51455	**2.4**	**10.4**
C (+ N2)	-2986.70221	-3367.83136	-2987.17331	0.4711	0.50455	**-8.0**	
C_rotated (+ N2)	-2986.70116	-3367.83031	-2987.17146	0.4703	0.50372	**-7.4**	
TS2 (+ N2)	-2986.69702	-3367.82617	-2987.16368	0.46666	0.49888	**-4.8**	**3.3**
D (+ N2)	-2986.71967	-3367.84882	-2987.19086	0.47119	0.50419	**-19.0**	
TS3 (+ N2)	-2986.69664	-3367.82579	-2987.16682	0.47018	0.50271	**-4.5**	**14.5**
F + A_toluene_adduct (+ N2)	-615.03986	-3367.89945	-615.24626	0.2064	0.21966	**-50.8**	
D (+ N2)	-2986.71967	-3367.84882	-2987.19086	0.47119	0.50419	**-19.0**	
E + A_toluene_adduct (+ N2)	-614.95806	-3367.81765	-615.16006	0.202	0.21659	**0.6**	
TS4 + A_toluene_adduct (+ N2)	-614.95424	-3367.81383	-615.15628	0.20204	0.21572	**3.0**	**22.0**
F + A_toluene_adduct (+ N2)	-615.03986	-3367.89945	-615.24626	0.2064	0.21966	**-50.8**	
D'	-3026.02786	-3407.15701	-3026.52627	0.49841	0.53307	**0.0**	
TS5	-3026.00519	-3407.13434	-3026.50277	0.49758	0.53161	**14.2**	**14.2**
TS5' (Me other side)	-3026.0036	-3407.13275	-3026.50088	0.49728	0.53153	**15.2**	**15.2**
F' + A_toluene_adduct (+ N2)	-654.34563	-3407.20522	-654.57937	0.23374	0.24844	**-30.3**	
E'	-654.27476	-3407.13435	-654.50408	0.22932	0.24512	**14.2**	
TS8	-654.27322	-3407.13281	-654.50009	0.22687	0.24154	**15.2**	**15.2**
G	-654.30671	-3407.1663	-654.53665	0.22994	0.24626	**-5.8**	

BP86, def2-TZVP, m4, disp3						
		SCF+ZPE	SCF	ZPE_cor	H_corr	kcal/mol
E'	trans	-654.2748	-654.50408	0.22932	0.24512	**0.0**
E''	cis	-654.2681	-654.4967	0.22864	0.24508	**4.2**
TS8		-654.2732	-654.50009	0.22687	0.24154	**1.0**
G		-654.3067	-654.53665	0.22994	0.24626	**-20.0**
TS6	cis	-654.2593	-654.4885	0.22919	0.24447	**9.7**
TS7	trans	-654.2559	-654.48507	0.22918	0.24428	**7.6**
F'		-654.3456	-654.57937	0.23374	0.24844	**-44.5**

Table S6. SCF Barriers.

BP86, def2-TZVP, disp3, m4	SCF		SCF	ZPE_corr	H_corr	kcal/mol	barriers
A	-2371.97065	-2643.64871	-2371.97065	0.26715	0.2858	**18.2**	
A_toluene_adduct -	-2643.67769	-2643.67769	-2643.67769	0.39317	0.41947	**0.0**	
toluene	-271.67806	-2915.35575	-271.67806	0.12398	0.13134		
diazo_substrate	-724.74601	-3368.4237	-724.74601	0.21199	0.22881	**0.0**	
N2	-109.58042		-109.58042	0.00535	0.00866		
B	-3096.75714	-3368.4352	-3096.75714	0.47994	0.51552	**-7.2**	
TS1	-3096.73979	-3368.41785	-3096.73979	0.47918	0.51455	**3.7**	**10.9**
C (+ N2)	-2987.17331	-3368.43179	-2987.17331	0.4711	0.50455	**-5.1**	
C_rotated (+ N2)	-2987.17146	-3368.42994	-2987.17146	0.4703	0.50372	**-3.9**	
TS2 (+ N2)	-2987.16368	-3368.42216	-2987.16368	0.46666	0.49888	**1.0**	**6.0**
D (+ N2)	-2987.19086	-3368.44934	-2987.19086	0.47119	0.50419	**-16.1**	
TS3 (+ N2)	-2987.16682	-3368.4253	-2987.16682	0.47018	0.50271	**-1.0**	**15.1**
F + A_toluene_adduct (+ N2)	-615.24626	-3368.50437	-615.24626	0.2064	0.21966	**-50.6**	
D (+ N2)	-2987.19086	-3368.44934	-2987.19086	0.47119	0.50419	**-16.1**	
E + A_toluene_adduct (+ N2)	-615.16006	-3368.41817	-615.16006	0.202	0.21659	**3.5**	
TS4 + A_toluene_adduct (+ N2)	-615.15628	-3368.41439	-615.15628	0.20204	0.21572	**5.8**	**21.9**
F + A_toluene_adduct (+ N2)	-615.24626	-3368.50437	-615.24626	0.2064	0.21966	**-50.6**	
D'	-3026.52627	-3407.78475	-3026.52627	0.49841	0.53307	**0.0**	
TS5	-3026.50277	-3407.76125	-3026.50277	0.49758	0.53161	**14.7**	**14.7**
TS5' (Me other side)	-3026.50088	-3407.75936	-3026.50088	0.49728	0.53153	**15.9**	**15.9**
F' + A_toluene_adduct (+ N2)	-654.57937	-3407.83748	-654.57937	0.23374	0.24844	**-33.1**	
E'	-654.50408	-3407.76219	-654.50408	0.22932	0.24512	**14.2**	
TS8	-654.50009	-3407.7582	-654.50009	0.22687	0.24154	**16.7**	**16.7**
G	-654.53665	-3407.79476	-654.53665	0.22994	0.24626	**-6.3**	

BP86, def2-TZVP, m4, disp3						
		SCF	SCF	ZPE_cor	H_corr	kcal/mol
E'	trans	-654.5041	-654.5041	0.22932	0.24512	**0.0**
E''	cis	-654.4967	-654.4967	0.22864	0.24508	**4.6**
TS8		-654.5001	-654.5001	0.22687	0.24154	**2.5**
G		-654.5367	-654.5367	0.22994	0.24626	**-20.4**
TS6	cis	-654.4885	-654.4885	0.22919	0.24447	**9.8**
TS7	trans	-654.4851	-654.4851	0.22918	0.24428	**7.3**
F'		-654.5794	-654.5794	0.23374	0.24844	**-47.2**

Optimized Geometries

N_2

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2
 N2
N      0.0000000    0.0000000    0.9863040
N      0.0000000    0.0000000   -0.1163040
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toluene

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15
 toluene
C     -0.0178842    0.0000899    1.0525150
C      0.0132356   -0.0000101    3.8750033
C     -0.0119504   -1.2033840    1.7734632
C     -0.0120285    1.2035135    1.7735456
C      0.0041801    1.2066012    3.1703468
C      0.0042753   -1.2065729    3.1702562
H     -0.0226446   -2.1515267    1.2308571
H     -0.0227564    2.1516923    1.2310052
H      0.0055441    2.1550015    3.7100966
H      0.0056993   -2.1550132    3.7099346
H      0.0226728   -0.0000515    4.9657486
C     -0.0009101    0.0000885   -0.4557340
H      1.0331991   -0.0005296   -0.8360819
H     -0.4991930    0.8899279   -0.8646515
H     -0.4994391   -0.8898268   -0.8643049
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diazo substrate

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28
 diazo substrate
C     3.351737    -0.4791113   -1.543548
H     3.2120787    0.5867124   -1.7084272
C     4.1545404   -1.0284046   -0.4643852
C     5.6613673   -2.0529556    1.6903527
C     4.9575463   -0.1508181    0.3231891
C     4.1328119   -2.4028995   -0.1514086
C     4.8759788   -2.9087158    0.9095317
C     5.6932761   -0.693127     1.3931731
H     3.5146202   -3.0818146   -0.7415811
H     4.8420649   -3.9765608    1.1291948
H     6.3364809   -0.029088     1.9705571
H     6.2545896   -2.4462979    2.5160354
C     5.0705247    1.2650562   -0.0335595
H     5.1694123    1.4776527   -1.1013976
C     5.0737109    2.3331635    0.8022436
C     5.2708401    3.7090704    0.2614203
O     5.2808658    4.71392      0.955461
O     5.44204      3.7504544   -1.0933374
C     5.6347338    5.0737431   -1.6351047
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H     6.5323321    5.5404479   -1.2066399
H     4.7675435    5.7123307   -1.4175175
H     5.7505744    4.9325751   -2.7147445
C     4.859067     2.2792191    2.2889371
H     4.4176209    1.3237676    2.595855
H     4.2065966    3.1046563    2.6025689
H     5.8064819    2.4146506    2.8336189
N     2.6881173   -1.2529323   -2.3605285
N     2.1164486   -1.954694    -3.061959
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A

```
37
 A
C     0.1929408    2.1101905   -2.370403
N     0.1213381    0.7726809   -2.0183592
H     0.0853592    3.2300402   -4.3085728
C    -0.0552166    0.1012487   -3.216715
C    -0.0949132    1.0251479   -4.3206291
H    -0.2253955    0.7350583   -5.3596115
C     0.060763     2.2727771   -3.7951195
C    -0.1722191   -1.2702096   -3.3555359
N     0.0456697   -1.8218461   -0.9687307
C     0.0423494   -3.0298464   -0.2913395
C    -0.1249767   -4.1296108   -1.2057963
H    -0.1586544   -5.1745631   -0.9097897
C    -0.2283351   -3.5914539   -2.4534547
H    -0.3643648   -4.0983925   -3.4048628
C    -0.1203876   -2.1636678   -2.3005481
C     0.3607739    3.162047    -1.4875924
H     0.8134221    4.0865377    3.0031898
C     0.6962774    3.5783121    2.0499592
C     0.5781543    2.1512292    1.8980046
H     0.6856144    5.1573829    0.5006256
N     0.4408737    1.8074398    0.5634262
C     0.4731197    3.0134567   -0.116738
C     0.6326431    4.1137544    0.7984742
C     0.1730136   -3.1796847    1.0777564
H     0.6646232   -0.746204     4.9588588
C     0.5551934   -1.037746     3.9178469
C     0.4388972   -2.2880711    3.3885687
H     0.4313406   -3.2464955    3.9003985
C     0.3189002   -2.1263265    1.962665
N     0.3629251   -0.7869366    1.6132613
C     0.5090286   -0.1134174    2.8145427
C     0.6069298    1.2593478    2.9552027
Co    0.2429206   -0.0071919   -0.202618
H    -0.3076814   -1.6723126   -4.3592768
H     0.1543007   -4.1902817    1.4850589
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A_toluene_adduct

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52
 A_toluene_adduct
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C     1.7816146    1.7011128   -6.2039420
C     0.6780587    1.4690000   -5.3066927
H     0.7835762    1.2106873   -4.2564721
C    -0.4620421    1.6597561   -6.0287658
C     3.1100341    1.6726922   -5.8180951
N     4.0466078    2.3459562   -7.9874259
C     5.3316487    2.6657590   -8.3892875
C     6.2555968    2.5397924   -7.2911523
H     7.3211529    2.7417859   -7.3578298
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C    -0.9343952    2.1825964   -8.4204419
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C     5.7110440    2.9713028   -9.6850604
H     4.0794413    2.9785972  -13.9967528
C     4.1658482    2.9272650  -12.9148144
C     5.2720060    3.1058170  -12.1378391
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C     4.8524514    2.9341229  -10.7702852
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C     3.0645360    2.6789622  -12.0196175
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C     3.2621965   -0.6805074   -8.9634035
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C     2.8182320   -1.1663738   -7.7235770
C     1.4621175   -1.3772958   -7.4780534
C     0.9358309   -0.6273121   -9.7083874
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B

65
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C     1.5499009   -0.6244613    1.9713592
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H     4.6976413    1.5176998    2.7740989
H     4.9867376    3.2861181    2.7637654
H     6.3531701    2.1727185    2.7020295
H    -0.5264138   -0.9451349   -5.0992191
H     2.0552221    4.1343231   -2.2109837
H     2.064804     0.944203     3.3098168
H     0.4107847   -4.3770512    0.1992639
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C

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63
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C     4.9176562   -0.2558634    0.2715772
C     3.666283    -2.3258795   -0.1020533
C     4.5296465   -3.015226     0.7364243
C     5.7875741   -0.9828158    1.1042231
H     2.8341016   -2.8384341   -0.5831262
H     4.3766267   -4.079878     0.9187712
H     6.6337065   -0.4670466    1.5591392
H     6.3002208   -2.8834191    1.9815708
C     5.0799171    1.1830559    0.0697994
H     4.8968046    1.5531093   -0.939836
C     5.3526802    2.119531     1.0120542
C     5.4189702    3.5564573    0.6303296
O     5.5100297    4.4742448    1.4331948
O     5.3581934    3.7698348   -0.7176455
C     5.3615926    5.1547839   -1.1080457
H     6.2857661    5.650677    -0.7803076
H     4.5053477    5.6841204   -0.6667425
H     5.2912847    5.150608    -2.2008103
C     0.982737     2.1631395   -2.8871774
N     0.8062209    0.8183185   -2.6155226
H     0.8868843    3.4112665   -4.7476605
C     0.5710152    0.2340519   -3.8476314
C     0.5720124    1.2263964   -4.8918047
H     0.3942854    1.0132234   -5.9422737
C     0.8156407    2.4265646   -4.2938814
C     0.3276412   -1.1110034   -4.0589738
N     0.4052171   -1.7859035   -1.6985347
C     0.1146321   -2.9808228   -1.0631375
C    -0.2618489   -3.9901317   -2.0191545
H    -0.5454902   -5.0066225   -1.7603928
C    -0.1803471   -3.4137312   -3.2519169
H    -0.3894587   -3.8532921   -4.2233284
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C    2.2760275    3.2019198    1.4929962
C    1.9327516    1.8205049    1.2773136
H    2.1931985    4.9032195    0.0867197
N    1.4951525    1.6209009   -0.0215884
C    1.5875786    2.8644404   -0.6236526
C    2.0491876    3.8517202    0.3173497
C    0.2186458   -3.2044143    0.2984274
H    1.8445693   -1.2633743    4.1432337
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C    0.9474829   -2.5565587    2.5888267
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N    1.0620751   -0.9721955    0.8901593
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C    2.0058434    0.842306     2.2505411
Co   1.076715    -0.1046697   -0.8900435
C    5.4890936    1.8591816    2.4861935
H    5.0342347    0.8998803    2.7613255
H    5.011852     2.6705098    3.0512418
H    6.5446127    1.8428821    2.7999921
H    0.1590443   -1.4448667   -5.0825375
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C_rotated

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63
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 C    4.2438191   -0.2342466    0.4473690
 C    4.4571071    1.9342995   -0.6526336
 C    5.3349379    2.3752642    0.3286836
 C    5.0977541    0.2558123    1.4570592
 H    4.1602757    2.6082668   -1.4586622
 H    5.7575369    3.3792754    0.2712433
 H    5.3586443   -0.4098692    2.2826268
 H    6.3127294    1.8742264    2.1985834
 C    3.8534322   -1.6375421    0.5578581
 H    3.7088064   -1.9821198    1.5838227
 C    3.7620817   -2.5777182   -0.4194474
 C    3.4108613   -3.9749074   -0.0521040
 O    3.2841262   -4.8956865   -0.8465946
 O    3.2205688   -4.1585926    1.2944049
 C    2.8413536   -5.4927669    1.6685404
 H    3.6085262   -6.2199939    1.3685867
 H    1.8911040   -5.7767154    1.1925734
 H    2.7338684   -5.4730280    2.7584584
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C	0.2899298	2.4485016	-4.7618027
C	0.6664535	-1.0886274	-4.3295139
N	0.6535659	-1.5894350	-1.9293362
C	0.5098586	-2.7717706	-1.2258558
C	0.4552552	-3.8965241	-2.1239536
H	0.3723661	-4.9309929	-1.8055169
C	0.5809406	-3.3986926	-3.3856426
H	0.5897026	-3.9361410	-4.3296639
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C	0.9334358	3.2377335	-1.1275302
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Co	0.9795798	0.2213900	-1.2119726
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H	3.9088760	-3.2512235	-2.4553166
H	5.0085846	-1.8958350	-2.0351555
H	0.3107607	-3.8610562	0.5870000
H	0.6670007	-1.5062402	-5.3359634
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D

63
D

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C	3.8415408	-1.6719452	1.5122688
C	4.2051509	-2.9754744	1.8360087
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H	4.1370366	-4.308536	-1.2892385
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C	3.6739263	-1.9708028	-2.2797621
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O	3.0564633	-1.8039751	-5.0079323
O	4.087658	0.2048072	-5.1718364
C	3.6897924	0.2346482	-6.5559401
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H	2.5942319	0.2439617	-6.6380987
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C	1.1545146	1.7151254	-2.5987626
N	0.9119838	0.5027371	-1.9734525
H	1.1927466	2.4027269	-4.7320233
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C	0.8575984	-1.363642	3.9422305
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N	0.8974952	-0.2638426	1.8932913
C	0.9779836	0.6455918	2.9362568
C	1.103442	2.0153752	2.7927072
Co	1.0284471	0.109176	-0.039758
C	4.914397	0.1648265	-2.5894922
H	5.3210046	0.1450197	-1.5797226
H	5.2054643	0.9819191	-3.2436012
H	3.2853913	0.7594761	0.8123335
H	1.5979168	3.7926675	-2.5578817
H	1.1618138	2.6200245	3.6975938
H	0.3305592	-2.3308532	-3.776301
H	0.7394732	-3.6226764	2.4571658

D′

66
D′

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C	3.7801825	-2.2389008	-0.8555337
C	3.7328407	-1.7149307	1.5301475
C	4.0580582	-3.0279101	1.8525711
C	3.9995054	-3.5937422	-0.4901584
H	3.5656555	-0.9890893	2.3282396
H	4.1908429	-3.3162853	2.8959385
H	4.0965386	-4.3321664	-1.2882023
H	4.3624121	-5.0286192	1.0703641
C	3.7706624	-1.9525388	-2.2630875
H	3.4194885	-2.7686090	-2.8991041
C	4.2173292	-0.8143623	-2.9865320
C	3.7327415	-0.7787435	-4.4128803
O	3.1361843	-1.6858033	-4.9703926
O	4.0443034	0.3849001	-5.0482047
C	3.6188654	0.4600671	-6.4220142
H	3.9781152	1.4284282	-6.7858071
H	2.5239959	0.4066206	-6.4873962
H	4.0513962	-0.3615046	-7.0090917
C	1.0289247	1.6673599	-2.6276298
N	0.8639836	0.4505216	-1.9849890
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C	0.6639017	0.1970494	-4.2906198
H	0.5223481	-0.3188456	-5.2352612
C	0.9064857	1.5166746	-4.0550998
C	0.5175104	-1.8236618	-2.8527132
N	0.6314818	-1.8315045	-0.3995359
C	0.5664117	-2.8595040	0.5271299
C	0.4254684	-4.1348059	-0.1272358
H	0.3562626	-5.0865060	0.3921308
C	0.3929991	-3.8868747	-1.4663235
H	0.2903364	-4.5892812	-2.2887971
C	0.5186647	-2.4610669	-1.6262456
C	1.2527763	2.8780093	-1.9985330
H	1.5415156	4.7801237	2.1880556
C	1.4391542	4.0748579	1.3677352
C	1.2341948	2.6588885	1.5320802
H	1.6037014	5.2582528	-0.4946922
N	1.1157344	2.0306718	0.3032419
C	1.2795791	3.0442910	-0.6259671
C	1.4711134	4.3138220	0.0261370
C	0.6082277	-2.6990224	1.8979544
H	1.0336409	0.5227075	5.1620716
C	0.9544769	0.0098836	4.2072886
C	0.7782790	-1.3200770	3.9629408
H	0.6837504	-2.1365289	4.6737014
C	0.7296251	-1.4768091	2.5331189
N	0.8631713	-0.2549182	1.8965802
C	1.0092227	0.6626824	2.9248859
C	1.1887119	2.0241677	2.7601573
Co	0.9939778	0.0860780	-0.0456866
C	5.1464894	0.1330767	-2.5873957

H	5.3492001	0.9426737	-3.2882405
H	3.2511689	0.7459549	0.7918817
H	1.3877390	3.7609362	-2.6230648
H	1.3002205	2.6360660	3.6552157
H	0.4281846	-2.4322300	-3.7513152
H	0.5463547	-3.5924217	2.5185660
C	5.9669625	0.1126978	-1.3446198
H	6.9749758	0.5009757	-1.5516057
H	6.0465398	-0.8920575	-0.9107685
H	5.5357316	0.7596303	-0.5593089

E

26
E

H	1.4598097	1.5696417	0.2616948
C	0.7841259	1.2715462	1.0659108
C	-0.9717025	0.5069360	3.1170752
C	-0.1293391	0.1658734	0.7910445
C	0.7371932	1.9807213	2.2226462
C	-0.2055774	1.6214042	3.2510957
C	-0.8859405	-0.3692592	1.9551630
H	1.3949017	2.8383252	2.3704012
H	-0.2729181	2.2275296	4.1554548
H	-1.6349155	0.1986622	3.9278939
C	-0.2624684	-0.2288275	-0.5058132
H	-1.0197540	-0.9226255	-0.8450687
H	0.3939536	0.1939743	-1.2682312
C	-1.3578009	-1.6504635	2.1370900
H	-1.7249887	-1.8559101	3.1472786
C	-1.3022455	-2.8381219	1.2929826
C	-1.8169215	-2.9677288	0.0525001
H	-1.7297303	-3.9176240	-0.4752824
H	-2.3919045	-2.1692653	-0.4105394
C	-0.6884129	-4.0863310	1.8831237
O	-0.3234044	-3.8975741	3.1800003
O	-0.5232651	-5.1359552	1.2902793
C	0.2674985	-5.0518540	3.8174907
H	-0.4368677	-5.8947380	3.8185454
H	0.4959303	-4.7340670	4.8396253
H	1.1817440	-5.3542691	3.2896386

E′

29
TS8

H	0.8984042	2.1414293	0.1375660
C	0.5828517	1.6378924	1.0536136
C	-0.2681283	0.3523042	3.4003268
C	-0.1731044	0.4022980	0.9084092
C	0.8437453	2.1901389	2.2672276
C	0.3693669	1.5524832	3.4677143
C	-0.4707490	-0.3599151	2.1493323
H	1.3886892	3.1325411	2.3381068

H	0.5415872	2.0283427	4.4339288
H	-0.5926163	-0.1448292	4.3169140
C	-0.6325334	0.0580704	-0.3289785
H	-1.2743650	-0.8057423	-0.4911417
H	-0.4198358	0.6933892	-1.1893454
C	-0.9460037	-1.6539506	2.2605256
H	-1.3061828	-1.9066576	3.2618927
C	-1.0506111	-2.7620393	1.3295224
C	-0.1283290	-3.1447886	0.3990382
H	-0.3692574	-4.0527276	-0.1594354
C	1.1289075	-2.4442357	0.0758662
H	1.8823438	-3.1241572	-0.3420559
H	1.5408598	-1.9008073	0.9393251
H	0.9257020	-1.6527809	-0.6820396
C	-2.2193173	-3.6998298	1.4859164
O	-2.4411930	-4.6791422	0.7957648
O	-3.0440123	-3.3167681	2.5020841
C	-4.1878380	-4.1735084	2.7088617
H	-3.8668203	-5.1943455	2.9566820
H	-4.8104569	-4.2081422	1.8047713
H	-4.7391036	-3.7265218	3.5426067

E’’

29
E’’

H	0.5055901	1.9535053	0.0432676
C	0.3368331	1.4672918	1.0063528
C	-0.1305425	0.2235400	3.4963148
C	-0.4829077	0.2591828	1.0172123
C	0.8014575	2.0257431	2.1525604
C	0.5106746	1.4191386	3.4323513
C	-0.5212786	-0.5080993	2.2982187
H	1.3730495	2.9545029	2.1197823
H	0.8395265	1.9155279	4.3462683
H	-0.2984922	-0.2619885	4.4601763
C	-1.2445593	-0.0368763	-0.0675823
H	-1.9379081	-0.8748820	-0.0842887
H	-1.1899520	0.5823964	-0.9639735
C	-0.8480532	-1.8292430	2.4424260
H	-0.9585961	-2.1909061	3.4693836
C	-1.0271686	-2.8540792	1.3980076
C	-0.0407864	-3.0982447	0.5008025
C	-2.2889135	-3.6518546	1.4191724
O	-2.6907750	-4.4155260	0.5564559
O	-2.9924162	-3.4080298	2.5654426
C	-4.2375302	-4.1294471	2.6785122
H	-4.6780604	-3.8024471	3.6258131
H	-4.0571320	-5.2130350	2.6879986
H	-4.9010107	-3.8888058	1.8369733
H	0.8420562	-2.4578883	0.6007086
C	0.0007509	-4.0723373	-0.6255339
H	1.0028217	-4.5194235	-0.7063260
H	-0.1740487	-3.5312278	-1.5737841

H	-0.7616283	-4.8524874	-0.5487126

F

26
F

H	0.0297263	1.9912538	-0.1593652
C	0.0904589	1.6186063	0.8656713
C	0.2264240	0.6834676	3.4894153
C	-0.1517519	0.2682154	1.1161977
C	0.4050289	2.4984354	1.9081423
C	0.4699476	2.0303455	3.2235814
C	-0.0749156	-0.2111752	2.4471954
H	0.5960907	3.5504278	1.6917070
H	0.7102823	2.7140744	4.0385529
H	0.2790701	0.3077367	4.5135436
C	-0.5722329	-0.6999987	0.0356582
H	-1.6777027	-0.7303661	0.0169580
H	-0.2524981	-0.3377558	-0.9519685
C	-0.3036354	-1.6246068	2.7074611
H	-0.4392738	-1.9433627	3.7423202
C	-0.3002902	-2.5454615	1.7124478
C	-0.0449082	-2.1166041	0.2874499
H	1.0437998	-2.1579622	0.0989752
H	-0.4994596	-2.8365152	-0.4052969
C	-0.4550020	-3.9958464	1.9615067
O	-0.3949466	-4.8497250	1.0888097
O	-0.6703778	-4.2972193	3.2766825
C	-0.8206705	-5.7045838	3.5541630
H	-1.6767252	-6.1193197	3.0042083
H	0.0843588	-6.2561410	3.2645419
H	-0.9857968	-5.7729196	4.6344410

F′

29
F′

H	0.0437935	1.9972897	-0.1512857
C	0.0932272	1.6266455	0.8750856
C	0.2075283	0.6946104	3.5014057
C	-0.1585057	0.2782417	1.1263437
C	0.4026723	2.5068485	1.9188035
C	0.4557329	2.0406445	3.2356274
C	-0.0895300	-0.1996622	2.4577500
H	0.5992653	3.5579168	1.7023879
H	0.6923112	2.7248848	4.0512601
H	0.2549248	0.3191640	4.5259047
C	-0.5735568	-0.6923823	0.0478410
H	-1.6783230	-0.7300118	0.0321826
H	-0.2572483	-0.3276422	-0.9410585
C	-0.3116389	-1.6142612	2.7131087
H	-0.4404876	-1.9366581	3.7478667
C	-0.3081165	-2.5329594	1.7159163

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C    -0.0342867   -2.1126441    0.2853906
H    -0.5619838   -2.8092834   -0.3820374
C    -0.4500026   -3.9847010    1.9660253
O    -0.3687017   -4.8394506    1.0952647
O    -0.6795834   -4.2877498    3.2781841
C    -0.8146774   -5.6967553    3.5554161
H    -1.6599357   -6.1226417    2.9972203
H     0.1001154   -6.2369512    3.2750008
H    -0.9896859   -5.7664863    4.6340039
C     1.4735314   -2.2226866   -0.0120214
H     2.0476630   -1.5409165    0.6326891
H     1.6803456   -1.9613296   -1.0604716
H     1.8251533   -3.2480726    0.1621960
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G

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29
 G
H     0.8428574    2.4764432   -0.1531029
C     0.6429395    1.9299739    0.7712974
C     0.0772804    0.5904899    3.1271626
C    -0.1042697    0.7455160    0.7005242
C     1.1233119    2.4315332    1.9813309
C     0.8332940    1.7592482    3.1708633
C    -0.3697567    0.0489004    1.9057807
H     1.7053056    3.3540460    1.9967872
H     1.1852713    2.1473046    4.1274923
H    -0.1592368    0.0621656    4.0529608
C    -0.6067988    0.2676960   -0.6352367
H    -1.5756624   -0.2421148   -0.5488006
H    -0.7135857    1.1071599   -1.3351350
C    -1.1575562   -1.1946544    1.9690964
H    -2.0098799   -1.1634266    2.6527600
C    -0.9474466   -2.3703840    1.3206085
C     0.2039550   -2.7149403    0.4730885
H    -0.0016683   -3.4624116   -0.2967180
C     1.4561462   -2.2601101    0.6295107
H     2.2549126   -2.5948850   -0.0327155
H     1.7247042   -1.5521048    1.4142896
H     0.0935056   -0.4574526   -1.0780178
C    -1.9530251   -3.4769759    1.4452343
O    -1.9145494   -4.5085854    0.7948721
O    -2.9330184   -3.2204642    2.3564041
C    -3.9209586   -4.2646034    2.4895400
H    -4.6198529   -3.9073948    3.2526726
H    -4.4390059   -4.4306265    1.5353044
H    -3.4492127   -5.2053428    2.8041458
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TS1

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65
 TS1
C     3.0556836   -0.3753812   -1.4316951
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H	3.4014427	0.5745210	-1.8560570
C	3.9513268	-0.9317067	-0.3990240
C	5.5057661	-2.0595549	1.6607031
C	4.8323145	-0.1018707	0.3583870
C	3.8817875	-2.3049462	-0.1021003
C	4.6388459	-2.8681797	0.9164047
C	5.5992890	-0.7007052	1.3801424
H	3.1978408	-2.9264958	-0.6794047
H	4.5567293	-3.9340573	1.1314555
H	6.3148920	-0.0924229	1.9302603
H	6.1205217	-2.4933258	2.4506059
C	4.9653992	1.3154007	0.0343483
H	4.8101867	1.5731617	-1.0132730
C	5.2245353	2.3570134	0.8643105
C	5.3133016	3.7336495	0.3021762
O	5.4574330	4.7430908	0.9761134
O	5.2053004	3.7769164	-1.0597623
C	5.2146243	5.0997382	-1.6244150
H	6.1532622	5.6200738	-1.3897401
H	4.3781346	5.6953780	-1.2309873
H	5.1107019	4.9566397	-2.7050880
C	1.3387158	2.2384905	-2.8865798
N	0.9290521	0.9371732	-2.6542163
H	1.3782512	3.5707220	-4.6904584
C	0.4651464	0.4866068	-3.8768572
C	0.5850864	1.5143490	-4.8796023
H	0.2754447	1.4016156	-5.9149591
C	1.1409604	2.5981609	-4.2679338
C	-0.0457774	-0.7758051	-4.1181848
N	0.3593241	-1.6857977	-1.8689344
C	0.1882916	-2.9546528	-1.3397923
C	-0.3815879	-3.8458455	-2.3171802
H	-0.6138863	-4.8912913	-2.1337911
C	-0.5695542	-3.1162002	-3.4517976
H	-0.9789070	-3.4351317	-4.4062823
C	-0.0931454	-1.7861926	-3.1747442
C	1.7896979	3.1153008	-1.9150976
H	2.3810857	3.4660270	2.6392258
C	2.1716533	3.0891581	1.6426883
C	1.8568714	1.7186633	1.3377347
H	2.4117544	4.8113750	0.2814556
N	1.6321026	1.5580515	-0.0193887
C	1.8625088	2.8092098	-0.5681559
C	2.1870977	3.7636956	0.4584236
C	0.4777383	-3.3208995	-0.0377564
H	1.8172581	-1.5510454	3.9996844
C	1.5547015	-1.6798499	2.9533537
C	1.1671619	-2.8127876	2.3031244
H	1.0422002	-3.8166537	2.6996006
C	0.9197417	-2.4406754	0.9339159
N	1.1597547	-1.0930086	0.7380375
C	1.5455867	-0.6183880	1.9796802
C	1.8500008	0.6986573	2.2713592
Co	1.1687395	-0.1095578	-0.9830671
C	5.3534961	2.2854745	2.3597680
H	4.7938717	1.4318938	2.7625761

H	4.9804899	3.2144425	2.8074617
H	6.4054052	2.1869046	2.6723372
H	-0.4064007	-0.9983379	-5.1220072
H	2.0530221	4.1274077	-2.2209998
H	2.0991460	0.9498467	3.3020027
H	0.3145562	-4.3594638	0.2492584
N	3.3644651	-1.3609732	-2.8914918
N	2.8295596	-2.2476049	-3.3537704

TS2

63
TS2

C	2.9162008	0.4414839	-1.3445702
H	3.0875378	1.2429183	-2.0794621
C	3.8222648	0.5065043	-0.1985841
C	5.2659556	0.8427691	2.2057813
C	4.1759346	-0.6411288	0.5847537
C	4.2942694	1.7709607	0.2046767
C	5.0117225	1.9476254	1.3864837
C	4.8517190	-0.4247673	1.8039351
H	4.0336359	2.6371312	-0.4067659
H	5.3432406	2.9443926	1.6801668
H	5.0773966	-1.2894676	2.4314430
H	5.7959521	0.9673407	3.1511212
C	3.8918464	-2.0172311	0.2111404
H	3.8221363	-2.7219499	1.0409967
C	3.7994407	-2.5304045	-1.0588399
C	3.4963562	-3.9642132	-1.2849103
O	3.4710775	-4.5056474	-2.3810276
O	3.2509231	-4.6573976	-0.1280572
C	2.9991688	-6.0608694	-0.3194812
H	3.8712670	-6.5569114	-0.7682611
H	2.1340554	-6.2127613	-0.9798324
H	2.7999861	-6.4628300	0.6799318
C	0.6789718	1.9257362	-3.5615579
N	0.7160994	0.6958665	-2.9285471
H	0.5645801	2.5824092	-5.7023688
C	0.7082947	-0.2334132	-3.9544664
C	0.6548560	0.4216005	-5.2359877
H	0.6260367	-0.0972512	-6.1902093
C	0.6205055	1.7623956	-4.9916794
C	0.6728187	-1.6057838	-3.7830805
N	0.6632910	-1.5765165	-1.3271578
C	0.4869526	-2.5795684	-0.3861396
C	0.2555224	-3.8464828	-1.0280050
H	0.0827245	-4.7777523	-0.4967613
C	0.3453342	-3.6322025	-2.3701278
H	0.2679333	-4.3498949	-3.1810531
C	0.5861396	-2.2241352	-2.5494361
C	0.7330485	3.1525606	-2.9235021
H	1.4818040	5.0423989	1.2110803
C	1.3052725	4.3366973	0.4040044
C	1.2801746	2.9073073	0.5654158
H	0.9904887	5.5482520	-1.4213762

N	1.0120048	2.2826533	-0.6398790
C	0.8989655	3.3135734	-1.5594178
C	1.0565797	4.5901141	-0.9131953
C	0.6269871	-2.4237882	0.9777101
H	1.7642808	0.7262911	4.1426538
C	1.5122998	0.2282370	3.2107383
C	1.2221929	-1.0854705	2.9944587
H	1.1870247	-1.9022835	3.7100169
C	0.9559135	-1.2255430	1.5858184
N	1.0731983	-0.0093863	0.9390694
C	1.3946550	0.8930466	1.9387146
C	1.5062387	2.2590702	1.7669411
Co	1.0128005	0.3435423	-1.0086051
C	3.9883833	-1.7172367	-2.2587461
H	3.2001325	-0.7048901	-2.0436086
H	3.7077924	-2.1984711	-3.1984342
H	4.9390791	-1.1732887	-2.3131410
H	0.5274134	-3.3081180	1.6059018
H	0.6485185	-2.2342807	-4.6727401
H	1.7544674	2.8662425	2.6365711
H	0.6821364	4.0502168	-3.5395099

TS3

63
TS3

C	3.1806256	-0.0620320	-0.3197697
H	2.7910453	0.1492862	-1.3073279
C	3.6104300	-1.4049096	0.1049726
C	4.1995808	-4.0153532	1.0149967
C	3.8120692	-2.4659800	-0.8338997
C	3.7888856	-1.6749799	1.4656513
C	4.0878084	-2.9633483	1.9228339
C	4.0618807	-3.7601146	-0.3522533
H	3.6381236	-0.8686409	2.1848191
H	4.2046131	-3.1406928	2.9925855
H	4.1779589	-4.5721291	-1.0722858
H	4.4008272	-5.0289431	1.3634246
C	3.7645018	-2.2224833	-2.2665400
H	3.4053750	-3.0157229	-2.9234512
C	4.1476488	-1.0285513	-2.8338346
C	3.8191988	-0.8277789	-4.2722916
O	3.2991080	-1.6569525	-5.0025378
O	4.1605364	0.4226392	-4.6981211
C	3.8264575	0.7067243	-6.0712879
H	4.1845950	1.7250461	-6.2541555
H	2.7397990	0.6478327	-6.2173062
H	4.3189345	-0.0068377	-6.7455823
C	0.7630086	1.7107856	-2.7302746
N	0.7381696	0.4798543	-2.0956936
H	0.6010478	2.3772169	-4.8649360
C	0.6115534	-0.4442090	-3.1206625
C	0.5373290	0.2147513	-4.3979907
H	0.4419433	-0.3059629	-5.3462616
C	0.6210728	1.5543214	-4.1554688

C	0.5703310	-1.8152911	-2.9529625
N	0.6467114	-1.8097955	-0.4935270
C	0.5501458	-2.8287997	0.4390597
C	0.4174345	-4.1081212	-0.2113636
H	0.3252134	-5.0559448	0.3115274
C	0.4420348	-3.8708802	-1.5524289
H	0.3658836	-4.5798944	-2.3721999
C	0.5700039	-2.4447212	-1.7201335
C	0.9556166	2.9262034	-2.0969131
H	1.8544655	4.7771878	2.0262310
C	1.6332215	4.0803026	1.2223711
C	1.4743114	2.6589312	1.3959854
H	1.4573329	5.2935520	-0.6189597
N	1.1849792	2.0436083	0.1899210
C	1.1668476	3.0732414	-0.7368869
C	1.4315414	4.3388942	-0.1005219
C	0.6014979	-2.6606276	1.8092077
H	1.5110355	0.5087303	5.0258000
C	1.3100993	0.0101764	4.0813918
C	0.9927852	-1.2970783	3.8558188
H	0.8841484	-2.1047682	4.5744842
C	0.8254724	-1.4458855	2.4338461
N	1.0108019	-0.2360925	1.7883704
C	1.3140107	0.6636995	2.7980219
C	1.5610534	2.0131094	2.6169369
Co	0.9999087	0.1045057	-0.1477358
C	4.7291577	0.0202788	-2.0411899
H	5.4564453	-0.2375690	-1.2724526
H	4.7596085	1.0371281	-2.4257508
H	3.5068229	0.7888996	0.2778887
H	0.9663833	3.8253994	-2.7128745
H	1.7975995	2.6115872	3.4965560
H	0.5274271	-2.4352046	-3.8472963
H	0.5085401	-3.5465973	2.4364275

TS4

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TS4

H	0.8145409	1.7337865	0.0513506
C	0.3712721	1.3815021	0.9850571
C	-0.8360580	0.5096991	3.3667006
C	-0.5095971	0.2475135	0.9300545
C	0.5278011	2.0985526	2.1437101
C	-0.1385964	1.6895176	3.3369700
C	-0.9291815	-0.3299323	2.2019940
H	1.1317415	3.0068573	2.1466481
H	-0.0458012	2.2928970	4.2408632
H	-1.2565823	0.1415567	4.3047792
C	-0.9558869	-0.2249274	-0.2951886
H	-1.9678625	-0.5928500	-0.3924024
H	-0.4812707	0.1182065	-1.2166595
C	-1.0719582	-1.7119209	2.4055684
H	-1.1462397	-2.0113687	3.4529576
C	-0.7264210	-2.7422416	1.4870474

C	-0.9861670	-2.7730117	0.1305459
H	-0.4359431	-3.4799861	-0.4917305
H	-1.9168655	-2.3979242	-0.2650598
C	0.1433014	-3.8627851	1.9971396
O	0.8161028	-4.5951774	1.2942481
O	0.0944013	-3.9825455	3.3542466
C	0.8847665	-5.0646324	3.8926049
H	0.5526007	-6.0280871	3.4824906
H	1.9465374	-4.9234340	3.6496758
H	0.7263654	-5.0292646	4.9753886

TS5

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TS5

C	3.1791523	-0.0505641	-0.3430582
H	2.8409278	0.1281898	-1.3533516
C	3.6051302	-1.3742609	0.1161593
C	4.2033809	-3.9621631	1.0839836
C	3.7973923	-2.4580056	-0.7952085
C	3.8046492	-1.6098611	1.4817889
C	4.1065449	-2.8865620	1.9663763
C	4.0497948	-3.7405653	-0.2876341
H	3.6648882	-0.7846383	2.1817150
H	4.2371652	-3.0380997	3.0385553
H	4.1578500	-4.5697996	-0.9891575
H	4.4059977	-4.9672055	1.4554941
C	3.7592331	-2.2442145	-2.2346246
H	3.3887087	-3.0526190	-2.8676978
C	4.1511444	-1.0852586	-2.8492107
C	3.8313738	-0.9573178	-4.2983446
O	3.2817593	-1.8036080	-4.9861069
O	4.2242336	0.2545932	-4.7914433
C	3.8899178	0.4820560	-6.1751170
H	4.3072664	1.4646940	-6.4189582
H	2.7992635	0.4830963	-6.3052949
H	4.3271572	-0.2973648	-6.8138101
C	0.8332795	1.6724457	-2.8021907
N	0.7713786	0.4603720	-2.1348915
H	0.7152587	2.2845517	-4.9561845
C	0.6342464	-0.4875990	-3.1362311
C	0.5908555	0.1377959	-4.4319501
H	0.4944456	-0.4064139	-5.3668107
C	0.7065107	1.4808687	-4.2247469
C	0.5636484	-1.8526828	-2.9336705
N	0.6408197	-1.7874847	-0.4749101
C	0.5431077	-2.7837690	0.4816973
C	0.3964441	-4.0771029	-0.1372026
H	0.3005380	-5.0115744	0.4086071
C	0.4132492	-3.8716550	-1.4836234
H	0.3262321	-4.5990977	-2.2860147
C	0.5531705	-2.4510282	-1.6856822
C	1.0395460	2.9009000	-2.1990010
H	1.8769534	4.8530054	1.8900415
C	1.6638709	4.1370446	1.1008434

C	1.4873937	2.7223897	1.3090119
H	1.5398005	5.3015460	-0.7759693
N	1.2128464	2.0777794	0.1148078
C	1.2258496	3.0821028	-0.8394985
C	1.4926903	4.3616829	-0.2325260
C	0.6041662	-2.5844335	1.8473091
H	1.4966061	0.6621483	4.9910081
C	1.3022974	0.1402376	4.0578734
C	0.9926755	-1.1734418	3.8619576
H	0.8843864	-1.9645268	4.5989416
C	0.8306648	-1.3559948	2.4430992
N	1.0147461	-0.1615176	1.7694923
C	1.3097939	0.7628328	2.7589685
C	1.5564605	2.1076584	2.5469878
Co	1.0131931	0.1319151	-0.1752503
C	4.7630417	0.0222835	-2.1218938
H	3.5142975	0.8164023	0.2265060
H	1.0773996	3.7825079	-2.8389014
H	1.7843129	2.7278406	3.4137970
H	0.5129845	-2.4941422	-3.8122495
H	0.5114319	-3.4555121	2.4951199
C	6.0450601	-0.1463001	-1.3678464
H	6.8935186	-0.1118679	-2.0772523
H	6.0991025	-1.1091923	-0.8435116
H	6.1958326	0.6624929	-0.6396682
H	4.5629611	1.0230106	-2.5084471

TS5′

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TS5′

C	3.1559716	-0.0370428	-0.3373327
H	2.7527871	0.1160488	-1.3280907
C	3.6098883	-1.3531169	0.1263565
C	4.2601734	-3.9323163	1.0769787
C	3.8354002	-2.4219240	-0.7955273
C	3.7897975	-1.5960142	1.4921701
C	4.1184874	-2.8696782	1.9688916
C	4.1183532	-3.7023572	-0.2941969
H	3.6165570	-0.7817825	2.1972783
H	4.2361976	-3.0289799	3.0414673
H	4.2545585	-4.5229776	-1.0009707
H	4.4863681	-4.9348965	1.4416269
C	3.7704053	-2.2095204	-2.2319765
H	3.4454726	-3.0426130	-2.8572403
C	4.0969053	-1.0306958	-2.8635183
C	3.7792173	-0.9832530	-4.3203155
O	3.1865269	-1.8551998	-4.9382819
O	4.2309852	0.1549904	-4.9187909
C	3.8902569	0.2814079	-6.3136820
H	4.3292443	1.2313622	-6.6358894
H	2.7988579	0.2986265	-6.4369462
H	4.3026254	-0.5554648	-6.8932640
C	0.7958763	1.6996662	-2.7854692
N	0.7387683	0.4820247	-2.1278204
H	0.6926379	2.3259053	-4.9363945

C	0.6166985	-0.4601861	-3.1366810
C	0.5793181	0.1743762	-4.4279359
H	0.4942440	-0.3640321	-5.3672212
C	0.6833054	1.5172638	-4.2104496
C	0.5649406	-1.8278208	-2.9443472
N	0.6358571	-1.7825960	-0.4841866
C	0.5505074	-2.7886518	0.4631706
C	0.4290178	-4.0789643	-0.1678740
H	0.3475012	-5.0198004	0.3692860
C	0.4472291	-3.8611847	-1.5122045
H	0.3765354	-4.5826381	-2.3215375
C	0.5627362	-2.4363848	-1.7013924
C	0.9997912	2.9235555	-2.1718995
H	1.8366834	4.8447897	1.9318344
C	1.6239868	4.1345453	1.1373793
C	1.4424983	2.7190153	1.3358109
H	1.5096297	5.3115498	-0.7322748
N	1.1718961	2.0827724	0.1361783
C	1.1883500	3.0936430	-0.8113792
C	1.4583406	4.3682588	-0.1951713
C	0.5982315	-2.5994411	1.8307830
H	1.4334106	0.6337434	5.0039970
C	1.2491663	0.1169979	4.0659590
C	0.9538654	-1.1982241	3.8585797
H	0.8493158	-1.9957571	4.5891328
C	0.8033465	-1.3723640	2.4373618
N	0.9790441	-0.1709628	1.7737858
C	1.2599925	0.7489507	2.7715785
C	1.5033103	2.0960677	2.5701506
Co	0.9792458	0.1384409	-0.1671357
C	4.6498191	0.0811173	-2.1072619
H	3.4833781	0.8439712	0.2135893
H	1.0408250	3.8098609	-2.8050751
H	1.7243819	2.7108050	3.4425932
H	0.5319638	-2.4630045	-3.8280312
H	0.5134802	-3.4767680	2.4712101
C	4.6290176	1.5190917	-2.5166532
H	5.4082300	1.7308302	-3.2683089
H	4.8147663	2.1637644	-1.6468087
H	3.6675576	1.8034947	-2.9651559
H	5.3992653	-0.1983243	-1.3624569

TS6

29
TS6

H	0.8972045	1.6947887	0.1240446
C	0.4433676	1.4115444	1.0761901
C	-0.7871975	0.7217032	3.5025457
C	-0.4779307	0.3074922	1.0835949
C	0.6260979	2.1893656	2.1908877
C	-0.0520494	1.8746545	3.4058282
C	-0.9117731	-0.1811279	2.3885358
H	1.2616244	3.0745887	2.1404546
H	0.0628762	2.5252875	4.2735935
H	-1.2167309	0.4212883	4.4603275

C	-0.9327143	-0.2176100	-0.1166259
H	-1.9556438	-0.5540346	-0.2125018
H	-0.4321376	0.0524442	-1.0492714
C	-1.0985560	-1.5413325	2.6811167
H	-1.1739620	-1.7768921	3.7458956
C	-0.8020178	-2.6570663	1.8496935
C	-1.1036298	-2.7504015	0.4930204
H	-2.0392803	-2.2862523	0.2100020
C	-0.1211646	-3.7650957	2.6031417
O	-0.2750304	-3.9865489	3.7923218
O	0.6918390	-4.5241423	1.8162525
C	1.3571593	-5.6079074	2.5035487
H	1.9752186	-5.2223507	3.3253730
H	0.6228064	-6.3140249	2.9136687
H	1.9794690	-6.0925074	1.7443154
C	-0.5522263	-3.7067839	-0.5208647
H	0.5433343	-3.7243707	-0.5213451
H	-0.9084856	-3.4354439	-1.5232594
H	-0.8824670	-4.7392642	-0.3154843

TS7

29
TS7

H	1.1816599	1.6483652	0.2987823
C	0.5843002	1.4126845	1.1821163
C	-0.9879020	0.8354368	3.4243034
C	-0.2956867	0.2765500	1.1094606
C	0.5704541	2.2690450	2.2530008
C	-0.2770291	2.0051366	3.3681862
C	-0.9330255	-0.1345890	2.3617685
H	1.1859771	3.1694832	2.2405543
H	-0.3140163	2.7097092	4.2000076
H	-1.5530468	0.5791813	4.3224673
C	-0.4719752	-0.3489247	-0.1201685
H	-1.4378057	-0.6954534	-0.4445762
H	0.2427011	-0.1403200	-0.9204856
C	-1.1239938	-1.4821702	2.7084693
H	-1.2140361	-1.6837482	3.7787731
C	-0.8290668	-2.5990961	1.8854441
C	-1.2163612	-2.7309636	0.5570877
C	-0.0284946	-3.6724602	2.5548077
O	0.1401462	-3.7653292	3.7593930
O	0.4945154	-4.5676892	1.6662839
C	1.2973025	-5.6080941	2.2630052
H	2.1419631	-5.1766670	2.8176189
H	0.6942713	-6.2137611	2.9531368
H	1.6545572	-6.2161225	1.4253473
C	-2.6076266	-2.3912963	0.0953371
H	-2.6596073	-2.1627516	-0.9793792
H	-3.0508642	-1.5651938	0.6666444
H	-3.2416534	-3.2814920	0.2559721
H	-0.7076568	-3.4954695	-0.0343583

TS8

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29
 TS8
H     1.1871595    2.4393732    0.0302709
C     0.7890709    1.9472402    0.9202641
C    -0.2966076    0.7181553    3.1754118
C     0.0553749    0.7287191    0.7348493
C     0.9436844    2.5257141    2.1532846
C     0.3610991    1.9141546    3.2987294
C    -0.3990531    0.0141670    1.9227967
H     1.4821824    3.4689688    2.2540564
H     0.4507304    2.3912857    4.2753775
H    -0.7148325    0.2370126    4.0619677
C    -0.1971790    0.2801720   -0.5704688
H    -1.0326703   -0.3991717   -0.7535224
H     0.0871992    0.9229692   -1.4063954
C    -0.9686917   -1.2785891    2.0007293
H    -1.5299099   -1.4308102    2.9254456
C    -0.9543283   -2.4272848    1.1711070
C    -0.0303973   -2.7822790    0.1857293
H    -0.2678140   -3.6825937   -0.3833938
C     1.1287434   -2.0277962   -0.1617319
H     1.8191868   -2.5103794   -0.8598522
H     1.6432523   -1.5361429    0.6777384
H     0.7156508   -0.9805917   -0.6688904
C    -2.0083053   -3.4804119    1.4147035
O    -2.1695835   -4.4757640    0.7294602
O    -2.7995685   -3.2045901    2.4904392
C    -3.8164052   -4.1923745    2.7613996
H    -4.3617143   -3.8160257    3.6330473
H    -4.4880791   -4.3015205    1.8992795
H    -3.3601947   -5.1676064    2.9801677
```

References in the Supporting Information

(1) TURBOMOLE Version 7.0.1 (TURBOMOLE Gmbh, Karlsruhe, Germany).

(2) (a) PQS version 2.4, **2001**, Parallel Quantum Solutions, Fayetteville, Arkansas, USA (the Baker optimizer is available separately from PQS upon request); b) Baker, J., *J. Comput. Chem.* **1986**, *7*, 385–395.

(3) Budzelaar, P. H. M., *J. Comput. Chem*. **2007**, *28*, 2226–2236.

(4) (a) Becke, A. D., *Phys. Rev. A* **1988***, 38*, 3098–3100. (b) Perdew, J. P., *Phys. Rev. B* **1986**, *33*, 8822–8824.

(5) (a) Weigend, F.; Ahlrichs, R., *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305. (b) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R., *Chem. Phys. Lett.* **1998**, *294*, 143–152.

(6) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.* **2010**, *132*, 154104.

(7) In solution the catalyst is completely surrounded by solvent molecules, leading to small translational entropy contributions to the toluene molecule association/dissociation steps. These are of little influence on the translational entropy contributions associated with substrate/product association/dissociation. Hence, the latter are not canceled by the former in toluene solution.