Supporting Information

for

Intramolecular Palladium-Catalyzed Alkane C–H Arylation from Aryl Chlorides

Part 1: Synthetic procedures, characterization data and computational studies

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Table des matières

General information

Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] Reagents were commercially available and were used without further purification unless otherwise stated including pivalic acid. Palladium(II) acetate was obtained from Strem or Johnson Matthew. P(*t*-Bu)$_3$•HBF$_4$ and P(Cy)$_3$•HBF$_4$ was purchased from Strem. P(Cyp)$_3$•HBF$_4$ was received from Aldrich Chemical Co. K_2CO_3 was received from Acros Organics and dried under vaccum at 140 °C for 24 hours then stored under argon atmosphere in a glovebox. Cs_2CO_3 was purchased from Aldrich, stored in a dessicator and weighed to air. The solvents were dried prior to use using standard methods.[2] Anhydrous solvents were obtained by distillation over calcium hydride (Et_3N, DCM, pyridine) or by distillation over sodium/benzophenone (THF, toluene, Et_2O). Mesitylene was dried over molecular sieves.

Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). Flash chromatography was performed using EM Silica Gel 60 (60-200 mesh) with the indicated solvent system according to standard technique.[3]

GC analyses were performed with a Shimadzu QP2010 GCMS apparatus, with simultaneous double injection on a DB-5ms column lined with a mass (EI) or a FID detection system.

Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm^{-1}).

Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{19}F, DEPT 135, COSY, HMQC, NOESY) were recorded either on a Bruker ALS 300, AV 300, DRX 300, AV 400 or ARX 400 spectrometer (300, 300, 300, 400 et 400 MHz respectively) in deuterated chloroform (^1H δ 7.26 ppm, ^{13}C δ 77.0 ppm) unless otherwise noted. The ^{19}F spectrawere calibrated using $CFCl_3$ as internal reference. All spectra were obtained with complete proton decoupling. Data are reported in

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[1] Shriver, D. F.; Drezdzon, M. A. The manipulation of air-sensitive compounds; 2nd Edition ed.; Wiley: New York, 1986.
[2] Armarego W. L. F.; Perrin, D. D. Purification of Laboratory Chemicals, Fourth Edition, Butterworth-Heinemann, 1996.
[3] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

parts per million (ppm) as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz and integration. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments.

High-resolution mass spectra were measured under chemical ionization (CI), electrospray ionization (ESI) or electronic impact (EI) mode.

General procedures

General procedure A: Synthesis of cyclobutarenes by C-H activation (Table 2)

In a glovebox, a Schlenk tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (0.1 equiv), P(*t*-Bu)$_3$•HBF_4 (0.2 equiv) and dry K_2CO_3 (1.3 equiv). The flask was closed with a rubber septum. The vessel was connected to a combined argon/vacuum line and evacuated for 1 hour (in order to remove traces of oxygen and water) then backfilled with argon twice. To this flask was added a solution of aryl chloride (1.00 equiv) in dry DMF (0.25M). The mixture is stirred for 15 minutes at room temperature then stirred at 140 °C (preheated oil bath) until the reaction showed completion by GC/MS analysis. After cooling, the mixture was diluted with ether and filtered through Celite®. The organic solution was washed with brine, dried over magnesium sulfate, and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography or preparative TLC to afford the desired benzocyclobutene.

General procedure B: Synthesis of indanes by alkane arylation (Table 4)

In a glovebox, a Schlenk tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (0.05 equiv), P(Cyp)$_3$•HBF_4 (0.2 equiv) and K_2CO_3 (2 equiv). The flask was closed with a rubber septum. The vessel was connected to a combined argon/vacuum line and evacuated for 1 hour (in order to remove traces of oxygen and water) then backfilled with argon twice. To this flask was added a solution of aryl chloride (1.00 equiv) in dry DMF (0.2M). The mixture is stirred for 15 minutes at room temperature then stirred at 140 °C (preheated oil bath) until the reaction showed completion by GC/MS analysis. After cooling, the mixture was diluted with ether and filtered through Celite®. The organic solution was washed with brine, dried over magnesium sulfate, and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography or preparative TLC to afford the desired indane.

General procedure C: Synthesis of dihydrobenzofurans, indolines and indanones by alkane arylation (Table 5 and 6)

A 4 mL screw cap vial equipped with a magnetic stir bar was charged with the starting material (if a solid, 1 equiv), $Pd(OAc)_2$ (5 mol%), PCy_3•HBF_4 (10 mol%), Cs_2CO_3 (1.1 equiv)

and PivOH (30 mol%). The vial was purged with argon for at least 5 minutes after which the starting material (if a liquid, 1 equiv) was added as a stock solution in mesitylene (0.17 M). The resulting mixture was placed in a preheated bath at 140 °C and stirred overnight (16 h). Upon cooling to room temperature, the reaction was diluted with EtOAc and purified by silica gel flash chromatography.

General procedure D: Synthesis of dihydrobenzofuran precursors

The desired alcohol (1.1 equiv) was added dropwise to a solution of KH (1.1 equiv) in THF (0.15 M) under argon at 0 ºC. The resulting mixture was stirred for 10 minutes after which the desired *ortho*-chloro-fluorobenzene was added and the flask was warmed to room temperature. The reaction was stirred for 2 hours (or until judged complete by TLC) and the crude product was extracted with CH_2Cl_2 (x3), washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

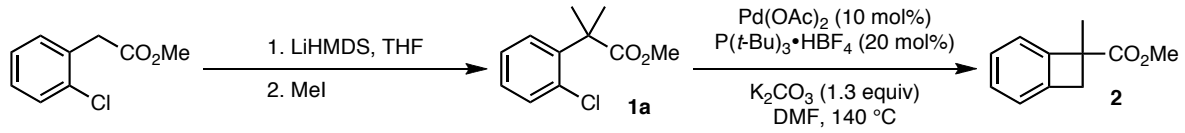
General procedure E: Synthesis of (*o*-chloro)ketophenones

The desired aryl halide (1.0 equiv) was added to a solution of KH (3.5 equiv) in THF (0.2 M) at 0 °C under argon. The resulting mixture was stirred for 10 minutes after which MeI was added (12 equiv). The solution was stirred at 0 °C for 3 hours before warming to room temperature and stirring overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the crude product was extracted with EtOAc, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General procedure F : Synthesis of (*o*-chloro)ketophenones

To a solution of 1-(2-chlorophenyl)-2-methylpropan-1-one (1.0 equiv) in THF (0.2 M) was added a base (1.1-1.5 equiv). The reaction was stirred for 10 minutes before the desired electrophile (1.5-2.0 equiv) was added. The mixture was then stirred at room temperature until judged complete by TLC. The reaction was quenched with NH_4Cl sat. and the crude product was extracted with EtOAc, dried with $MgSO_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

Synthesis of cyclobutarenes by alkane arylation (Table 2)



Methyl 2-(2-chlorophenyl)-2-methylpropanoate (1a).

LiHMDS (1.06M in THF, 30.6 mL, 32.50 mmol) was added dropwise at 0 °C to a solution of the ester (2 g, 10.83 mmol) in THF (10 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (2.02 mL, 32.50 mmol) was added dropwise. The reaction was stirred at r.t for 1 h. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous phase was extracted with Et_2O (twice) and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography afforded **1a** as a pale yellow oil in quantitative yield (2.30 g, 10.83 mmol, 100 % yield). R_f 0.35 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.30-7.18 (m, 2H), 3.67 (s, 3H), 1.61 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 142.3, 133.6, 130.6, 128.0, 126.9, 126.7, 52.3, 46.6, 26.0 ppm.

IR (neat) ν 2982, 2948, 1733, 1472, 1432, 1142 cm^{-1}.

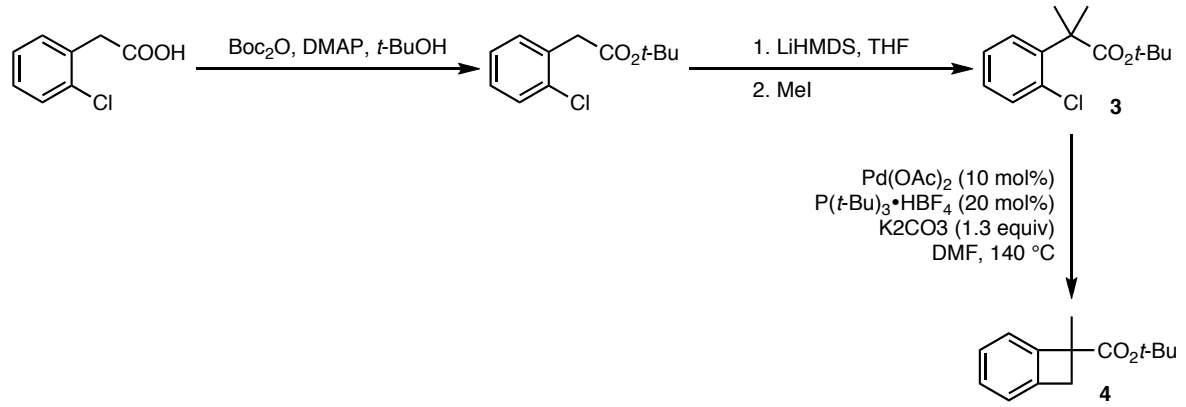
HRMS (CI) calculated for $C_{11}H_{13}ClO_2$ $[M+H]^+$: 213.0682, found: 213.0683.

Methyl 1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (2).[4]

The title compound was prepared from **1a** according to the ***general procedure A***. **1a** (100 mg, 0.47 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (10.5 mg, 0.047 mmol, 0.10 equiv), $P(t\text{-}Bu)_3$•HBF_4 (27.2 mg, 0.094 mmol, 0.20 equiv) and K_2CO_3 (84 mg, 0.61 mmol, 1.3 equiv) in DMF (2 mL) at 140 °C. The desired cyclobutarene **2** (69 mg, 83%) was obtained as a colorless oil after flash chromatography (5% EtOAc/cyclohexane). R_f 0.35 (5% Ethyl acetate/cyclohexane).

[4] Chaumontet, M.; Piccardi, R.; Audic, N.; Hitce, J.; Peglion, J.-L.; Clot, E.; Baudoin, O. *J. Am. Chem. Soc.* **2008**, *130*, 15157-15166.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.20 (m, 2H), 7.16-7.14 (m, 1H), 7.12-7.10 (m, 1H), 3.72 (d, *J* = 14.0 Hz, 1H), 3.70 (s, 3H), 3.05 (d, *J* = 14.0 Hz, 1H), 1.69 (s, 3H) ppm.



Tert-butyl 2-(2-chlorophenyl)acetate.

DMAP (143 mg, 1.17 mmol) was added to a solution of the acid (2 g, 11.72 mmol), Boc_2O (3.84 g, 17.59 mmol) in *tert*-butanol (30 mL). The reaction mixture was stirred at 50 °C for 16 hours, after which the solvent was evaporated. The residue was dissolved in Et_2O, washed successively with HCl 1N, water and brine then dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Purification by flash chromatography (2% Ethyl acetate/cyclohexane) afforded the title compound as a pale yellow oil (1.76 g, 7.76 mmol, 66%). R_f 0.31 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.28-7.26 (m, 1H), 7.23-7.20 (m, 2H), 3.68 (s, 2H), 1.45 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 134.5, 133.1, 131.3, 129.3, 128.4, 126.7, 81.1, 40.4, 27.9 ppm.

IR (neat) ν 2978, 1731, 1367, 1225, 1142, 746 cm^{-1}.

HRMS (CI) calculated for $C_{12}H_{16}ClO_2^+$ $[M+H]^+$: 227.0839, found: 227.0835.

Tert-butyl 2-(2-chlorophenyl)-2-methylpropanoate (3).

LiHMDS (1.06M in THF, 12.5 mL, 13.23 mmol) was added dropwise at 0°C to a solution of the *tert*-butyl 2-(2-chlorophenyl)acetate (1 g, 4.41 mmol) in THF (2 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (824 μL, 13.23 mmol) was added

dropwise. The reaction was stirred at r.t for 3 h. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous phase was extracted with Et_2O (twice) and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography afforded **3** as a yellow oil (874 mg, 3.43 mmol, 78 % yield). R_f 0.37 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.39-7.15 (m, 4H), 1.40 (s, 9H), 1.39 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 142.7, 133.7, 128.1, 127.9, 127.6, 126.6, 80.3, 47.4, 27.8, 25.9 ppm.

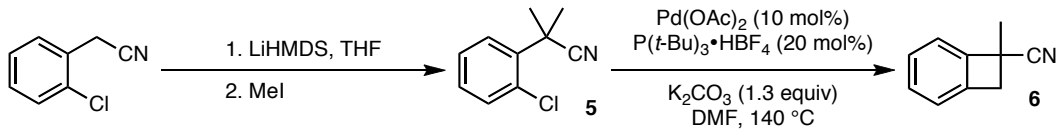
IR (neat) ν 2977, 2933, 1725, 1366, 1255 cm^{-1}.

HRMS (CI) calculated for $C_{14}H_{20}ClO_2^+$ $[M+H]^+$: 255.1152, found: 255.1153.

***Tert*-butyl 1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (4).[4]**

The title compound was prepared from **3** according to the ***general procedure A***. **3** (200 mg, 0.78 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (17.6 mg, 0.078 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (45.5 mg, 0.157 mmol, 0.20 equiv) and K_2CO_3 (141 mg, 1.02 mmol, 1.3 equiv) in DMF (3 mL) at 140 °C. The desired cyclobutarene **4** (122 mg, 71%) was obtained as a colorless oil after flash chromatography (5% EtOAc/cyclohexane). R_f 0.36 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.19 (m, 2H), 7.15-7.12 (m, 1H), 7.09-7.07 (m, 1H), 3.67 (d, *J* = 14.0 Hz, 1H), 2.99 (d, *J* = 14.0 Hz, 1H), 1.65 (s, 3H), 1.44 (s, 9H) ppm.



2-(2-chlorophenyl)-2-methylpropionitrile (5).

LiHMDS (1.06M in THF, 18.67 mL, 19.79 mmol) was added dropwise at 0 °C to a solution of the (2-chlorophenyl)acetonitrile (1 g, 6.59 mmol) in THF (10 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (1.23 mL, 19.79 mmol) was added dropwise. The reaction was stirred at r.t for 1 h. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous phase was extracted with Et_2O (twice) and the combined organic layer were

washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography afforded **5** as a yellow oil (1.06 g, 5.93 mmol, 90 % yield). R_f 0.42 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.36-7.34 (m, 1H), 7.32-7.30 (m, 1H), 7.17-7.13 (m, 2H), 1.74 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 133.2, 131.8, 129.3, 127.2, 126.9, 123.4, 36.2, 27.1 ppm.

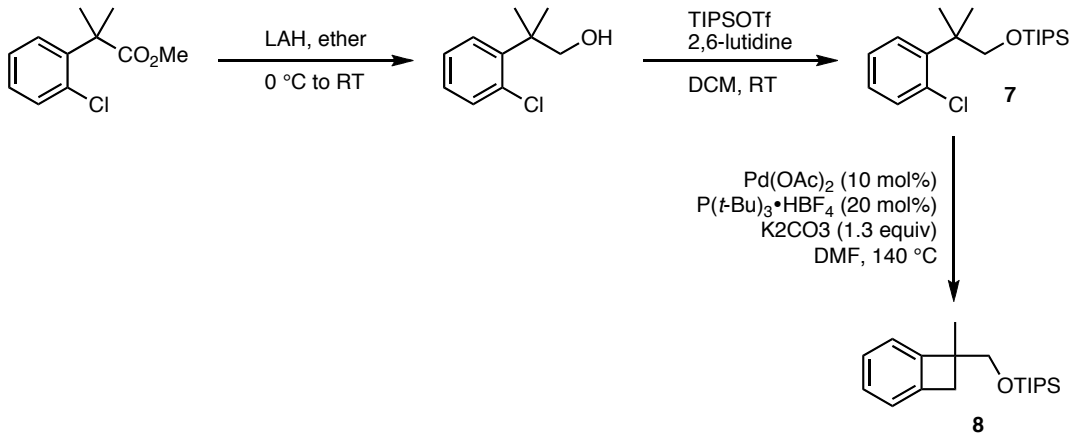
IR (neat) ν 2954, 2235, 1472, 1430 cm^{-1}.

HRMS (EI) calculated for $C_{10}H_{10}ClN$ [$M^{+\bullet}$]: 179.0502, found: 179.0500.

1-methyl-1,2-dihydrocyclobutabenzene-1-carbonitrile (6).[4]

The title compound was prepared from **5** according to the ***general procedure A***. **5** (100 mg, 0.56 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (12.0 mg, 0.055 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (32.0 mg, 0.111 mmol, 0.20 equiv) and K_2CO_3 (100 mg, 0.72 mmol, 1.3 equiv) in DMF (2.2 mL) at 140 °C. The desired cyclobutarene **6** (52 mg, 65%) was obtained as a colorless oil after flash chromatography (3% EtOAc/cyclohexane). R_f 0.42 (10% EtOAc/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.21-7.19 (1H), 7.16-7.14 (m, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.26 (d, *J* = 14.0 Hz, 1H), 1.78 (s, 3H) ppm.



2-(2-Chlorophenyl)-2-methyl-propan-1-ol.

A solution of methyl 2-(2-chlorophenyl)-2-methylpropanoate (500 mg, 2.35 mmol) in ether (5 mL) was added at 0 °C to a suspension of lithium aluminium hydride (2.33 mg, 5.88 mmol) in ether (5 mL). The reaction was stirred overnight and quenched by addition of 20% NaOH aqueous. The resulting mixture was vigorously stirred for 30 min at room temperature. The white suspension was filtered through a pad of celite, washed with Et_2O, and concentrated to give a visquous yellow oil. Purification by flash chromatography afforded the title compound as a white solid in quantitative yield (432 mg, 2.35 mmol, 100 % yield). R_f = 0.35 (20% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.35 (dd, *J* = 7.6, 1.6 Hz), 7.23 (ddd, *J* = 7.8, 7.6, 1.6 Hz, 1H), 7.16 (ddd, *J* = 7.8, 7.6, 1.8 Hz, 1H), 3.99 (s, 2H), 1.48 (s, 6H), 1.34 (s(br), 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 133.4, 132.0, 129.7, 127.8, 126.8, 69.6, 41.7, 24.9 ppm.

IR (neat) ν 3372, 2968, 2875, 1470, 1427, 1032, 752 cm^{-1}.

HRMS (CI) calculated for C10H14ClO $[M+H]^+$: 185.0733, found 185.0736.

(2-(2-Chlorophenyl)-2-methylpropoxy)triisopropylsilane (7).

2,6-Lutidine (0.75 mL, 6.51 mmol) and triisopropylsilyl triflate (1.16 mL, 4.33 mmol) were added successively at 0 °C to a solution of alcohol (400 mg, 2.17 mmol) in DCM (10 mL). The reaction mixture was then stirred for 2 h at room temperature, hydrolyzed with a saturated aqueous solution of $NaHCO_3$ and the aqueous layer was extracted twice with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Purification by flash chromatography afforded **7** as a colorless oil (702 mg, 2.06 mmol, 95 %). R_f = 0.45 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.6 Hz), 7.18 (ddd, *J* = 8.0, 7.8, 1.6 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.8, 1.8 Hz, 1H), 4.01 (s, 2H), 1.47 (s, 6H), 1.04-0.96 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 133.4, 131.6, 129.7, 127.2, 126.4, 69.7, 42.0, 24.7, 17.9, 11.9 ppm.

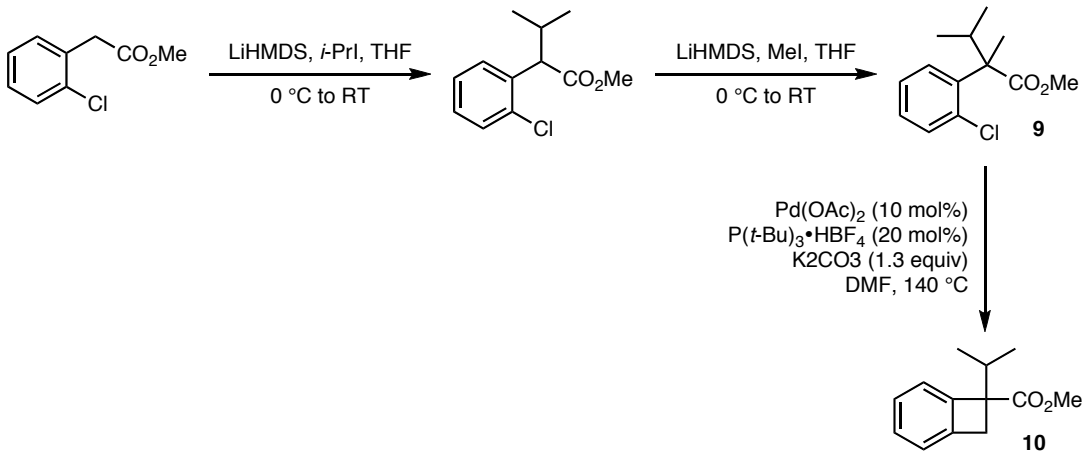
IR (neat) ν 2941, 2864, 1463, 1099, 881, 751 cm^{-1}.

HRMS (CI) calculated for $C_{19}H_{34}ClOSi$ $[M+H]^+$: 341.2067, found 341.2065.

Triisopropyl((1-methyl-1,2-dihydrocyclobutabenzen-1-yl)methoxy)silane (8).[4]

The title compound was prepared from **7** according to the ***general procedure A***. **7** (100 mg, 0.29 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (6.6 mg, 0.029 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (17.0 mg, 0.059 mmol, 0.20 equiv) and K_2CO_3 (53 mg, 0.38 mmol, 1.3 equiv) in DMF (1.1 mL) at 140 °C. The desired cyclobutarene **8** (59 mg, 66%) was obtained as a colorless oil after flash chromatography (1% EtOAc/cyclohexane). R_f 0.39 (10% EtOAc/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13 (m, 2H), 7.09-7.06 (m, 2H), 3.82 (d, *J* = 9.2 Hz, 1H), 3.79 (d, *J* = 9.2 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.84 (d, *J* = 14.0 Hz, 1H), 1,46 (s, 3H), 1.05 (s, 21H) ppm.



Methyl 2-(2-chlorophenyl)-3-methylbutanoate.

To a solution of lithium hexamethyldisilazide (1.81 g, 13.54 mmol) in THF (10 mL) was added dropwise a solution of methyl (2-chlorophenyl)acetate (2 g, 10.83 mmol) in THF (5 mL). The reaction mixture was stirred at 0 °C for 30 minutes then *i*-PrI (3.24 mL, 32.50 mmol) was added. The reaction was stirred at r.t overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layer were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (1% Ethyl acetate/cyclohexane) afforded the title compound as a colorless oil (2.26 g, 9.96 mmol, 92 % yield). R_f = 0.42 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.56 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.39 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.28-7.16 (m, 2H), 3.98 (d, *J* = 10.5 Hz, 1H), 3.67 (s, 3H), 2.41-2.29 (m, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 136.1,134.5, 129.4, 128.8, 128.1, 127.0, 53.9, 51.8, 32.4, 21.3, 19.5 ppm.

IR (neat) ν 2963, 2873, 1734, 1158 cm^{-1}.

HRMS (EI): calculated for $C_{12}H_{15}ClO_2$ [$M^{+\bullet}$]: 226.0761, found: 226.0761.

Methyl 2-(2-chlorophenyl)-2,3-dimethylbutanoate (9).

LiHMDS (1.06M in THF, 16.6 mL, 17.64 mmol) was added dropwise at 0 °C to a solution of the methyl 2-(2-chlorophenyl)-3-methylbutanoate (500 mg, 2.20 mmol) in THF (2 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (2.02 mL, 32.50 mmol) was added dropwise. The reaction was stirred at r.t overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (1% EtOAc/cyclohexane) afforded **9** as a colorless oil (514 mg, 2.13 mmol, 97 % yield). R_f = 0.25 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.19-7.14 (m, 1H), 7.11-7.06 (m, 1H), 3.56 (s, 3H), 2.69 (sept, *J* = 6.9 Hz, 1H), 1.43 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 1H), 0.63 (d, *J* = 6.9 Hz, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 142.1, 134.3, 131.2, 128.7, 128.1, 126.8, 53.6, 52.2, 32.1, 20.6, 19.7, 19.1 ppm.

IR (neat) ν 2947, 1734, 1220, 1101 cm^{-1}.

HRMS (EI): calculated for $C_{13}H_{17}ClO_2$ [$M^{+\bullet}$]: 240.0917, found: 240.0920.

Methyl 1-isopropyl-1,2-dihydrocyclobutabenzene-1-carboxylate (10).

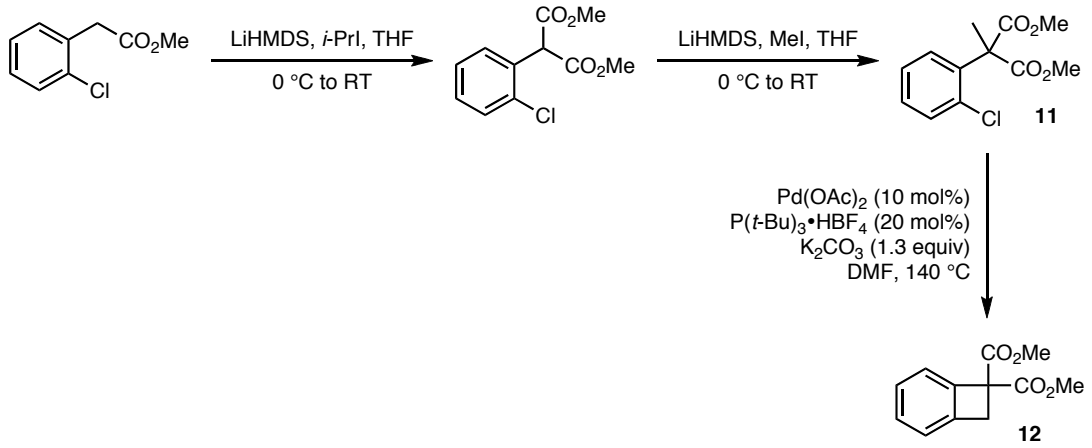
The title compound was prepared from **9** according to the ***general procedure A***. **9** (200 mg, 0.83 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (18.6 mg, 0.083 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (48.0 mg, 0.166 mmol, 0.20 equiv) and K_2CO_3 (150 mg, 1.08 mmol, 1.3 equiv) in DMF (3.3 mL) at 140 °C. The desired cyclobutarene **10** (119 mg, 70%) was obtained as a colorless oil after flash chromatography (5% EtOAc/cyclohexane). R_f 0.25 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.20 (m, 3H), 7.09-7.06 (m, 1H), 3.70 (s, 3H), 3.55 (d, *J* = 14.4 Hz, 1H), 3.16 (d, *J* = 14.4 Hz, 1H), 2.32 (qq, *J* = 7.2, 6.8 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 146.4, 142.9, 128.0, 127.0, 122.8, 122.7, 61.7, 51.8, 37.8, 33.8, 18.4, 18.3 ppm.

IR (neat) ν 2962, 1726, 1457, 1432, 1247 cm^{-1}.

HRMS (EI) calculated for $C_{13}H_{17}ClO_2$ [$M^{+\bullet}$]: 205.1229, found: 205.1227.



Dimethyl 2-(2-chlorophenyl)malonate.

NaHMDS (2M in THF, 16.25 mL, 32.50 mmol) was added dropwise at 0 °C to a stirred solution of methyl (2-chlorophenyl)acetate (2.0 g, 10.83 mmol) in freshly distilled THF (5 mL). The mixture was stirred at 0 °C for 15 min and dimethylcarbonate (2.74 mL, 32.50 mmol) was added dropwise. After stirring at room temperature overnight, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography (10% ethyl acetate/cylohexane) to afford the title product as a yellow oil (2.26 g, 9.31 mmol, 86%). R_f 0.47 (20% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.43 (m, 1H), 7.39-7.36 (m, 1H), 7.29-7.23 (m, 2H), 5.23 (s, 1H), 3.75 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 134.2, 130.2, 129.5, 127.1, 54.0, 52.9 ppm.

IR (neat) ν 3026, 2954, 1735, 1434, 1221, 1149 cm^{-1}.

HRMS (EI): calculated for $C_{11}H_{11}ClO_4$ [$M^{+\bullet}$]: 242.0346, found: 242.0344.

Dimethyl 2-(2-chlorophenyl)-2-methylmalonate (11).

A solution of dimethyl 2-(2-chlorophenyl)malonate the starting material (1.00 g, 4.12 mmol) in anhydrous DMF (5 mL) was added dropwise at 0 °C to a solution of sodium hydride (60% in oil, 6.18 mmol) in anhydrous DMF (10 mL). The mixture was stirred for 20 min at room temperature and iodomethane (770 μL, 12.36 mmol) was added dropwise. After stirring at room temperature vernight, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and the aqueous layer was extracted twice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography (10% ethyl acetate/cyclohexane) to afford **11** as a yellow oil (841 mg, 3.25 mmol, 79%). R_f 0.27 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 1H), 7.27-7.22 (m, 2H), 7.14-7.12 (m, 1H), 3.80 (s, 6H), 1.92 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 137.5, 133.7, 131.1,128.8, 128.1, 126.9, 59.8, 53.1, 21.9 ppm.

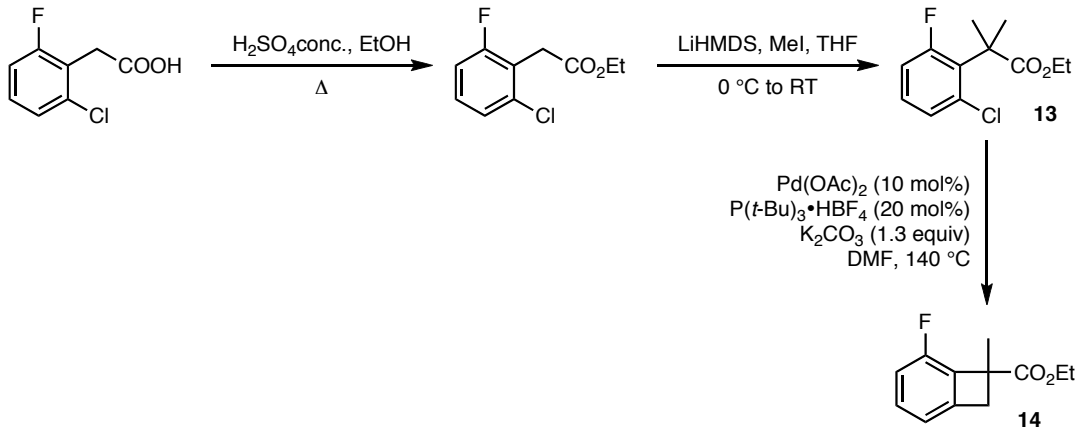
IR (neat) ν 3001, 2951, 1728, 1431, 1240, 1211, 1108, 1037 cm^{-1}.

HRMS (CI): calculated for $C_{12}H_{24}ClO_4$ [M+H]$^+$: 257.0581, found: 257.0580.

Dimethyl cyclobutabenzene-1,1-(*2H*)-dicarboxylate(12).[4]

The title compound was prepared from **11** according to the ***general procedure A***. **11** (100 mg, 0.39 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (8.7 mg, 0.039 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (23.0 mg, 0.078 mmol, 0.20 equiv) and K_2CO_3 (70 mg, 0.51 mmol, 1.3 equiv) in DMF (1.6 mL) at 140 °C. The desired cyclobutarene **12** (63 mg, 74%) was obtained as a yellow oil after flash chromatography (2% EtOAc/cyclohexane). R_f 0.24 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.26 (m, 3H), 7.15-7.12 (m, 1H), 3.78 (s, 6H), 3.77 (s, 2H) ppm.



Ethyl 2-(2-chloro-6-fluorophenyl)acetate.

One drop of H_2SO_4 conc. was added to a solution of 2-(2-chloro-6-fluorophenyl)acetic acid (1 g, 5.30 mmol) in EtOH (30 mL). The reaction mixture was stirred under reflux overnight. After concentration under vaccum, the residue was diluted in Et_2O then washed with water, a saturated aqueous solution of $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$. Evaporation of the solvent afforded the desired product as a colorless oil in quantitative yield (1.15 mg, 5.30 mmol, 100%). R_f 0.28 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.24 (m, 2H), 7.08-7.02 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 1.8 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 161.4 (d, *J* = 247.1), 135.7, 128.9 (d, *J* = 9.4 Hz), 125.0 (d, *J* = 3.3 Hz), 121.1 (d, *J* = 18.5 Hz), 113.8 (d, *J* = 22.5 Hz), 61.1, 31.9 (d, *J* = 3.3 Hz), 14.0 ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ -113.0 ppm.

IR (neat) ν 2983, 1735, 1579, 1452, 1175, 952, 778 cm^{-1}.

HRMS (CI): calculated for $C_{10}H_{10}ClFO_2$ $[M+H]^+$: 217.0432, found: 217.0432.

Ethyl 2-(2-chloro-5-fluorophenyl)-2-methylpropanoate (13).

LiHMDS (1.06M in THF, 6.5 mL, 6.86 mmol) was added dropwise at 0 °C to a solution of the ethyl 2-(2-chloro-6-fluorophenyl)acetate (500 mg, 2.29 mmol) in THF (2 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (427 μL, 6.86 mmol) was added dropwise. The reaction was stirred at room temperature for 3 hours. After hydrolysis with a

saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (2% Ethyl acetate/cyclohexane) afforded **13** as a colorless oil (532 mg, 2.17 mmol, 95 % yield). R_f 0.23 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.16-7.11 (m, 2H), 7.00-7.92 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.70 (d, *J* = 3.9 Hz, 6H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 161.8 (d, *J* = 248.1 Hz), 134.9 (d, *J* = 7.0 Hz), 129.8 (d, *J* = 12.5 Hz), 128.0 (d, *J* = 10.9 Hz), 126.7 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 26.6 Hz), 61.1, 47.4 (d, *J* = 2.7 Hz), 26.5 (d, *J* = 8.0 Hz), 13.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -107.7 ppm.

IR (neat) ν 2983, 1731, 1445, 1236, 1143, 881 cm^{-1}.

HRMS (CI): calculated for $C_{11}H_{13}ClO_2$ $[M+H]^+$: 245.0745, found: 245.0742.

Methyl 6-fluoro-1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (14).[4]

The title compound was prepared from **13** according to the ***general procedure A***. **13** (100 mg, 0.47 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (10.5 mg, 0.047 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (27.2 mg, 0.094 mmol, 0.20 equiv) and K_2CO_3 (84 mg, 0.61 mmol, 1.3 equiv) in DMF (2 mL) at 140 °C. The desired cyclobutarene **14** (69 mg, 83%) was obtained as a colorless oil after flash chromatography (5% EtOAc/cyclohexane). R_f 0.23 (5% Ethyl acetate/cyclohexane).

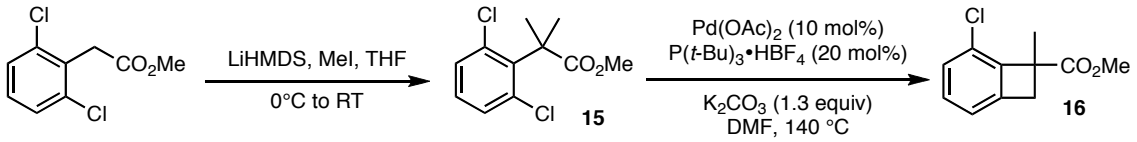
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.18 (m, 1H), 6.92-6.84 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.65 (d, *J* = 14.1 Hz, 1H), 3.05 (d, *J* = 14.1 Hz, 1H), 1.74 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9 (d, *J* = 1.5 Hz), 155.3 (d, *J* = 256.4 Hz), 144.8 (d, *J* = 8.7 Hz), 131.9 (d, *J* = 14.3 Hz), 130.0 (d, *J* = 5.8 Hz), 119.4 (d, *J* = 4.3 Hz), 114.2 (d, *J* = 19.7 Hz), 61.0, 51.2, 42.5, 22.3, 14.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -122.0 ppm;

IR (neat) ν 2979, 2933, 1727, 1601, 1473, 1274, 1241, 1145, 752 cm^{-1}.

HRMS (EI) calculated for $C_{12}H_{13}FO_2$ $[M^{+\bullet}]$: 208.0900, found: 208.0902.



Methyl 2-(2,6-dichlorophenyl)-2-methylpropanoate (15).

LiHMDS (1.06M in THF, 29.84 mL, 27.39 mmol) was added dropwise at 0°C to a solution of the methyl (2,6-dichlorophenyl)acetate (2 g, 9.13 mmol) in THF (5 mL). The reaction mixture was stirred at 0 °C for 30 minutes then MeI (1.70 mL, 27.39 mmol) was added dropwise. The reaction was stirred at room temperature overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (2% , Ethyl acetate/cyclohexane) afforded **15** as a yellow oil (1.85 g, 7.48 mmol, 82 % yield). R_f 0.33 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.27 (d, *J* = 8 Hz, 2H), 7.06 (t, *J* = 8 Hz, 1H), 3.69 (s, 3H), 1.79 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 139.0, 135.2, 130.5, 127.8, 52.5, 50.0, 27.0 ppm.

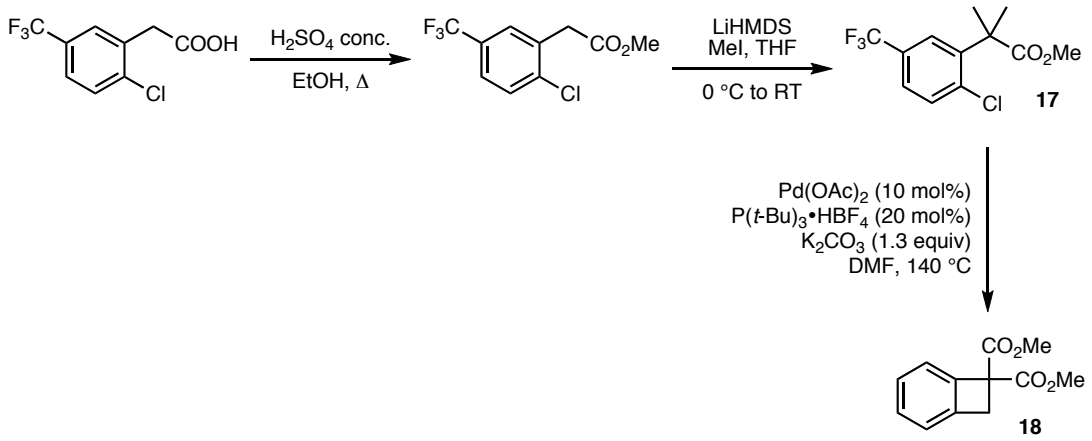
IR (neat) ν 2984, 2947, 1734, 1425, 1202, 1144, 1121, 779, 749 cm^{-1}.

HRMS (CI): calculated for $C_{11}H_{13}Cl_2O_2$ $[M+H]^+$: 247.0292, found: 247.0288.

Methyl 6-chloro-1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (16).[4]

The title compound was prepared from **15** according to the ***general procedure A***. **15** (100 mg, 0.40 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (9.0 mg, 0.040 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (23.5 mg, 0.081 mmol, 0.20 equiv) and K_2CO_3 (72 mg, 0.52 mmol, 1.3 equiv) in DMA (1.6 mL) at 140 °C. The desired cyclobutarene **16** (61 mg, 72%) was obtained as a colorless oil after flash chromatography (2% Ethyl acetate/cyclohexane). R_f 0.33 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.14 (m, 3H), 7.02-7.00 (m, 1H), 3.72 (s, 3H), 3.62 (d, *J* =18.8 Hz, 1H), 3.04 (d, *J* = 18.8 Hz, 1H), 1.74 (s, 3H) ppm.



Methyl 2-(2-chloro-5-trifluoromethylphenyl)acetate.

Concentrated sulfuric acid 98% (1 drop) was added to a solution of 2-(2-chloro-5-trifluoromethylphenyl)acetic acid (500 mg, 2.09 mmol) in MeOH (50 mL). The reaction mixture was stirred under reflux overnight. After concentration under vaccum, the residue was diluted in Et_2O then washed with water, a saturated aqueous solution of $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$. Evaporation of the solvent afforded the desired product as a colorless oil in near quantitative yield (523 mg, 2.07 mmol, 99%). R_f 0.26 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.49 (m, 3H), 3.82 (s, 2H), 3.72 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 138.4 (q, J = 1.4 Hz), 133.3, 130.0, 129.3 (q, J = 32.7 Hz), 128.3 (q, J = 3.8 Hz), 125.5 (q, J = 3.7 Hz), 123.5 (q, J = 270.6 Hz), 52.2, 38.7 ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ -63.0 ppm;

IR (neat) ν 2956, 1739, 1326, 1120, 1081 cm^{-1}.

HRMS (CI): calculated for $C_{10}H_9ClF_3O_2$ $[M+H]^+$: 253.0243, found: 253.0241.

Methyl 2-(2-chloro-5-trifluoromethylphenyl)-2-methylpropanoate (17).

LiHMDS (1.06M in THF, 3.36 mL, 3.56 mmol) was added dropwise at 0 °C to a solution of methyl 2-(2-chloro-5-trifluoromethylphenyl)acetate (300 mg, 1.19 mmol) in THF (1 mL). The reaction mixture was stirred at 0 °C for 15 minutes then MeI (222 μL, 3.56 mmol) was added dropwise. The reaction was stirred at room temperature for 1 hour. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the

solvent and purification of the residue by flash chromatography (2% Ethyl acetate/cyclohexane) afforded **17** as a yellow oil (298 mg, 1.06 mmol, 89% yield). R_f = 0.20 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 8.09 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.4, 2.1 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 3.65 (s, 3H), 1.64 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 145.0, 135.0, 130.1 (q, *J* = 32.7 Hz), 127.8, 125.1 (q, *J* = 3.7 Hz), 124.7 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 373.0 Hz), 52.7, 48.3, 26.3 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8 ppm.

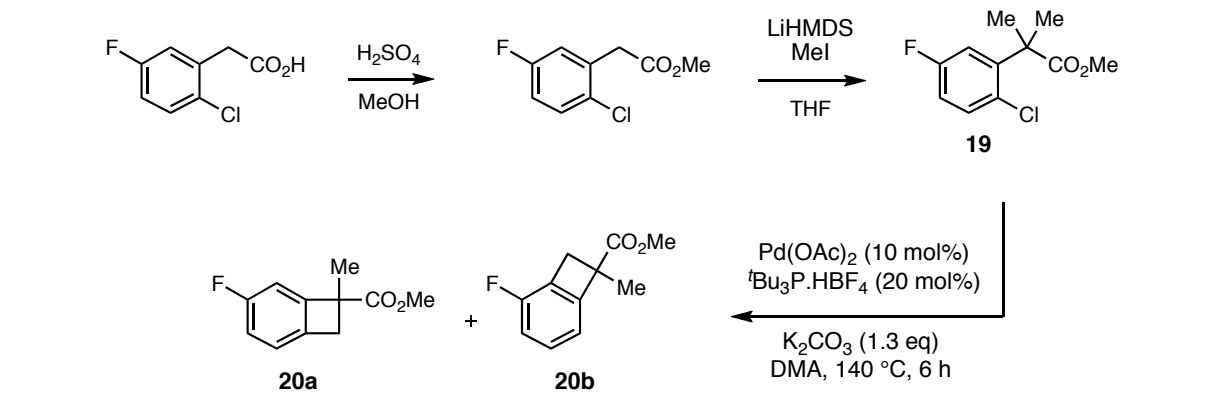
IR (neat) ν 2950, 1710, 1327, 1116, 1078, 827 cm^{-1}.

HRMS (ESI) calculated for $C_{12}H_{13}ClF_3O_2$ $[M+H]^+$: 281.0556, found: 247.0560.

Methyl 1-methyl-5-(trifluoromethyl)-1,2-dihydrocyclobutabenzene-1-carboxylate (18).[4]

The title compound was prepared from **17** according to the ***general procedure A***. **17** (100 mg, 0.36 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (8.0 mg, 0.036 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (20.6 mg, 0.071 mmol, 0.20 equiv) and K_2CO_3 (64 mg, 0.46 mmol, 1.3 equiv) in DMF (1.4 mL) at 140 °C. The desired cyclobutarene **18** (76 mg, 87%) was obtained as a colorless oil after flash chromatography (2% EtOAc/cyclohexane). R_f 0.20 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz,1H), 7.42 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 3.76 (d, *J* = 14.8 Hz, 1H), 3.72 (s, 3H), 3.10 (d, *J* = 14.8 Hz, 1H), 1.71 (s, 3H) ppm.



Methyl-2-(2-chloro-5-fluorophenyl)acetate.

Concentrated sulfuric acid 98% (1 drop) was added to a solution of (2-Chloro-5-fluorophenyl) acetic acid (1 g, 5.3 mmol, 1 equiv) in MeOH. The reaction mixture was stirred under reflux overnight. After concentration under vacuum, the residue was diluted with ethyl acetate, washed with $NaHCO_3$, dried over $MgSO_4$, and evaporated affording the title compound as a yellow oil (1.056 g, 5.23 mmol, 98%). R_f 0.74 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.02 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.91 (ddd, *J* = 8.6, 8.1, 2.9 Hz, 1H), 3.72 (s, 2H), 3.69 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 161.0 (d, *J* = 246.4 Hz), 134.2 (d, *J* = 8.3 Hz), 130.5 (d, *J* = 8.3 Hz), 129.3 (d, *J* = 3.1 Hz), 118.3 (d, *J* = 23.5 Hz), 115.6 (d, *J* = 22.7 Hz), 52.0, 38.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.73 ppm.

IR (neat) ν 2954, 1737, 1476, 1239, 1152, 1114, 812 cm^{-1}.

GC/MS (m/z) $C_9H_8{}^{35}ClFO_2$ [$M^{+\bullet}$] 202, (m/z) $C_9H_8{}^{37}ClFO_2$ [M+.] 204.

Methyl-2-(2-chloro-5-fluorophenyl)-2-methylpropanoate (19).

LiHMDS 1.06 M in THF (9.3 mL, 9.9 mmol, 4 eq) was added dropwise with a syringe at 0 °C to a solution of methyl-2-(2-chloro-5-fluorophenyl)acetate (500 mg, 2.47 mmol, 1 equiv) and MeI (614 μL, 9.9 mmol, 4 equiv) in THF (13 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The crude was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the title compound **19** as a yellow oil (553 mg, 2.40 mmol, 97%). R_f 0.76 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.14 (dd, *J* = 10.3, 3.0 Hz, 1H), 6.94-6.88 (m, 1H), 3.67 (s, 3H), 1.60 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 161.5 (d, *J* = 245.7 Hz), 144.6 (d, *J* = 7.0 Hz), 131.8 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 3.3 Hz), 114.8 (d, *J* = 22.6 Hz), 114.5 (d, *J* = 24.6 Hz), 52.5, 46.7, 25.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.04 ppm.

IR (neat) ν 2950, 1734, 1465, 1242, 1142, 1104, 812 cm^{-1}.

HRMS (CI) calculated for $C_{11}H_{12}ClFO_2$ $[M+H]^+$: 243.0588, found: 231.0585.

Methyl 5-fluoro-1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (20).

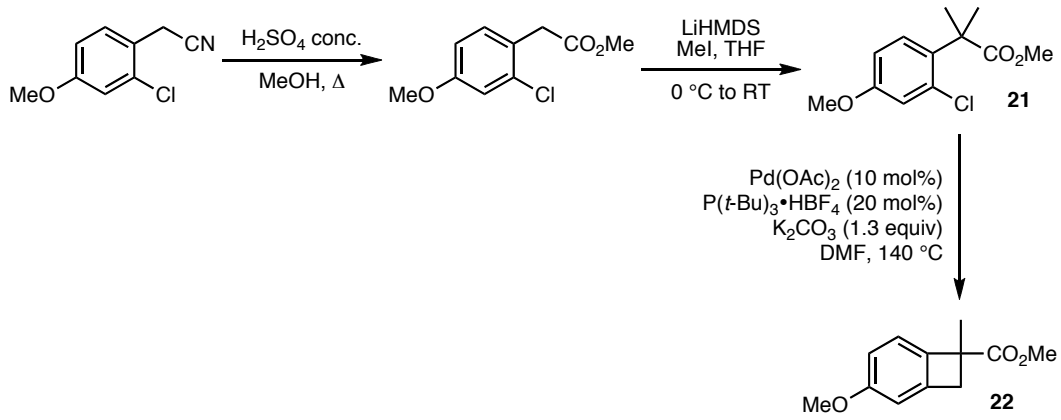
The title compound was prepared from **19** according to the ***general procedure A***. **19** (50 mg, 0.22 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (4.8 mg, 0.022 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (12.5 mg, 0.043 mmol, 0.20 equiv) and K_2CO_3 (39 mg, 0.28 mmol, 1.3 equiv) in DMA (0.86 mL) at 140 °C. After flash chromatography (1% EtOAc/cyclohexane), a 3.9:1 inseparable mixture of **20a** and **20b** was isolated as a pale yellow oil (26 mg, 0.26 mmol, 75 %). R_f 0.36 (5% Ethyl acetate/cyclohexane).

Major regioisomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.94-6.87 (m, 2H), 3.71 (s, 3H), 3.64 (d, *J* = 14.0 Hz, 1H), 3.00 (d, *J* = 14.0 Hz, 1H), 1.67 (s, 3H) ppm.

Minor regioisomer

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.19 (m, 1H), 6.97 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.94-6.87 (m, 1H), 3.74 (d, *J* = 14.2 Hz, 1H), 3.71 (s, 3H), 3.07 (d, *J* = 14.2 Hz, 1H), 1.69 (s, 3H) ppm.



Methyl 2-(2-chloro-4-methoxyphenyl)acetate.

Concentrated sulfuric acid 98% (2 mL) was added dropwise to a stirred solution of 2-chloro-4-methoxyphenylacetonitrile (500 mg, 2.75 mmol) in MeOH (4 mL) at 0 °C. The mixture was then refluxed overnight. After cooling, water (80 mL) was added and the mixture was extracted with DCM (3 x 20 mL). The combined extracts were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (5% ethyl acetate/cyclohexane) afforded the title compound as a yellow oil (413 g, 1.92 mmol, 70 % yield). R_f = 0.25 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 2.7 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 5H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 159.3, 134.9, 131.8, 124.3, 114.8, 113.0, 55.4, 52.0, 38.0 ppm.

IR (neat) ν 3019, 1716, 1610, 1500, 1437, 1214 cm^{-1}.

HRMS (EI): calculated for $C_{10}H_{11}ClO_3$ $[M^{+\bullet}]$: 214.0397, found: 214.0394.

Methyl 2-(2-chloro-4-methoxyphenyl)-2-methylpropanoate (21).

LiHMDS (1.06M in THF, 6.6 mL, 6.98 mmol) was added dropwise with a syringe at 0 °C to a solution of methyl 2-(2-chloro-4-methoxyphenyl)acetate (500 mg, 2.33 mmol) in THF (5 mL). The reaction mixture was then stirred at room temperature for 30 minutes, then MeI (435 μL, 6.98 mmol) was added dropwise. The reaction was stirred at room temperature overnight, then a saturated solution of NH_4Cl was added. The aqueous layer was extracted with Et_2O and the combined organic layer were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (5% ethyl acetate/cyclohexane) afforded **21** as a colorless oil in quanttative yield (564 mg, 2.33 mmol, 100 % yield).

^{1}H NMR (300 MHz $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 2.7 Hz, 1H), 6.80 (dd, *J* 8.7, 2.7 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 1.58 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 158.7, 134.4, 134.0, 127.2, 116.1, 112.4, 55.4, 52.3, 45.9, 26.2 ppm.

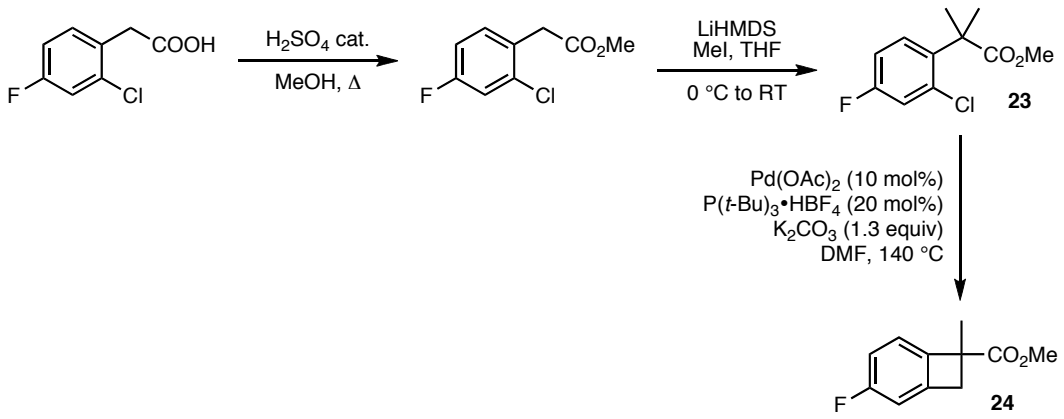
IR (neat) ν 2980, 2946, 1731, 1602, 1488, 1230, 1143, 1034, 836 cm^{-1}.

HRMS (CI) calculated for $C_{12}H_{16}ClO_3$ $[M+H]^+$: 243.0788, found: 243.0786.

Methyl 4-methoxy-1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate (22).[4]

The title compound was prepared from **21** according to the ***general procedure A***. **21** (100 mg, 0.41 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (9.2 mg, 0.04 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (23.9 mg, 0.08 mmol, 0.20 equiv) and K_2CO_3 (74 mg, 0.53 mmol, 1.3 equiv) in DMF (1.6 mL) at 140 °C. The desired cyclobutarene **22** (56 mg, 66%) was obtained as a colorless oil after flash chromatography (5% Ethyl acetate/cyclohexane). R_f 0.26 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.64 (d, *J* = 14.0 Hz), 2.98 (d, *J* = 14.0 Hz), 1.66 (s, 3H) ppm.



Methyl 2-(2-chloro-4-fluorophenyl)acetate.

Concentrated sulfuric acid 98% (1 drop) was added to a solution of 2-(2-chloro-4-fluorophenyl)acetic acid (1 g, 5.30 mmol) in MeOH (30 mL). The reaction mixture was stirred under reflux overnight. After concentration under vaccum, the residue was diluted in Et_2O then washed with water, a saturated aqueous solution of $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$. Evaporation of the solvent afforded the desired product as a colorless oil (932 mg, 4.61 mmol, 87%). R_f 0.29 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 1H), 7.15-7.12 (m, 1H), 6.98-6.93 (m, 1H), 3.74 (s, 2H), 3.71 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 162.1 (d, *J* = 247.9 Hz), 135.5 (d, *J* = 10.3 Hz), 132.7 (d, *J* = 8.6 Hz), 128.7 (d, *J* = 4.0 Hz), 117.3 (d, *J* = 19.2 Hz), 114.5 (d, *J* = 21.1 Hz), 52.6, 38.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.4 ppm.

IR (neat) ν 2954, 1737, 1605, 1493, 1236, 1158, 856 cm^{-1}.

HRMS (EI): calculated for $C_9H_8ClFO_2$ [$M^{+\bullet}$]: 202.0197, found: 202.0197.

Methyl 2-(2-chloro-4-fluorophenyl)-2-methylpropanoate (23).

LiHMDS (1.06M in THF, 7.0 mL, 7.40 mmol) was added at 0 °C to a solution of methyl 2-(2-chloro-4-fluorophenyl)acetate (500 mg, 2.47 mmol) in THF (2 mL). The reaction mixture was then stirred at room temperature for 30 minutes and MeI (460 μL, 7.40 mmol) was added dropwise. The reaction was stirred at room temperature overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (5% ethyl acetate/cyclohexane) afforded **23** as a colorless oil (458 mg, 1.98 mmol, 80% yield). R_f 0.23 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.98 (m, 1H), 3.67 (s, 3H), 1.59 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.1, 161.1 (d, *J* = 247.6 Hz), 138.3 (d, *J* = 3.8 Hz), 134.2 (d, *J* = 9.8 Hz), 127.7 (d, *J* = 8.6 Hz), 117.8 (d, *J* = 24.4 Hz), 113.7 (d, *J* = 20.3 Hz), 52.4, 46.2, 26.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -114.9 ppm.

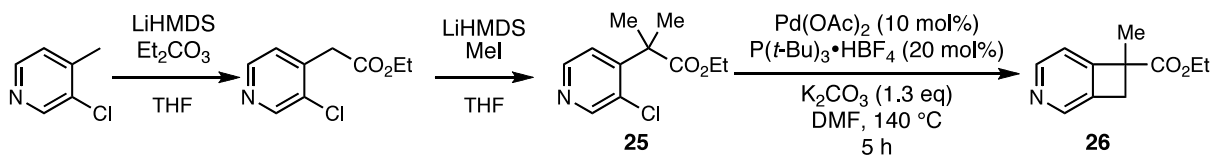
IR (neat) ν 2983, 2949, 1733, 1599, 1488, 1241, 1143, 1103, 846 cm^{-1}.

HRMS (CI): calculated for $C_{11}H_{13}ClFO_2^+[M+H]^+$: 231.0588, 231.0588.

Methyl 4-fluoro-1-methyl-1,2-dihydrocyclobutabenzene-1-carboxylate(24).[4]

The title compound was prepared from **23** according to the ***general procedure A***. **23** (100 mg, 0.43 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (9.6 mg, 0.043 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (25.2 mg, 0.087 mmol, 0.20 equiv) and K_2CO_3 (78.0 mg, 0.56 mmol, 1.3 equiv) in DMF (1.7 mL) at 140 °C. The desired cyclobutarene **24** (63 mg, 76%) was obtained as a colorless oil after flash chromatography (5% EtOAc/cyclohexane). R_f 0.23 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.08 (m, 1H), 6.93-6.88 (m, 1H), 6.85-6.83 (m, 1H), 3.70 (s, 3H), 3.67 (d, *J* = 14.4 Hz, 1H), 3.00 (d, *J* = 14.4 Hz, 1H), 1.66 (s, 3H) ppm.



Ethyl (3-chloro-pyridin-4-yl)acetate.

LiHMDS 1.06 M in THF (29.6 mL, 31.4 mmol, 4 equiv) was added at 0 °C to a solution of 3-chloro-4-methylpyridine (863 μL, 7.84 mmol, 1 equiv) and Et_2CO_3 (1.23 mL, 10.19 mmol, 1.3 equiv) in THF (8.9 mL) under argon atmosphere. The solution was then stirred for 3 h. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether and the combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (15% Ethyl acetate/cyclohexane) affording the title compound as an incolor oil (1.443 g, 7.23 mmol, 92%). Rf 0.34 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.39 (d, *J* = 5 Hz, 1H), 7.20 (d, *J* = 5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 149.4, 147.8, 141.1, 132.5, 125.8, 61.4, 38.3, 14.1 ppm.

IR (neat) υ = 2962, 1732, 1229, 1158, 1096, 1028, 826 cm^{-1}.

GC/MS (m/z) $C_9H_{10}{}^{35}ClNO_2$ [$M^{+\bullet}$] 199, (m/z) $C_9H_{10}{}^{37}ClNO_2$ [$M^{+\bullet}$] 201.

Ethyl 2-(3-chloro-pyridin-4-yl)-2-methylpropionate (25).

LiHMDS 1.06 M in THF (19 mL, 20.3 mmol, 3 equiv) was added dropwise with a syringe at 0 °C to a solution of compound ethyl (3-chloro-pyridin-4-yl)acetate (1.35 g, 6.76 mmol, 1 equiv) in THF (28 mL). The reaction mixture was then stirred at room temperature for 2 h. MeI (1.3 mL, 20.3 mmol, 3 equiv) was added dropwise and the reaction was stirred at room temperature overnight. Monitoring GCMS showed about 80% conversion. Therefore 4 mL of LiHMDS were added and the reaction mixture stirred for two extra hours. Then 300 μL of MeI were added and the solution was stirred for three hours. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. Organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (15% Ethyl acetate/cyclohexane) affording the title compound **25** as a yellow oil (1.377 g, 6.05 mmol, 90%). R_f 0.41 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.45 (d, *J* = 5.2 Hz, 1H), 7.29 (d, *J* = 5.2 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.58 (s, 6H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 150.9, 150.2, 148.3, 131.6, 121.6, 61.4, 46.5, 25.1, 13.9 ppm.

IR (neat) υ 2962, 1732, 1248, 1146, 1126, 1040, 1024 cm^{-1}.

HRMS (CI) calculated for $C_{11}H_{14}ClNO_2$ $[M^+H]^+$: 228.0791, found: 228.0791.

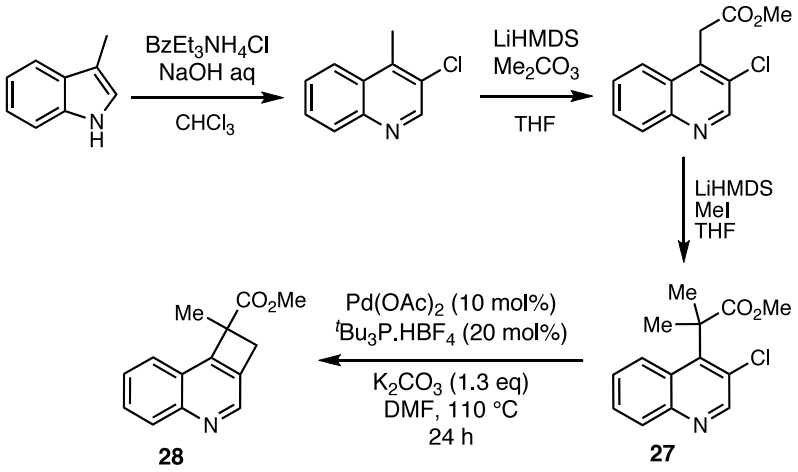
7-methyl-3-aza-bicyclo[4.2.0]octa-1(6), 2,4-triene-7-carboxylic acid ethyl ester (26).

The title compound was prepared from **25** according to the ***general procedure A***. **26** (300 mg, 1.32 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (29.6 mg, 0.132 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (76.6 mg, 0.087 mmol, 0.20 equiv) and K_2CO_3 (237.0 mg, 1.72 mmol, 1.3 equiv) in DMF (5.0 mL) at 140 °C. The desired cyclobutarene **26** (146 mg, 0.76 mmol, 76%) was obtained as a pale yellow oil after flash chromatography (30% Ethyl acetate/cyclohexane). R_f 0.21 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.7 Hz, 1H), 8.31 (s, 1H), 7.09 (d, *J* = 4.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 14.3 Hz, 1H), 3.14 (d, *J* = 14.3 Hz, 1H), 1.67 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 157.5, 148.5, 143.9, 139.0, 116.9, 61.3, 53.6, 41.8, 22.6, 14.2 ppm.

HRMS (EI) calculated for $C_{11}H_{13}NO_2$ $[M^{+\bullet}]$: 191.0946, found: 191.0942.



3-chloro-4-methylquinoline.

NaOH (1.14 mL) in water (2.28 mL) was added to a vigorously stirred solution of 3-methylindole (500 mg, 3.8 mmol, 1 eq) and benzyltriethylammonium chloride (86 mg, 0.38 mmol, 10 mol%) in chloroform (5 mL) under ice-cooling bath. The reaction mixture was

stirred at 0 °C for 3 h and left overnight at room temperature. The aqueous layer was separated and extracted with chloroform. The organic layers were dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a brown oil (450 mg, 2.54 mmol, 67%). R_f 0.61 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 2.75 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 146.3, 140.8, 130.2, 129.1, 128.6, 128.5, 127.5, 123.9, 15.1 ppm.

IR (neat) υ 2920, 1455, 1159, 1118, 1011, 749 cm^{-1}.

GC/MS (m/z) $C_{10}H_8{}^{35}ClN$ [$M^{+\bullet}$] 177, (m/z) $C_{10}H_8{}^{37}ClN$ [$M^{+\bullet}$] 179.

Methyl 2-(3-chloroquinolin-4-yl)acetate.

LiHMDS 1.06 M in THF (3.2 mL, 3.4 mmol, 4 eq) was added at 0 °C to a solution of 3-chloro-4-methylquinoline (150 mg, 0.84 mmol, 1 eq) and Me_2CO_3 (92 μL, 1.09 mmol, 1.3 eq) in THF (1 mL) under argon atmosphere. The solution was then stirred for 3 h. A saturated solution of NH_4Cl was added. The aqueous layer was extracted with ether and the combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a pale yellow solid (143 mg, 0.67 mmol, 79%). Mp: 103.4 °C. R_f 0.52 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 4.28 (s, 2H), 3.69 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 149.9, 146.7, 136.7, 130.5, 129.5, 129.4, 128.2, 128.1, 123.5, 52.7, 34.7 ppm.

IR (neat) υ 2962, 1719, 1333, 1234, 1213, 1184, 957, 764 cm^{-1}.

GC/MS (m/z) $C_{12}H_{10}{}^{35}ClNO_2$ [$M^{+\bullet}$] 235, (m/z) $C_{12}H_{10}{}^{37}ClNO_2$ [$M^{+\bullet}$] 237.

Methyl 2-(3-chloroquinolin-4-yl)-2-methylpropanoate (27).

LiHMDS 1.06 M in THF (1.31 mL, 1.39 mmol, 3 eq) was added dropwise with a syringe at 0 °C to a solution of compound methyl 2-(3-chloroquinolin-4-yl)acetate (100 mg, 0.46 mmol, 1 eq) in THF (2.3 mL). The reaction mixture was then stirred at room temperature for 30 min. MeI (100 μL, 1.39 mmol, 3 eq) was added dropwise and the reaction was stirred at room

temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with EtOAc. Organic layers were dried over Na_2SO_4. After filtration and evaporation, the crude was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound **27** as a yellow oil (99 mg, 0.41 mmol, 88%). R_f 0.57 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.49 (s, 3H), 1.86 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 152.0, 147.0, 144.5, 130.8, 128.4, 127.9, 127.6, 126.9, 123.6, 52.5, 49.1, 27.7 ppm.

IR (neat) υ 2948, 1732, 1255, 1148, 1130, 760 cm^{-1}.

HRMS (EI) calculated for $C_{14}H_{14}ClNO_2$ [$M^{+\bullet}$]: 263.0713, found:263.0712.

Methyl 1,2-dihydro-1-methylcyclobuta[*c*]quinoline-1-carboxylate (28).

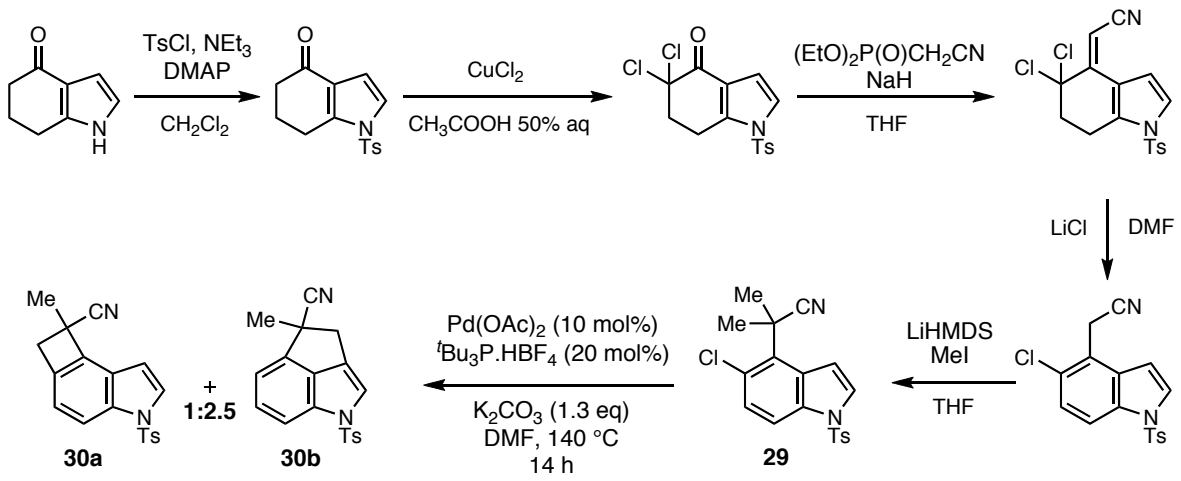
The title compound was prepared from **27** according to the ***general procedure A***. **27** (50 mg, 0.19 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (4.3 mg, 0.019 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (11.0 mg, 0.038 mmol, 0.20 equiv) and K_2CO_3 (34.0 mg, 0.25 mmol, 1.3 equiv) in DMF (760 μL) at 140 °C. The desired cyclobutarene **28** (27 mg, 0.12 mmol, 63%) was obtained as a yellow oil after flash chromatography (20% Ethyl acetate/cyclohexane). R_f 0.27 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.56 (t, *J* = 7.1 Hz, 1H), 3.91 (d, *J* = 13.7 Hz, 1H), 3.73 (s, 3H), 3.25 (d, *J* = 13.7 Hz, 1H), 1.86 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 153.0, 146.4, 144.5, 134.7, 129.8, 128.1, 126.5, 122.6, 121.8, 52.7, 51.6, 40.8, 21.4 ppm.

IR (neat) υ 2931, 1728, 1282, 1147, 766, 756 cm^{-1}.

HRMS (EI) calculated for $C_{14}H_{13}NO_2$ [$M^{+\bullet}$]: 227.0946, found: 227.0947.



6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-one.

To a solution of 1,5,6,7-Tetrahydro-4*H*-indol-4-one (500 mg, 3.7 mmol, 1 equiv) in dichloromethane (9.3 mL) was added Et_3N (1.5 mL, 11.1 mmol, 3 equiv) dropwise at room temperature. To the resulting suspension was added TsCl (705 mg, 3.7 mmol, 1 equiv) and DMAP (45 mg, 0.37 mmol, 10 mol%). The reaction mixture was stirred until TsCl was consumed. The mixture was poured into water and extracted twice with dichloromethane. Combined organic layers were dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the title compound **30d** as a pale pink solid (884 mg, 3.05 mmol, 83%). Mp: 135.8 °C. R_f 0.39 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 3.5 Hz, 1H), 6.62 (d, *J* = 3.5 Hz, 1H), 2.97 (t, *J* = 6.2 Hz, 2H), 2.44-2.40 (m, 5H), 2.14-2.04 (m, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 146.0, 143.8, 135.4, 130.5, 127.3, 124.9, 122.4, 108.3, 37.5, 23.4, 21.8 ppm.

IR (neat) υ 2964, 1660, 1373, 1119, 701, 673, 656 cm^{-1}.

GC/MS m/z $C_{15}H_{15}NO_3S$ [$M^{+\cdot}$] 289.

5,5-dichloro-6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-one.

Compound 6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-one (2 g, 6.9 mmol, 1 equiv) was dissolved in 50% acetic acid solution (10 mL). Then $CuCl_2$ (5.6 g, 41.4 mmol, 6 equiv) was added and the mixture stirred under reflux for 4 h. Mainly monochlorinated compound was observed. $CuCl_2$ (1 g, 3.46 mmol, 0.5 equiv) was added and the mixture stirred under reflux overnight. The mixture was poured into water and extracted twice with dichloromethane. Combined organic layers were dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (30% Ethyl acetate/cyclohexane) affording the title compound as a pale pink solid (884 mg, 3.05 mmol, 83%). Mp: 144.1 °C. R_f 0.65 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 3.5 Hz, 1H), 6.67 (d, *J* = 3.5 Hz, 1H), 3.19 (t, *J* = 5.8 Hz, 2H), 2.88 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.1, 146.6, 141.5, 134.9, 130.7, 127.3, 123.9, 120.1, 109.9, 85.7, 43.6, 22.1 ppm.

IR (neat) υ = 3123, 1688, 1378, 1174, 1134, 1108, 715, 678, 659 cm^{-1}.

GC/MS m/z $C_{15}H_{13}Cl_2NO_3S$ [$M^{+\bullet}$] 357.

2-(5,5-dichloro-6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-ylidene)acetonitrile.

A solution prepared from diethylcyanomethylphosphonate (666 µL, 4.10 mmol, 1.47 equiv) and NaH 60% oil (123 mg, 3.069 mmol, 1.1 equiv) was stirred at room temperature for 30 min under argon atmosphere. Compound 5,5-dichloro-6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-one (1 g, 2.79 mmol, 1 equiv) was added to this solution of sodium salt of diethylcyanomethylphosphonate at 0 °C. The resulting mixture was stirred for 3 h at room temperature. GC/MS monitoring did not show a complete conversion and another solution of sodium salt of diethylcyanomethylphosphonate was added. The mixture was washed with water and extracted twice with EtOAc. Organic layers were dried over $MgSO_4$. After filtration and evaporation, the crude was purified by flash chromatography (50% Ethyl acetate/cyclohexane) affording the title compound as an orange solid in quantitative yield (1.065 g, 2.79 mmol, 100%). Mp: 96.8 °C. R_f 0.73 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.33-7,36 (m, 3H), 7.26 (d, *J* = 3.7 Hz, 1H), 6.06 (s, 1H), 3.13 (t, *J* = 5.9 Hz, 2H), 2.70 (t, *J* = 5.9 Hz, 2H), 2.48 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 146.2, 135.2, 132.8, 130.5, 127.1, 123.4, 118.3, 117.5, 109.7, 92.1, 85.6, 43.3, 22.4, 21.8 ppm.

IR (neat) υ 2956, 1171, 1158, 1144, 688, 660 cm^{-1}.

GC/MS m/z $C_{17}H_{14}Cl_2N_2O_2S$ [$M^{+\cdot}$(-HCl)] 344.

2-(5-chloro-1-tosyl-1*H*-indol-4-yl)acetonitrile.

A mixture of compound 2-(5,5-dichloro-6,7-dihydro-1-tosyl-1*H*-indol-4(5*H*)-ylidene)acetonitrile (1.065 g, 2.79 mmol, 1 equiv) and LiCl (201 mg, 4.75 mmol, 1.7 equiv) was stirred in DMF (100 mL) under argon atmosphere at refluxing temperature for 3 h. The mixture was poured into water and extracted with dichloromethane. The dichloromethane solution was dried over $MgSO_4$ and concentrated. The crude was purified by flash chromatography (25% Ethyl acetate/cyclohexane) affording the title compound as a pale brown solid (815 mg, 2.36 mmol, 85%). Mp: 200.1 °C. R_f 0.67 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 3.7 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 3.4 Hz, 1H), 3.99 (s, 2H), 2.36 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 134.8, 133.4, 131.2, 130.3, 129.0, 128.4, 126.9, 125.8, 120.2, 116.5, 114.9, 106.3, 21.7, 18.8 ppm.

IR (neat) υ = 3137, 1372, 1167, 1144, 1123, 708, 667 cm^{-1}.

GC/MS (m/z) $C_{17}H_{13}{}^{35}ClN_2O_2S$ [$M^{+\cdot}$] 344, (m/z) $C_{17}H_{13}{}^{37}ClN_2O_2S$ [$M^{+\cdot}$] 346.

2-(5-chloro-1-tosyl-1*H*-indol-4-yl)-2-methylpropanenitrile (29).

LiHMDS 1.06 M in THF (2.19 mL, 2.32 mmol, 4 equiv) was added dropwise with a syringe at 0 °C to a solution of compound 2-(5-chloro-1-tosyl-1*H*-indol-4-yl)acetonitrile (200 mg, 0.58 mmol, 1 equiv) in THF (3 mL). The reaction mixture was then stirred at room temperature for 30 min. MeI (144 μL, 2.32 mmol, 4 equiv) was added dropwise and the reaction was stirred at room temperature overnight. After hydrolysis with a saturated aqueous solution of NH_4Cl, the aqueous layer was extracted twice with EtOAc. Organic layers were dried over Na_2SO_4. After filtration and evaporation, the crude was purified by flash chromatography (15% Ethyl acetate/cyclohexane) affording the title compound **29** as a pale brown solid (182 mg, 0.49 mmol, 84%). R_f 0.65 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 3.9 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H), 2.03 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 134.6, 134.2, 130.1, 129.5, 129.2, 128.3, 128.3, 127.1, 126.9, 124.7, 114.2, 108.2, 37.8, 28.9, 21.6 ppm.

IR (neat) υ = 3143, 2230, 1379, 1159, 1137 cm^{-1}.

HRMS (EI) calculated for $C_{19}H_{17}ClN_2O_2S$ [$M^{+\bullet}$]: 372.0699, found: 372.0701.

6,7-dihydro-7-methyl-3-tosyl-3*H*-cyclobuta[*e*]indole-7-carbonitrile (30).

The title compound was prepared from **29** according to the ***general procedure A***. **29** (100 mg, 0.27 mmol, 1 equiv) was reacted with $Pd(OAc)_2$ (6.1 mg, 0.027 mmol, 0.10 equiv), P(*t*-Bu)$_3$•HBF_4 (15.7 mg, 0.054 mmol, 0.20 equiv) and K_2CO_3 (48.5 mg, 0.25 mmol, 1.3 equiv) in DMF (1.1 mL) at 140 °C. Mixture was stirred under argon atmosphere at 140 °C overnight. After preparative thin layer chromatography (10% Ethyl acetate/cyclohexane), a mixture of **30a** and **30b** (ratio: **1:2.5**) was isolated as a colorless oil (60 mg, 0.18 mmol, 69%). After an other preparative thin layer chromatography (15% Ethyl acetate/cylohexane) with several elutions, the major product **30b** was isolated as a pure fraction, and the minor product as an inseparable mixture of **30a** and **30b** (ratio: **3.4:1**). R_f 0.54 (50% Ethyl acetate/cyclohexane).

Major product 30b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.04 (s, 1H), 3.88 (dd, *J* = 16.9, 1.5 Hz, 1H), 3.43 (dd, *J* = 16.9, 1.5 Hz, 1H), 2.39 (s, 3H), 1.82 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 143.2, 136.5, 135.7, 130.3, 130.1, 129.1, 126.9, 123.4, 122.9, 117.9, 117.0, 113.8, 48.6, 44.3, 27.4, 21.7 ppm.

Minor product 30a

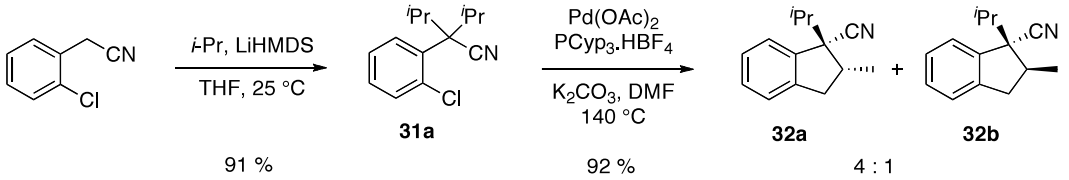
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 3.7 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 3.81 (d, *J* = 13.5 Hz, 1H), 3.29 (d, *J* = 13.6 Hz, 1H), 2.36 (s, 3H), 1.82 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 135.7, 135.4, 135.1, 130.1, 129.0, 128.4, 127.0, 124.5, 122.3, 119.4, 115.4, 104.6, 44.6, 37.7, 23.6, 21.7 ppm.

IR (neat) υ 2926, 1360, 1173, 1158, 1073, 764, 670 cm^{-1}.

HRMS (EI) calculated for $C_{19}H_{16}N_2O_2S$ [$M^{+\bullet}$]: 336.0932, found: 336.0931.

Synthesis of indanes by alkane arylation (Table 4).



2-(2-Chloro-phenyl)-2-isopropyl-3-methyl-butyronitrile (31a).

LiHMDS 1.06 M in THF (30 mL, 30.8 mmol, 2.4 equiv) was added dropwise with a syringe at 0 °C to a solution of 2-bromophenylacetonitrile (1.6 mL, 12.9 mmol, 1 equiv) and isopropyliodide (4 mL, 40 mmol, 3 equiv) in Et_2O (3 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. Combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a colorless oil (2.6 g, 11 mmol, 91%). R_f 0.83 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.38 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.25 (m, 2H), 2.99 (s, *2*H), 1.21 (d, *J* = 6.7 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 134.8, 132.3, 132.2, 128.7, 126.5, 120.2, 60.7, 32.8, 20.1 ppm.

HRMS (EI) calculated for $C_{14}H_{18}ClN$ [$M^{+\bullet}$]: 235.1128, found: 235.1127.

IR (neat) ν 2971, 1038, 752, 718 cm^{-1}.

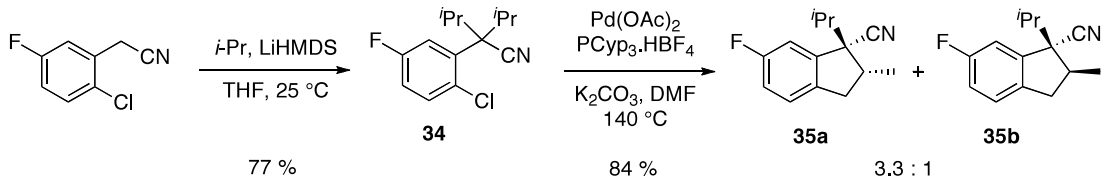
1-Isopropyl-2-methyl-indan-1-carbonitrile (32a).[5]

Following ***general procedure B*** starting from K_2CO_3 (61.8 mg, 0.44 mmol, 2 equiv), $Pd(OAc)_2$ (2.9 mg, 0.012 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (15.6 mg, 0.048 mmol, 0.20 equiv), compound **31a** (51.7 mg, 0,22 mmol, 1 equiv) and DMF (1.1 mL). Mixture was stirred for 2.5 h. The crude was purified by preparative thin layer chromatography (10% Ethyl

[5] Hitce, J.; Retailleau, P.; Baudoin, O. *Chem. Eur. J.* **2007**, *13*, 792-799.

acetate/cyclohexane) affording the title compound as a yellow oil (40.4 mg, 0.20 mmol, 92%). R_f 0.72 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.25 (m, 3H), 3.20 (dd, *J* = 21.4, 9.5 Hz, 1H), 2.69 (m, 1H), 2.59 (dd, *J* = 21.2, 4.3 Hz, 1H), 2.06 (sept, *J* = 8.9 Hz, 1H), 1.26 (d, *J* = 9.3 Hz, 1H), 1.07 (d, *J* = 9 Hz, 3H), 1.05 (d, *J* = 9 Hz, 3H) ppm.



2-(2-Chloro-5-fluoro-phenyl)-2-isopropyl-3-methyl-butyronitrile (34).

LiHMDS 1.06 M in THF (10 mL, 10.6 mmol, 6 equiv) was added dropwise with a syringe at 0 °C to a solution of 2-bromo-4-fluorophenylacetonitrile (290 mg, 1.71 mmol, 1 equiv) and isopropyliodide (1.5 mL, 15 mmol, 9 equiv) in THF (2 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. Combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a yellow solid (331 mg, 1.3 mmol, 76%). Mp: 55.2 °C. R_f 0.81 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34 (dd, *J* = 8.7, 5.5 Hz, 1H), 6.96 (m, 1H), 2.94 (s, 2H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245.8 Hz), 133.7 (d, *J* = 8.0 Hz), 128.3 (d, *J* = 15.4 Hz), 119.9, 119.8, 116.9 (d, *J* = 22 Hz), 61.1, 33.0, 20.3 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.4 ppm.

HRMS (EI) calculated for $C_{14}H_{17}ClFN$ [$M^{+\bullet}$]: 253.1034, found 253.1035.

IR (neat) ν 2986, 1463, 1231, 822 cm^{-1}.

6-Fluoro-1-isopropyl-2-methyl-indan-1-carbonitrile (35a).

Following ***general procedure B*** starting from K_2CO_3 (67.9 mg, 0.49 mmol, 2 equiv), $Pd(OAc)_2$ (2.6 mg, 0.011 mmol, 0,05 equiv), $Cyp_3P{\bullet}HBF_4$ (17.9 mg, 0.055 mmol, 0.20 equiv), compound **34** (51.7 mg, 0.20 mmol, 1 equiv) and DMF (1.1 mL). Mixture was stirred for 12 h. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (37.2 mg, 0.17 mmol, 84%). R_f 0.70 (10% Ethyl acetate/cyclohexane).

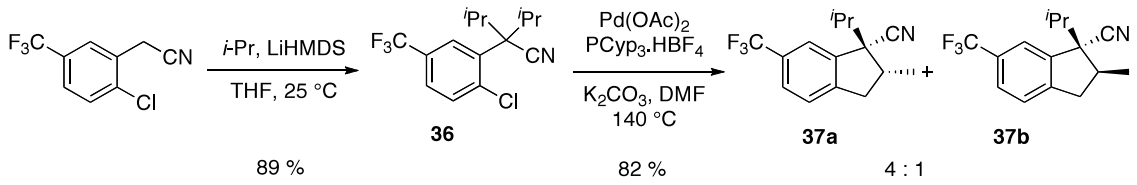
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.3, 4.9 Hz, 1H), 7.05 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.96 (td, *J* = 8.7, 2.4 Hz, 1H), 3.15 (dd, *J* = 15.9, 7.4 Hz, 1H), 2.69 (m, 1H), 2.55 (dd, *J* = 15.9, 3.4 Hz, 1H), 2.05 (sept, *J* = 7.9 Hz, 1H), 1.25 (d, *J* = 7 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 243.0 Hz), 142.9 (d, *J* = 7.8 Hz), 126.4 (d, *J* = 8.6 Hz), 120.6, 115.8 (d, *J* = 22.1 Hz), 112.5 (d, *J* = 23.0 Hz), 58.6, 39.3, 38.5, 34.9, 19.8, 18.7, 18.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.0 ppm.

HRMS (EI) calculated for $C_{14}H_{19}FN$ [$M^{+\bullet}$]: 217.1267, found: 217.1265.

IR (neat) ν 2968, 1488, 1260, 812 cm^{-1}.



2-(2-Chloro-5-trifluoromethyl-phenyl)-2-isopropyl-3-methyl-butyronitrile (36).

LiHMDS 1.06 M in THF (10 mL, 10.6 mmol, 4 equiv) was added dropwise with a syringe at 0°C to a solution of compound 2-chloro-5-trifluoromethylphenylacetonitrile (492 mg, 2.24 mmol, 1 equiv) and isopropyliodide (1.5 mL, 15 mmol, 6 equiv) in THF (2 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a white solid (610 mg, 2.01 mmol, 89%). Mp: 52.8 °C. R_f 0.80 (5% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.51 (m, 2H), 2.94 (s, 2H), 1.20 (d, *J* = 6.8 Hz, 6H), 0.85 (d, *J* = 6.8 Hz 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 129.2 (q, *J* = 32.9 Hz), 129.0, 128.4, 128.3, 125.6 (q, *J* = 3.2 Hz), 123.5 (q, *J* = 270.6 Hz), 119.7, 61.1, 33.2, 20.1 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.1 ppm.

HRMS (EI) calculated for $C_{15}H_{17}F_3N$ [$M^{+\bullet}$]: 303.1002, found: 303.1004.

IR (neat) ν 2977, 1162, 1124, 1087 cm^{-1}.

1-Isopropyl-2-methyl-6-trifluoromethyl-indan-1-carbonitrile (37a).

Following ***general procedure B*** starting from K_2CO_3 (97.7 mg, 0.70 mmol, 2 equiv), $Pd(OAc)_2$ (3.9 mg, 0.017 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (24.3 mg, 0.074 mmol, 0.20 equiv), compound **36** (100 mg, 0.33 mmol, 1 equiv) and DMF (1.65 mL). Mixture was stirred for 6 h. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (72.5 mg, 0.27 mmol, 82%). R_f 0.70 (10% Ethyl acetate/cyclohexane).

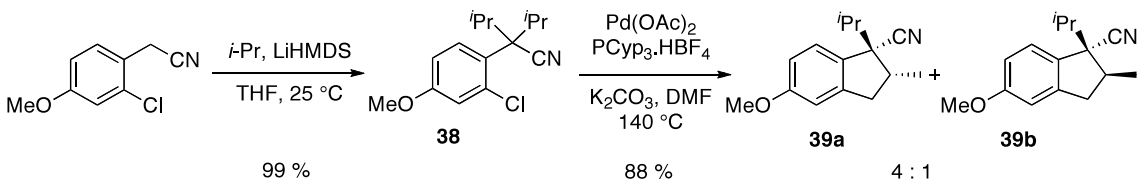
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 3.25 (dd, *J* = 16.6, 7.4 Hz, 1H), 2.73 (m, 1H), 2.65 (dd, *J* = 16.7, 2.8 Hz, 1H), 2.07 (sept, *J* = 6.8 Hz, 1H), 1.26 (d, *J* = 7 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.96, 141.96, 129.7 (q, *J* = 32.1 Hz), 125.9 (q, *J* = 3.1 Hz), 125.8, 124.2 (q, *J* = 270.6 Hz), 122.4 (q, *J* = 3.9 Hz), 120.3, 58.5, 39.1, 38.9, 34.9, 19.8, 18.7, 18.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5 ppm.

HRMS (EI) calculated $C_{15}H_{16}F_3N$ [$M^{+\bullet}$]: 267.1235, found: 267.1235.

IR (neat) ν 2921, 1320, 1162, 1120 cm^{-1}.



2-(2-Chloro-4-methoxy-phenyl)-2-isopropyl-3-methyl-butyronitrile (38).

LiHMDS 1.06 M in THF (6 mL, 6.36 mmol, 6 equiv) was added dropwise with a syringe at 0 °C to a solution of 2-chloro-5-methoxyphenylacetonitrile (205.1 mg, 1.13 mmol, 1 equiv) and isopropyliodide (0.8 mL, 8 mmol, 7 equiv) in THF (2 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. Combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a colorless oil (297 mg, 0.12 mmol, 99%). R_f 0.82 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.92 (d, *J* = 2.8 Hz, 2H), 6.80 (dd, *J* = 2.8, 8.9 Hz, 1H), 3.79 (s, 3H), 2.91 (s, 2H), 1.17 (d, *J* = 6.7 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.1, 125.7, 120.8, 117.6, 112.2, 59.7, 55.4, 33.1, 20.1 ppm.

HR/MS (EI) calculated for $C_{15}H_{20}ClNO$ [$M^{+\bullet}$]: 263.1233, found: 265.1235.

IR (neat) ν 2970, 1495, 1298, 1234, 1036 cm^{-1}.

1-Isopropyl-5-methoxy-2-methyl-indan-1-carbonitrile (39a).

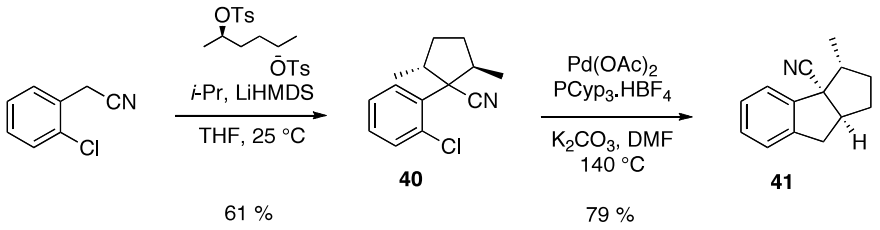
Following ***general procedure B*** starting from K_2CO_3 (110 mg, 0.80 mmol, 2 equiv), $Pd(OAc)_2$ (4.7 mg, 0.021 mmol, 5 mol%), $Cyp_3P{\bullet}HBF_4$ (27.9 mg, 0.085 mmol, 0.20 equiv), compound **38** (104 mg, 0.39 mmol, 1 equiv) and DMF (2 mL). Mixture was stirred for 12 h. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (80.3 mg, 0.35 mmol, 88%). R_f 0.67 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 3.07 (dd, *J* = 16.1, 7.5 Hz, 1H), 1.21 (m, 1H), 2.45 (dd, *J* = 16.1, 3.5 Hz, 1H), 1.94 (sept, *J* = 6.8 Hz, 1H), 1.17 (d, *J* = 7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 143.4, 133.0, 126.1, 121.3, 112.9, 110.3, 57.8, 55.4, 39.3, 39.0, 34.9, 19.9, 18.7, 18.6 ppm.

HRMS (EI) calculated for $C_{15}H_{19}NO$ [$M^{+\bullet}$]: 229.1467, found: 229.1463.

IR (neat) ν 2965, 1490, 1258, 1081 cm^{-1}.



1-(2-Chloro-phenyl)-2,5-dimethyl-cyclopentanecarbonitrile (40).

LiHMDS 1.06 M in THF (3.18 mL, 3 mmol, 6 equiv) was added dropwise with a syringe at 0 °C to a solution 2-bromophenylacetonitrile (72 mg, 0.47 mmol, 1 equiv) in THF (2 mL). The mixture was added to a solution of ditosylate[6] (205 mg, 0.48 mmol, 1 equiv) in THF (2 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. Combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (68 mg, 0.29 mmol, 61%). R_f 0.85 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 1H), 7.27 (m, 2H), 7.21 (m, 1H), 3.36 (m, 1H), 2.76 (m, 1H), 2.32 (m, 1H), 2.08 (m, 1H), 1.78 (m, 1H), 1.39 (m, 1H), 1.32 (d, J = 6.5 Hz, 3H), 0.50 (d, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.7, 131.6, 129.2, 128.8, 126.9, 121.1, 55.1, 41.2, 38.0, 31.0, 30.3, 18.8, 15.7 ppm.

HRMS (EI) calculated for $C_{14}H_{16}ClN$ [$M^{+\bullet}$]: 233.0971, found: 233.0974.

IR (neat) ν 2952, 1065, 780, 754 cm^{-1}.

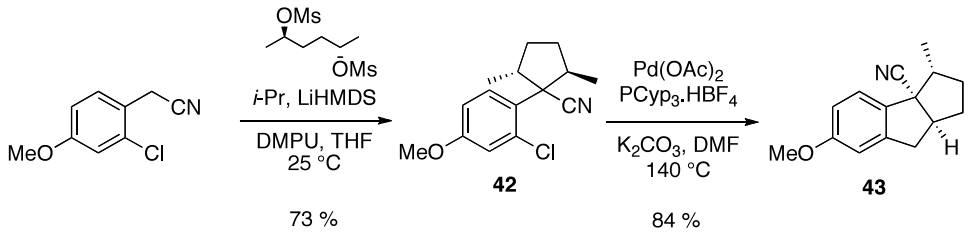
3-Methyl-2,3,8,8a-tetrahydro-1*H*-cyclopenta[a]indene-3a-carbonitrile (41).[5]

Following ***general procedure B*** starting from K_2CO_3 (64.3 mg, 0.46 mmol, 2 equiv), $Pd(OAc)_2$ (2 mg, 0.009 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (13.1 mg, 0.040 mmol, 0.20 equiv), compound **40** (45 mg, 0.19 mmol, 1 equiv) and DMF (1.1 mL). Mixture was stirred over

[6] McKinstry, L.; Livinghouse, T. *Tetrahedron*, **1995**, *51*, 3237.

night. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (30 mg, 0.15 mmol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 1H), 7.25 (m, 2H), 7.19 (m, 1H), 3.36 (m, 2H), 2.75 (m, 1H), 2.21 (m, 2H), 1.84 (m, 1H), 1.57 (m, 1H), 1.44 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 6H) ppm.



1-(2-Chloro-4-methoxy-phenyl)-2,5-dimethyl-cyclopentanecarbonitrile (42).

LiHMDS 1.06 M in THF (5 mL, 5.3 mmol, 5 equiv) was added dropwise with a syringe at 0°C to a solution of 2-bromo-5-methoxyphenylacetonitrile (184 mg, 1 mmol, 1 eq) in THF (2 mL). The mixture was added to a solution of dimesylate[7] (880 mg, 3.2 mmol, 3 equiv) in THF (2 mL). The reaction mixture was then stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a yellow solid (195 mg, 0.74 mmol, 74%). Mp: 64.9 °C. R_f 0.72 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.9 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.80 (dd, *J* = 2.7, 8.8 Hz, 1H), 3.80 (s, 1H), 3.29 (m, 1H), 2.69 (m, 1H), 2.31 (m, 1H), 2.06 (m, 1H), 1.74 (m, *1*H), 1.38 (m, 1H): 7.10 (d, *J* = 8.9 Hz, 3H), 0.50 (d, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 135.7, 129.3, 125.5, 121.4, 116.8, 112.7, 55.6, 54.6, 41.3, 38.1, 30.9, 30.2, 18.7, 15.7 ppm.

HRMS (EI) calculated for $C_{15}H_{18}ClNO$ [$M^{+\bullet}$]: 263.1077, found: 263.1074.

[7] Boren, L.; Leijondahl, K.; Baeckvall, J.-E. *Tetrahedron. Lett.* **2009**, *50*, 3237.

IR(neat) ν 2963, 1239, 1042, 1031 cm^{-1}.

6-Methoxy-3-methyl-2,3,8,8a-tetrahydro-1H-cyclopenta[a]indene-3a-carbonitrile (43).

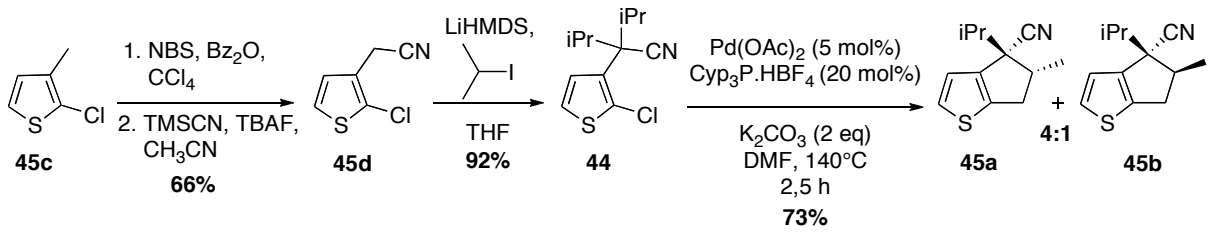
Following ***general procedure B*** starting from K_2CO_3 (104 mg, 0.75 mmol, 2 equiv), $Pd(OAc)_2$ (5 mg, 0.022 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (28 mg, 0.085 mmol, 0.20 equiv), compound **42** (101.5 mg, 0.38 mmol, 1 equiv) and DMF (1.8 mL). Mixture was stirred over night. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (68 mg, 0.32 mmol, 84%). R_f 0.68 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.63 (d, *J* = 2.5 Hz, 1H), 3.69 (s, 3H), 3.25 (m, *2*H), 2.63 (m, 1H), 2.10 (m, 2H), 1.73 (m, 1H), 1.46 (m, 1H), 1.35 (m, 1H), 1.26 (d, *3*H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 143.9, 134.5, 124.2, 122.5, 113.8, 110.1, 57.4, 55.4, 51.5, 45.5, 39.3, 35.1, 32.5, 16.7 ppm.

HRMS (EI) calculated for $C_{18}H_{17}NO$ [$M^{+\bullet}$]: 227.1310, found: 227.1309.

IR (neat) ν 2962, 1491, 1242, 1043 cm^{-1}



2-(2-chlorothiophen-3-yl)acetonitrile (45d).

NBS (939 mg, 5.28 mmol, 1 equiv) and benzoyl peroxide (256 mg, 1 mmol, 0.20 equiv) were added to a solution of 2-chloro-3-methylthiophene **45c** (700 mg, 5.28 mmol, 1 equiv) in CCl_4 (15 mL). The reaction mixture was stirred for 40 min. After cooling, the solvent was evaporated under reduced pressure. The residue obtained was dissolved in dry CH_3CN (52 mL) and TMSCN (919 μL, 6.86 mmol, 1.3 equiv). TBAF 1M in THF (6.86 mL, 6.86 mmol, 1.3 equiv) was added dropwise at 0 °C, and the reaction mixture was stirred at r.t for 3 h. Then the solvent was evaporated under reduced pressure. The residue was purified by flash

chromatography (5% Ethyl acetate/cyclohexane) affordind the title compound **45d** as an orange oil (550 mg, 3.49 mmol, 66% for the two steps). R_f 0.64 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.7 Hz, 1H), 6.98 (d, *J* = 5.8 Hz, 1H), 3.65 (s, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 127.7, 126.9, 126.5, 123.9, 116.6, 16.8 ppm.

IR (neat) υ = 3112, 2252, 1414, 1034, 827, 689 cm^{-1}.

GC/MS (m/z) $C_6H_4{}^{35}ClNS$ [$M^{+\bullet}$] 157, (m/z) $C_6H_4{}^{37}ClNS$ [$M^{+\bullet}$] 159.

2-(2-chlorothiophen-3-yl)-2-isopropyl-3-methylbutanenitrile (44).

LiHMDS 1.06 M in THF (2.4 mL, 2.54 mmol, 4 equiv) was added dropwise with a syringe at 0 °C to a solution of compound **45d** (100 mg, 0.63 mmol, 1 equiv) in THF (3 mL). The reaction mixture was then stirred at room temperature for 30 min. Isopropyl iodide (642 μL, 2.54 mmol, 4 equiv) was added dropwise and the reaction was stirred at room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4. After filtration and evaporation, the crude was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound **44** as a pale yellow solid (141 mg, 0.58 mmol, 92%). Mp: 56.3 °C. R_f 0.71 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 5.9 Hz, 1H), 6.93 (d, *J* = 5.8 Hz, 1H), 2.65 (m, *J* = 6.7 Hz, 2H), 1.11 (d, *J* = 6.7 Hz, 6H), 0.94 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 130.2, 129.9, 126.7, 122.1, 120.9, 55.2, 33.4, 19.0, 18.3 ppm.

IR (neat) υ 2976, 2229, 1467, 1392, 1021, 849, 721 cm^{-1}.

HRMS (EI) calculated for $C_{12}H_{16}Cl^{35}NS$ [$M^{+\bullet}$]: 241.0686, found: 241.0689.

5,6-dihydro-4-isopropyl-5-methyl-4*H*-cyclopenta[*b*]thiophene-4-carbonitrile (45).

Following ***general procedure B*** starting from K_2CO_3 (84.6 mg, 0.61 mmol, 2 equiv), $Pd(OAc)_2$ (3.5 mg, 0.016 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (20.6 mg, 0.062 mmol, 0.20 equiv), compound **44** (74 mg, 0.31 mmol, 1 equiv) and DMF (1.47 mL). Mixture was stirred for 2.5 h. After preparative thin layer chromatography (5% Ethyl acetate/cyclohexane), a mixture of inseparable diastereoisomers **45a** and **45b** was isolated as a yellow oil (46 mg, 0.23 mmol, 72%). R_f 0.68 (50% Ethyl acetate/cyclohexane)

Major diastereoisomer 45a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.1 Hz, 1H), 6.90 (d, *J* = 5.1 Hz, 1H), 3.16 (dd, *J* = 15.5, 7.8 Hz, 1H), 3.02-2.91 (m, 1H), 2.60 (dd, *J* = 15.5, 5.2 Hz, 1H), 2.13-2.01 (m, *J* = 6.8 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H), 1.08 (dd, *J* = 6.3, 6.5 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 128.9, 121.9, 120.5, 55.0, 45.1, 36.1, 35.5, 19.9, 18.7, 18.4 ppm.

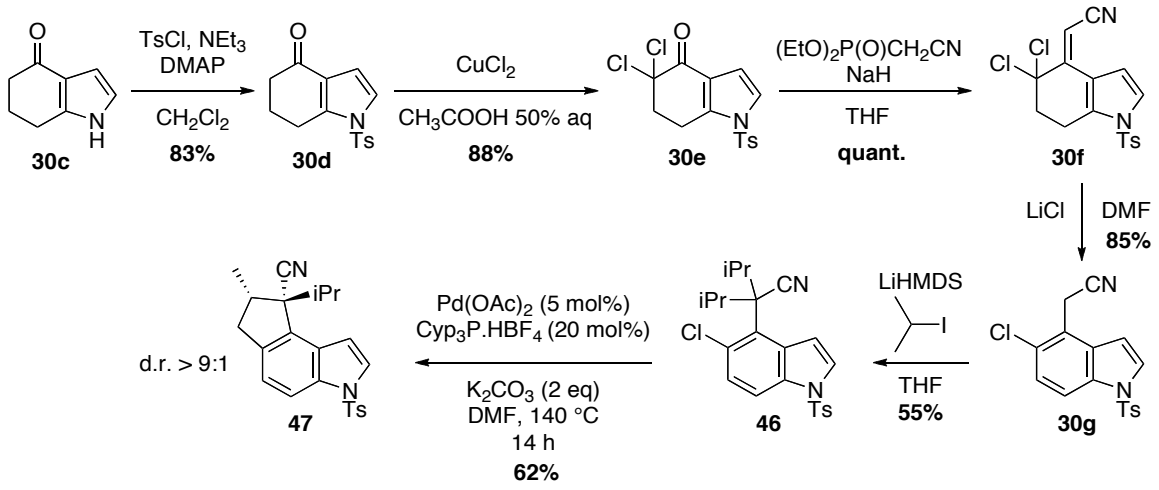
Minor diastereoisomer 45b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 5.1 Hz, 1H), 3.49-3.36 (m, 1H), 3.05 (dd, *J* = 15.4, 8.2 Hz, 1H), 2.24-2.15 (m, *J* = 6.7 Hz, 1H), 1.36 (d, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 141.9, 128.1, 123.5, 122.4, 51.4, 50.8, 35.9, 32.3, 20.3, 17.8, 14.3 ppm.

IR (neat) υ 2966, 1465, 1389, 838, 713 cm^{-1}.

HRMS (EI) calculated for $C_{12}H_{15}NS$ [$M^{+\bullet}$]: 205.0925, found: 205.0928.



2-(5-chloro-1-tosyl-1*H*-indol-4-yl)-2-isopropyl-3-methylbutanenitrile (46).

LiHMDS 1.06 M in THF (1.09 mL, 1.16 mmol, 4 equiv) was added dropwise with a syringe at 0 °C to a solution of compound **30g**[8] (100 mg, 0.29 mmol, 1 equiv) and isopropyliodide (1.44 mL, 14.5 mmol, 50 equiv) in THF (0.75 mL). The reaction mixture was then stirred at

[8] See part "*Synthesis of cyclobutarenes by alkane arylation*".

room temperature overnight. After hydrolysis with a saturated solution of NH_4Cl, the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and evaporation, the reaction was run on the residue an extra time. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound **46** as a colorless oil (69 mg, 0.16 mmol, 55%). R_f 0.72 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 3.9 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 3.9 Hz, 1H), 7.29 (d, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.29 (m, *J* = 6.7 Hz, 2H), 2.36 (s, 3H), 1.19 (d, *J* = 6.6 Hz, 6H), 0.84 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 135.1, 133.8, 133.1, 130.2, 129.0, 127.9, 127.8, 127.0, 126.5, 121.8, 113.8, 109.8, 58.7, 33.9, 21.7, 20.6, 20.5 ppm.

IR (neat) υ 3026, 1604, 1495, 1171, 1030 cm^{-1}.

HR/MS (EI) calculated for $C_{23}H_{25}ClN_2O_2S$ [$M^{+\bullet}$]: 428.1325, found: 428.1325.

3,6,7,8-tetrahydro-8-isopropyl-7-methyl-3-tosylcyclopenta[*e*]indole-8-carbonitrile (47).

Following ***general procedure B*** starting from K_2CO_3 (27 mg, 0.19 mmol, 2 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 0.05 equiv), $Cyp_3P{\bullet}HBF_4$ (6.39 mg, 0.019 mmol, 0.20 equiv), compound **46** (42 mg, 0.098 mmol, 1 equiv) and DMF (490 μL). Mixture was stirred overnight. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound **47** as a white oil (24 mg, 0.061 mmol, 62%). R_f 0.72 (50% Ethyl acetate/cyclohexane).

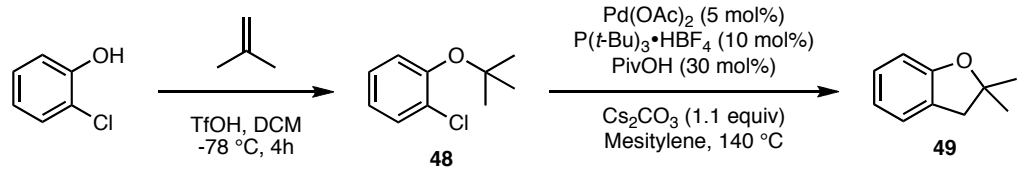
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 3.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 3.28 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.76-2.69 (m, 1H), 2.59 (dd, *J* = 15.9, 2.2 Hz, 1H), 2.35 (s, 3H), 2.23 (m, *J* = 13.6 Hz, 1H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 136.7, 135.4, 134.6, 132.5, 130.1, 127.8, 127.3, 127.0, 121.4, 120.9, 113.9, 106.7, 58.6, 39.5, 38.2, 35.8, 21.7, 20.5, 19.5, 18.3 ppm.

IR (neat) υ = 2967, 1371, 1174, 1136, 1088, 685, 663 cm^{-1}.

HR/MS (EI) calculated for $C_{23}H_{24}N_2O_2S$ [$M^{+\bullet}$]: 392.1558, found: 392.1563.

Synthesis of dihydrobenzofurans and indolines by alkane arylation (Table 5).



1-*tert*-butoxy-2-chlorobenzene (48).[9]

A large excess of isobutene was added *via* cold finger to a solution of 2-chlorophenol (1.29 g, 10.00 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL, 1.0 M) under argon at -78 ºC. TfOH (60 μL, 0.80 mmol, 0.08 equiv) was then added dropwise and the solution was sittred at -78 ºC for 4 hours. Et_3N (0.20 mL) was added and the mixture was brought to room temperature. The crude reaction mixture was concentrated and purified by silica gel flash chromatography (1% Et_2O in petroleum ether) to afford 1.30 g of a clear oil in 70% yield.

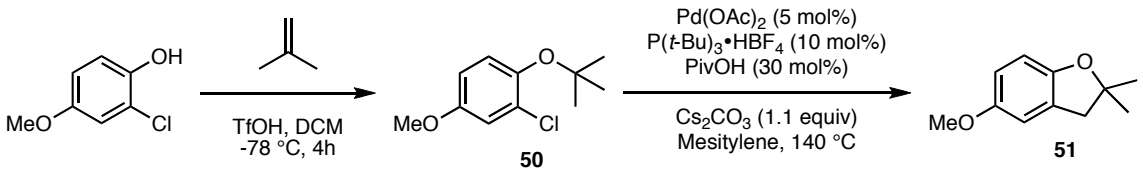
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 3.1 Hz, 1H), 6.71 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.77 (s, 3H), 1.37 (s, 9H) ppm.

2,3-dihydro-2,2-dimethylbenzofuran (49).[9]

The title compound was prepared according to the ***general procedure C*** using 1-*tert*-butoxy-2-chlorobenzene **48** (130 mg, 0.704 mmol, 1 equiv). The product was purified by silica gel flash chromatography (1% Et_2O in petroleum ether) to afford 80 mg of clear oil in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.08 (m, 2H), 6.81 (td, *J* = 7.4, 0.9 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.01 (s, 2H), 1.47 (s, 6H) ppm.

[9] Lafrance, M.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 14570.



1-*tert*-butoxy-2-chloro-4-methoxybenzene (50).

A large excess of isobutene was added *via* cold finger to a solution of 2-chloro-4-methoxyphenol (1.60g, 10.00 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL, 1.0 M) under argon at -78 ºC. TfOH (60 μL, 0.80 mmol, 0.08 equiv) was then added dropwise and the solution was stirred at -78 ºC for 4 hours. Et_3N (0.20 mL) was added and the mixture was brought to room temperature. The crude reaction mixture was concentrated and purified by silica gel flash chromatography (2% Et_2O in petroleum ether) to afford 1.40 g of a clear oil in 65% yield. R_f = 0.33 (1% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.9 Hz, 1H), 6.92 (d, *J* = 3.1 Hz, 1H), 6.71 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.77 (s, 3H), 1.37 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 145.6, 129.9, 125.6, 115.3, 113.0, 81.0, 55.8, 28.9 ppm.

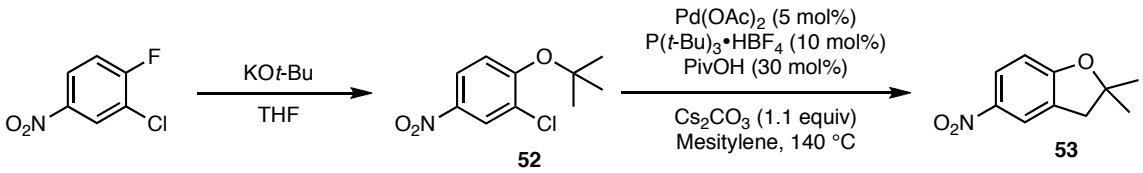
HRMS Calculated for $C_{11}H_{15}O_2Cl$ (M^+) 214.0761, found 214.0738.

IR (neat) 3075, 2978, 2837, 1490, 1367, 1163, 1053, 861 cm^{-1}.

2,3-dihydro-5-methoxy-2,2-dimethylbenzofuran (51).[9]

The title compound was prepared according to the ***general procedure C*** using 1-*tert*-butoxy-2-chloro-4-methoxybenzene **50** (150 mg, 0.700 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_2O in petroleum ether) to afford 120 mg of yellow oil in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 2.2, 1.0 Hz, 1H), 6.67-6.62 (m, 2H), 3.75 (s, 3H), 2.99 (s, 2H), 1.46 (s, 6H) ppm.



1-*tert*-butoxy-2-chloro-4-nitrobenzene (52).

Prepared according to ***general procedure D*** using potassium *tert*-butoxide (352 mg, 3.13 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (500 mg, 2.85 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 470 mg of a clear oil in 72% yield. R_f = 0.33 (1% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.20 (d, *J* = 9.1 Hz, 1H), 1.51 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 142.3, 128.6, 126.1, 123.0, 121.1, 83.5, 29.0 ppm.

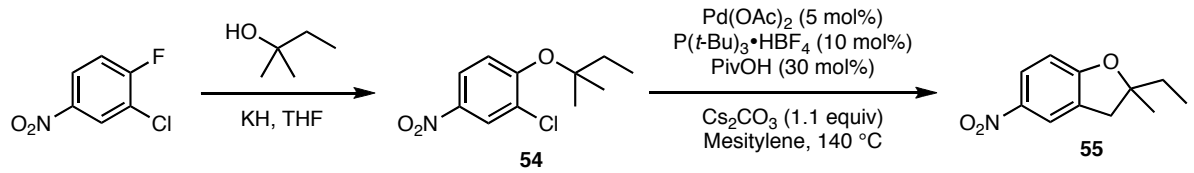
HRMS Calculated for $C_{10}H_{12}NO_3Cl$ (M^+ - CH_3) 214.0271, found 214.0268.

IR (neat) 3093, 2983, 2938, 1584, 1520, 1345, 1160, 730 cm^{-1}.

2,3-dihydro-2,2-dimethyl-5-nitrobenzofuran (53).[9]

The title compound was prepared according to the ***general procedure C*** using 1-*tert*-butoxy-2-chloro-4-nitrobenzene **52** (62 mg, 0.270 mmol, 1 equiv). The product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 46 mg of yellow oil in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.06-8.05 (m, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 3.08 (s, 2H), 1.52 (s, 6H) ppm.



1-(*tert*-pentyloxy)-2-chloro-4-nitrobenzene (54).

Prepared according to ***general procedure D*** using 2-methylbutan-2-ol (271 μL, 2.51 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (400 mg, 2.28 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (3.5% Et_2O in petroleum ether) to afford 426 mg of a yellow oil in 77% yield. R_f = 0.37 (4% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.8 Hz, 1H), 8.07 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.17 (d, *J* = 9.1 Hz, 1H), 1.85 (q, *J* = 7.5 Hz, 2H), 1.46 (s, 6H), 1.04 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 141.9, 128.1, 126.1, 123.0, 120.1, 85.7, 35.1, 26.1, 8.5 ppm.

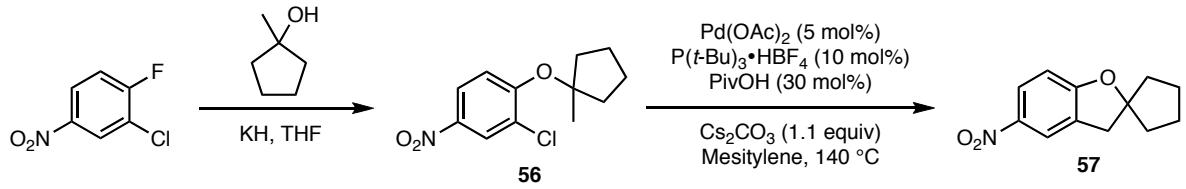
HRMS Calculated for $C_{11}H_{17}NO_3Cl$ (M^+) 243.0662, found 243.0602.

IR (neat) 3089, 2980, 2942, 1517, 1345, 1281, 744 cm^{-1}.

2-ethyl-2,3-dihydro-2-methyl-5-nitrobenzofuran (55).[9]

The title compound was prepared according to the ***general procedure C*** using 1-(*tert*-pentyloxy)-2-chloro-4-nitrobenzene **54** (150 mg, 0.616 mmol, 1 equiv). The product was purified by silica gel flash chromatography (5% Et_2O in petroleum ether) to afford 107 mg of orange oil in 84% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.06-8.05 (m, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.14 (d, *J* = 16.0 Hz, 1H), 2.99 (d, *J* = 16.0 Hz, 1H), 1.81 (q, *J* = 7.5 Hz, 2H), 1.48 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm.



1-(1-methylcyclopentyloxy)-2-chloro-4-nitrobenzene (56).

Prepared according to ***general procedure D*** using 1-methylcyclopentanol (314 mg, 3.13 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (500 mg, 2.85 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (2% Et_2O in petroleum ether) to afford 405 mg of a pale yellow solid in 63% yield. M.p.: 60-62 °C. R_f = 0.38 (4% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.08 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 1H), 2.31-2.23 (m, 2H), 1.86-1.76 (m, 4H), 1.74-1.68 (m, 2H), 1.62 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 140.9, 126.4, 126.1, 123.2, 116.6, 92.2, 40.1, 24.9, 24.5 ppm.

HRMS Calculated for $C_{12}H_{14}NO_3Cl$ (M^+ - CH_3) 240.0427, found 240.0436.

IR (neat) 2967, 1584, 1343, 1282, 742 cm^{-1}.

2,3-dihydro-2,2-*spiro*cyclopentyl-5-nitrobenzofuran (57).

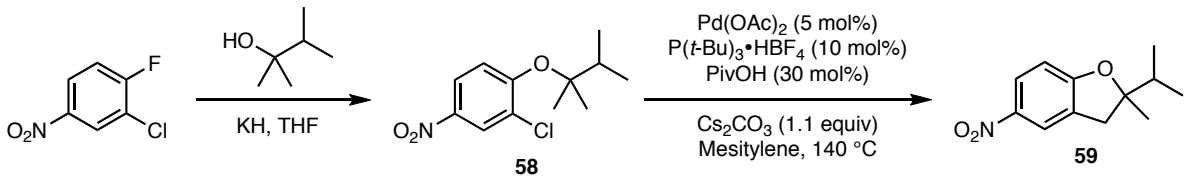
The title compound was prepared according to the ***general procedure C*** using 1-(1-methylcyclopentyloxy)-2-chloro-4-nitrobenzene **56** (150 mg, 0.665 mmol, 1 equiv). The product was purified by silica gel flash chromatography (4% Et_2O in petroleum ether) to afford 93 mg of a yellow solid in 64% yield. M.p.: 74-75 °C. R_f = 0.26 (4% Et_2O in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.06-8.04 (m, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.24 (s, 2H), 2.19-2.09 (m, 2H), 1.94-1.71 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 141.6, 128.8, 125.9, 121.3, 109.2, 100.4, 39.6, 39.1, 23.9 ppm.

HRMS Calculated for $C_{12}H_{13}NO_3$ (M^+) 219.0895, found 219.0900.

IR (neat) 2963, 1597, 1340, 1276 cm^{-1}.



1-(2,3-dimethylbutan-2-yloxy)-2-chloro-4-nitrobenzene (58).

Prepared according to ***general procedure D*** using 2,3-dimethylbutan-2-ol (1.12 mL, 9.02 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (1.44 g, 8.20 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 1.44 g of an orange oil in 68% yield. R_f = 0.36 (4% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.05 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.18 (d, *J* = 9.1 Hz, 1H), 2.15 (sept, *J* = 6.8 Hz, 1H), 1.42 (s, 6H), 1.05 (d, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 141.8, 128.1, 126.2, 123.1, 119.9, 88.3, 38.5, 23.7, 17.7 ppm.

HRMS Calculated for $C_{12}H_{16}NO_3Cl$ (M^+ - CH_3) 242.0584, found 242.0589.

IR (neat) 2979, 2880, 1584, 1518, 1344, 1282, 1137, 735 cm^{-1}.

2,3-dihydro-2-isopropyl-2-methyl-5-nitrobenzofuran (59).

The title compound was prepared according to the ***general procedure C*** using 1-(2,3-dimethylbutan-2-yloxy)-2-chloro-4-nitrobenzene **58** (150 mg, 0.582 mmol, 1 equiv). The product was purified by silica gel flash chromatography (4% Et_2O in petroleum ether) to

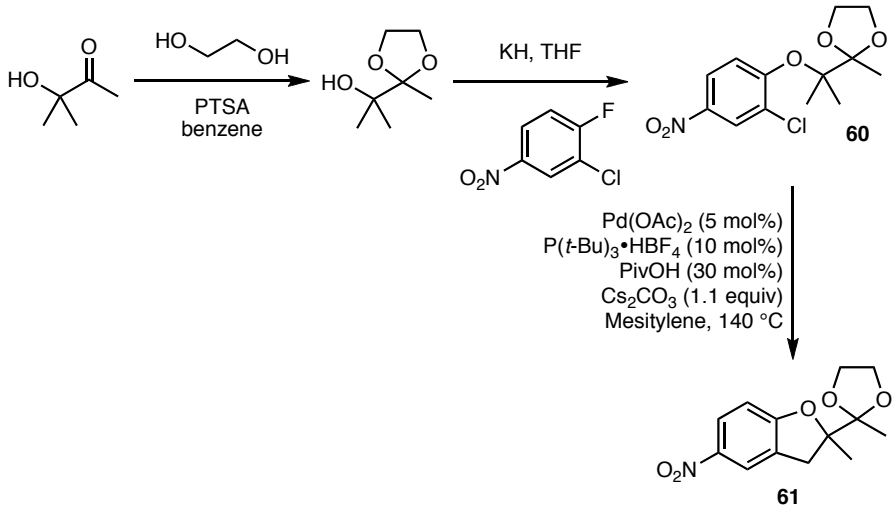
afford 99 mg of a yellow solid in 77% yield. M.p.: 66-68 °C. R_f = 0.24 (4% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (ddd, *J* = 8.8, 2.4, 0.5 Hz, 1H), 8.04-8.03 (m, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.19 (d, *J* = 16.1 Hz, 1H), 2.87 (d, *J* = 16.1 Hz, 1H), 2.03 (sept, *J* = 6.8 Hz, 1H), 1.39 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 141.5, 128.6, 125.9, 121.6, 109.1, 95.4, 38.2, 37.2, 23.5, 17.4, 17.3 ppm.

HRMS Calculated for $C_{12}H_{15}NO_3$ (M^+) 221.1052, found 221.1045.

IR (neat) 2969, 2879, 1597, 1343, 1277 cm^{-1}.



2-(2-methyl-1,3-dioxolan-2-yl)propan-2-ol.

Synthesized according to a reported procedure,[10] using 3-hydroxy-3-methylbutan-2-one (1.05 mL, 9.80 mmol, 1.0 equiv), ethylene glycol (26.4 mL, 473.4 mmol, 48.3 equiv), *p*-toluenesulfonic acid (100 mg, 0.58 mmol, 0.06 equiv) and benzene (165 mL, 0.06 M). The product was obtained in 25% yield (354 mg).

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[10] Bernstein, S. ; Heller, M. ; Stolar, S. M. *J. Am. Chem. Soc.* **1954**, *76*, 5674.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (s, 4H), 2.02 (s, 1H), 1.34 (s, 3H), 1.27 (s, 6H) ppm.

2-(2-(2-chloro-4-nitrophenoxy)propan-2-yl)-2-methyl-1,3-dioxolane (60).

Prepared according to ***general procedure D*** using 2-(2-methyl-1,3-dioxolan-2-yl)propan-2-ol (350 mg, 2.39 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (382 mg, 2.18 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (20% Et_2O in petroleum ether) to afford 238 mg of a green oil in 36% yield. R_f = 0.30 (20% Et_2O in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.8 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 4.10-3.99 (m, 4H), 1.50 (s, 3H), 1.45 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.4, 128.6, 125.7, 122.7, 122.4, 111.8, 88.3, 65.4, 22.2, 19.8 ppm.

HRMS Calculated for $C_{12}H_{13}NO_5Cl$ (M^+ - CH_3) 286.0482, found 286.0460.

IR (neat) 3107, 2989, 2888, 1583, 1348, 1103, 752 cm^{-1}.

2,3-dihydro-2-methyl-2-(2-methyl-1,3-dioxolan-2-yl)-5-nitrobenzofuran (61).

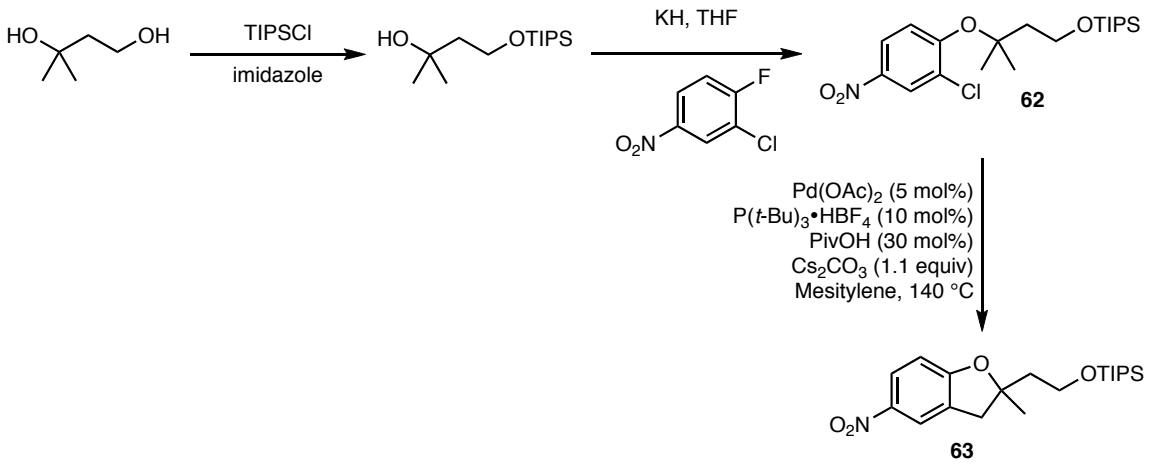
The title compound was prepared according to the ***general procedure C*** using 2-(2-(2-chloro-4-nitrophenoxy)propan-2-yl)-2-methyl-1,3-dioxolane **60** (130 mg, 0.431 mmol, 1 equiv). The product was purified by silica gel flash chromatography (30% Et_2O in petroleum ether) to afford 109 mg of a yellow solid in 95% yield. M.p.: 81-83 °C. R_f = 0.26 (4% Et_2O in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.05-8.04 (m, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.12-3.92 (m, 4H), 3.48 (d, *J* = 16.2 Hz, 1H), 2.94 (d, *J* = 16.2 Hz, 1H), 1.54 (s, 3H), 1.39 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 141.9, 128.6, 125.8, 121.3, 111.2, 109.0, 95.0, 66.1, 66.1, 37.7, 23.1, 20.2 ppm.

HRMS Calculated for $C_{13}H_{15}NO_5$ (M^+) 265.0950, found 265.0926.

IR (neat) 2991, 2899, 1514, 1335, 1275 cm^{-1}.



3-hydroxy-3-methylbutoxytriisopropylsilane.

Synthesized according to a reported procedure,[11] using 3-methylbutane-1,3-diol (2.05 mL, 19.20 mmol, 1.0 equiv), triisopropylsilyl chloride (4.52 mL, 21.12 mmol, 1.1 equiv), imidazole (2.61 g, 38.40 mmol, 2.0 equiv) and dimethylformamide (19 mL, 1.0 M). The product was purified by silica gel flash chromatography (10% Et_2O in petroleum ether) to give 4.54 g of a clear oil in 91% yield. R_f = 0.62 (40% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (t, *J* = 5.7 Hz, 2H), 1.72 (t, *J* = 5.7 Hz, 2H), 1.26 (s, 6H), 1.17-1.05 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 71.0, 61.6, 43.1, 29.4, 18.1, 11.8 ppm.

HRMS Calculated for $C_{13}H_{29}O_2Si$ (M^+ - CH_3) 245.1937, found 245.1922.

IR (neat) 3390, 2941, 2869, 1464, 1088 cm^{-1}.

(3-(2-chloro-4-nitrophenoxy)-3-methylbutoxy)triisopropylsilane (62).

Prepared according to ***general procedure D*** using 2-(2-methyl-1,3-dioxolan-2-yl)propan-2-ol (2.00 g, 7.68 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (1.23 g, 6.98 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (1% Et_2O in

[11] Ogilvie, K. K.; Thompson, E. A.; Quilliam, M. A.; Westmore, J. B. *Tetrahedron Lett.* **1974**, *15*, 2865.

petroleum ether) to afford 1.30 g of a green oil in 45% yield. R_f = 0.35 (2% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.07 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 3.96 (t, *J* = 6.9 Hz, 2H), 2.11 (t, *J* = 6.9 Hz, 2H), 1.51 (s, 6H), 1.14-1.02 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 142.1, 128.4, 126.1, 123.1, 120.5, 84.7, 59.5, 45.3, 27.2, 18.2, 12.1 ppm.

HRMS Calculated for $C_{17}H_{27}ClNO_4Si$ (M^+ - C_3H_7) 372.1398, found 372.1403.

IR (neat) 2944, 2866, 1520, 1345, 1126, 747 cm^{-1}.

(2-(2,3-dihydro-2-methyl-5-nitrobenzofuran-2-yl)ethoxy)triisopropylsilane (63).

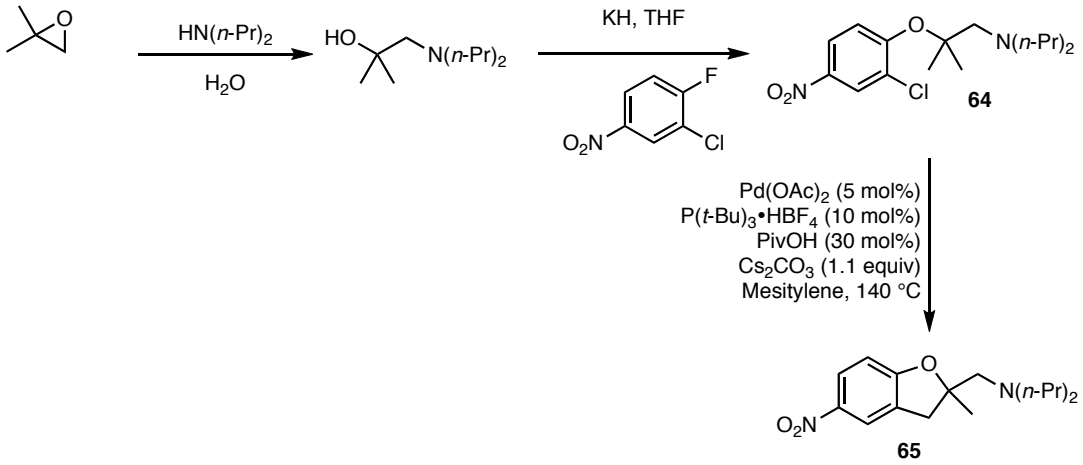
The title compound was prepared according to the ***general procedure C*** using (3-(2-chloro-4-nitrophenoxy)-3-methylbutoxy)triisopropylsilane **62** (200 mg, 0.481 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_2O in petroleum ether) to afford 159 mg of a yellow oil in 87% yield. R_f = 0.27 (2% Et_2O in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.04-8.03 (m, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 3.88 (t, *J* = 6.3 Hz, 2H), 3.41 (d, *J* = 16.0 Hz, 1H), 3.00 (d, *J* = 16.0 Hz, 1H), 2.05 (td, *J* = 6.3, 4.3 Hz, 2H), 1.52 (s, 3H), 1.10-1.01 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 141.7, 128.9, 125.9, 121.7, 109.2, 91.6, 59.4, 43.4, 41.0, 26.9, 18.1, 12.0 ppm.

HRMS Calculated for $C_{17}H_{26}NO_4Si$ (M^+ - C_3H_7) 336.1631, found 336.1632.

IR (neat) 2943, 2866, 1597, 1518, 1481, 1337, 1101 cm^{-1}.



1-(dipropylamino)-2-methylpropan-2-ol.

Synthesized according to a reported procedure,[12] using 2,2-dimethyloxirane (1.85 mL, 20.80 mmol, 1.0 equiv), dipropylamine (3.42 mL, 24.96 mmol, 1.2 equiv) and H_2O (8 mL, 2.6 M). The product was obtained as 1.95 g of a clear oil 55% yield. R_f = 0.44 (40% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (br, 1H), 2.51-2.47 (m, 4H), 2.39 (s, 2H), 1.52-1.43 (m, 4H), 1.15 (s, 6H), 0.88 (t, *J* = 7.4 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 69.1, 66.3, 58.5, 28.5, 20.8, 11.9 ppm.

HRMS Calculated for $C_{10}H_{23}NO$ (M^+) 173.1780, found 173.1758.

IR (neat) 3431, 2962, 2874, 1468, 1076 cm^{-1}.

***N*-(2-(2-chloro-4-nitrophenoxy)-2-methylpropyl)-*N*-propylpropan-1-amine (64).**

Prepared according to ***general procedure D*** using 1-(dipropylamino)2-methylpropan-2-ol (542 mg, 3.13 mmol, 1.1 equiv) and 2-chloro-1-fluoro-4-nitrobenzene (500 mg, 2.85 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (8% Et_2O in

[12] Azizi, N.; Saidi, M. R. *Org. Lett.* **2005**, *7*, 3649.

petroleum ether) to afford 528 mg of a yellow oil in 56% yield. R_f = 0.35 (2% Et_3N and 6% Et_2O in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.06 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.36 (d, *J* = 9.1 Hz, 1H), 2.72 (s, 2H), 2.56-2.51 (m, 4H), 1.52-1.40 (m, 10H), 0.87 (t, *J* = 7.3 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 142.0, 128.0, 126.1, 122.9, 121.0, 87.2, 65.4, 57.8, 25.1, 20.3, 11.9 ppm.

HRMS Calculated for $C_{14}H_{20}ClN_2O_3$ (M^+ - C_2H_5) 299.1162, found 299.1126.

IR (neat) 3094, 2961, 2873, 1584, 1345, 1124, 748 cm^{-1}.

***N*-((2,3-dihydro-2-methyl-5-nitrobenzofuran-2-yl)methyl)-*N*-propylpropan-1-amine (65).**

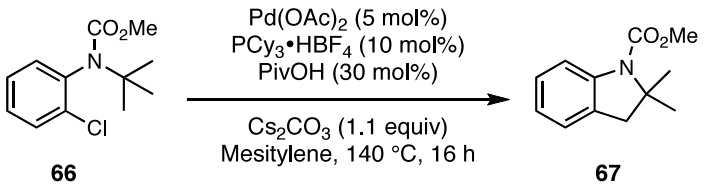
The title compound was prepared according to the ***general procedure C*** using *N*-(2-(2-chloro-4-nitrophenoxy)-2-methylpropyl)-*N*-propylpropan-1-amine **64** (150 mg, 0.457 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_3N and 6% Et_2O in petroleum ether) to afford 74 mg of a yellow oil in 55% yield. R_f = 0.45 (2% Et_3N and 6% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.03 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 3.42 (d, *J* = 15.7 Hz, 1H), 2.87 (d, *J* = 15.7 Hz, 1H), 2.71 (d, *J* = 14.7 Hz, 1H), 2.57 (d, *J* = 14.7 Hz, 1H), 2.52-2.37 (m, 4H), 1.43 (s, 3H), 1.41-1.26 (m, 4H), 0.77 (t, *J* = 7.3 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 141.6, 129.4, 125.7, 121.4, 108.9, 93.8, 62.8, 57.8, 38.3, 25.5, 20.6, 11.9 ppm.

HRMS Calculated for $C_{16}H_{24}N_2O_3$ (M^+) 292.1787, found 292.1754.

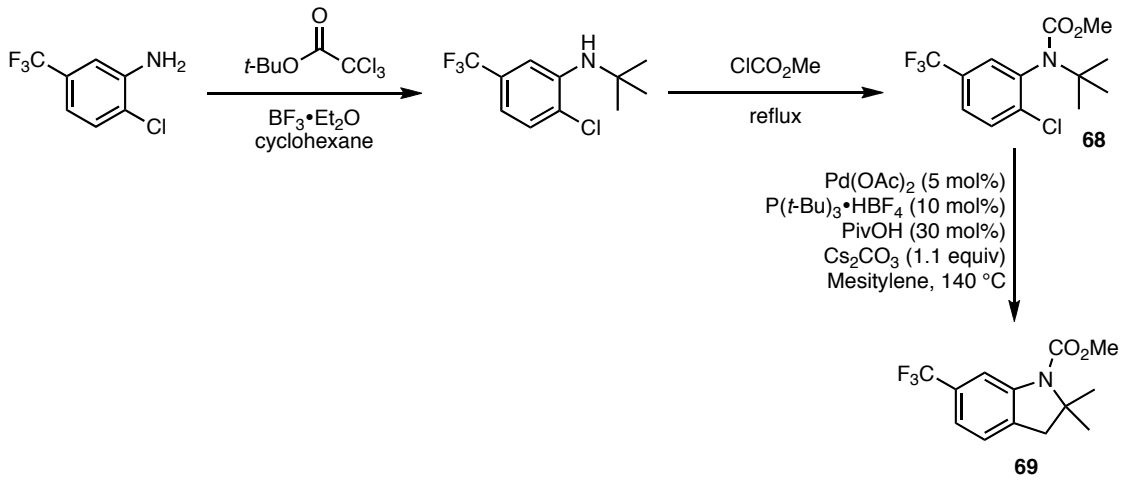
IR (neat) 2959, 2930, 1598, 1336, 1272, 1060 cm^{-1}.



Methyl-2,2-dimethylindoline-1-carboxylate (67).[13]

The title compound was prepared according to the ***general procedure C*** using compound **66**[13] (50 mg, 0.207 mmol, 1 equiv). The product was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) to afford 35 mg of a pale yellow oil in 83% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s(br), 1H), 7.20-7.10 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 3.85 (s, 3H), 3.02 (s, 2H), 1.57 (s, 6H) ppm.



[13] Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2008**, *10*, 1759-1762.

***tert*-Butyl-(2-chloro-5-trifluoromethyl-phenyl)-amine.**

To a solution of 2-chloro-5-(trifluoromethyl)aniline (1 mL, 7.3 mmol, 1 equiv) in cyclohexane (5 mL) were added *tert*-butyl-2,2,2-trichloroacetimidate (3.4 mL, 19 mmol, 3 equiv) and BF_3•Et_2O (200 μL, 1.5 mmol, 0.15 equiv) at room temperature under argon. The mixture was stirred at room temperature overnight. The mixture was diluted with ethyl acetate, washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under vaccum. The crude material was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a colorless oil (1.17 g, 4.6 mmol, 63%). R_f 0.42 (10% Ethyl acetate/cyclohexane).

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 1H), 7.08 (s, 1H), 6.77 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.46 (s, 1H), 1.37 (s, *9*H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 129.9 (q, *J* = 31.9 Hz), 129.7, 124.3 (q, *J* = 270.5 Hz), 123.6, 113.3 (q, *J* = 3.9 Hz), 110.3 (q, *J* = 3.8 Hz), 51.6, 29.7 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.2 ppm.

HRMS (EI) calculated for $C_{11}H_{13}ClF_3N$ [$M^{+\bullet}$]: 251.0684, found 251.0686.

IR (neat) ν 3421, 2979, 1120, 1080 cm^{-1}.

***tert*-Butyl-(2-chloro-5-trifluoromethyl-phenyl)-carbamic acid methyl ester (68).**

A solution of *tert*-Butyl-(2-chloro-5-trifluoromethyl-phenyl)-amine (690 mg, 2.7 mmol, 1 equiv) and methyl chloroformate (20 mL) was heated under reflux overnight. Methyl chloroformate was concentrated under vaccum and the crude material was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a white solid (760 mg, 2.4 mmol, 88%). Mp: 91.5 °C. R_f 0.71 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 3.56 (s, 3H), 1.40 (s, *9*H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 140.1, 139.0, 130.5, 129.7 (q, *J* = 33 Hz), 128.1 (q, *J* = 3.6 Hz), 125.4 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 270.6 Hz), 58.5, 52.6, 29.3 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9 ppm.

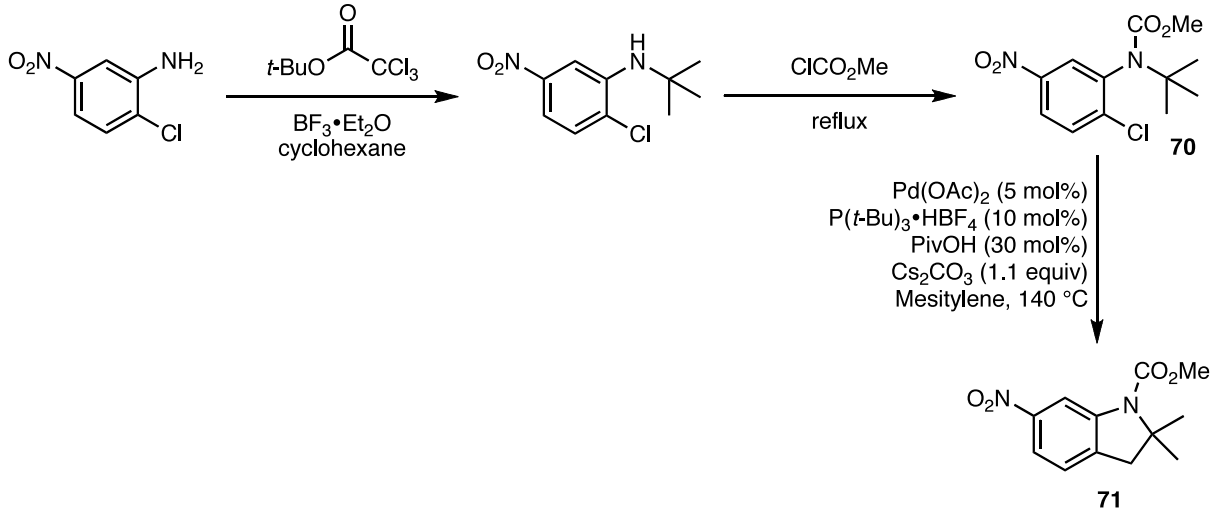
HRMS (CI) calculated for $C_{13}H_{16}ClF_3NO_2$ $[M+H]^+$: 310.0822, found: 310.0822.

IR (neat) ν 3003, 1706, 1323, 1116, 1084 cm^{-1}.

Methyl 2,2-Dimethyl-6-(trifluoromethyl)indoline-1-carboxylate (69).

Following ***general procedure C*** starting from Cs_2CO_3 (94.7 mg, 0.29 mmol, 1.1 equiv), $Pd(OAc)_2$ (2.6 mg, 0.011 mmol, 0.05 equiv), $Cy_3P{\bullet}HBF_4$ (9.7 mg, 0.026 mmol, 0.10 equiv), compound **68** (73.6 mg, 0.23 mmol, 1 equiv) and mesitylene (2 mL). Mixture was stirred at 140 °C for 20 h. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (52.7 mg, 0.19 mmol, 84%). R_f 0.67 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.20 (m, 2H), 3.87 (s, 3H), 3.05 (s, 2H), 1.57 (s, 6H) ppm.



***tert*-Butyl-(2-chloro-5-nitro-phenyl)-amine.**

To a solution of 2-chloro-5-nitroaniline (500 mg, 2.8 mmol, 1 equiv) in cyclohexane (4 mL) were added *tert*-butyl-2,2,2-trichloroacetimidate (2.54 mL, 4.2 mmol, 5 equiv) and $BF_3{\cdot}Et_2O$ (160 µL, 1.2 mmol, 0.5 equiv) at room temperature under argon. The mixture was stirred at room temperature overnight. The mixture was diluted with ethyl acetate, washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under vaccum. The crude material was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a colorless oil (291 mg, 1.3 mmol, 51%). R_f 0.45 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 2.4 Hz, 1H), 7.42 (dd, J = 8.6, 2.2 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 4.60 (s, 1H), 1.45 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 143.1, 129.4, 126.2, 111.1, 107.3, 51.6, 29.4 ppm.

HRMS (EI) calculated for $C_{10}H_{13}ClN_2O_2$ [$M^{+\bullet}$]: 228.0666, found 228.0666.

IR (neat) ν 3414, 2977, 1522, 1342 cm^{-1}.

***tert*-Butyl-(2-chloro-5-nitro-phenyl)-carbamic acid methyl ester (70).**

A solution of *tert*-Butyl-(2-chloro-5-nitro-phenyl)-amine (209 mg, 0.91 mmol, 1 equiv) and methyl chloroformate (20 mL) was heated under reflux overnight. Methyl chloroformate was concentrated under vacuum and the crude material was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound as a yellow solid (205 mg, 0.72 mmol, 80%). Mp: 72.1 °C. R_f 0.68 (10% Ethyl acetate/cyclohexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.8, 2.7 Hz, 1H), 8.01 (d, *J* = 2.7 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 3.57 (s, 3H), 1.43 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 142.5, 140.6, 130.5, 126.1, 123.4, 58.7, 52.8, 29.3 ppm.

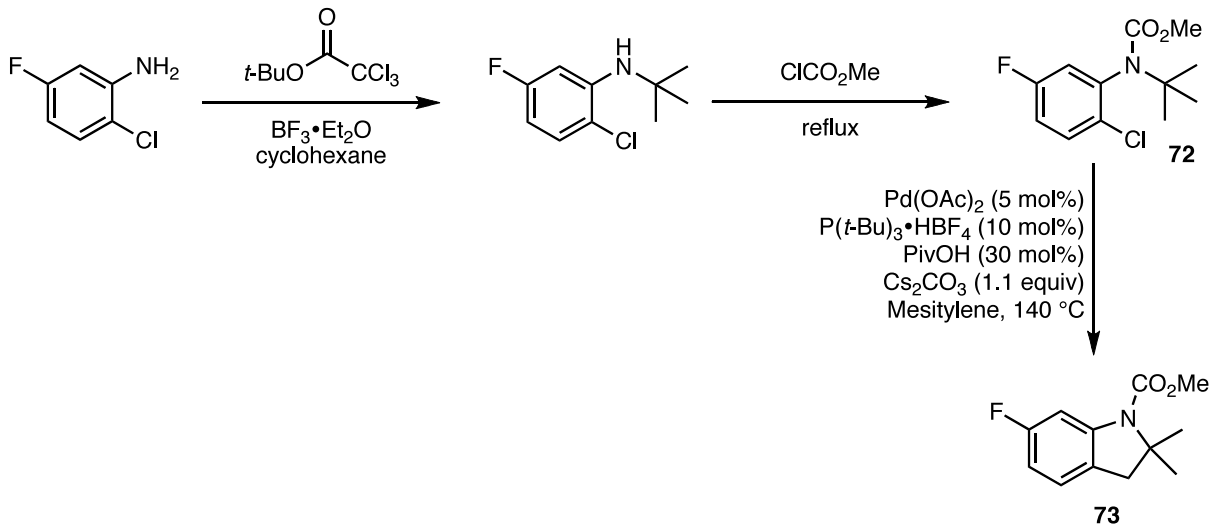
HRMS (CI) calculated for $C_{12}H_{16}ClN_2O_4$ [M+H]$^+$: 287.0799, found: 287.0799.

IR (neat) ν 2977, 1776, 1320, 1095 cm^{-1}.

Methyl 2,2-Dimethyl-6-(nitro)indoline-1-carboxylate (71).[13]

Following ***general procedure C*** starting from Cs_2CO_3 (62.4 mg, 0.19 mmol, 1.1 equiv), $Pd(OAc)_2$ (1.96 mg, 0.0087 mmol, 0.05 equiv), PCy_3•HBF_4 (6.41 mg, 0.017 mmol, 0.10 equiv), PivOH (5.3 mg, 0.052 mmol, 0.30 equiv) and compound **70** (50 mg, 0.17 mmol, 1 equiv) in mesytilene (900 μL). Mixture was stirred at 140 °C for 20 h. The crude was purified by preparative thin layer chromatography (10% Ethyl acetate/cyclohexane) affording the title compound as a yellow oil (27 mg, 0.17 mmol, 62%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s(br), 1H), 7.20-7.10 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 3.85 (s, 3H), 3.02 (s, 2H), 1.57 (s, 6H) ppm.



***N-tert*-butyl-2-chloro-5-fluorobenzenamine.**

To a solution of 2-chloro-5-fluoroaniline (500 mg, 3.45 mmol, 1 equiv) in cyclohexane (5 mL) were added *tert*-butyl-2,2,2-trichloroacetimidate (1.54 mL, 8.63 mmol, 2.5 equiv) and BF_3•OEt_2 (100 μL, 25.8 mL/mol) at room temperature under argon atmosphere. The mixture was stirred at room temperature for 6 h then *tert*-butyl-2,2,2-trichloroacetimidate (1 mL) and BF_3•OEt_2 (100 μL) were added. The reaction mixture was stirred for four extra hours. The mixture was diluted with ethyl acetate, washed with $NaHCO_3$, dried over $MgSO_4$, and evaporated. The crude material was purified by flash chromatography (100% cyclohexane) affording the title compound as a pale yellow oil (655 mg, 3.25 mmol, 94%). R_f 0.79 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.7, 6.1 Hz, 1H), 6.64 (dd, *J* = 11.8, 2.8 Hz, 1H), 6.32-6.25 (m, 1H), 4.43 (s(br), 1H), 1.38 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 240.3 Hz), 144.0 (d, *J* = 11.7 Hz), 129.8 (d, *J* = 10.3 Hz), 115.2 (d, *J* =2.8 Hz), 103.2 (d, *J* = 23.3), 101.3 (d, *J* = 27.8), 51.4, 29.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.07 ppm.

IR (neat) υ 3418, 2977, 1609, 1514, 1203, 831 cm^{-1}.

GC/MS (m/z) $C_{10}H_{13}{}^{35}ClFN$ [$M^{+\cdot}$] 201, (m/z) $C_{10}H_{13}{}^{37}ClFN$ [$M^{+\cdot}$] 203.

Methyl *tert*-butyl-2-chloro-5-fluorophenylcarbamate (72).

A mixture of *N-tert*-butyl-2-chloro-5-fluorobenzenamine (320 mg, 1.59 mmol, 1 equiv) and methyl chloroformate (20 mL) was refluxed overnight. The mixture was evaporated and the residue was purified by flash chromatography (5% Ethyl acetate/cyclohexane) affording the title compound **72** as a white solid (386 mg, 1.49 mmol, 93%). Mp: 61.2 °C. R_f 0.93 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.9, 5.7 Hz, 1H), 6.99-6.93 (m, 1H), 6.88 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.56 (s, 3H), 1.41 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, *J* = 246.7 Hz), 154.6, 140.6 (d, *J* = 8.9 Hz), 130.4 (d, *J* = 8.9 Hz), 130.3 (d, *J* = 3.8 Hz), 118.4 (d, *J* = 22.0 Hz), 115.9 (d, *J* = 22.3 Hz), 58.4, 52.6, 21.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.97 ppm.

IR (neat) υ 2986, 1709, 1328, 1294, 1098, 826 cm^{-1}.

GC/MS (m/z) $C_9H_{13}{}^{35}ClN_2$ [$M^{+\cdot}$] 184, (m/z) $C_9H_{13}{}^{37}ClN_2$ [$M^{+\cdot}$] 186.

Methyl-6-fluoro-2,2-dimethylindoline-1-carboxylate (73).

Following ***general procedure C*** starting from Cs_2CO_3 (68 mg, 0.21 mmol, 1.1 equiv), $Pd(OAc)_2$ (2.16 mg, 0.0096 mmol, 0.05 equiv), PCy_3•HBF_4 (6.99 mg, 0.019 mmol, 0.10 equiv), PivOH (5.82 mg, 0.057 mmol, 0.30 equiv) and compound **72** (50 mg, 0.19 mmol, 1 equiv) in mesytilene (1 mL). Mixture was stirred at 140 °C for 20 h under argon atmosphere. The crude was purified by preparative thin layer chromatography (5% Ethyl acetate/cyclohexane) affording the title compound **73** as a yellow oil (35 mg, 0.16 mmol, 83%). R_f 0.76 (50% Ethyl acetate/cyclohexane).

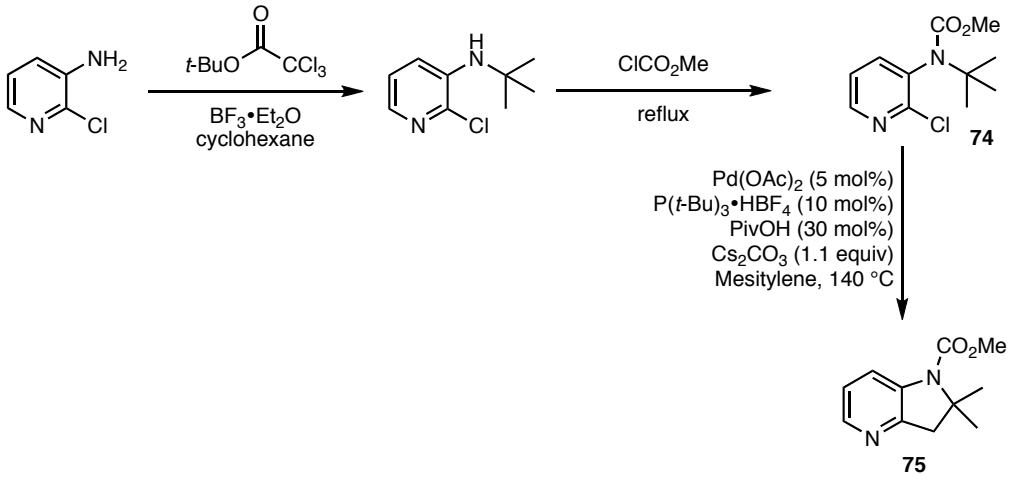
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s(br), 1H), 7.00 (dd, *J* = 6.1, 7.2 Hz, 1H), 6.64 (td, *J* = 2.4, 8.5 Hz, 1H), 3.85 (s, 3H), 2.96 (s, 3H), 1.56 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 239.0 Hz), 153.9, 127.0, 125.0 (d, *J* = 9.4 Hz), 124.0, 109.0 (d, *J* = 22.7 Hz), 104.0 (d, *J* = 29.2 Hz), 52.4, 44.9, 27.3 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.17 ppm.

IR (neat) υ = 2957, 1702, 1368, 1315, 1073, 764 cm^{-1}.

HRMS (EI) calculated for $C_{12}H_{14}FNO_2$ [$M^{+\bullet}$]: 223.1009, found: 223.1008.



***N-tert*-butyl-2-chloropyridin-3-amine.** [14]

To a solution of 3-amino-2-chloropyridine (1 g, 7.75 mmol, 1 equiv) in cyclohexane (10 mL) were added *tert*-butyl-2,2,2-trichloroacetimidate (3.46 mL, 19.3 mmol, 2.5 equiv) and BF_3•OEt_2 (200 μL, 25.8 mL/mol) at room temperature under argon atmosphere. The mixture was stirred at room temperature for 6 h. Monitoring GC/MS did not show a complete conversion. Therefore *tert*-butyl-2,2,2-trichloroacetimidate (1 mL) and BF_3•OEt_2 (100 μL) were added. The reaction mixture was stirred for two extra hours. The mixture was diluted with ethyl acetate, washed with $NaHCO_3$, dried over $MgSO_4$, and evaporated. The crude material was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the title compound **75b** as an incolor oil (1.374 g, 7.47 mmol, 96%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 4.5 Hz, 1H), 7.17 (d, *J* = 8.13 Hz, 1H), 7.04 (dd, *J* = 8.1, 4.6 Hz, 1H), 4.41 (s(br), 1H), 1.40 (s, 9H) ppm.

Methyl *tert*-butyl-2-chloropyridin-3-ylcarbamate (74).

A mixture of *N-tert*-butyl-2-chloropyridin-3-amine (600 mg, 3.26 mmol, 1 equiv) and methyl chloroformiate (16 mL) was heated at 45 °C overnight. The mixture was evaporated and the residue was purified by flash chromatography (10% Ethyl acetate/cyclohexane) affording the

[14] Morris, J.; Wishka, D. *J. Org. Chem.* **1995**, 60, 2642-2644.

title compound **74** as a white solid (250 mg, 1.03 mmol, 32%). R_f 0.5 (50% Ethyl acetate/cyclohexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.26 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.57 (s, 3H), 1.42 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 152.3, 148.1, 139.4, 136.3, 122.6, 58.6, 52.6, 29.3 ppm.

IR (neat) υ = 2952, 1709, 1403, 1331, 1289, 1094, 771 cm^{-1}.

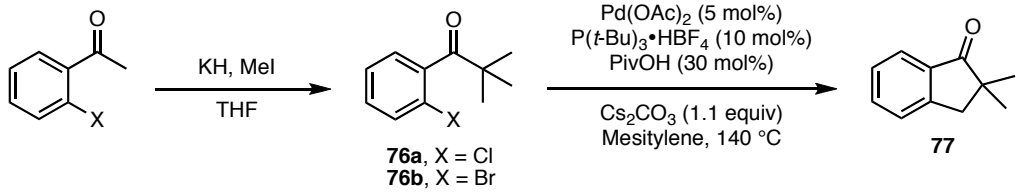
HRMS (CI) calculated for $C_{11}H_{15}ClN_2O_2$ $[M+H]^+$: 243.0900, found: 243.0899.

Methyl-2,2-dimethyl-2,3-dihydropyrrolo[3,2-*b*]pyridine-1-carboxylate (75).[13]

Following ***general procedure C*** starting from Cs_2CO_3 (75 mg, 0.23 mmol, 1.1 equiv), $Pd(OAc)_2$ (2.36 mg, 0.0105 mmol, 0.05 equiv), PCy_3•HBF_4 (7.73 mg, 0.021 mmol, 0.10 equiv), PivOH (6.43 mg, 0.063 mmol, 0.30 equiv) and compound **74** (50 mg, 0.21 mmol, 1 equiv) in mesytilene (1 mL). Mixture was stirred at 140 °C for 16 h. The crude was purified by preparative thin layer chromatography (20% Ethyl acetate/cyclohexane) affording the title compound **75** as a yellow oil (38 mg, 0.18 mmol, 88%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.6 Hz, 1H), 7.62-8.20 (s(br), 1H), 7.04 (dd, *J* = 5.0, 8.0 Hz, 1H), 3.84 (s, 3H), 3.14 (s, 2H), 1.59 (s, 6H) ppm.

Synthesis of indanones by alkane arylation (Table 6)



1-(2-chlorophenyl)-2,2-dimethylpropanone (74a)[15]

Prepared according to ***general procedure E*** using 2'-chloroacetophenone (400 g, 2.59 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (1% Et_2O in petroleum ether) to afford 214 mg of clear oil in 42% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (m, 1H), 7.31 (ddd, *J* = 7.2, 7.2, 1.8 Hz, 1H), 7.27 (ddd, *J* = 7.2, 7.2, 1.5 Hz, 1H), 7.16-7.13 (m, 1H), 1.27 (s, 9H) ppm.

1-(2-bromophenyl)-2,2-dimethylpropanone (74b)[15]

Prepared according to ***general procedure E*** using 2'-bromoacetophenone (0.17 mL, 1.29 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (gradient from 100% petroleum ether to 2% Et_2O in petroleum ether) to afford 186 mg of clear oil in 60% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 7.9, 1.2, 0.4 Hz, 1H), 7.32 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.26-7.20 (m, 1H), 7.13 (dd, *J* = 7.5, 1.8 Hz, 1H), 1.29 (s, 9H) ppm.

2,3-dihydro-2,2-dimethylindenone (75)[16]

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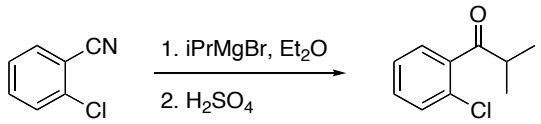
[15] Cahiez, G.; Luart, D.; Lecomte, F. *Org. Lett.* **2004**, *6*, 4395.

[16] Murphy, J. A.; Zhou, S.-z.; Thomson, D. W.; Schoenebeck, F.; Mahesh, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. A. *Angew. Chem. Int. Ed.* **2007**, *46*, 5178.

The title compound was prepared according to the ***general procedure C*** using 1-(2-bromophenyl)-2,2-dimethylpropanone (or 1-(2-chlorophenyl)-2,2-dimethylpropanone) (140 mg, 0.581 mmol, 1 equiv). The product was purified by silica gel flash chromatography (4% Et_2O in petroleum ether) to afford 92 mg of a clear oil in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.59 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.01 (s, 2H), 1.24 (s, 6H) ppm.



1-(2-chlorophenyl)-2-methylpropanone.[17]

A flame dried flask containing magnesium (3.11 g, 128 mmol, 2.2 equiv) under argon was fitted with a condenser. Ether (4 ml) was added to the flask after which 2-bromopropane (14.30 g, 116 mmol, 2.0 equiv) was slowly added as a solution in ether (100 mL, 1.2 M), keeping the reaction at reflux. A solution of 2-chlorobenzonitrile (8 g, 58.2 mmol, 1.0 equiv) in benzene (100 ml, 0.58 M) was slowly added. The reaction was refluxed overnight. The solution was then cooled in an ice bath and the reaction was quenched by the slow addition of 10% H_2SO_4 (200 ml). The solution was heated to reflux for 48 hours to complete the hydrolysis after which the organic layer was separated and the aqueous phase was extracted with Et_2O (2x100 ml). The combined organic extracts were washed with 10% HCl, water and saturated $NaHCO_3$. The organic layer was dried with Na_2SO_4, filtered and concentrated. The crude product was purified by distillation to afford 7.60 g of a clear oil in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 4H), 3.39-3.29 (m, 1H), 1.19-1.17 (m, 6H) ppm.

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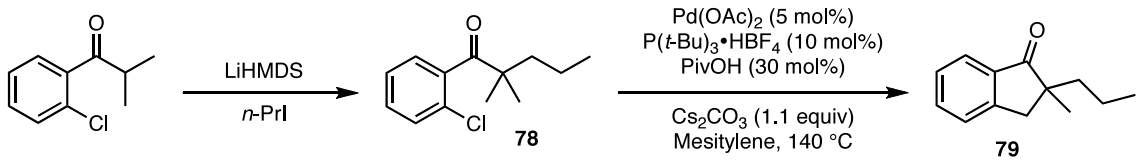
[17] Yoshida, H.; Mimura, Y.;Ohshita, J.; Kunai, A. *Chem. Commun.* **2007**, 2405.



1-(2-chlorophenyl)-2,2-dimethylpentanone (78).

Prepared according to ***general procedure F*** using LiHMDS (1.06M in THF) (5.3 mL, 5.34 mmol, 1.3 equiv) and iodopropane (0.80 mL, 8.21 mmol, 2.0 equiv). The crude product was purified by neutral aluminum oxide flash chromatography (10% toluene in petroleum ether) to afford 281 mg of a pale pink oil in 30% yield. R_f 0.20 (10% toluene in petroleum ether on aluminum TLC plate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 1H), 7.32-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.12-7.10 (m, 1H), 1.64-1.60 (m, 2H), 1.41-1.32 (m, 2H), 1.22 (s, 6H), 0.94 (t, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 140.7, 130.1, 129.8, 129.7, 126.3, 126.1, 48.7, 42.2, 24.7, 17.9, 14.8 ppm.

HRMS calculated for $C_{13}H_{17}OCl$ (M^+ - C_3H_7): 181.0420, found 181.0398.

IR (ν_{max}/cm^{-1}) 3066, 2962, 2873, 1696, 1471, 741 cm^{-1}.

2,3-dihydro-2-methyl-2-propylindenone (79)

The title compound was prepared according to the ***general procedure C*** using 1-(2-chlorophenyl)-2,2-dimethylpentanone **78** (140 mg, 0.623 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_2O in petroleum ether) to afford 59 mg of a yellow oil in 50% yield.

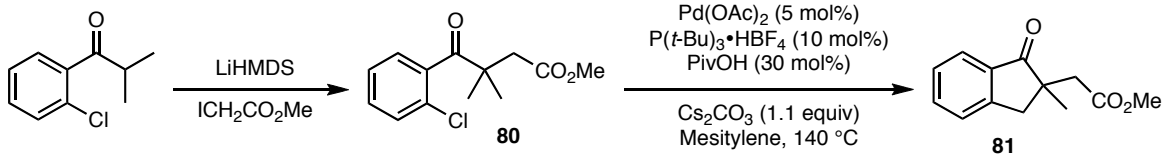
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 1H), 7.58 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H), 7.43 (ddd, J = 7.7, 0.8, 0.8 Hz, 1H), 7.38-7.34 (m, 1H), 3.11 (d, J = 17.2 Hz, 1H), 2.87 (d, J =

17.2 Hz, 1H), 1.64-1.50 (m, 2H), 1.32-1.24 (m, 1H), 1.20 (s, 3H), 1.16-1.08 (m, 1H), 0.86 (t, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 152.9, 136.3, 134.9, 127.5, 126.6, 124.3, 49.3, 40.9, 40.4, 24.1, 18.1, 14.7 ppm.

HRMS (EI) calculated for $C_{13}H_{16}O$ ($M^{+\bullet}$): 188.1201, found 188.1204.

IR (neat) 3074, 3040, 2959, 2930, 1714, 1609, 1466 cm^{-1}.



Methyl 4-(2-chlorophenyl)-3,3-dimethyl-4-oxobutanoate (80).

Prepared according to ***general procedure F*** using LiHMDS (1M solution in THF) (2.71 mL, 2.71 mmol, 1.1 equiv) and methyl 2-iodoacetate (739 mg, 3.70 mmol, 1.5 equiv). The crude product was purified by silica gel flash chromatography (15% Et_2O in petroleum ether) to afford 330 mg of a clear oil in 53% yield. R_f = 0.27 (15% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.41-7.38 (m, 1H), 7.34-7.27 (m, 2H), 3.69 (s, 3H), 2.76 (s, 2H), 1.34 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 172.1, 139.7, 130.1, 130.0, 129.6, 127.6, 126.3, 51.7, 47.0, 44.0, 25.6 ppm.

HRMS calculated for $C_{13}H_{15}ClO_3$ (M^+) 254.0710, found 254.0701.

IR (neat) 3075, 2973, 1737, 1700, 1199, 743 cm^{-1}.

Methyl 2-(2,3-dihydro-2-methyl-1-oxo-1*H*-inden-2-yl)acetate (81).

The title compound was prepared according to the ***general procedure C*** using methyl 4-(2-chlorophenyl)-3,3-dimethyl-4-oxobutanoate **80** (150 mg, 0.589 mmol, 1 equiv). The

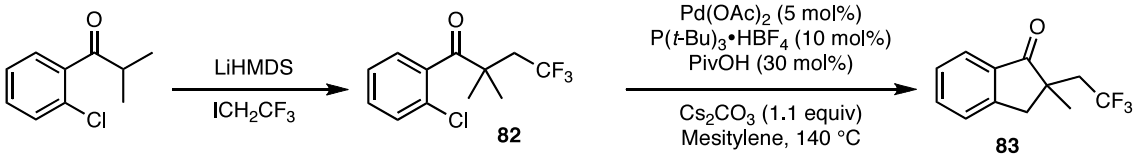
product was purified by silica gel flash chromatography (15% Et_2O in petroleum ether) to afford 99 mg of a white solid in 77% yield. M.p.: 49-52 °C. R_f = 0.17 (15% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.60 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.58 (s, 3H), 3.31 (d, *J* = 17.1 Hz, 1H), 2.97 (d, *J* = 17.1 Hz, 1H), 2.83 (d, *J* = 16.4 Hz, 1H), 2.69 (d, *J* = 16.4 Hz, 1H), 1.23 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 171.9, 152.3, 135.3, 134.9, 127.6, 126.7, 124.5, 51.7, 46.8, 41.5, 40.3, 24.8 ppm.

HRMS calculated for $C_{13}H_{14}O_3$ (M^+) 218.0943, found 218.0958.

IR (neat) 3073, 2958, 2927, 1746, 1710, 1210 cm^{-1}.



1-(2-chlorophenyl)-4,4,4-trifluoro-2,2-dimethylbutanone (82).

Prepared according to ***general procedure F*** using KH (30 wt%) (403 mg, 3.01 mmol, 1.1 equiv) and 1,1,1-trifluoro-2-iodoethane (0.40 mL, 4.11 mmol, 1.5 equiv). The crude product was purified by silica gel flash chromatography (gradient 10% toluene in petroleum ether to 1% Et_2O and 10% toluene in petroleum ether) to afford 103 mg of a clear oil in 14% yield. R_f 0.27 (2% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.35 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.30 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.7 Hz, 1H), 2.62 (q, *J* = 11.5 Hz, 2H), 1.38 (d, *J* = 1.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 139.2, 130.4, 130.0, 129.7, 126.8, 126.6 (q, *J* = 276 Hz), 126.5, 46.0, 41.6 (q, *J* = 27 Hz), 25.1 ppm.

HRMS calculated for $C_{10}H_{10}ClO$ (M^+ - CH_2CF_3) 181.0420, found 181.0339.

IR (neat) 3068, 2988, 1704, 1109, 742 cm^{-1}.

2-(2,2,2-trifluoroethyl)-2,3-dihydro-2-methylindenone (83).

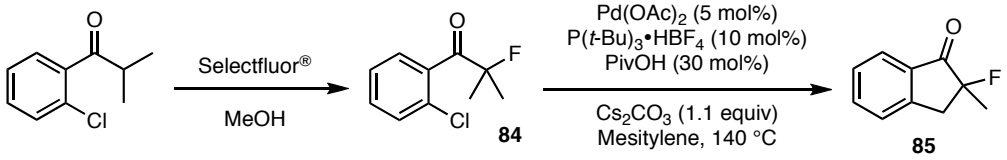
The title compound was prepared according to the ***general procedure C*** using 1-(2-chlorophenyl)-4,4,4-trifluoro-2,2-dimethylbutanone **82** (65 mg, 0.246 mmol, 1 equiv). The crude product was purified by silica gel flash chromatography (3% Et_2O in petroleum ether) to afford 50 mg of a yellow oil in 89% yield. R_f 0.29 (3% Et_2O in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 0.4 Hz, 1H), 7.65 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 7.48 (ddd, *J* = 7.7, 0.9, 0.9 Hz, 1H), 7.44-7.40 (m, 1H), 3.41 (d, *J* = 17.5 Hz, 1H), 3.05 (d, *J* = 17.4 Hz, 1H), 2.62 (dq, *J* = 15.3, 11.1 Hz, 1H), 2.41 (dq, *J* = 15.3, 11.5 Hz, 1H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 152.1, 135.6, 134.2, 128.0, 126.9 (q, *J* = 276 Hz), 126.8, 125.0, 46.0 (q, *J* = 1.7 Hz), 40.0 (q, *J* = 27.6 Hz), 39.9 (q, *J* = 1.6 Hz), 24.4 (q, *J* = 1.4 Hz) ppm.

HRMS calculated for $C_{12}H_{11}OF_3$ (M^+) 228.0762, found 228.0765.

IR (neat) 3085, 2939, 1717, 1609, 1260 cm^{-1}.



1-(2-chlorophenyl)-2-fluoro-2-methylpropanone (84).

To a solution of 1-(2-chlorophenyl)-2-methylpropan-1-one (400 mg, 2.19 mmol, 1.0 equiv) in MeOH (22 ml, 0.1 M) was added Selectfluor® (1.55 g, 4.38 mmol, 2.0 equiv). The reaction was refluxed for 24 hours after which the mixture was cooled to room temperature, extracted with Et_2O (x3), dried with $MgSO_4$ and concentrated. The crude product was purified by silica

gel flash chromatography (10% toluene in petroleum ether) to afford 310 mg of a pale yellow oil in 71% yield. R_f = 0.24 (10% toluene in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 4H), 1.70 (s, 3H), 1.65 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7 (d, *J* = 31.0 Hz), 137.6 (d, *J* = 2.1 Hz), 131.2, 130.7 (d, *J* = 1.4 Hz), 130.1, 127.9 (d, *J* = 4.5 Hz) 126.4, 99.0 (d, *J* = 180.3 Hz), 25.2 (d, *J* = 23.9 Hz) ppm.

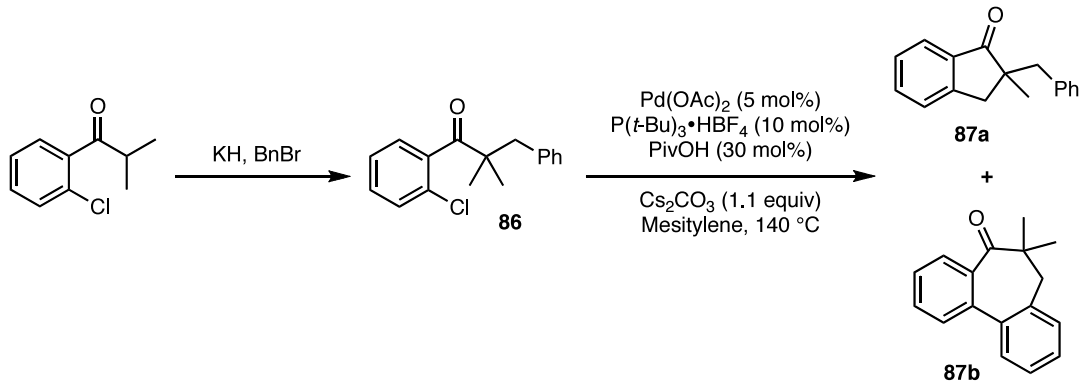
HRMS calculated for $C_{10}H_{10}ClOF$ (M^+) 200.0404, found 200.0391.

IR (neat) 3073, 2989, 1716, 1436, 1195, 741 cm^{-1}.

2-fluoro-2,3-dihydro-2-methylindenone (85).[18]

The title compound was prepared according to the ***general procedure C*** using 1-(2-chlorophenyl)-2-fluoro-2-methylpropanone **84** (139 mg, 0.691 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (gradient of 2% to 4% Et_2O in petroleum ether) to afford 53 mg of a yellow oil in 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.66 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 7.46-7.41 (m, 2H), 3.46 (dd, *J* = 22.4, 17.5 Hz, 1H), 3.30 (dd, *J* = 17.4, 11.2 Hz, 1H), 1.63 (d, *J* = 22.7 Hz, 3H) ppm.



[18] Takeuchi, Y.; Suzuki, T.; Satoh, A.; Shiragami, T.; Shibata, N. *J. Org. Chem.* **1999**, *64*, 5708.

2-benzyl-1-(2-chlorophenyl)-2-methylpropanone (86).

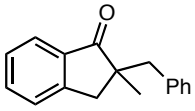
Prepared according to ***general procedure F*** using KH (30 wt%) (659 mg, 4.93 mmol, 1.5 equiv) and benzyl bromide (843 mg, 4.93 mmol, 1.5 equiv). The product was purified by silica gel flash chromatography (2% Et_2O and 20% toluene in petroleum ether) to afford 636 mg of a clear oil in 71% yield. R_f = 0.24 (2% Et_2O and 20% toluene in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 7.19-7.14 (m, 3H), 6.65 (ddd, *J* = 7.6, 1.6, 0.3 Hz, 1H), 2.99 (s, 2H), 1.22 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 140.8, 137.6, 131.1, 129.9, 129.8, 129.3, 128.2, 126.6, 126.4, 125.9, 49.5, 45.5, 24.9 ppm.

HRMS calculated for $C_{17}H_{17}ClO$ (M^+) 272.0968, found 272.0978.

IR (neat) 3029, 2972, 2933, 1696, 703 cm^{-1}.



87a

2-benzyl-2,3-dihydro-2-methylindenone (87a).

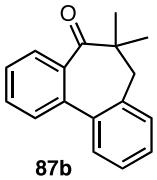
The title compound was prepared according to the ***general procedure C*** using 2-benzyl-1-(2-chlorophenyl)-2-methylpropanone **86** (109 mg, 0.400 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_2O and 20% toluene in petroleum ether) to afford 61 mg of a clear oil in 65% yield. R_f = 0.14 (2% Et_2O and 20% toluene in petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.52 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.34-7.30 (m, *J* = 7.8 Hz, 2H), 7.22-7.13 (m, 5H), 3.24 (d, *J* = 17.2 Hz, 1H), 3.03 (d, *J* = 13.4 Hz, 1H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.74 (d, *J* = 17.2 Hz, 1H), 1.24 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 152.6, 137.9, 135.8, 134.9, 130.3, 128.2, 127.4, 126.6, 126.5, 124.4, 50.5, 43.4, 39.0, 24.7 ppm.

HRMS calculated for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1207.

IR (neat) 3063, 3029, 2924, 1712, 1609, 980 cm^{-1}.



87b

6,6-Dimethyl-6,7-dihydro-dibenzo[a,c]cyclohepten-5-one (87b).

The title compound was prepared according to the ***general procedure C*** using 2-benzyl-1-(2-chlorophenyl)-2-methylpropanone **86** (109 mg, 0.400 mmol, 1 equiv). The product was purified by silica gel flash chromatography (2% Et_2O and 20% toluene in petroleum ether) to afford 30 mg of a clear oil in 32% yield. R_f = 0.19 (2% Et_2O and 20% toluene in petroleum ether)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.47-7.32 (m, 5H), 7.29 (ddd, *J* = 7.3, 7.3, 1.6 Hz, 1H), 7.22 (dd, *J* = 7.4, 1.1 Hz, 1H), 2.83 (s, 2H), 1.21 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 139.9, 138.8, 138.3, 137.0, 131.4, 130.0, 129.3, 128.6, 128.1, 128.0, 127.8, 127.7, 54.0, 44.3, 25.3 ppm.

HRMS calculated for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1193.

IR (neat) 2962, 2927, 1684, 1207, 914 cm^{-1}.

Computational studies

Complete reference for Gaussian03:

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

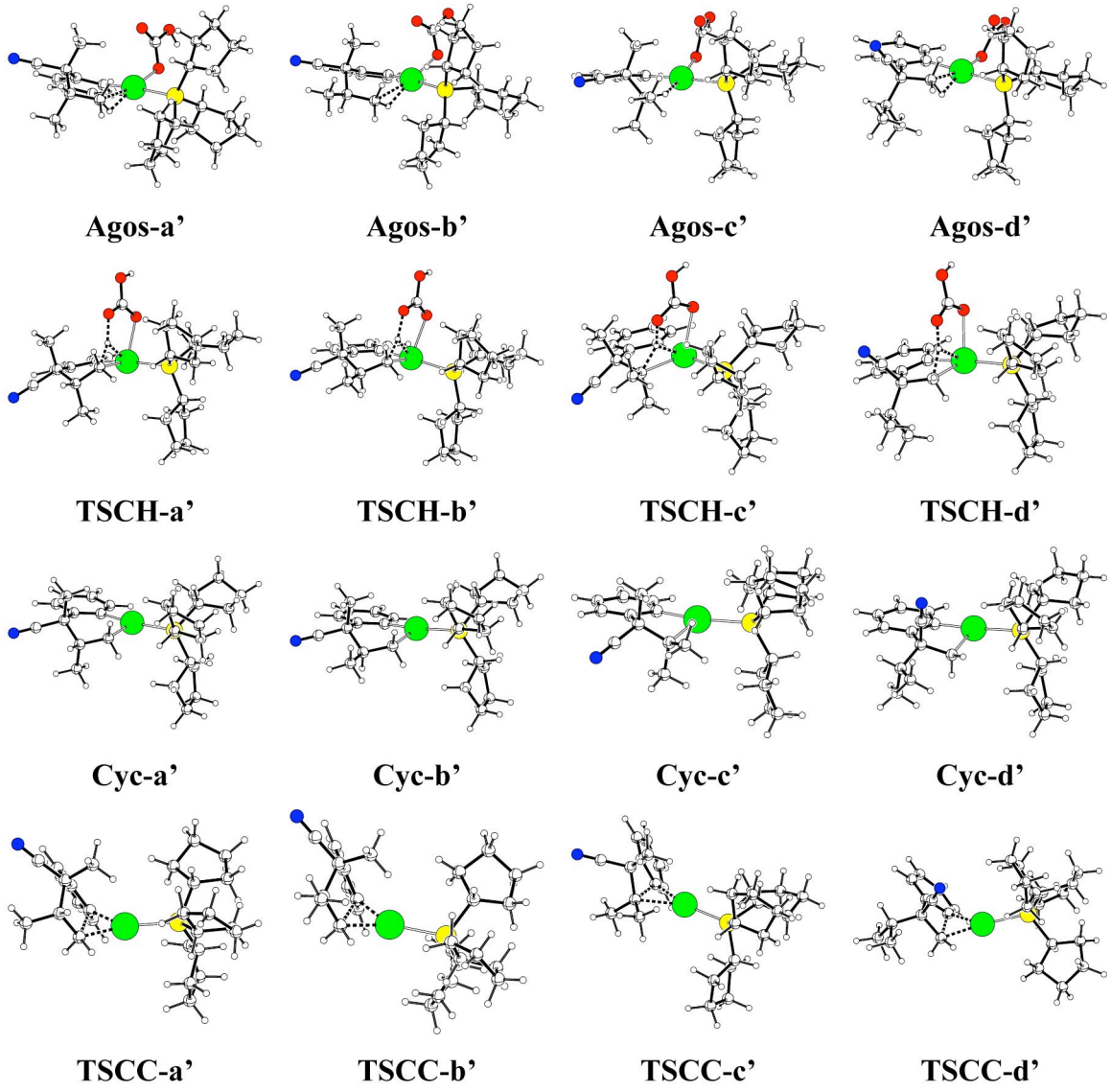


Figure S1. Optimized geometries for the various extrema along pathways a, b, c and d corresponding to C–H activation of **9'** by Pd(PCyp$_3$).

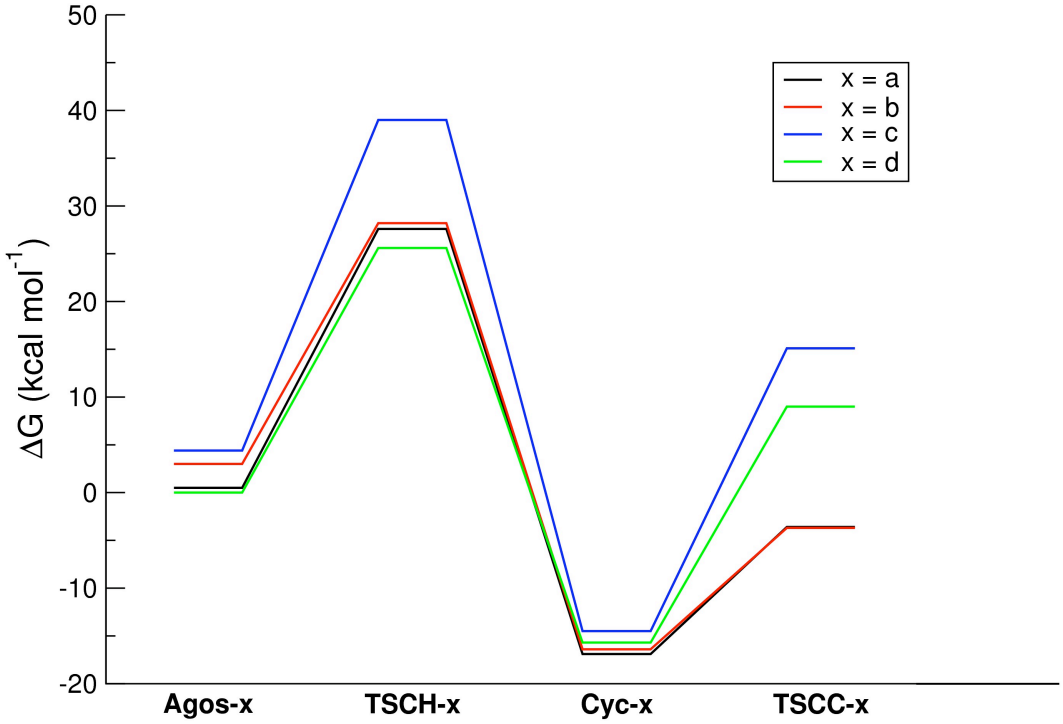


Figure S2. Comparison of the Gibbs free energy profiles along pathways a, b, c and d for C–H activation of **9'** by Pd($PCyp_3$).

Cartesian coordinates (Å), Gibbs free energy G (a.u.) for the molecules optimized.

Agos-a

Sum of PCM and thermal Free Energies= -1919,437208

C,0,2.1905692565,-1.1050942706,2.4798493573
C,0,3.3299347113,-1.5390874055,3.1572923878
C,0,4.5614228784,-1.5067571696,2.5125256983
C,0,4.6389263588,-1.052842365,1.1993531946
C,0,3.5009793514,-0.6223617848,0.5004198585
C,0,2.2565127476,-0.6497924224,1.1579597844
H,0,1.2329652508,-1.1085617845,2.9922420962
H,0,3.2505071812,-1.8919923209,4.1826007915
H,0,5.4637482929,-1.8296123621,3.0243756976
H,0,5.6062405921,-1.0262170882,0.7053177355
C,0,3.6251996255,-0.1480292765,-0.9580393897
H,0,0.9905808693,-1.5205077291,-0.7917877553
Pd,0,0.4571625359,-0.2127741477,0.3472621709
C,0,0.4704167295,2.0135881125,2.0727831686
O,0,0.0087959818,0.7896666519,2.0719238946
O,0,0.3192078991,2.6195727823,3.2802930714
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H,0,0.8010973711,-1.6211874647,-2.4943716753
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H,0,2.7659589603,-3.1866916077,-2.5335048895
H,0,4.3573719475,-2.665292503,-1.9680409968
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H,0,-3.1701000557,4.8726163285,0.0930580851
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H,0,-3.7337511981,-2.1898438463,-3.850543579

Agos-b

Sum of PCM and thermal Free Energies= -1919,430637

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C,0,3.4771983399,-0.2043275977,-0.5377438474
C,0,2.2530398891,-0.7053761813,-1.0182250331
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Agos-c

Sum of PCM and thermal Free Energies=   -1919,426375

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C,0,-4.983249982,0.3039538649,-0.4300816155
C,0,-3.6494825306,0.0806654122,-0.0741787589
C,0,-2.6399264587,0.8741446415,-0.6516430759
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Pd,0,-0.7276623686,0.4042425008,-0.3221316973
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H,0,-6.3607370963,1.4668376489,-1.6017960071
H,0,-5.7666817848,-0.3094557556,0.0075859357
H,0,-1.2321536347,-1.3460407509,0.0427720382
P,0,1.6452653373,-0.2143399339,-0.0720100228
C,0,1.9531448874,-1.1694626546,1.5132368694
C,0,3.2694947813,-1.9619580279,1.6978216226
C,0,1.8418699857,-0.3244282023,2.7934903943
C,0,3.4759578831,-2.0619935475,3.2356154254
C,0,2.2896352366,-1.3117726352,3.8737737972
C,0,2.8190925709,1.2470801786,-0.0355828787
C,0,4.3317216128,0.9609727051,0.1089421805
C,0,2.6942339604,2.2005942559,-1.2688324437
C,0,5.0008885666,2.1806405459,-0.5329147899
C,0,4.1324109125,2.4294848449,-1.7673318918
C,0,2.2752648471,-1.3751704174,-1.3993087038

C,0,2.0842271309,-0.8706378488,-2.8422296413
C,0,1.5429481625,-2.7260063695,-1.4235092169
C,0,2.1229545006,-2.1415650207,-3.7287760869
C,0,1.9760966599,-3.3404828999,-2.7619737932
H,0,1.1226424641,-1.890821456,1.5277383397
H,0,4.1136763882,-1.4434923607,1.2372723499
H,0,3.2125325531,-2.947476492,1.2256732209
H,0,0.8473782252,0.100476549,2.946823754
H,0,2.5424131275,0.5187204305,2.7527774068
H,0,3.5347599164,-3.1004215614,3.5756667007
H,0,4.421198905,-1.5865260938,3.5184294688
H,0,1.4725264161,-2.0102393723,4.0945656871
H,0,2.5554034699,-0.8217601967,4.8154256671
H,0,2.474748202,1.7913587165,0.8504604079
H,0,4.623179048,0.064377264,-0.4524938302
H,0,4.6282877142,0.8050179002,1.1505149944
H,0,2.2497881009,3.1433891053,-0.941781674
H,0,2.0374800356,1.8144463185,-2.0516381679
H,0,4.9441250143,3.0400615082,0.1472585022
H,0,6.0573808894,2.013504518,-0.7670346397
H,0,4.2701213978,3.4246356849,-2.2015164264
H,0,4.3911887178,1.7003341173,-2.5464481455
H,0,3.3414478498,-1.5614120005,-1.2131339255
H,0,2.8382236096,-0.1352958917,-3.1351982095
H,0,1.1055375251,-0.3810457606,-2.9266083205
H,0,0.4588550987,-2.5503212054,-1.4262628833
H,0,1.7729221847,-3.3645831021,-0.5655517394
H,0,1.3167856938,-2.1201966118,-4.4684483161
H,0,3.0601130703,-2.2052661037,-4.290262273
H,0,1.2682501323,-4.0927848957,-3.123278191
H,0,2.939929881,-3.8466303238,-2.6349977468
C,0,-0.0645555801,2.9383484598,0.679716561
O,0,-0.32839063,2.3992519422,-0.4788634202
O,0,0.1369058028,4.2816524996,0.5838305691
O,0,0.0364687308,2.3827664909,1.7629154991
H,0,-0.0294994421,4.5196814783,-0.3380221207
C,0,-1.7458551605,-3.1986090675,0.9538271991
H,0,-1.1197944709,-3.8203462058,0.307352766
H,0,-1.1836049031,-2.9814392729,1.8593502619
H,0,-2.6225518559,-3.7922473628,1.233391903
C,0,-2.7023315701,-2.3897489848,-1.1891046165
H,0,-2.9775871026,-1.5506888092,-1.8278975748
H,0,-1.9379281822,-2.982999284,-1.6996100126
H,0,-3.5838127345,-3.0281473,-1.061007604
C,0,-2.7220656922,-0.2850713151,2.2387282987
H,0,-1.8597499807,0.3169873093,1.9113839558
C,0,-4.3738793081,-1.8567393103,1.2859584795
N,0,-5.2538795948,-2.5503023654,1.5948152694
C,0,-2.2809493461,-1.2012004194,3.386502025
H,0,-2.189932316,-0.6068505445,4.3007416819
H,0,-3.0137098537,-1.9915292088,3.5826214803
H,0,-1.3067419425,-1.6630613282,3.2189013258
C,0,-3.7864897174,0.6848710215,2.7674887512
H,0,-4.6740269988,0.1452564633,3.1186760069
H,0,-3.3758369579,1.2413286846,3.6148304048
H,0,-4.1007250488,1.4092885463,2.0141686371

TSCH-a

Sum of PCM and thermal Free Energies= -1919,395489

C,0,2.1642593053,1.198581867,2.0512214965
C,0,3.2462504962,1.3406126853,2.9216015367
C,0,4.4599613132,0.7456691162,2.5899157281
C,0,4.585258169,0.0310836762,1.4004236347
C,0,3.5064610131,-0.1251182607,0.5167025048
C,0,2.2797654951,0.4356725502,0.8869249893
H,0,1.2199936682,1.6965552065,2.2804491514
H,0,3.1413674227,1.9218982035,3.8338338043
H,0,5.3186931182,0.8462376704,3.2476170037
H,0,5.5414566139,-0.4214894993,1.1515708481
C,0,3.6797498548,-0.8630483217,-0.8164271105
H,0,0.9704224911,0.3278277979,-1.4085726212
Pd,0,0.4261000003,0.154399701,0.2725684928
C,0,0.5770392515,2.5908107048,-1.3111005494
O,0,0.1893109731,2.4973925402,-0.115292932
O,0,0.6656369453,3.8341988838,-1.8435262225
O,0,0.8925926126,1.6514909201,-2.0984777396
H,0,0.4234922376,4.4368284272,-1.1269831089
C,0,2.4594893641,-1.8048651985,-1.0950508438
H,0,2.7397899374,-2.3864320829,-1.9842939704
C,0,3.91865848,0.1669781345,-1.9871621331
H,0,3.0302860306,0.8074039303,-1.9993359942
C,0,1.1711990763,-1.0613089514,-1.4453663021
H,0,1.2092976774,-0.721766919,-2.4921841107
H,0,0.32259054,-1.74791581,-1.4140238911
C,0,2.2403202857,-2.8138789728,0.0338751823
H,0,1.4799526735,-3.5444728932,-0.262386317
H,0,3.1576024622,-3.3638115376,0.2648332753
H,0,1.8957984535,-2.3154818385,0.9463851196
C,0,4.053603711,-0.509654129,-3.3553195509
H,0,3.1596232288,-1.0686310767,-3.6467362853
H,0,4.218965681,0.2525453281,-4.1230439764
H,0,4.9069976153,-1.1968736618,-3.379283532
C,0,5.1343282364,1.0622401233,-1.7327709464
H,0,5.2225982795,1.7958796082,-2.5401595186
H,0,5.0504592207,1.6111687475,-0.7917058396
H,0,6.0626461268,0.479781865,-1.7092787222
C,0,4.8672737169,-1.7349556342,-0.756768927
N,0,5.8009963509,-2.4271616886,-0.7546454997
P,0,-1.9877756083,-0.1764417255,0.0551263257
C,0,-2.6409724382,-0.4174618755,-1.683730668
C,0,-2.8701475996,1.3138912586,0.7629461333
C,0,-2.6444750476,-1.6737217737,0.9635600427
C,0,-4.1056832683,-0.8860458558,-1.8763790259
C,0,-2.49807301,0.8055442347,-2.6065019974
H,0,-1.9782222511,-1.1974245002,-2.0850735817
C,0,-4.3883603536,1.2697437066,1.0137058573
C,0,-2.247096742,1.791514215,2.1094100064
H,0,-2.6648068934,2.0926514805,0.0191244585
C,0,-2.2188945755,-1.7684960196,2.4391452747
C,0,-2.1183932445,-2.9971967816,0.3859516957
H,0,-3.7405987297,-1.6675638181,0.8974982145
C,0,-4.5517894237,-0.3013817258,-3.2447432224
H,0,-4.7552265527,-0.520644139,-1.0763914483
H,0,-4.1722919379,-1.9781800107,-1.8551626986
C,0,-3.3048082536,0.3789695408,-3.8360428885
H,0,-1.4568688946,1.0601140997,-2.8222959522
H,0,-2.9689469669,1.6872732536,-2.1523494968
C,0,-4.6069925818,2.4346866328,1.9850565022
H,0,-4.6832291299,0.3297921315,1.4979340982

H,0,-4.97351827,1.3660801574,0.0942356831
C,0,-3.4307076939,2.3092191628,2.9613544772
H,0,-1.5065405346,2.5686627521,1.9063216705
H,0,-1.7199371026,0.986966325,2.6324953976
C,0,-2.3922800578,-3.2608267088,2.8121650284
H,0,-2.7910853937,-1.1026880404,3.0919008938
H,0,-1.1622353621,-1.4822754643,2.5287811985
C,0,-2.4714662924,-4.0292859402,1.4693928836
H,0,-1.0290089393,-2.9290926948,0.2705374407
H,0,-2.5418119146,-3.2464216832,-0.5917528289
H,0,-4.9628247656,-1.0678479094,-3.9087140149
H,0,-5.343973651,0.4401510776,-3.0926973643
H,0,-2.720277577,-0.3393935908,-4.4245537063
H,0,-3.5501412128,1.2149263138,-4.4982485664
H,0,-4.5457051936,3.3839080094,1.4376478934
H,0,-5.5831418925,2.4051188309,2.4800956199
H,0,-3.1992670866,3.2506117876,3.4686644341
H,0,-3.6810594325,1.5809672856,3.7421645279
H,0,-1.5578927309,-3.605772157,3.4300286458
H,0,-3.3019588677,-3.4135899856,3.4013618705
H,0,-1.8073030565,-4.898232263,1.4409542066
H,0,-3.4887559986,-4.4019291842,1.3049965567

TSCH-b

Sum of PCM and thermal Free Energies= -1919,386802

C,0,1.8502113251,-1.5401407147,2.0858160971
C,0,2.8343103261,-2.3710683757,2.6235602304
C,0,4.089048483,-2.4026229104,2.0219546998
C,0,4.352855872,-1.6047617244,0.9102810862
C,0,3.3731889506,-0.7697667394,0.3523398845
C,0,2.1006164165,-0.7894515991,0.9353994638
H,0,0.8765763293,-1.4678804596,2.576135057
H,0,2.6250262555,-2.9663090018,3.5083779033
H,0,4.8746192717,-3.0358163273,2.424575613
H,0,5.3420326458,-1.6316399144,0.4611615621
C,0,3.6886204114,0.149362499,-0.8416360789
H,0,0.9837048031,1.3533056764,-0.1953438822
Pd,0,0.3171260227,-0.2162230741,0.3241724393
C,0,0.5107138631,2.2475886298,1.861154889
O,0,0.0508850859,1.1469896049,2.266347072
O,0,0.5990607532,3.2579031069,2.7606650188
O,0,0.9015025101,2.5421149354,0.6928557709
H,0,0.2928614765,2.8816284612,3.5973275168
C,0,2.5063681055,0.0184507292,-1.8755458084
C,0,3.9743435562,1.6080609889,-0.3095304201
H,0,3.0591329663,1.9131511574,0.2079538778
C,0,1.2397781613,0.7601153331,-1.4449939738
H,0,1.3754586767,1.8418134195,-1.6065383001
H,0,0.4137161705,0.4937036804,-2.1076340897
C,0,4.2686402953,2.6320853134,-1.4100520211
H,0,3.4015960928,2.8384863162,-2.041279781
H,0,4.5573447178,3.5823345876,-0.9496627127
H,0,5.0961155678,2.3107159003,-2.052592808
C,0,5.1162004732,1.6269564034,0.7127533932
H,0,5.2360173306,2.6422986923,1.1034346316

H,0,4.9260484925,0.9649644067,1.560818314
H,0,6.0676005464,1.3325813745,0.2546991901
C,0,4.9128043614,-0.3291155849,-1.5052089581
N,0,5.8875176994,-0.6769028949,-2.034524545
P,0,-2.0493278619,-0.0181366959,-0.2452379186
C,0,-2.5456632464,1.5030002452,-1.2176646602
C,0,-3.0669068503,-0.0088642125,1.3270429455
C,0,-2.6988181248,-1.4233863391,-1.2943736408
C,0,-3.9589516062,1.5567440446,-1.8517121196
C,0,-2.4087915361,2.8321326755,-0.4536434508
H,0,-1.804769321,1.5264415455,-2.0293926597
C,0,-4.5979408085,-0.1634700725,1.2556518762
C,0,-2.5908307151,-1.0828466675,2.3526900669
H,0,-2.836597756,0.9727147472,1.7573203826
C,0,-2.4340601785,-2.8281703081,-0.7225314389
C,0,-2.0362755677,-1.5020579093,-2.6794528232
H,0,-3.7793509666,-1.2818701772,-1.4299741116
C,0,-4.3401768244,3.0618957742,-1.8884955034
H,0,-4.6872799706,0.9934512552,-1.2620941331
H,0,-3.9560111755,1.1101916041,-2.8508041533
C,0,-3.0947828201,3.821312787,-1.399689017
H,0,-1.3710870146,3.083499534,-0.218685622
H,0,-2.9656297006,2.7910922966,0.491703948
C,0,-4.9679492851,-0.6088874562,2.6749559858
H,0,-4.8850829294,-0.9461207465,0.5417021607
H,0,-5.1022218784,0.759066926,0.9522433766
C,0,-3.874853952,-1.625887829,3.0216428226
H,0,-1.915935584,-0.6169632283,3.0752154572
H,0,-2.0284457054,-1.8941689959,1.8796774836
C,0,-2.5252179077,-3.7854212647,-1.9379058251
H,0,-3.1292247134,-3.0979673512,0.0778013381
H,0,-1.4220518124,-2.8620665139,-0.2974751144
C,0,-2.4626036987,-2.8846092953,-3.1950296452
H,0,-0.9451126828,-1.4650876679,-2.5621500209
H,0,-2.3270829504,-0.6885740449,-3.351269321
H,0,-4.6623289441,3.3842353485,-2.8832689662
H,0,-5.1796611562,3.2501466198,-1.2098527997
H,0,-2.4273119737,4.0447022976,-2.2415638163
H,0,-3.3391719143,4.7739692815,-0.919803709
H,0,-4.9160684608,0.2506842343,3.3554141799
H,0,-5.9796365452,-1.0215691437,2.7458395302
H,0,-3.7545013421,-1.7709099059,4.099472559
H,0,-4.1381060425,-2.6023206169,2.5970713208
H,0,-1.7054676237,-4.5099115225,-1.9199417622
H,0,-3.4541321086,-4.3636849825,-1.9166640189
H,0,-1.7806956501,-3.2709106657,-3.9584621496
H,0,-3.4526994923,-2.8119935233,-3.6594230583
C,0,2.8441097844,0.3721030677,-3.3335650998
H,0,2.0031918995,0.0793267543,-3.9716944146
H,0,3.0145087607,1.4398843126,-3.4863297497
H,0,3.7289163625,-0.1654530417,-3.6849439851
H,0,2.2765126353,-1.0538652786,-1.8755399869

TSCH-c

Sum of PCM and thermal Free Energies=   -1919,372541

C,0,-2.5946852531,-2.2492145582,-1.029586263
C,0,-3.7691867274,-3.0008223206,-0.9361623687
C,0,-4.8622619752,-2.4883855595,-0.2389085913

C,0,-4.8005449228,-1.2191596008,0.3355051469
C,0,-3.6396706869,-0.4447789349,0.2297978941
C,0,-2.5272716404,-1.0033499533,-0.4078419378
C,0,-3.5054744206,0.9833193242,0.7376004043
C,0,-1.9673951184,1.1824762962,1.1098698475
Pd,0,-0.7124793523,-0.3293159937,-0.1680643479
H,0,-1.7364433877,-2.6392118135,-1.5764870184
H,0,-3.82522107,-3.9797650446,-1.4052306409
H,0,-5.7723661651,-3.0746058424,-0.1481382015
H,0,-5.6585384033,-0.829283084,0.8772297951
H,0,-1.3399678903,1.3302389195,-0.287416844
P,0,1.7197833059,-0.0543504354,0.2153961001
C,0,2.3386876431,1.6101331148,0.8178581618
C,0,3.7969160346,1.7407330065,1.3269526643
C,0,2.1797674389,2.7534397166,-0.1990879027
C,0,4.2096004096,3.2089811414,1.0304044023
C,0,2.9510713299,3.8940830395,0.4690550993
C,0,2.6108765214,-0.3830760001,-1.4016180786
C,0,4.1471304887,-0.4919778814,-1.4238625841
C,0,2.0954008361,-1.6593450818,-2.1365666764
C,0,4.4229104918,-1.2238739439,-2.7412349571
C,0,3.3454092209,-2.3139820725,-2.768036202
C,0,2.4687467675,-1.2504996685,1.4478685967
C,0,2.1460821134,-2.7351767765,1.1976452651
C,0,1.9875660525,-1.0524174601,2.8929833364
C,0,2.4114891407,-3.4393574702,2.5524325754
C,0,2.5013904031,-2.3106226446,3.6078994176
H,0,1.6662347908,1.8292192069,1.6588154486
H,0,4.4692405477,1.0461374302,0.8165487028
H,0,3.8603153483,1.5058031795,2.3938963033
H,0,1.1357216646,2.9853481109,-0.424546117
H,0,2.6701237541,2.4922479758,-1.1460851023
H,0,4.5992163124,3.7173773881,1.9174706153
H,0,5.0089737717,3.2276533374,0.281206049
H,0,2.3490974238,4.3159350616,1.2838578785
H,0,3.1839694587,4.7136265732,-0.2178074607
H,0,2.3221158439,0.4783729363,-2.0147977217
H,0,4.5157923653,-1.0999830404,-0.5878285673
H,0,4.6405991227,0.4829155524,-1.3653978181
H,0,1.3561857888,-1.3656506368,-2.8845196684
H,0,1.5893501798,-2.3582459697,-1.4634267479
H,0,4.2836395181,-0.5326547157,-3.5824348709
H,0,5.4413732675,-1.6202666206,-2.8082869287
H,0,3.15237743,-2.6984624356,-3.774153306
H,0,3.6760758414,-3.1652164913,-2.1599165803
H,0,3.5576185217,-1.1105267179,1.4228134301
H,0,2.7329700512,-3.1647700215,0.3809991067
H,0,1.0868716358,-2.8365352576,0.9250780213
H,0,0.8914039895,-1.0353554633,2.9123092618
H,0,2.342971063,-0.1248751357,3.3522959813
H,0,1.6079487933,-4.144998801,2.7840213913
H,0,3.3383728977,-4.0203554392,2.5201164529
H,0,1.9315626114,-2.5330193283,4.5149326993
H,0,3.5427955908,-2.1593582899,3.9144115973
C,0,-0.84068755,1.4189100785,-2.4588772581
O,0,-0.5255913746,0.2039479264,-2.4856137651
O,0,-0.911886147,2.0846001291,-3.6342051805
O,0,-1.1029379369,2.1302954515,-1.4373711208
H,0,-0.708431481,1.4279490837,-4.3148724907
C,0,-1.5594035922,2.6355458071,1.3724497447
H,0,-0.4954422117,2.6728388636,1.6258720242

H,0,-1.7180780456,3.3031500496,0.5257776747
H,0,-2.1108416958,3.0206882184,2.2419116952
C,0,-1.6549253371,0.4126180822,2.4125110273
H,0,-1.9481086041,-0.6398853106,2.3793740319
H,0,-0.5910992736,0.4704972596,2.6507233807
H,0,-2.1965915827,0.8804196698,3.248273272
C,0,-4.0530477923,2.0337493987,-0.3293064798
H,0,-3.1969419916,2.2580557543,-0.970548687
C,0,-4.3178167493,1.1328661645,1.9586859955
N,0,-4.9678312485,1.2541940463,2.9151995314
C,0,-4.549029527,3.3453257664,0.2969413429
H,0,-3.839103199,3.7927900216,0.9939105914
H,0,-4.7337208767,4.0737423249,-0.4995534371
H,0,-5.4895855779,3.1943846747,0.8364953714
C,0,-5.1660261884,1.4801566133,-1.2237110645
H,0,-5.4761997736,2.2610974438,-1.9261063922
H,0,-4.8463546745,0.6132470224,-1.8057950743
H,0,-6.0505699077,1.1938979939,-0.6431297458

Cyc-a

Sum of PCM and thermal Free Energies= -1654,556691

C,0,4.4923600389,-1.0530061796,-2.5970448224
C,0,4.617266507,-0.3907713203,-1.376157077
C,0,3.4883202248,0.0557749444,-0.6800674759
C,0,2.2111057283,-0.1513186394,-1.2177809275
C,0,2.1032074599,-0.824692675,-2.4440967796
C,0,3.2290141261,-1.2783359778,-3.1353696577
C,0,3.6089944926,0.7445943635,0.6852429684
C,0,2.6447554987,1.9771534584,0.7363504367
C,0,1.1768687675,1.589493548,0.7992980158
H,0,5.3824909477,-1.3868824404,-3.1232579871
H,0,5.6075078384,-0.2174832441,-0.9621422117
H,0,1.1194795148,-0.9894703832,-2.8918170947
H,0,3.117661046,-1.7876115311,-4.0896538372
H,0,2.8660241556,2.4905765258,1.685310582
H,0,0.5603445812,2.4882012561,0.6767801531
H,0,0.9209253004,1.1210849258,1.7568485269
Pd,0,0.386625156,0.2859595583,-0.5415231312
C,0,4.9748334992,1.2563797563,0.8902444813
N,0,6.044946567,1.6611247338,1.0966447388
C,0,3.3192641332,-0.2902828477,1.8375915064
C,0,4.2629642999,-1.4943239026,1.7871942536
H,0,2.3039656973,-0.650516898,1.6302254386
H,0,3.9935038361,-2.2098900959,2.5711667349
H,0,5.3024293158,-1.191646913,1.9579060237
H,0,4.2121295879,-2.0117419921,0.8262654744
C,0,2.9283829864,2.9798177335,-0.3845547065
H,0,2.6657836457,2.5615692706,-1.3602623089
H,0,2.3335402245,3.8866942704,-0.2304086466
H,0,3.9826777333,3.272505536,-0.4046342233
C,0,3.3563516682,0.3389850862,3.233912039
H,0,4.3448918004,0.7593896281,3.4502524604
H,0,2.6162043029,1.1338292269,3.3640316864
H,0,3.151244673,-0.426007768,3.9903083741
P,0,-1.9584289005,0.5817867836,-0.0479812486
C,0,-2.3904537288,1.1443636414,1.685528019
C,0,-2.90266338,-1.0232893056,-0.3125518783

C,0,-2.7985829288,1.8633402536,-1.1196200233
C,0,-3.8594908738,1.4747078306,2.0129745755
C,0,-1.9881266774,0.1748042113,2.8074251927
H,0,-1.7870369045,2.0553182364,1.8108407332
C,0,-4.4256824604,-1.0041567243,-0.6273652015
C,0,-2.2707125676,-1.8849458784,-1.427859743
H,0,-2.749781522,-1.5641270108,0.6297082942
C,0,-2.6414359206,1.6132363689,-2.6289470272
C,0,-2.2090615578,3.2738553589,-0.957431878
H,0,-3.865185432,1.8948608718,-0.8607620582
C,0,-3.9486646373,1.4304511273,3.561747367
H,0,-4.5224929372,0.7185447073,1.5792322333
H,0,-4.1685062859,2.4405633183,1.6024677353
C,0,-2.6136886223,0.8195547122,4.0513030762
H,0,-0.9066864431,0.0341373014,2.8888621705
H,0,-2.4348653542,-0.8132786857,2.6358975557
C,0,-4.6439238942,-2.0715834972,-1.7286789882
H,0,-4.7761558364,-0.0249772036,-0.9650443777
H,0,-4.9984395527,-1.2437461513,0.2742387779
C,0,-3.3614202599,-2.9125330952,-1.7365554921
H,0,-1.3208432643,-2.3317675054,-1.114940599
H,0,-2.0723345254,-1.2804618003,-2.3227962647
C,0,-2.9252064107,2.9823314202,-3.2915389781
H,0,-3.2968125686,0.8200113124,-3.0017555099
H,0,-1.6069380712,1.3060270089,-2.8328586887
C,0,-2.7714614955,4.0383452674,-2.1679081866
H,0,-1.1149425928,3.2181146904,-1.0199251407
H,0,-2.464358433,3.7465063678,-0.0035489385
H,0,-4.103415747,2.4280854207,3.9836613429
H,0,-4.8022320665,0.8229159589,3.8787584122
H,0,-1.9499911921,1.6097304982,4.4211305029
H,0,-2.7497248704,0.1083706805,4.8716277155
H,0,-5.5450257648,-2.6688816956,-1.5592828399
H,0,-4.7650676897,-1.583247394,-2.7028818398
H,0,-3.3947886549,-3.666208688,-0.939301906
H,0,-3.2011931234,-3.4414348568,-2.6812190174
H,0,-2.2341439244,3.1643729318,-4.1199351231
H,0,-3.9348349255,3.0098693982,-3.7136659524
H,0,-2.1264162557,4.8724163055,-2.4596595608
H,0,-3.7478011015,4.4663934948,-1.9141872493

Cyc-b

Sum of PCM and thermal Free Energies=   -1654,554671

C,0,-4.4912519905,-2.8240042795,-0.9316560368
C,0,-4.6042154961,-1.4751645246,-0.5945709042
C,0,-3.4750708374,-0.7221072362,-0.2570774802
C,0,-2.2072534306,-1.3245368436,-0.2541025263
C,0,-2.1131837108,-2.6828959834,-0.5942870381
C,0,-3.2408127297,-3.4339859906,-0.9354993259
C,0,-3.5722388166,0.7691441878,0.1121175991
C,0,-2.7333792532,0.9432566416,1.433702389
C,0,-1.2328531593,0.903591082,1.1924000279
H,0,-5.3820926224,-3.3927157474,-1.1842531287
H,0,-5.585204057,-1.0065364674,-0.5922892212
H,0,-1.1416887062,-3.1815775878,-0.5807503108
H,0,-3.141167029,-4.4875451815,-1.1857937913
H,0,-0.7185293435,0.7602737597,2.150499235

H,0,-0.8766652548,1.8409703176,0.7454140383
Pd,0,-0.4003696346,-0.518150498,0.0078993008
C,0,-4.9686014815,1.1259382744,0.4026110219
N,0,-6.0670818278,1.4395279025,0.6191342458
C,0,-3.1012626024,1.6384691519,-1.1146513568
C,0,-3.9280122474,1.3416843114,-2.3697248539
H,0,-2.0725803047,1.3023808209,-1.2999178129
H,0,-3.5255326137,1.903586014,-3.2192704697
H,0,-4.9728852928,1.6454495564,-2.237309221
H,0,-3.9128642169,0.2803818799,-2.6285353575
C,0,-3.0930059549,3.1475080793,-0.8553300395
H,0,-4.0752851444,3.5021092508,-0.5235559584
H,0,-2.3537966927,3.4440904348,-0.1076650367
H,0,-2.8491588512,3.6782334747,-1.7821845274
P,0,1.915712404,0.1630825904,0.0366743871
C,0,2.235011542,2.0075236038,0.0386144062
C,0,2.7378158108,-0.4996282181,-1.5200074029
C,0,2.94843407,-0.4367384585,1.4756700659
C,0,3.6911868409,2.5107478446,0.0940283777
C,0,1.6356284623,2.7699393064,-1.1527177245
H,0,1.7090853755,2.3502865803,0.9416282229
C,0,4.2803785934,-0.6736104909,-1.5942469989
C,0,2.1579470903,-1.8686225223,-1.9355697083
H,0,2.4305496353,0.2197063607,-2.2895157666
C,0,2.8987587196,-1.9570186447,1.6994897826
C,0,2.4638959519,0.1088729584,2.8287992155
H,0,3.9888855865,-0.1217064669,1.318376138
C,0,3.6403739887,3.9681455777,-0.4410580627
H,0,4.3293007404,1.8969697027,-0.5497705445
H,0,4.1090199222,2.4500117843,1.1034614743
C,0,2.2008598603,4.182710028,-0.9632697044
H,0,0.5427793326,2.7348435968,-1.1787369497
H,0,2.0002656649,2.3485695929,-2.098875654
C,0,4.5207497102,-2.010344869,-2.3409142903
H,0,4.7496896622,-0.6950174872,-0.6068137498
H,0,4.7291926252,0.1673566476,-2.1323072465
C,0,3.1683719372,-2.3761333988,-2.9667507944
H,0,1.1383101651,-1.7837831969,-2.3283894046
H,0,2.127225469,-2.5560514201,-1.0804329393
C,0,3.3722437931,-2.1556809468,3.157559594
H,0,3.5053871002,-2.5173200766,0.9813065897
H,0,1.8610353184,-2.2988174863,1.5899957692
C,0,3.1722209114,-0.7882832378,3.8596175083
H,0,1.3765075819,-0.0199183776,2.8987766562
H,0,2.6808819084,1.171925597,2.973112614
H,0,3.893934074,4.6946005376,0.3368374301
H,0,4.3718814494,4.1038506224,-1.2441548379
H,0,1.6019041314,4.7145673676,-0.2145455494
H,0,2.1680380976,4.7790184441,-1.8801394643
H,0,5.3248162549,-1.9374606731,-3.0795140977
H,0,4.8151603597,-2.7889855986,-1.6274457521
H,0,3.0289168571,-1.8398028193,-3.9140830426
H,0,3.0693458656,-3.4453876702,-3.1778639882
H,0,2.8090542134,-2.955662676,3.6471922845
H,0,4.4258113595,-2.4518978206,3.1848539414
H,0,2.5975448845,-0.8723425519,4.7867759733
H,0,4.1416698855,-0.3538103424,4.1275026159
C,0,-3.084848817,2.15908675,2.3092215183
H,0,-2.5658741068,2.0673116848,3.2694648098
H,0,-2.7833199914,3.1099748769,1.8635997756
H,0,-4.1580603056,2.2084200043,2.5156558947

H,0,-2.9962221939,0.0591049714,2.0273796379

Cyc-c

Sum of PCM and thermal Free Energies= -1654,548194

C,0,2.1494651957,-2.6470420206,1.4435792619
C,0,3.3708239972,-3.2284707085,1.8003453163
C,0,4.5651463603,-2.7190742185,1.2928503108
C,0,4.5481138834,-1.6139032234,0.4395127741
C,0,3.3289841153,-1.0266251702,0.1056720148
C,0,2.1142704223,-1.5401855937,0.5876449321
C,0,3.1332706892,0.2019498927,-0.7654316778
C,0,1.7645489798,-0.0792316155,-1.5140463855
Pd,0,0.4258899848,-0.6913870405,-0.0503290678
H,0,1.2257073947,-3.0767660041,1.829697906
H,0,3.386653611,-4.090666639,2.4632913146
H,0,5.5115092846,-3.1839538419,1.5563184306
H,0,5.4782311136,-1.2216835779,0.0347263998
P,0,-1.8636699671,0.0870813844,-0.3876823991
C,0,-2.2088457076,1.8728958196,-0.8399364183
C,0,-3.6716114297,2.3315364894,-1.0393380346
C,0,-1.6179401334,2.9075777113,0.1306789745
C,0,-3.6727343909,3.8571901981,-0.7426017584
C,0,-2.2185335573,4.2200927117,-0.3822235217
C,0,-2.6752214877,-0.1894748769,1.2896454539
C,0,-4.1905337917,-0.4264707328,1.410458762
C,0,-2.0320163523,-1.394015973,2.0355044309
C,0,-4.328669601,-1.0114180337,2.8201895518
C,0,-3.1480339536,-1.9887563198,2.9335097295
C,0,-2.9154448471,-0.8659171082,-1.6056216765
C,0,-2.8000834161,-2.3945866148,-1.4682404117
C,0,-2.5133286983,-0.6406580676,-3.0712420657
C,0,-3.3005071927,-2.9550301499,-2.8206066499
C,0,-3.2334358933,-1.7738574512,-3.8211479409
H,0,-1.6762704662,1.990426277,-1.7937219573
H,0,-4.3449853804,1.813557015,-0.3506294837
H,0,-4.0250879668,2.1046741657,-2.0497474894
H,0,-0.5243401662,2.9004268328,0.1486477296
H,0,-1.9631274017,2.7185127319,1.1555229205
H,0,-4.0410808847,4.4423522367,-1.5904534406
H,0,-4.3374044571,4.0747352916,0.1002254756
H,0,-1.6736116723,4.5412943676,-1.2784042059
H,0,-2.1521489765,5.035163103,0.3449630462
H,0,-2.4333936532,0.7204351206,1.8537315104
H,0,-4.5345677186,-1.1599278402,0.6712675415
H,0,-4.7812906753,0.4832522689,1.2702876654
H,0,-1.1640843699,-1.0654949768,2.6170678214
H,0,-1.6685650622,-2.152402767,1.3310956675
H,0,-4.2282117172,-0.2076714551,3.5605181665
H,0,-5.2975814563,-1.4913127227,2.9918563634
H,0,-2.8198489876,-2.127419613,3.9676405507
H,0,-3.4438586588,-2.9753339756,2.5601757016
H,0,-3.9615530878,-0.5589002535,-1.4716753523
H,0,-3.357822813,-2.7935681668,-0.6152173215
H,0,-1.7448471465,-2.6576913965,-1.3170562239
H,0,-1.4263187556,-0.7565185418,-3.1683691748
H,0,-2.7757253149,0.3524728762,-3.449367624
H,0,-2.6842419996,-3.7993003819,-3.1438717509

H,0,-4.3248627085,-3.3309789143,-2.733059278
H,0,-2.7224126535,-2.0380971594,-4.7517388334
H,0,-4.2439163747,-1.4508583321,-4.0955428396
C,0,1.1746927069,1.1247591999,-2.2310563522
H,0,0.2736075226,0.8311507584,-2.7775700427
H,0,0.9144689333,1.9459341315,-1.5599309325
H,0,1.8884354994,1.5065066179,-2.9779638092
C,0,1.9042086387,-1.2326634149,-2.5095233434
H,0,2.3753205623,-2.1111550615,-2.0654743082
H,0,0.9229141235,-1.5305966028,-2.8914221213
H,0,2.510975596,-0.9161054054,-3.3715401784
C,0,3.0963522476,1.5178022244,0.1199648388
H,0,2.055964485,1.5642258554,0.4721891786
C,0,4.2194341117,0.3293040082,-1.750102901
N,0,5.0736581212,0.4362657114,-2.5320765848
C,0,3.4383303027,2.804560448,-0.6441540612
H,0,2.8707665191,2.935405305,-1.5663800212
H,0,3.2395343439,3.6715501527,-0.0045632126
H,0,4.5004429086,2.8266315773,-0.9090909076
C,0,4.001184226,1.4413113349,1.3532585379
H,0,3.9389128752,2.3838820688,1.9083251177
H,0,3.7197616178,0.6299621627,2.0269328542
H,0,5.0498955709,1.2972389126,1.0688025084

TSCC-a

Sum of PCM and thermal Free Energies= -1654,540145

C,0,-4.4533898206,-3.3733919841,-0.5509656607
C,0,-4.4769457346,-1.9793570902,-0.604654451
C,0,-3.3987176768,-1.2364116952,-0.1231395018
C,0,-2.2709339949,-1.8919424222,0.3981341693
C,0,-2.281436218,-3.292476643,0.5062822454
C,0,-3.3599293635,-4.0285633674,0.011107097
C,0,-3.3641136778,0.2862322365,-0.0509828781
C,0,-2.7776899773,0.6140669478,1.3795211233
C,0,-1.7852762492,-0.4697513324,1.8201041834
H,0,-5.3012550466,-3.941819834,-0.922788251
H,0,-5.3479806459,-1.4657211286,-1.0037174544
H,0,-1.4485766936,-3.8096696031,0.9751207893
H,0,-3.349720481,-5.1134270473,0.0828100008
H,0,-2.2332434675,1.5597909676,1.2937485753
H,0,-2.222091055,-1.1446749518,2.5577143867
H,0,-0.8911550145,-0.0226382396,2.2818051921
Pd,0,-0.3821999844,-1.2040017288,0.3757957528
C,0,-4.7140370475,0.8409080297,-0.212150996
N,0,-5.7706574109,1.2942349557,-0.3840360953
C,0,-2.4708770312,0.8992861171,-1.1919373656
C,0,-2.845031372,0.3613317345,-2.5734457558
H,0,-1.4528301728,0.5460204875,-0.9470113661
H,0,-2.1835235063,0.7904922488,-3.3336001085
H,0,-3.8730411484,0.6345777787,-2.8396607654
H,0,-2.7588556915,-0.7269858019,-2.623962196
C,0,-3.8629527447,0.781997336,2.4473089438
H,0,-4.4783849017,-0.1218790479,2.521243461
H,0,-3.4002911415,0.9542319563,3.4247926432
H,0,-4.5259716911,1.624868072,2.2323423216
C,0,-2.4834054172,2.4298800758,-1.2077967576
H,0,-3.4762799314,2.814324244,-1.4660901214

H,0,-2.1938909745,2.8716776503,-0.2495849608
H,0,-1.7791494438,2.7970157948,-1.9615651711
P,0,1.9230729599,-1.0167198114,-0.19651117
C,0,2.6275696217,0.7190820712,-0.1160952496
C,0,2.2837971839,-1.6084240974,-1.9464133481
C,0,3.077254001,-1.959102928,0.9352980992
C,0,4.0828540617,0.9666187806,-0.5404269887
C,0,1.8189493155,1.7588935666,-0.9236963496
H,0,2.5407612042,0.9746224483,0.9491138094
C,0,3.7255829099,-2.0453016386,-2.3424748995
C,0,1.3742438222,-2.7860174214,-2.3627367098
H,0,2.0008918922,-0.7454018352,-2.5631824712
C,0,2.7843616795,-3.4642790566,1.0303450242
C,0,2.9875014909,-1.4581693881,2.4006390068
H,0,4.1046487499,-1.8232171837,0.5752562945
C,0,4.1540813705,2.4971737168,-0.5947700744
H,0,4.2689088001,0.5502489635,-1.5376648161
H,0,4.8150123372,0.5256663032,0.1436346002
C,0,2.8083539673,2.9187521222,-1.2197485663
H,0,0.9343358457,2.083774578,-0.3697692661
H,0,1.4526298575,1.3272856018,-1.8623039761
C,0,3.5639800969,-3.3538138321,-3.1515987757
H,0,4.3800617875,-2.1963086082,-1.4797456015
H,0,4.1963120887,-1.2676342491,-2.9526081481
C,0,2.0918719508,-3.3770897134,-3.5769806133
H,0,0.3483674123,-2.4623877858,-2.5615620584
H,0,1.3220784477,-3.5359788794,-1.5634016695
C,0,3.483561959,-3.8694807539,2.3314528397
H,0,3.1329964102,-4.0256360726,0.1575461735
H,0,1.7010648103,-3.6235448105,1.1206551986
C,0,3.1576365899,-2.7162975402,3.293889754
H,0,2.0130758978,-0.9908164648,2.5883811089
H,0,3.7519234301,-0.7016329965,2.6036609915
H,0,4.2385689605,2.892962852,0.4248328437
H,0,5.0183476058,2.8669580789,-1.1557775954
H,0,2.4553331814,3.8730822385,-0.8176098458
H,0,2.9173670558,3.0562002322,-2.3007475396
H,0,4.2582109251,-3.4118636011,-3.9958283958
H,0,3.7701844202,-4.2190430085,-2.5098824518
H,0,1.9388905656,-2.7317852853,-4.4520842318
H,0,1.7371844953,-4.3780723677,-3.8423982944
H,0,3.1572516667,-4.8443066614,2.7078301386
H,0,4.5662451486,-3.9318982107,2.1624953426
H,0,2.2210387815,-2.9261171344,3.8216572057
H,0,3.9289619393,-2.581413553,4.0582227572

TSCC-b

Sum of PCM and thermal Free Energies=   -1654,534648

C,0,3.8921408332,-2.9756668507,1.0815938526
C,0,4.1305453969,-1.6024334262,1.0061609123
C,0,3.2379578228,-0.7693258171,0.3330785208
C,0,2.0746175552,-1.3047080391,-0.243115091
C,0,1.8773556673,-2.6946413389,-0.2232933361
C,0,2.7750776008,-3.5230730266,0.4554933406
C,0,3.4803215314,0.7135971305,0.0550587824
C,0,3.1878456651,0.7725807222,-1.4957744649
C,0,1.8630205026,0.0718302332,-1.8300632275

H,0,4.5986218327,-3.6173262046,1.6007246826
H,0,5.0303367069,-1.1824844181,1.4487755437
H,0,1.021559384,-3.132028357,-0.7306024523
H,0,2.6051869861,-4.5966796604,0.4796055516
H,0,1.9806203233,-0.6891848182,-2.6017808818
H,0,1.1182612121,0.8026099377,-2.1849805596
Pd,0,0.3122897426,-0.3618421365,-0.4120331532
C,0,4.8927928139,1.0529382499,0.269973405
N,0,6.0052530969,1.3454124748,0.4383927186
C,0,2.6046933137,1.6325308103,0.9820269565
C,0,2.6542531263,1.1592581097,2.4384869776
H,0,1.5734701304,1.4915722069,0.6147327318
H,0,2.0316965567,1.8097225921,3.062210095
H,0,3.6762427917,1.2058233955,2.8336381793
H,0,2.2945452857,0.1336986205,2.5498279342
C,0,2.9666667906,3.1209028497,0.9349595346
H,0,3.9874176561,3.288617836,1.2958287351
H,0,2.8899613666,3.5578053587,-0.0608265168
H,0,2.290416958,3.6783037441,1.592031892
P,0,-1.9808617696,0.1783933877,-0.0486147472
C,0,-2.4699281577,1.918637256,-0.547358483
C,0,-2.4938941436,0.0243471781,1.7548600727
C,0,-3.1789988751,-0.8633408004,-1.0389800265
C,0,-3.909517348,2.4000056687,-0.3144703752
C,0,-1.600339308,3.0211662857,0.095640533
H,0,-2.2832931109,1.9277570625,-1.6303568915
C,0,-3.9950695509,-0.1504596746,2.1309825135
C,0,-1.7584491725,-1.1293257787,2.4729738654
H,0,-2.131953958,0.9623648218,2.1955419939
C,0,-3.0684842893,-2.3746999358,-0.785520618
C,0,-2.9467711663,-0.7150597626,-2.5650855142
H,0,-4.2003276173,-0.541364798,-0.8007895378
C,0,-3.8038281603,3.9038232891,-0.5952631822
H,0,-4.2053918572,2.2357312044,0.7286078114
H,0,-4.6442172398,1.8951812315,-0.9498076486
C,0,-2.4533768132,4.3170326462,0.0270109174
H,0,-0.6391119582,3.1147075503,-0.4166262984
H,0,-1.3711700376,2.777540714,1.1394793414
C,0,-4.0349544003,-1.2599636327,3.2082953278
H,0,-4.6233146407,-0.4116216674,1.2750785061
H,0,-4.3918213641,0.78965672,2.5277626009
C,0,-2.5974032279,-1.3557827786,3.7314088908
H,0,-0.7100211253,-0.887607595,2.6704520313
H,0,-1.7653134062,-2.0372274962,1.8568511002
C,0,-3.7458136413,-2.9806480234,-2.0184822277
H,0,-3.5273964165,-2.68731612,0.1578983105
H,0,-2.0099638359,-2.6675286718,-0.7560877105
C,0,-3.2376469232,-2.1107221959,-3.1796793441
H,0,-1.908934635,-0.4228086764,-2.7668895704
H,0,-3.5893884443,0.0641070501,-2.9867188961
H,0,-3.787735535,4.0702591328,-1.6793288188
H,0,-4.6484221812,4.4743205947,-0.1957916039
H,0,-1.9621852541,5.1006360267,-0.5576161638
H,0,-2.603819617,4.7250410694,1.0319742932
H,0,-4.7674765774,-1.0533461802,3.9948939565
H,0,-4.3193974623,-2.2156947333,2.751557645
H,0,-2.4034433151,-0.5562330808,4.4585296655
H,0,-2.3830722036,-2.308059523,4.2268057906
H,0,-3.5207812646,-4.0436749425,-2.1517443565
H,0,-4.8351282742,-2.8890755703,-1.9207114206
H,0,-2.314806122,-2.5362870119,-3.5882869079

H,0,-3.9547434987,-2.0594618617,-4.0046154773
C,0,3.2834395037,2.1410437694,-2.1713616531
H,0,4.2053404379,2.6658876471,-1.9001827899
H,0,3.286276407,2.0081881923,-3.2584621773
H,0,2.4300425855,2.7808134066,-1.9264536719
H,0,3.9913257755,0.1547652381,-1.9170637779

TSCC-c

Sum of PCM and thermal Free Energies=   -1654,508816

C,0,-2.4275942006,-2.8228184439,-0.0477846625
C,0,-3.4213427488,-3.3990057136,-0.8473653394
C,0,-4.3968326882,-2.6171623727,-1.4719684672
C,0,-4.4227207281,-1.2309268552,-1.2858566305
C,0,-3.4074987141,-0.6603417647,-0.5316372395
C,0,-2.3814032453,-1.420819651,0.0437938393
C,0,-3.2147283248,0.6907516956,0.1229449443
C,0,-2.3260700778,0.0597621493,1.2861508096
Pd,0,-0.4295955576,-0.8728233355,0.1553348126
H,0,-1.7126408203,-3.4524250091,0.4731291672
H,0,-3.4456463831,-4.4795401046,-0.9675623722
H,0,-5.1718575709,-3.0964550679,-2.0636809128
H,0,-5.2394427326,-0.6322011634,-1.680030528
P,0,1.8490699346,-0.9933097427,-0.3334786656
C,0,2.6302686423,0.6549693454,-0.7900059681
C,0,4.1687837438,0.7387226942,-1.0163341755
C,0,1.992996522,1.3206058615,-2.0279506179
C,0,4.3598414704,1.5842609747,-2.2951654046
C,0,3.0418865005,2.3495832777,-2.4573523052
C,0,2.1944876963,-2.1395795978,-1.7848496879
C,0,3.6267065211,-2.6152821124,-2.0894201063
C,0,1.3501859692,-3.4436401445,-1.7237245099
C,0,3.3958164583,-3.7958580372,-3.0392510785
C,0,2.2044096513,-4.536621601,-2.4145153211
C,0,2.9679452794,-1.5790726426,1.0513733103
C,0,2.5824236548,-2.9317906628,1.6661823167
C,0,2.944656474,-0.6178594487,2.2604240453
C,0,3.3543327539,-2.9424447543,2.9909040295
C,0,3.2641264909,-1.4906946264,3.5039632788
H,0,2.3737191276,1.2751700922,0.0780214077
H,0,4.6395890296,-0.2421920513,-1.1152794635
H,0,4.6424627398,1.2216052626,-0.155019358
H,0,1.0125011528,1.7501903394,-1.8046033812
H,0,1.84857762,0.5941381347,-2.83822318
H,0,5.2363348699,2.2377269798,-2.24260302
H,0,4.5035355012,0.925565159,-3.1608893787
H,0,3.0184659222,3.2121581107,-1.7784052629
H,0,2.885297881,2.7275395698,-3.4728913402
H,0,1.8466052089,-1.5614042481,-2.6505002045
H,0,4.1275173288,-2.9686555275,-1.1787805635
H,0,4.253108554,-1.8333018013,-2.5288854578
H,0,0.385571018,-3.2911123522,-2.2152809336
H,0,1.1197270718,-3.7249407118,-0.6920552426
H,0,3.1275040675,-3.4162543787,-4.0335653816
H,0,4.2802953884,-4.4297837017,-3.161667814
H,0,1.6339191434,-5.1078320452,-3.1531759042
H,0,2.5670822528,-5.2561148852,-1.6710955507
H,0,3.9924534685,-1.6456771854,0.6628440592

H,0,2.8247711643,-3.7856192791,1.0254278412
H,0,1.499925298,-2.9489314224,1.8528922553
H,0,1.9446774785,-0.1770281254,2.3576316033
H,0,3.6508617096,0.2086185091,2.1363401308
H,0,2.9600200322,-3.671203731,3.70624065
H,0,4.4003924212,-3.2128949732,2.8009932411
H,0,2.467358315,-1.3934355539,4.2485724998
H,0,4.1911355711,-1.1786959367,3.9947402479
C,0,-1.3236799025,0.9960248226,1.9751214734
H,0,-0.7241188746,0.4456359133,2.7054089093
H,0,-0.6430818706,1.5157521099,1.2989635669
H,0,-1.8994916387,1.7524279892,2.5361242753
C,0,-3.1678174711,-0.5737028313,2.3963256675
H,0,-4.0141221167,-1.1491694833,2.0159726104
H,0,-2.5412741918,-1.244231571,2.9921524955
H,0,-3.5557048594,0.2065205274,3.0647366939
C,0,-2.4986225478,1.7395549823,-0.7915976226
H,0,-1.4700535029,1.3537163773,-0.8824655706
C,0,-4.4712789516,1.2562345762,0.6245337417
N,0,-5.466593996,1.7182776835,1.0091392399
C,0,-2.4700601554,3.1563291643,-0.2078386477
H,0,-2.0502670196,3.2004726306,0.7987024526
H,0,-1.8657191605,3.8064150976,-0.8494591388
H,0,-3.4793411301,3.5791041018,-0.1647947021
C,0,-3.1186037944,1.7800201215,-2.1903393733
H,0,-2.5939926239,2.5145368678,-2.8102275622
H,0,-3.0592924079,0.8105804436,-2.6912001956
H,0,-4.1721140211,2.081270493,-2.1463019438

H2CO3

Sum of PCM and thermal Free Energies= -264,907371

C,0,0.1197986569,0.0000006218,-0.0717787744
O,0,1.3121499717,-0.0000022174,0.0710108047
O,0,-0.7862749961,0.0000035612,0.936146101
H,0,-0.2764305766,0.0000026812,1.7578846571
O,0,-0.498095189,0.0000013652,-1.2568035788
H,0,-1.4538208669,0.0000035959,-1.1121232097

Agos-a'

Sum of PCM and thermal Free Energies = -1840,900224

C,0,2.9160853975,2.581977251,0.0248874944
C,0,4.2436128628,3.0009793373,-0.0463625183
C,0,5.2711584781,2.0610383625,-0.0964540834
C,0,4.9602166523,0.7071860798,-0.0541477912
C,0,3.6295318311,0.277975818,0.0370464891
C,0,2.5836860626,1.2235359119,0.0580387181
C,0,3.3385641554,-1.2193463229,0.1587926493
C,0,1.8273674591,-1.4542780598,-0.0055873247
Pd,0,0.6632525447,0.5803579625,0.1012027233
H,0,2.1183473489,3.3167929674,0.0496357651
H,0,4.4725896886,4.0634535484,-0.0748717502
H,0,6.3074846937,2.3779173798,-0.1724548317
H,0,5.7587333244,-0.0302556951,-0.1073445149

H,0,1.501863777,-1.1515570458,-1.0116762033
P,0,-1.6393256838,-0.3003695566,0.1156565547
C,0,-1.7517406724,-1.6595231136,-1.1729679981
C,0,-2.9890470722,-2.603772062,-1.2000490549
C,0,-1.5895058221,-1.156901701,-2.6221732833
C,0,-3.2931504781,-2.847041489,-2.6989161553
C,0,-2.0450942697,-2.361914986,-3.447533062
C,0,-2.9947391023,0.9283326267,-0.2908513417
C,0,-4.4455920449,0.402403569,-0.3784944182
C,0,-3.0582322313,2.1620844613,0.6684235933
C,0,-5.2999616864,1.6404510489,-0.0885637601
C,0,-4.5407686282,2.3116038318,1.0575503129
C,0,-2.1738722151,-1.1565716107,1.6943004822
C,0,-2.0712508312,-0.2902861506,2.9675466307
C,0,-1.3507894057,-2.4021098997,2.0579699552
C,0,-1.9478920109,-1.2936880247,4.1456137494
C,0,-1.7815719403,-2.6873984126,3.5020380572
H,0,-0.8705919943,-2.2744800179,-0.9445577433
H,0,-3.8570174586,-2.1817059221,-0.6893952414
H,0,-2.7542631089,-3.5419219141,-0.6867120857
H,0,-0.5755441448,-0.8143130025,-2.8425630206
H,0,-2.2507106269,-0.3055057068,-2.8173259803
H,0,-3.5426723656,-3.8914592717,-2.9100003558
H,0,-4.1572073755,-2.2454711014,-3.0055045889
H,0,-1.2684264134,-3.1379264211,-3.4369392046
H,0,-2.2434395459,-2.1126131303,-4.494420449
H,0,-2.6877854831,1.2849723429,-1.2794006918
H,0,-4.6491507048,-0.3508913476,0.392975751
H,0,-4.6631346206,-0.0547738523,-1.3482609511
H,0,-2.7168508445,3.0482494155,0.1283047514
H,0,-2.4085953011,2.069138644,1.5413981496
H,0,-5.3161119907,2.2982102941,-0.966818811
H,0,-6.3375604003,1.3938059878,0.1593415996
H,0,-4.8275226559,3.3559373559,1.2148418347
H,0,-4.7484814723,1.7759583546,1.9933627788
H,0,-3.2160893192,-1.4726654438,1.5551082717
H,0,-2.92872475,0.3785689969,3.0796323228
H,0,-1.1773168406,0.3427735599,2.9133906726
H,0,-0.2793337837,-2.1630317128,2.034052387
H,0,-1.5186077626,-3.2483552545,1.3851700698
H,0,-1.0837986225,-1.0435907925,4.7692369923
H,0,-2.8245276656,-1.2599781765,4.799315122
H,0,-1.0679240445,-3.3210737954,4.0375521291
H,0,-2.7397904653,-3.2202278767,3.4948482442
C,0,-0.4000247259,2.7842466082,-1.2760445052
O,0,0.0330747662,2.4987974,-0.0773084591
O,0,-0.7432195684,4.0975598508,-1.3943065386
O,0,-0.536913259,2.0303099991,-2.2257978407
H,0,-0.5424742698,4.5116608749,-0.544349783
H,0,1.5219359139,-2.4945205976,0.1247632534
H,0,1.3030054562,-0.9431651943,0.8697517292
C,0,4.0077958002,-1.9362262183,-0.9418537202
N,0,4.5317908363,-2.5173213869,-1.8009609037
C,0,3.8914368492,-1.7937006863,1.5168688305
C,0,3.748997329,-3.3137884522,1.6298839313
C,0,3.2853526902,-1.0946020565,2.7346249914
H,0,4.9633532582,-1.5601908275,1.5019952888
H,0,4.1843914548,-3.8323434616,0.7708243818
H,0,4.2627551482,-3.6671980021,2.5294128664
H,0,2.7004649725,-3.6204371943,1.7202364877
H,0,3.3613594146,-0.0067430197,2.663134731

H,0,2.2295876576,-1.3559431791,2.8741523536
H,0,3.8126452954,-1.4142212141,3.6390464087

Agos-b'

Sum of PCM and thermal Free Energies = -1840,896355

C,0,2.1354182682,-2.0929554267,-1.8780311255
C,0,3.2836567986,-2.605338259,-2.4812856732
C,0,4.5178843001,-2.0326819139,-2.1953939387
C,0,4.5918056335,-0.9562736249,-1.3164571495
C,0,3.4457027914,-0.4232066251,-0.7070269739
C,0,2.1988479146,-1.0064883257,-0.9986651157
H,0,1.1734565376,-2.5526508545,-2.0857327691
H,0,3.2087580087,-3.4485496087,-3.1635104474
H,0,5.4265539109,-2.4203844356,-2.6474792382
H,0,5.5633183401,-0.5236798987,-1.0946636401
C,0,3.5697418719,0.776186604,0.2536251915
H,0,1.1018269991,1.1170232316,-1.2943201209
Pd,0,0.3955122567,-0.3169069637,-0.4144080309
C,0,0.2154533165,-2.6210429924,1.1927186973
O,0,-0.1298086104,-2.245856623,-0.0118750864
O,0,0.0036580455,-3.9479376002,1.3978546248
O,0,0.6591843745,-1.9279097121,2.0939557559
H,0,-0.2873521485,-4.314087021,0.5525380045
C,0,2.8748360354,2.046704867,-0.3617809221
C,0,3.0522185016,0.4052391879,1.6636025067
H,0,2.0371857793,0.0011444634,1.6245396614
C,0,1.3636684498,1.8936289482,-0.4993452896
H,0,0.8851454956,1.7560128799,0.4782925969
H,0,0.9166925481,2.7897275458,-0.9383929888
C,0,4.9900696185,1.1384828919,0.417025482
N,0,6.0960655235,1.4558398085,0.5783712957
P,0,-1.9697437265,0.326713759,-0.056490575
C,0,-2.4716874799,0.6726638717,1.7175785735
C,0,-3.0078822612,-1.1237598118,-0.6219052695
C,0,-2.621510038,1.811966452,-0.9998270692
C,0,-3.8956733329,1.2330518233,2.0094584836
C,0,-2.3142833086,-0.538249396,2.6600516592
H,0,-1.7367147872,1.4241372664,2.0371550618
C,0,-4.5433658978,-1.021926078,-0.5959957905
C,0,-2.6517559966,-1.6153246753,-2.0573918639
H,0,-2.7021650672,-1.9130078572,0.0737377946
C,0,-2.1634868248,1.8771759225,-2.4819074129
C,0,-2.2175039326,3.175565827,-0.4083939467
H,0,-3.716445088,1.7531022541,-0.9682341481
C,0,-4.3587628364,0.5361470954,3.3128654079
H,0,-4.5986421934,1.0463136432,1.1937503531
H,0,-3.8529489858,2.3188660557,2.13931774
C,0,-3.0920883648,-0.0975856052,3.9009304125
H,0,-1.2696911303,-0.8008303683,2.8433954945
H,0,-2.8030875026,-1.4248385733,2.234535422
C,0,-4.9773460038,-2.1617825503,-1.5232663437
H,0,-4.8885462865,-0.0668929244,-1.0132226266
H,0,-4.9567212755,-1.1100515794,0.413015731
C,0,-3.9907929649,-2.0594732606,-2.6927730072
H,0,-1.9348982762,-2.4368108169,-1.9882729311
H,0,-2.1725772238,-0.8406865624,-2.6617674029
C,0,-1.9360282341,3.3790643756,-2.7968984071
H,0,-2.9163920594,1.4327886144,-3.1397316576

H,0,-1.240079285,1.3068267565,-2.6345794722
C,0,-2.4650231909,4.1396560192,-1.572553668
H,0,-1.1549638551,3.1851416984,-0.1365370718
H,0,-2.7851544789,3.4334390392,0.4894601085
H,0,-4.85444587,1.2275341281,4.0013906087
H,0,-5.0840842446,-0.2521275601,3.0776393827
H,0,-2.5121151739,0.6499335589,4.4576723911
H,0,-3.3045378245,-0.922685257,4.5877201002
H,0,-4.856060077,-3.1222811369,-1.0063695363
H,0,-6.0245407555,-2.0876399987,-1.8340307504
H,0,-3.8977710372,-2.9949780859,-3.2526448754
H,0,-4.3428940997,-1.2993060459,-3.4005202873
H,0,-0.8655999875,3.5776621742,-2.9241053873
H,0,-2.423640318,3.6885943052,-3.7258845049
H,0,-1.9856417436,5.113721826,-1.4324345031
H,0,-3.5428528018,4.3193241392,-1.6727135634
C,0,3.1550773713,3.3372433874,0.4194944281
H,0,2.7381449233,4.1971440918,-0.114981199
H,0,2.6991821779,3.3150777341,1.4151179027
H,0,4.2273664941,3.5080393108,0.5402643871
H,0,3.3033235607,2.1593468452,-1.3660254012
H,0,3.0863368794,1.2647589892,2.3392894769
H,0,3.6802596746,-0.3830609928,2.0850794857

Agos-c'

Sum of PCM and thermal Free Energies = **-1840,894037**

C,0,-2.563490196,-2.7435223028,0.7544132222
C,0,-3.8564531552,-3.2206755727,0.9812040519
C,0,-4.9418865211,-2.3558509702,0.8808344907
C,0,-4.7331453734,-1.0144109621,0.5652269408
C,0,-3.4413396919,-0.5248872254,0.3473786089
C,0,-2.3426910018,-1.4014278493,0.4447686082
C,0,-3.1778146759,0.938823233,-0.0179449877
C,0,-2.1055177441,1.5532378634,0.9493615727
Pd,0,-0.4902266723,-0.6719306373,0.2632102845
H,0,-1.7166180534,-3.4215208353,0.8045138133
H,0,-4.0106086144,-4.2684033288,1.2274113539
H,0,-5.9525337124,-2.7184495918,1.0463426386
H,0,-5.5835907415,-0.3412790853,0.4917201964
H,0,-1.13296678,0.971854019,0.7999138642
P,0,1.8075831755,0.2113533611,0.1435554525
C,0,1.8789065111,1.8240748577,-0.8163474904
C,0,3.1384037363,2.7275792715,-0.7071778851
C,0,1.6277410371,1.6752356575,-2.3286634134
C,0,3.2842638391,3.4087823997,-2.0938681502
C,0,2.000233964,3.0600556803,-2.8621010272
C,0,3.0524468787,-0.9293827933,-0.6687739148
C,0,4.5154413903,-0.4431313874,-0.7837061382
C,0,3.1378434758,-2.3510831898,-0.0232875899
C,0,5.3289213304,-1.7394941364,-0.8539761685
C,0,4.6381331083,-2.6259980776,0.1839476831
C,0,2.5174925162,0.680449972,1.8122727241
C,0,2.5168942201,-0.456731617,2.852854978
C,0,1.7175707581,1.7833027226,2.5225753764
C,0,2.5509847107,0.2475188457,4.2340503209
C,0,2.25688465,1.7406947536,3.95877413

H,0,1.0303112881,2.3862246499,-0.4032426991
H,0,4.0377280131,2.1578808818,-0.4641125619
H,0,3.0121626274,3.4636741343,0.0930493824
H,0,0.6092512171,1.3593867058,-2.5654215418
H,0,2.2976425943,0.922541437,-2.7611593846
H,0,3.4493973281,4.4875105674,-2.0130276375
H,0,4.1510835137,2.9949629137,-2.6216615367
H,0,1.2047138328,3.7770654577,-2.6201707809
H,0,2.1348756447,3.0793608139,-3.9480015198
H,0,2.6365675674,-1.0397813514,-1.6762020997
H,0,4.8224243458,0.1139399299,0.1101444965
H,0,4.6691915371,0.212364845,-1.6461354743
H,0,2.7092880342,-3.0795302638,-0.7155967103
H,0,2.564170428,-2.4406450477,0.9016387475
H,0,5.2378411213,-2.1862876952,-1.8522757525
H,0,6.3949077313,-1.5846925693,-0.6573355503
H,0,4.8857882896,-3.6871315175,0.0819029189
H,0,4.950563926,-2.3183390134,1.1906453034
H,0,3.5442280456,1.0403086527,1.6635244649
H,0,3.3528334331,-1.1479596218,2.7164076817
H,0,1.5945938625,-1.0425325704,2.7507928499
H,0,0.6507676611,1.5211974761,2.5154223527
H,0,1.8219007907,2.7675035955,2.0558924598
H,0,1.805469614,-0.1892283541,4.9056571338
H,0,3.5223400518,0.1223427629,4.7220766981
H,0,1.5590601993,2.1757653985,4.6808414033
H,0,3.1813453193,2.3268160482,4.0168822626
C,0,0.2125070109,-2.4432392022,-1.7867932613
O,0,0.0364987435,-2.4881052229,-0.494247195
O,0,0.4988004686,-3.6689142211,-2.3062152045
O,0,0.1727328529,-1.4654662254,-2.5171857365
H,0,0.4418654358,-4.2983132881,-1.5749775291
C,0,-1.7349880834,2.997154371,0.6136960346
H,0,-0.9828077379,3.3690018511,1.3153425253
H,0,-1.3408071131,3.1060873394,-0.3989443031
H,0,-2.6203125074,3.6357041713,0.7058795762
C,0,-2.4997078984,1.4176390836,2.4184680508
H,0,-2.7179189075,0.3822364565,2.6867069504
H,0,-1.7001989313,1.7876401144,3.0668549462
H,0,-3.3933406071,2.0199746435,2.6151122806
C,0,-2.760210114,1.0199141237,-1.5061148046
H,0,-1.8331865921,0.4539465798,-1.658418215
C,0,-4.3961488981,1.7517115306,0.1424281364
N,0,-5.3365932589,2.424092504,0.2573834399
H,0,-2.6212099829,2.0512303694,-1.83953996
H,0,-3.5332731858,0.5599742507,-2.126089853

Agos-d'

Sum of PCM and thermal Free Energies = -1840,901098

C,0,2.9160853975,2.581977251,0.0248874944
C,0,4.2436128628,3.0009793373,-0.0463625183
C,0,5.2711584781,2.0610383625,-0.0964540834

C,0,4.9602166523,0.7071860798,-0.0541477912
C,0,3.6295318311,0.277975818,0.0370464891
C,0,2.5836860626,1.2235359119,0.0580387181
C,0,3.3385641554,-1.2193463229,0.1587926493
C,0,1.8273674591,-1.4542780598,-0.0055873247
Pd,0,0.6632525447,0.5803579625,0.1012027233
H,0,2.1183473489,3.3167929674,0.0496357651
H,0,4.4725896886,4.0634535484,-0.0748717502
H,0,6.3074846937,2.3779173798,-0.1724548317
H,0,5.7587333244,-0.0302556951,-0.1073445149
H,0,1.501863777,-1.1515570458,-1.0116762033
P,0,-1.6393256838,-0.3003695566,0.1156565547
C,0,-1.7517406724,-1.6595231136,-1.1729679981
C,0,-2.9890470722,-2.603772062,-1.2000490549
C,0,-1.5895058221,-1.156901701,-2.6221732833
C,0,-3.2931504781,-2.847041489,-2.6989161553
C,0,-2.0450942697,-2.361914986,-3.447533062
C,0,-2.9947391023,0.9283326267,-0.2908513417
C,0,-4.4455920449,0.402403569,-0.3784944182
C,0,-3.0582322313,2.1620844613,0.6684235933
C,0,-5.2999616864,1.6404510489,-0.0885637601
C,0,-4.5407686282,2.3116038318,1.0575503129
C,0,-2.1738722151,-1.1565716107,1.6943004822
C,0,-2.0712508312,-0.2902861506,2.9675466307
C,0,-1.3507894057,-2.4021098997,2.0579699552
C,0,-1.9478920109,-1.2936880247,4.1456137494
C,0,-1.7815719403,-2.6873984126,3.5020380572
H,0,-0.8705919943,-2.2744800179,-0.9445577433
H,0,-3.8570174586,-2.1817059221,-0.6893952414
H,0,-2.7542631089,-3.5419219141,-0.6867120857
H,0,-0.5755441448,-0.8143130025,-2.8425630206
H,0,-2.2507106269,-0.3055057068,-2.8173259803
H,0,-3.5426723656,-3.8914592717,-2.9100003558
H,0,-4.1572073755,-2.2454711014,-3.0055045889
H,0,-1.2684264134,-3.1379264211,-3.4369392046
H,0,-2.2434395459,-2.1126131303,-4.494420449
H,0,-2.6877854831,1.2849723429,-1.2794006918
H,0,-4.6491507048,-0.3508913476,0.392975751
H,0,-4.6631346206,-0.0547738523,-1.3482609511
H,0,-2.7168508445,3.0482494155,0.1283047514
H,0,-2.4085953011,2.069138644,1.5413981496
H,0,-5.3161119907,2.2982102941,-0.966818811
H,0,-6.3375604003,1.3938059878,0.1593415996
H,0,-4.8275226559,3.3559373559,1.2148418347
H,0,-4.7484814723,1.7759583546,1.9933627788
H,0,-3.2160893192,-1.4726654438,1.5551082717
H,0,-2.92872475,0.3785689969,3.0796323228
H,0,-1.1773168406,0.3427735599,2.9133906726
H,0,-0.2793337837,-2.1630317128,2.034052387
H,0,-1.5186077626,-3.2483552545,1.3851700698
H,0,-1.0837986225,-1.0435907925,4.7692369923
H,0,-2.8245276656,-1.2599781765,4.799315122
H,0,-1.0679240445,-3.3210737954,4.0375521291
H,0,-2.7397904653,-3.2202278767,3.4948482442
C,0,-0.4000247259,2.7842466082,-1.2760445052
O,0,0.0330747662,2.4987974,-0.0773084591
O,0,-0.7432195684,4.0975598508,-1.3943065386
O,0,-0.536913259,2.0303099991,-2.2257978407
H,0,-0.5424742698,4.5116608749,-0.544349783
H,0,1.5219359139,-2.4945205976,0.1247632534
H,0,1.3030054562,-0.9431651943,0.8697517292

C,0,4.0077958002,-1.9362262183,-0.9418537202
N,0,4.5317908363,-2.5173213869,-1.8009609037
C,0,3.8914368492,-1.7937006863,1.5168688305
C,0,3.748997329,-3.3137884522,1.6298839313
C,0,3.2853526902,-1.0946020565,2.7346249914
H,0,4.9633532582,-1.5601908275,1.5019952888
H,0,4.1843914548,-3.8323434616,0.7708243818
H,0,4.2627551482,-3.6671980021,2.5294128664
H,0,2.7004649725,-3.6204371943,1.7202364877
H,0,3.3613594146,-0.0067430197,2.663134731
H,0,2.2295876576,-1.3559431791,2.8741523536
H,0,3.8126452954,-1.4142212141,3.6390464087

TSCH-a'

Sum of PCM and thermal Free Energies = **-1840,857137**

C,0,-2.317949572,-2.2180878624,-1.6209477786
C,0,-3.5595402612,-2.812384781,-1.8542608955
C,0,-4.6889202745,-2.3454920258,-1.1813448613
C,0,-4.5786868142,-1.296498413,-0.271475132
C,0,-3.3357225762,-0.7109956312,-0.0067265367
C,0,-2.2051139864,-1.1899675288,-0.6846149324
C,0,-3.146913704,0.4363030665,0.9789081463
C,0,-1.6352454979,0.7861605467,1.014517508
Pd,0,-0.3934977194,-0.5325729446,-0.2874324536
H,0,-1.4431430457,-2.5467884807,-2.1802098046
H,0,-3.6468817321,-3.6197788553,-2.576859115
H,0,-5.6612519996,-2.7884568402,-1.3779751788
H,0,-5.4699610899,-0.9196715976,0.2253134393
H,0,-1.2917288471,1.2246498492,-0.2694642738
P,0,1.9129616923,0.0119632138,0.2701683389
C,0,2.2165851388,1.749755841,0.8979418686
C,0,3.5957944788,2.1090533469,1.4830772136
C,0,1.9636209,2.8662621385,-0.1271124383
C,0,3.6395246672,3.6605411101,1.4736403749
C,0,2.426221514,4.1190930246,0.6275533802
C,0,3.0129177045,-0.2398363728,-1.2246629056
C,0,4.5388014163,-0.3586894493,-1.0662821847
C,0,2.5953769962,-1.4955669629,-2.0453717023
C,0,4.9699057376,-0.9811404502,-2.3986780836
C,0,3.9029209563,-2.0535223162,-2.6605852969
C,0,2.618559292,-1.0594034168,1.6305393468
C,0,2.451714179,-2.5712684459,1.4005892916
C,0,1.9223799898,-0.8578111965,2.9861052618
C,0,2.614575351,-3.2086828666,2.8009379057
C,0,2.3995703486,-2.0595002482,3.8180249556
H,0,1.4642509774,1.8583669471,1.6934794709
H,0,4.3911383887,1.7077714142,0.8476302313
H,0,3.7479567437,1.6904515295,2.4825755254
H,0,0.9254279132,2.9177218097,-0.4661675292
H,0,2.5960707376,2.7135836569,-1.0117941549
H,0,3.5902904319,4.0680648641,2.488082452
H,0,4.5815440777,4.0136268444,1.0421427557
H,0,1.6179615148,4.4663241933,1.2814339376
H,0,2.6682379057,4.9476810356,-0.0444574797
H,0,2.7997968465,0.6414849544,-1.84194655
H,0,4.7986879526,-1.0364458286,-0.2431712405
H,0,5.0255926988,0.6008658756,-0.8693941018
H,0,1.8588449908,-1.2116834385,-2.800600867
H,0,2.1164140451,-2.2532782508,-1.4155003657
H,0,4.9416720357,-0.2165089162,-3.1854369328

H,0,5.9874264011,-1.3847356911,-2.374494079
H,0,3.795837253,-2.2873155232,-3.7240098695
H,0,4.1882937895,-2.9857130319,-2.1591133809
H,0,3.6843282042,-0.8188510622,1.7401751817
H,0,3.1576503705,-2.9747542148,0.6685061982
H,0,1.4406605924,-2.7647980688,1.0164918082
H,0,0.834760795,-0.9056185112,2.8427043385
H,0,2.1512343909,0.1028244579,3.4571216329
H,0,1.8965439603,-4.02152204,2.9450195858
H,0,3.6108203929,-3.6471226646,2.9164877354
H,0,1.68743883,-2.3217572958,4.6061419873
H,0,3.3440946562,-1.8110790414,4.3146408872
C,0,-0.827706811,1.4110321615,-2.3954565894
O,0,-0.2799483718,0.2770161657,-2.4702928683
O,0,-0.9819009214,2.1060072016,-3.5421333696
O,0,-1.2475437338,2.0058183716,-1.3571462575
H,0,-0.6448024045,1.5291538235,-4.2417481624
H,0,-1.4305117774,1.8032736582,1.3675179031
H,0,-1.1546706204,0.1390398517,1.7648461646
C,0,-3.9148479654,1.5964483031,0.4893099221
N,0,-4.5658598947,2.4978319609,0.1517711071
C,0,-3.7248582318,0.0875331196,2.4033961659
C,0,-3.574204395,1.2470039845,3.390172551
C,0,-3.1352989293,-1.2017583314,2.9786864138
H,0,-4.7996121352,-0.081049225,2.2528382768
H,0,-4.013077698,2.1701889821,3.0008101892
H,0,-4.0776309992,1.0063438871,4.3321348981
H,0,-2.5207236954,1.4402627327,3.6212566637
H,0,-3.2348536589,-2.0422004134,2.2866306971
H,0,-2.0747228961,-1.0894385736,3.2306801137
H,0,-3.6573623991,-1.4623115046,3.9052424466

TSCH-b'

Sum of PCM and thermal Free Energies = **-1840,856133**

C,0,3.1087902355,-3.5067767592,0.4143918528
C,0,3.5831694865,-2.2196174978,0.6668443375
C,0,2.9697891901,-1.1144257472,0.0768618287
C,0,1.8387147801,-1.2852882992,-0.7386254314
C,0,1.4159566501,-2.5868579184,-1.0489282034
C,0,2.0393289276,-3.6891100724,-0.459724423
C,0,3.51134397,0.3071373237,0.1603598675
C,0,3.4703210934,0.809829184,-1.3297904051
C,0,2.1722392521,0.3586782019,-2.0127837217
H,0,3.5978353925,-4.3628848931,0.870376572
H,0,4.4573479996,-2.0755513397,1.2972289561
H,0,0.5933696253,-2.7423422795,-1.7406392633
H,0,1.6893445475,-4.6917000132,-0.6935563956
H,0,2.351326133,-0.2893198557,-2.8705414778
H,0,1.5882989652,1.2319181217,-2.373024396
Pd,0,0.3606074173,0.0851591045,-0.9626631043
C,0,4.9081768897,0.322014217,0.6172833474
N,0,6.0110423528,0.3640117889,0.9812495449
C,0,2.6935044923,1.1773034085,1.136601984
H,0,1.6541567847,1.2233764334,0.7826986819
P,0,-1.8722908201,0.3014020904,-0.1972636239
C,0,-2.5927166445,1.9518348322,-0.7254782138

C,0,-2.1139827135,0.2324074799,1.6651047192
C,0,-3.0873434322,-0.9076275775,-0.9476885573
C,0,-4.013369099,2.3437390596,-0.2896981493
C,0,-1.7197769777,3.1639310345,-0.3172826184
H,0,-2.58677689,1.8861604929,-1.8223209112
C,0,-3.5313372427,-0.0295479819,2.2556534856
C,0,-1.1954301774,-0.8123963134,2.3358885023
H,0,-1.7782424874,1.2241745371,1.9961892288
C,0,-2.8394494568,-2.3808767888,-0.5838800739
C,0,-3.0449636669,-0.8737136206,-2.4995216028
H,0,-4.095177179,-0.6310455479,-0.6140937841
C,0,-4.0701681371,3.831029933,-0.6540268324
H,0,-4.1323037096,2.2228319648,0.793438228
H,0,-4.7937916011,1.7501581965,-0.776482671
C,0,-2.6919714398,4.3714527217,-0.2294445755
H,0,-0.91389477,3.3221602505,-1.0400118269
H,0,-1.2335850692,2.9950379558,0.6503760251
C,0,-3.3316695893,-1.055547862,3.3961854858
H,0,-4.2418405095,-0.4013748823,1.5123839397
H,0,-3.9529362023,0.9037727601,2.6427979246
C,0,-1.8324311688,-1.009411555,3.7122985131
H,0,-0.1530108588,-0.48514079,2.3669023582
H,0,-1.2134676322,-1.7583778185,1.7812533573
C,0,-3.5683302903,-3.1381145114,-1.6980524153
H,0,-3.1962273138,-2.6385473823,0.4183916062
H,0,-1.7649262211,-2.6015284686,-0.6210657455
C,0,-3.2135867613,-2.3440795692,-2.9636119465
H,0,-2.0879733119,-0.4699069661,-2.8535784464
H,0,-3.8335474648,-0.2259956192,-2.8954143151
H,0,-4.201573069,3.9352723744,-1.7384331398
H,0,-4.9009911232,4.3598759649,-0.1758288617
H,0,-2.368887978,5.2096995241,-0.8539456448
H,0,-2.7359627639,4.7452497915,0.7992520822
H,0,-3.9627859074,-0.8426395879,4.2647313498
H,0,-3.5986191386,-2.0604953843,3.0476363305
H,0,-1.6065314559,-0.1486293013,4.3556449983
H,0,-1.4746646004,-1.9062092384,4.2279641058
H,0,-3.2799442447,-4.1924433863,-1.7596945461
H,0,-4.6507438223,-3.1063805799,-1.5183770462
H,0,-2.2688325892,-2.7128813857,-3.3781038644
H,0,-3.9670295067,-2.4488012398,-3.7502267915
C,0,3.7186712057,2.3113353707,-1.4714918685
H,0,4.6357223379,2.6154648564,-0.9551835068
H,0,3.8282921333,2.5774026314,-2.5274802396
H,0,2.8850377181,2.8957088464,-1.0676971182
H,0,4.299302975,0.2845412174,-1.8202735876
H,0,3.0999425773,2.1896758302,1.2095182111
H,0,2.7006420551,0.7267220337,2.1328830716

TSCH-c′

Sum of PCM and thermal Free Energies = **-1840,838936**

C,0,-3.7402475009,-3.1504441259,-0.7399266182
C,0,-4.8231100153,-2.6743294598,-0.0014345194
C,0,-4.7385413027,-1.4502643878,0.6601137782
C,0,-3.5637059178,-0.6939791131,0.603156902
C,0,-2.4694715996,-1.1994656754,-0.1071002728
C,0,-3.4248982342,0.6937160826,1.206483282
C,0,-1.8848917943,0.9963811207,1.4053526438
Pd,0,-0.6698672127,-0.4342975836,0.005570033
H,0,-1.7222314289,-2.757808546,-1.4022331504

H,0,-3.811969866,-4.0953587437,-1.2723839585
H,0,-5.7405618702,-3.2535478867,0.0533711084
H,0,-5.5867308217,-1.0828645746,1.233631026
H,0,-1.4756569852,1.1815717128,-0.0451206305
P,0,1.7545900981,0.033883813,0.0972929341
C,0,2.3137202296,1.7884091195,0.4482549395
C,0,3.8274915506,2.0753584059,0.6594548296
C,0,1.8519272203,2.8181184877,-0.6002885533
C,0,4.0814208239,3.4662762837,0.0240906404
C,0,2.6885427217,4.0503059224,-0.2492325214
C,0,2.438034617,-0.4037138193,-1.5953712973
C,0,3.961574692,-0.4316991602,-1.8281627979
C,0,1.9117983336,-1.7747973252,-2.1265113869
C,0,4.1117956548,-1.3154951955,-3.071319454
C,0,3.1197204145,-2.4526123519,-2.8089713768
C,0,2.7565943015,-0.9857645232,1.3083534903
C,0,2.4354671663,-2.4950725436,1.2919231411
C,0,2.5656422963,-0.6113011966,2.7861114679
C,0,2.8660110292,-3.0281515774,2.684797013
C,0,3.230181443,-1.7819935471,3.5207312113
H,0,1.7882200049,2.0238155074,1.3837258611
H,0,4.465353172,1.3172223083,0.1981666124
H,0,4.0676126439,2.0729256055,1.7272157055
H,0,0.7723034851,2.9859178801,-0.5849796624
H,0,2.1155688929,2.4838455328,-1.6121751131
H,0,4.696778639,4.1099394187,0.6600707526
H,0,4.6196448525,3.349705971,-0.9240511512
H,0,2.2878507798,4.5246975054,0.6559653905
H,0,2.6900469194,4.8073948241,-1.0396086325
H,0,2.0060659593,0.3733286968,-2.2359952126
H,0,4.4861102591,-0.9042556938,-0.9879783708
H,0,4.3853452326,0.5685715995,-1.9590464253
H,0,1.0945973433,-1.5934452537,-2.828351262
H,0,1.5025130768,-2.4107173085,-1.3348460425
H,0,3.8148924489,-0.7518433882,-3.965200745
H,0,5.1379465161,-1.6635181881,-3.2289361687
H,0,2.8374743665,-2.9940874823,-3.7170742248
H,0,3.5784634723,-3.1833705316,-2.1310038325
H,0,3.8159676804,-0.8405508878,1.0590919956
H,0,2.9371579973,-3.0164699386,0.471623502
H,0,1.3563072816,-2.6405995573,1.1521514118
H,0,1.4971002698,-0.5801491765,3.0292995848
H,0,2.9963844693,0.359093278,3.0502346222
H,0,2.0458265605,-3.585281193,3.1481917472
H,0,3.7107945779,-3.7194104733,2.609683755
H,0,2.9079767942,-1.8614628652,4.5633793998
H,0,4.3169131204,-1.6353073054,3.530406598
C,0,-1.2339525222,1.2667316689,-2.2539090553
O,0,-0.7519733271,0.1076928373,-2.3035756998
O,0,-1.508715094,1.891349804,-3.4212617613
O,0,-1.4993011226,1.9538247691,-1.2178631818
H,0,-1.2807512759,1.2556931979,-4.114002805
C,0,-1.6035148265,2.4844098711,1.6430292105
H,0,-0.536753156,2.6356017406,1.8351594892
H,0,-1.8862905369,3.1240016339,0.8060814377
H,0,-2.1460566521,2.8182304458,2.5399470681
C,0,-1.3734021857,0.2464266619,2.6561632751
H,0,-1.5900876976,-0.8253610253,2.6394012982
H,0,-0.2972783429,0.380698119,2.7787269531
H,0,-1.8534866152,0.6668710376,3.5526074173
C,0,-4.1632438816,1.7128914807,0.3000367476

H,0,-5.2020207729,1.3970887607,0.1735169814
H,0,-4.163073454,2.710113271,0.7471653306
H,0,-3.6826240727,1.7657733381,-0.676827749
C,0,-4.1081692334,0.7594768364,2.5143500843
N,0,-4.6642650021,0.8411048605,3.5319521924

TSCH-d'

Sum of PCM and thermal Free Energies = **-1840,860312**

C,0,-2.317949572,-2.2180878624,-1.6209477786
C,0,-3.5595402612,-2.812384781,-1.8542608955
C,0,-4.6889202745,-2.3454920258,-1.1813448613
C,0,-4.5786868142,-1.296498413,-0.271475132
C,0,-3.3357225762,-0.7109956312,-0.0067265367
C,0,-2.2051139864,-1.1899675288,-0.6846149324
C,0,-3.146913704,0.4363030665,0.9789081463
C,0,-1.6352454979,0.7861605467,1.014517508
Pd,0,-0.3934977194,-0.5325729446,-0.2874324536
H,0,-1.4431430457,-2.5467884807,-2.1802098046
H,0,-3.6468817321,-3.6197788553,-2.576859115
H,0,-5.6612519996,-2.7884568402,-1.3779751788
H,0,-5.4699610899,-0.9196715976,0.2253134393
H,0,-1.2917288471,1.2246498492,-0.2694642738
P,0,1.9129616923,0.0119632138,0.2701683389
C,0,2.2165851388,1.749755841,0.8979418686
C,0,3.5957944788,2.1090533469,1.4830772136
C,0,1.9636209,2.8662621385,-0.1271124383
C,0,3.6395246672,3.6605411101,1.4736403749
C,0,2.426221514,4.1190930246,0.6275533802
C,0,3.0129177045,-0.2398363728,-1.2246629056
C,0,4.5388014163,-0.3586894493,-1.0662821847
C,0,2.5953769962,-1.4955669629,-2.0453717023
C,0,4.9699057376,-0.9811404502,-2.3986780836
C,0,3.9029209563,-2.0535223162,-2.6605852969
C,0,2.618559292,-1.0594034168,1.6305393468
C,0,2.451714179,-2.5712684459,1.4005892916
C,0,1.9223799898,-0.8578111965,2.9861052618
C,0,2.614575351,-3.2086828666,2.8009379057
C,0,2.3995703486,-2.0595002482,3.8180249556
H,0,1.4642509774,1.8583669471,1.6934794709
H,0,4.3911383887,1.7077714142,0.8476302313
H,0,3.7479567437,1.6904515295,2.4825755254
H,0,0.9254279132,2.9177218097,-0.4661675292
H,0,2.5960707376,2.7135836569,-1.0117941549
H,0,3.5902904319,4.0680648641,2.488082452
H,0,4.5815440777,4.0136268444,1.0421427557
H,0,1.6179615148,4.4663241933,1.2814339376
H,0,2.6682379057,4.9476810356,-0.0444574797
H,0,2.7997968465,0.6414849544,-1.84194655
H,0,4.7986879526,-1.0364458286,-0.2431712405
H,0,5.0255926988,0.6008658756,-0.8693941018
H,0,1.8588449908,-1.2116834385,-2.800600867
H,0,2.1164140451,-2.2532782508,-1.4155003657
H,0,4.9416720357,-0.2165089162,-3.1854369328
H,0,5.9874264011,-1.3847356911,-2.374494079
H,0,3.795837253,-2.2873155232,-3.7240098695
H,0,4.1882937895,-2.9857130319,-2.1591133809
H,0,3.6843282042,-0.8188510622,1.7401751817
H,0,3.1576503705,-2.9747542148,0.6685061982
H,0,1.4406605924,-2.7647980688,1.0164918082

H,0,0.834760795,-0.9056185112,2.8427043385
H,0,2.1512343909,0.1028244579,3.4571216329
H,0,1.8965439603,-4.02152204,2.9450195858
H,0,3.6108203929,-3.6471226646,2.9164877354
H,0,1.68743883,-2.3217572958,4.6061419873
H,0,3.3440946562,-1.8110790414,4.3146408872
C,0,-0.827706811,1.4110321615,-2.3954565894
O,0,-0.2799483718,0.2770161657,-2.4702928683
O,0,-0.9819009214,2.1060072016,-3.5421333696
O,0,-1.2475437338,2.0058183716,-1.3571462575
H,0,-0.6448024045,1.5291538235,-4.2417481624
H,0,-1.4305117774,1.8032736582,1.3675179031
H,0,-1.1546706204,0.1390398517,1.7648461646
C,0,-3.9148479654,1.5964483031,0.4893099221
N,0,-4.5658598947,2.4978319609,0.1517711071
C,0,-3.7248582318,0.0875331196,2.4033961659
C,0,-3.574204395,1.2470039845,3.390172551
C,0,-3.1352989293,-1.2017583314,2.9786864138
H,0,-4.7996121352,-0.081049225,2.2528382768
H,0,-4.013077698,2.1701889821,3.0008101892
H,0,-4.0776309992,1.0063438871,4.3321348981
H,0,-2.5207236954,1.4402627327,3.6212566637
H,0,-3.2348536589,-2.0422004134,2.2866306971
H,0,-2.0747228961,-1.0894385736,3.2306801137
H,0,-3.6573623991,-1.4623115046,3.9052424466

Cyc-a'

Sum of PCM and thermal Free Energies = -1576,020736

C,0,-4.4134581617,-2.8647635021,-0.928643321
C,0,-4.5734776453,-1.5659348919,-0.4477452525
C,0,-3.4633916472,-0.7766255694,-0.1286527079
C,0,-2.1700165236,-1.2867876317,-0.2947459405
C,0,-2.0277120926,-2.5958770174,-0.7798052929
C,0,-3.1342132015,-3.3867201533,-1.0976232784
C,0,-3.6339232915,0.674466617,0.3359464357
C,0,-2.5876519668,1.0471173976,1.4321757692
C,0,-1.1641883925,1.1112216366,0.9050573858
H,0,-5.2880672832,-3.4648189643,-1.1645611132
H,0,-5.5757978899,-1.1656983964,-0.3139441914
H,0,-1.030360602,-3.0263793712,-0.9060332244
H,0,-2.9954702139,-4.4012219903,-1.4635803539
H,0,-2.844936122,2.0771324725,1.7344969589
H,0,-0.479556606,1.2778210069,1.745054937
H,0,-1.0322566336,1.9256179876,0.1833634348
Pd,0,-0.3605553648,-0.4802627755,-0.0665204295
C,0,-4.9717314008,0.8840578237,0.9182373759
N,0,-6.0226584287,1.0903764811,1.3693941286
C,0,-3.5261448986,1.61642658,-0.8875834185
H,0,-2.5777781451,1.4359517424,-1.3991710157
C,0,-2.7058876868,0.1618438179,2.6734793709
H,0,-2.4254773736,-0.8697594689,2.4411228498
H,0,-2.0372878615,0.5280525801,3.4599790873
H,0,-3.7246197618,0.163853428,3.0730077811
P,0,1.9633709228,0.1605866455,-0.0007385326
C,0,2.3204962753,1.9980582725,0.0525087576
C,0,2.8658203447,-0.4871614418,-1.518437947
C,0,2.9048440534,-0.4807958741,1.4822680676
C,0,3.783108064,2.4593360648,0.2483116978

C,0,1.835081639,2.7969110391,-1.1679648223
H,0,1.7283413145,2.3391378654,0.9133687137
C,0,4.4077150278,-0.6811857256,-1.5031357095
C,0,2.2967559366,-1.837348323,-2.0025547591
H,0,2.6173463296,0.2529679378,-2.2895896213
C,0,2.8342324873,-2.0095095963,1.6546687224
C,0,2.3532293863,0.0350789937,2.8212889916
H,0,3.9534995913,-0.1674042169,1.392277582
C,0,3.8607257062,3.8778208312,-0.3812808894
H,0,4.4781662015,1.7838743882,-0.2594727689
H,0,4.062159918,2.4589898119,1.3061990491
C,0,2.4486246754,4.1789514853,-0.9210216286
H,0,0.745789064,2.8111859471,-1.2643883937
H,0,2.2425259014,2.373705884,-2.0957188795
C,0,4.6775578845,-1.9909814578,-2.287493984
H,0,4.8128673312,-0.7521856011,-0.4896936996
H,0,4.901134852,0.1747053189,-1.9745201508
C,0,3.3563527083,-2.3235836432,-2.9937237847
H,0,1.299834161,-1.7313305855,-2.4440843452
H,0,2.2169564923,-2.5486316729,-1.1702451226
C,0,3.1112882006,-2.2669163455,3.1589165172
H,0,3.5348077869,-2.5392388354,1.0019083084
H,0,1.8247635062,-2.3553233836,1.3966590944
C,0,3.0235945612,-0.8862657237,3.8503115473
H,0,1.2644678947,-0.1013857898,2.844075472
H,0,2.5614127489,1.0949341579,2.9998714736
H,0,4.1911102633,4.6318198328,0.3393250813
H,0,4.5891540975,3.8860514015,-1.1990606158
H,0,1.8568332743,4.7070761918,-0.1633072844
H,0,2.4613581568,4.8083089797,-1.8162132946
H,0,5.5179612236,-1.8964138907,-2.9818287927
H,0,4.9315226643,-2.7979706493,-1.590294972
H,0,3.2712067094,-1.757916276,-3.9304327096
H,0,3.2597795481,-3.3849487114,-3.2425666568
H,0,2.3756852579,-2.9656146875,3.5687681464
H,0,4.0947336299,-2.7220807592,3.3115364785
H,0,2.4755226288,-0.9211767471,4.7966350677
H,0,4.0285774069,-0.5111860558,4.0768421884
H,0,-4.3372364162,1.4155844424,-1.5921437359
H,0,-3.5822917366,2.6668249425,-0.5819436815

Cyc-b′

Sum of PCM and Gibbs free energy = -1576,019842

C,0,-4.3098804655,-3.1999170415,-0.3856075755
C,0,-4.5083104915,-1.8453793886,-0.1227800203
C,0,-3.4241503698,-0.9888376148,0.0996360895
C,0,-2.117065642,-1.489922041,0.0432298194
C,0,-1.9356640411,-2.8576415781,-0.2155924151
C,0,-3.0172186194,-3.7140206244,-0.4310427596
C,0,-3.6375933109,0.5102557706,0.3547227344
C,0,-2.6466914896,1.0027149385,1.4602071961
C,0,-1.1939545432,1.0109468937,1.008828959
H,0,-5.1662277914,-3.8492645566,-0.5460451966
H,0,-5.5219716507,-1.4540733769,-0.0811796965
H,0,-0.9270280549,-3.2780551214,-0.242580129
H,0,-2.8494140685,-4.7712613356,-0.6221646598
H,0,-0.5531170293,1.1666328151,1.8848966496
H,0,-1.0098096267,1.8281723498,0.2987095818

Pd,0,-0.3461402117,-0.5857253394,0.0964826259
C,0,-5.0102525433,0.7401383781,0.838476251
N,0,-6.0933258215,0.9446676044,1.2070041126
C,0,-3.4801847523,1.2846929743,-0.9751871143
H,0,-2.4890205799,1.082217638,-1.3885401234
P,0,1.9496225373,0.1593979482,-0.039528884
C,0,2.2190385234,2.0047477711,-0.1929825612
C,0,2.7846904005,-0.6037290968,-1.5435143181
C,0,3.0123229298,-0.2943688077,1.4311037212
C,0,3.6604559588,2.5466976984,-0.2139369048
C,0,1.5790835525,2.654752886,-1.4294809044
H,0,1.7031445971,2.4067416673,0.6911537832
C,0,4.3307039448,-0.7612821554,-1.5955149841
C,0,2.2263818521,-2.0068604159,-1.863655821
H,0,2.4746479509,0.0554855686,-2.3641074493
C,0,3.0032026874,-1.7978471026,1.7619008983
C,0,2.5374922844,0.3427243665,2.7468990404
H,0,4.0414841572,0.0346351904,1.2349453351
C,0,3.5478336655,3.9718504531,-0.8188458252
H,0,4.2896181303,1.9176969793,-0.8523511891
H,0,4.1184357823,2.5485919736,0.7797272437
C,0,2.1033618474,4.0947972914,-1.360766176
H,0,0.4877502517,2.5854228965,-1.434614982
H,0,1.9417780181,2.170314623,-2.345736262
C,0,4.5941664147,-2.1470778751,-2.236695669
H,0,4.7936133181,-0.6998797632,-0.6066418302
H,0,4.7717477158,0.0425106433,-2.1935755572
C,0,3.2527487279,-2.5742217052,-2.8466040588
H,0,1.2085297844,-1.9643407791,-2.2665724857
H,0,2.1989370086,-2.6312127379,-0.9608720923
C,0,3.4026015236,-1.8910277402,3.2571431878
H,0,3.6666107358,-2.3765745174,1.1118609648
H,0,1.9870454092,-2.1889136271,1.6210910913
C,0,3.3040942801,-0.4512095054,3.8147479821
H,0,1.4575008166,0.1837163252,2.8602706461
H,0,2.7241005211,1.4200341773,2.8021965459
H,0,3.7558573651,4.7433886674,-0.0713663508
H,0,4.2829772027,4.1069563337,-1.6185082679
H,0,1.4855650556,4.6718519843,-0.6628387865
H,0,2.0559778814,4.6075382818,-2.3262478038
H,0,5.4059386527,-2.1204277987,-2.969996217
H,0,4.8885790532,-2.8666669716,-1.4636315004
H,0,3.1161084545,-2.1097022952,-3.8316319959
H,0,3.1688109577,-3.6571284141,-2.9808469882
H,0,2.7336833257,-2.5732294162,3.7904062841
H,0,4.4151075104,-2.2892925466,3.3750863573
H,0,2.8161357528,-0.4091634848,4.7931401417
H,0,4.3058904107,-0.023786464,3.9395031719
C,0,-2.9986593758,2.3977552037,2.0025510236
H,0,-2.3046753958,2.6713747378,2.8040796649
H,0,-2.9201119776,3.1662080401,1.2252691383
H,0,-4.0127279432,2.4307489162,2.4115844836
H,0,-2.7486340485,0.2864261079,2.2852586826
H,0,-4.2279398601,0.9462474874,-1.6969458082
H,0,-3.6031636357,2.3625067666,-0.8325227738

Cyc-c′

Sum of PCM and Gibbs free energy = -1576,016849

C,0,-2.4097969061,-2.7081409487,-0.9018619157
C,0,-3.6851078939,-3.2484879816,-1.0991464722
C,0,-4.820979676,-2.5023642205,-0.7881128522
C,0,-4.6899219503,-1.206648963,-0.2839625591
C,0,-3.4159354247,-0.6749713322,-0.0971166329
C,0,-2.2588282246,-1.4107275026,-0.3988523464
C,0,-3.0989025861,0.7314405376,0.3705098962
C,0,-1.7110152514,0.6431036891,1.1118993922
Pd,0,-0.4882715772,-0.5472278979,-0.0572379298
H,0,-1.5357777054,-3.3147173773,-1.1371185662
H,0,-3.7899392349,-4.2584496495,-1.489188803
H,0,-5.8098822538,-2.9292414778,-0.9328836006
H,0,-5.5740692299,-0.6255769689,-0.0304426072
P,0,1.8557192821,0.1161833333,0.0303294994
C,0,2.3551596811,1.888346475,-0.3084566716
C,0,3.8520031023,2.2291490006,-0.4478142509
C,0,1.7282165097,2.4931904412,-1.5739682742
C,0,3.8959489894,3.5662740476,-1.2369828231
C,0,2.4439476978,3.8444194892,-1.689291321
C,0,2.6271407395,-0.8847931831,-1.3685056539
C,0,4.0588413214,-1.4306739124,-1.2639393265
C,0,1.7892199783,-2.1440668875,-1.6900155844
C,0,4.1261376985,-2.4164924255,-2.43827678
C,0,2.7366374749,-3.0910242479,-2.4735225314
C,0,2.8450265774,-0.3317286834,1.5558838367
C,0,2.5236293271,-1.736629264,2.1021359385
C,0,2.5716140854,0.5710429495,2.7686656498
C,0,2.9330113293,-1.7021061766,3.5977571784
C,0,3.1940565295,-0.2144680013,3.9311661377
H,0,1.9457852618,2.4363669597,0.5515755834
H,0,4.3673379291,1.4467127763,-1.0138670218
H,0,4.3511512954,2.2969066036,0.523553412
H,0,0.6395204781,2.5774729413,-1.5133446867
H,0,1.9571079217,1.8722386553,-2.450282113
H,0,4.2863796785,4.3853304346,-0.6255163099
H,0,4.5635046489,3.4758169197,-2.0999115074
H,0,1.9682475638,4.5632703359,-1.0117020464
H,0,2.3885388178,4.269386078,-2.6960459575
H,0,2.5827124204,-0.2154617414,-2.2385302962
H,0,4.1954650617,-1.9694055179,-0.3187583048
H,0,4.8302534483,-0.6568055782,-1.314752222
H,0,0.8837076347,-1.8893428663,-2.2530902132
H,0,1.4623042181,-2.6272963329,-0.7601098123
H,0,4.2994022268,-1.8608808166,-3.3676891764
H,0,4.9443232238,-3.1367017054,-2.339024671
H,0,2.3948849246,-3.2495949688,-3.5003783732
H,0,2.7690690119,-4.0762588894,-1.9979691372
H,0,3.9118075456,-0.2641780057,1.3034519501
H,0,3.0293362202,-2.5329342086,1.5472212294
H,0,1.4452174443,-1.9179853218,2.0079048613
H,0,1.489085941,0.6707998766,2.9200378393
H,0,2.9866602011,1.5785930155,2.6657659795
H,0,2.135607032,-2.1169341773,4.221822641
H,0,3.8239112564,-2.3094552614,3.7844515651
H,0,2.7847089991,0.0814400818,4.9017595215
H,0,4.2721234761,-0.0178779693,3.9661926709
C,0,-1.0729416066,2.0104461189,1.3039041434
H,0,-0.1695048585,1.9348341949,1.915610769
H,0,-0.8093330335,2.4966114269,0.3619015784
H,0,-1.7703138496,2.6746846891,1.8393267761
C,0,-1.8436150628,-0.0694094499,2.4582522023

H,0,-2.3753663363,-1.0189830041,2.3685676935
H,0,-0.8583518531,-0.2715549632,2.889415156
H,0,-2.3926950302,0.5651836507,3.1705433393
C,0,-3.062073325,1.6672347895,-0.8608861554
H,0,-2.2638327571,1.3284558617,-1.5283223121
C,0,-4.1195019237,1.2624651582,1.292102864
N,0,-4.9148132067,1.7043262883,2.0160173504
H,0,-2.8860343073,2.7088204151,-0.5785209915
H,0,-4.0130166004,1.6119540548,-1.3973541944

Cyc-d'

Sum of PCM and Gibbs free energy = -1840,926071

C,0,-2.6609555251,-2.8438221187,-0.627034798
C,0,-3.9820248015,-3.2466537943,-0.8405245305
C,0,-5.0288200993,-2.3474084235,-0.6396387196
C,0,-4.7599540299,-1.0448197103,-0.217533093
C,0,-3.4406018513,-0.6500804797,0.006012431
C,0,-2.3717154033,-1.5371923817,-0.2142950102
C,0,-2.9945129061,0.7365525933,0.4560593018
C,0,-1.5635726387,0.5547051491,1.0242616179
Pd,0,-0.5121321429,-0.8266713529,-0.0148134541
H,0,-1.856292691,-3.5605255936,-0.7905285534
H,0,-4.1943027609,-4.262811484,-1.1651849752
H,0,-6.0557208051,-2.6593079656,-0.8108231245
H,0,-5.5826534411,-0.3491515956,-0.0675061947
P,0,1.7349334668,0.0178660605,0.0808067678
C,0,1.8909638221,1.8544674978,-0.2224641497
C,0,3.2851069631,2.4926889719,-0.294992032
C,0,1.2134002081,2.3341465155,-1.52082117
C,0,2.9829402553,3.9128396817,-0.7973360752
C,0,1.7753746588,3.7589319002,-1.7555466092
C,0,2.8077612028,-0.7961068492,-1.2323520688
C,0,4.3127574809,-0.9889785377,-0.99306945
C,0,2.3147468306,-2.2164750104,-1.5982920682
C,0,4.7110469146,-1.9392487778,-2.1286088356
C,0,3.533498693,-2.9316653399,-2.2408882636
C,0,2.6319135111,-0.2473076466,1.7014785285
C,0,2.5318078731,-1.6948772447,2.2200053599
C,0,2.0457476532,0.568330266,2.864950484
C,0,2.7583447208,-1.6022610771,3.7506598717
C,0,2.6568186968,-0.1000184337,4.1052300805
H,0,1.3530835198,2.3002453476,0.6269097647
H,0,3.9008816875,1.9600841625,-1.0300606019
H,0,3.8239797449,2.4806696269,0.6578253538
H,0,0.1226863043,2.3069165091,-1.4592770515
H,0,1.4950687952,1.6819922721,-2.3568435964
H,0,2.7119808512,4.549142728,0.0532344923
H,0,3.8491965699,4.3789021569,-1.2772892921
H,0,1.0150971867,4.5188033079,-1.5525628322
H,0,2.073925336,3.8895293871,-2.8001507422
H,0,2.6842254705,-0.1550361293,-2.1158977767
H,0,4.4876539883,-1.4745977492,-0.0251360731
H,0,4.8793936029,-0.0534392799,-0.9974665957
H,0,1.4480678214,-2.1775204837,-2.2667091531
H,0,1.996300065,-2.7538875445,-0.6965695692
H,0,4.814192727,-1.3685821998,-3.0594480425
H,0,5.6694214192,-2.4368277612,-1.9495976274
H,0,3.341285,-3.2110937276,-3.2808384169

H,0,3.7564026091,-3.8588058931,-1.7031377622
H,0,3.6860209082,0.0307089427,1.56891751
H,0,3.2400929627,-2.3703693057,1.7302457918
H,0,1.5240469647,-2.07728513,2.0110441636
H,0,0.9532335888,0.4605624301,2.8750619855
H,0,2.2738641778,1.6371298146,2.8045719528
H,0,2.0069194487,-2.1913164091,4.2853103821
H,0,3.7342133804,-2.0075119377,4.0357001454
H,0,2.0673601811,0.0829151035,5.0088106295
H,0,3.6554503308,0.3139118794,4.2873390398
H,0,-1.000463875,1.4916907277,1.0307712363
H,0,-1.6168551897,0.1456686596,2.0383625126
C,0,-2.8982049284,1.583275661,-0.7480204175
N,0,-2.8180109923,2.2668811149,-1.6856265938
C,0,-3.9704688501,1.4426486355,1.4619440559
C,0,-3.5033606931,2.8511008926,1.8389291322
C,0,-4.2277582146,0.6029470841,2.715590806
H,0,-4.9244501795,1.5475832986,0.9268692844
H,0,-3.3356000219,3.4740950484,0.9552678363
H,0,-4.2586202977,3.3446377356,2.459208634
H,0,-2.5735965787,2.8205909919,2.418005275
H,0,-4.5352100647,-0.4167211286,2.4701758423
H,0,-3.338741298,0.545714015,3.3526925033
H,0,-5.0225749933,1.063562607,3.3116914073

TSCC-a'

Sum of PCM and Gibbs free energy = -1575,999501

C,0,3.2092719061,-3.1880933141,1.0199051042
C,0,3.6101805246,-1.8543615902,1.089282461
C,0,2.9614035523,-0.881420932,0.3276043751
C,0,1.8689793731,-1.231829746,-0.4830708504
C,0,1.5216954794,-2.5869445708,-0.6054473806
C,0,2.1773625384,-3.5543607738,0.1580874035
C,0,3.4122660621,0.5706284239,0.2353563847
C,0,3.358454063,0.933901773,-1.2993787273
C,0,2.2048263957,0.1786026153,-1.9745695737
H,0,3.7249991708,-3.9398225472,1.6105947742
H,0,4.4533954775,-1.5718401258,1.7148615884
H,0,0.7337458129,-2.8883993371,-1.2893884561
H,0,1.8835389923,-4.5974791982,0.0689361874
H,0,3.1591899807,2.0111676109,-1.3574779608
H,0,2.5653305225,-0.6252602,-2.6179724814
H,0,1.5990128271,0.8545227292,-2.6121795386
Pd,0,0.3447373303,0.007154818,-0.9909694653
C,0,4.7694002334,0.741757578,0.7716072119
N,0,5.8260499874,0.9043654216,1.227233016
C,0,2.4948406619,1.5071299258,1.0536935217
H,0,1.4735798079,1.4340257973,0.6547403525
C,0,4.6713719018,0.6413141404,-2.0304423008
H,0,4.9401549042,-0.4167270504,-1.9328821351
H,0,4.5610857784,0.862873778,-3.0970158684
H,0,5.5017245042,1.2385132151,-1.6434466622

P,0,-1.8970707574,0.2704342551,-0.268608861
C,0,-2.588159624,1.9405487331,-0.7717725056
C,0,-2.1490470368,0.1762060517,1.5922260896
C,0,-3.1254312721,-0.9103602417,-1.040045541
C,0,-3.9997820765,2.3504931177,-0.3269774571
C,0,-1.6990235878,3.1300473503,-0.3413811926
H,0,-2.5827719441,1.8934770334,-1.8698700469
C,0,-3.57060178,-0.0902500827,2.1711756057
C,0,-1.2362551541,-0.8784909641,2.2550854989
H,0,-1.8128487061,1.1622623605,1.9392506844
C,0,-2.874704473,-2.3919678812,-0.7203921898
C,0,-3.0945367839,-0.8475169959,-2.5869848839
H,0,-4.130506591,-0.6414199701,-0.6912831716
C,0,-4.0395483094,3.8402145025,-0.6866203085
H,0,-4.1116219591,2.2263947568,0.7567762753
H,0,-4.7923237941,1.7697513825,-0.809555959
C,0,-2.6416382286,4.3634583484,-0.2990558181
H,0,-0.8574083734,3.2594345963,-1.0281682756
H,0,-1.2622093332,2.9542487112,0.6484189772
C,0,-3.379902825,-1.135755394,3.2953510634
H,0,-4.2793478462,-0.4474826908,1.4191345347
H,0,-3.9906468494,0.8378514586,2.5722011067
C,0,-1.8833862064,-1.0939851854,3.6238982882
H,0,-0.1938741206,-0.5528847001,2.296554649
H,0,-1.2499687946,-1.816822105,1.6875908573
C,0,-3.6712175944,-3.1165165972,-1.8102275336
H,0,-3.1787255942,-2.6698069681,0.293734543
H,0,-1.8043229835,-2.6153483526,-0.8192258819
C,0,-3.4080732764,-2.2867089713,-3.0791442885
H,0,-2.0998134247,-0.5384877643,-2.9330688218
H,0,-3.810390795,-0.1130174267,-2.968944116
H,0,-4.1990886594,3.9492116393,-1.7665083318
H,0,-4.8495739858,4.3803860291,-0.186079669
H,0,-2.306274115,5.1609595567,-0.9688141358
H,0,-2.6610130646,4.7895123007,0.7095992022
H,0,-4.0185470486,-0.9384830548,4.1621259869
H,0,-3.643063689,-2.1346874583,2.9269149279
H,0,-1.6627010478,-0.2419067462,4.2804619907
H,0,-1.5291737993,-1.9976296862,4.1299417667
H,0,-3.3855492213,-4.1673437767,-1.9217451855
H,0,-4.7387623935,-3.0965338145,-1.556904676
H,0,-2.5469753343,-2.6909761735,-3.6218405088
H,0,-4.2559051351,-2.3112543279,-3.7704562564
H,0,2.838239683,2.5440947067,0.981939477
H,0,2.4821595478,1.2108967278,2.106281131

TSCC-b′

Sum of PCM and Gibbs free energy = -1575,999616

C,0,3.1087902355,-3.5067767592,0.4143918528
C,0,3.5831694865,-2.2196174978,0.6668443375
C,0,2.9697891901,-1.1144257472,0.0768618287
C,0,1.8387147801,-1.2852882992,-0.7386254314
C,0,1.4159566501,-2.5868579184,-1.0489282034
C,0,2.0393289276,-3.6891100724,-0.459724423
C,0,3.51134397,0.3071373237,0.1603598675
C,0,3.4703210934,0.809829184,-1.3297904051
C,0,2.1722392521,0.3586782019,-2.0127837217
H,0,3.5978353925,-4.3628848931,0.870376572

H,0,4.4573479996,-2.0755513397,1.2972289561
H,0,0.5933696253,-2.7423422795,-1.7406392633
H,0,1.6893445475,-4.6917000132,-0.6935563956
H,0,2.351326133,-0.2893198557,-2.8705414778
H,0,1.5882989652,1.2319181217,-2.373024396
Pd,0,0.3606074173,0.0851591045,-0.9626631043
C,0,4.9081768897,0.322014217,0.6172833474
N,0,6.0110423528,0.3640117889,0.9812495449
C,0,2.6935044923,1.1773034085,1.136601984
H,0,1.6541567847,1.2233764334,0.7826986819
P,0,-1.8722908201,0.3014020904,-0.1972636239
C,0,-2.5927166445,1.9518348322,-0.7254782138
C,0,-2.1139827135,0.2324074799,1.6651047192
C,0,-3.0873434322,-0.9076275775,-0.9476885573
C,0,-4.013369099,2.3437390596,-0.2896981493
C,0,-1.7197769777,3.1639310345,-0.3172826184
H,0,-2.58677689,1.8861604929,-1.8223209112
C,0,-3.5313372427,-0.0295479819,2.2556534856
C,0,-1.1954301774,-0.8123963134,2.3358885023
H,0,-1.7782424874,1.2241745371,1.9961892288
C,0,-2.8394494568,-2.3808767888,-0.5838800739
C,0,-3.0449636669,-0.8737136206,-2.4995216028
H,0,-4.095177179,-0.6310455479,-0.6140937841
C,0,-4.0701681371,3.831029933,-0.6540268324
H,0,-4.1323037096,2.2228319648,0.793438228
H,0,-4.7937916011,1.7501581965,-0.776482671
C,0,-2.6919714398,4.3714527217,-0.2294445755
H,0,-0.91389477,3.3221602505,-1.0400118269
H,0,-1.2335850692,2.9950379558,0.6503760251
C,0,-3.3316695893,-1.055547862,3.3961854858
H,0,-4.2418405095,-0.4013748823,1.5123839397
H,0,-3.9529362023,0.9037727601,2.6427979246
C,0,-1.8324311688,-1.009411555,3.7122985131
H,0,-0.1530108588,-0.48514079,2.3669023582
H,0,-1.2134676322,-1.7583778185,1.7812533573
C,0,-3.5683302903,-3.1381145114,-1.6980524153
H,0,-3.1962273138,-2.6385473823,0.4183916062
H,0,-1.7649262211,-2.6015284686,-0.6210657455
C,0,-3.2135867613,-2.3440795692,-2.9636119465
H,0,-2.0879733119,-0.4699069661,-2.8535784464
H,0,-3.8335474648,-0.2259956192,-2.8954143151
H,0,-4.201573069,3.9352723744,-1.7384331398
H,0,-4.9009911232,4.3598759649,-0.1758288617
H,0,-2.368887978,5.2096995241,-0.8539456448
H,0,-2.7359627639,4.7452497915,0.7992520822
H,0,-3.9627859074,-0.8426395879,4.2647313498
H,0,-3.5986191386,-2.0604953843,3.0476363305
H,0,-1.6065314559,-0.1486293013,4.3556449983
H,0,-1.4746646004,-1.9062092384,4.2279641058
H,0,-3.2799442447,-4.1924433863,-1.7596945461
H,0,-4.6507438223,-3.1063805799,-1.5183770462
H,0,-2.2688325892,-2.7128813857,-3.3781038644
H,0,-3.9670295067,-2.4488012398,-3.7502267915
C,0,3.7186712057,2.3113353707,-1.4714918685
H,0,4.6357223379,2.6154648564,-0.9551835068
H,0,3.8282921333,2.5774026314,-2.5274802396
H,0,2.8850377181,2.8957088464,-1.0676971182
H,0,4.299302975,0.2845412174,-1.8202735876
H,0,3.0999425773,2.1896758302,1.2095182111
H,0,2.7006420551,0.7267220337,2.1328830716

TSCC-c′

Sum of PCM and Gibbs free energy = -1575,969692

C,0,-1.8315984977,-2.668616433,-0.0510883408
C,0,-2.5422887711,-3.4714826276,-0.9528259256
C,0,-3.6124459678,-2.9659614987,-1.6951793309
C,0,-4.0311444044,-1.6401844407,-1.5287524321
C,0,-3.2974966801,-0.842283849,-0.6665266687
C,0,-2.1714684138,-1.3071376729,0.0267676335
C,0,-3.5185597368,0.5012810996,-0.0135072696
C,0,-2.5994374002,0.1310669763,1.2238117582
Pd,0,-0.4236718399,-0.2921176122,0.2896270332
H,0,-1.0392983393,-3.097766355,0.5547417448
H,0,-2.2643973996,-4.5169960622,-1.0632834999
H,0,-4.1565311749,-3.6231516181,-2.3678830298
H,0,-4.9267543321,-1.2710518645,-2.0216983048
P,0,1.8414041143,0.2080985069,0.0889048946
C,0,2.2385693969,2.0473052802,0.0622137941
C,0,3.7260427771,2.4940434564,-0.0640705163
C,0,1.4767214934,2.8031262335,-1.057456928
C,0,3.7947311256,3.3474316723,-1.3405431393
C,0,2.3990192823,3.9676468597,-1.4353694726
C,0,2.6085055476,-0.4919974932,-1.4823943484
C,0,4.1325797007,-0.6768437459,-1.5976134273
C,0,2.0183500713,-1.8817810889,-1.8532084832
C,0,4.270078317,-1.6161031781,-2.8007335975
C,0,3.1480482555,-2.6441130915,-2.5908142601
C,0,2.9285748959,-0.4020625886,1.4867001793
C,0,2.8288514616,-1.9090864757,1.7669420852
C,0,2.5567964359,0.2403596594,2.8422405469
C,0,3.4494358501,-2.040503879,3.16173119
C,0,2.9359769667,-0.8046655226,3.9268732329
H,0,1.8481051342,2.3805606377,1.0305354391
H,0,4.4334880711,1.6614865218,-0.0841975446
H,0,3.9935502139,3.1055931806,0.8055044173
H,0,0.4834919884,3.1236993562,-0.7310966398
H,0,1.3250190534,2.1614441921,-1.9350032624
H,0,4.6018561994,4.0865772145,-1.3138971766
H,0,3.969963316,2.7070306271,-2.2151149493
H,0,2.3021985815,4.778975507,-0.7020185498
H,0,2.1742765214,4.3880181936,-2.4209373784
H,0,2.3015740945,0.2213990348,-2.2585230549
H,0,4.5378072412,-1.1657575357,-0.7027937284
H,0,4.6720815709,0.2648611525,-1.7327033557
H,0,1.121588041,-1.7616847259,-2.4673709625
H,0,1.697103991,-2.4273345429,-0.9608030592
H,0,4.0989264508,-1.0507542081,-3.7258685733
H,0,5.2625255329,-2.0723967951,-2.8787612594
H,0,2.8078704182,-3.087712539,-3.5314459883
H,0,3.5143329993,-3.4684313618,-1.9680552164
H,0,3.9717078288,-0.1582221278,1.246487392
H,0,3.3303082716,-2.5258944057,1.0140656601
H,0,1.7710383691,-2.20476185,1.7906549832
H,0,1.4779783399,0.4387622907,2.8705175971
H,0,3.0653562296,1.1980628364,2.9893472455
H,0,3.1923134485,-2.9831485752,3.6553842981
H,0,4.542982603,-2.008623138,3.0788705525
H,0,2.0560111726,-1.0627379709,4.5252514909
H,0,3.6867199791,-0.4188984736,4.623360863

C,0,-1.9622537118,1.3440689976,1.9180452716
H,0,-1.3224869111,1.0345516792,2.7484277738
H,0,-1.3784560302,1.9911887498,1.261068417
H,0,-2.7856775853,1.9441186283,2.3443432829
C,0,-3.3291548665,-0.6762258059,2.297529837
H,0,-3.9648022644,-1.4604147544,1.8805306673
H,0,-2.5985821611,-1.1489433635,2.9606185699
H,0,-3.9566823825,-0.011635052,2.906089226
C,0,-3.0070453543,1.6774259695,-0.8607691821
H,0,-1.9481667657,1.5052711184,-1.087623773
C,0,-4.9087684289,0.7586079694,0.3765126401
N,0,-6.0079447296,0.9813501788,0.6820300701
H,0,-3.1168171332,2.6304788449,-0.3353686566
H,0,-3.5644678902,1.7325055879,-1.7999766617

TSCC-d'

Sum of PCM and Gibbs free Energy = -1840,886792

C,0,2.3110135843,-2.3401374368,0.2483853788
C,0,3.2185060299,-2.7171229801,1.2454129863
C,0,4.1973615515,-1.8378511597,1.7179106753
C,0,4.3304777604,-0.5599972042,1.1638503617
C,0,3.4202954813,-0.1893811368,0.1857543544
C,0,2.3654991738,-1.0190393255,-0.2255498692
C,0,3.3505075935,0.9164043576,-0.8509450674
C,0,2.3331242431,0.114060526,-1.720096426
Pd,0,0.4739723131,-0.3441129356,-0.7059753123
H,0,1.5772002334,-3.048942659,-0.1212935247
H,0,3.160979355,-3.7208697396,1.6599406366
H,0,4.887929214,-2.1672286573,2.4893118299
H,0,5.1428340218,0.0966226214,1.4650982749
P,0,-1.7391958624,-0.2740328789,0.0590515653
C,0,-2.0782691273,-1.4632656015,1.4676579344
C,0,-3.4889337649,-1.517426824,2.0765771693
C,0,-1.735735224,-2.9390380438,1.1366336399
C,0,-3.4465209819,-2.8088644957,2.8998430058
C,0,-2.7135469089,-3.7990805591,1.9800565304
C,0,-3.0613650476,-0.6598124758,-1.2262644358
C,0,-4.5159761677,-0.1392128069,-1.028427337
C,0,-2.6488812635,-0.1848925327,-2.6366827592
C,0,-4.9485562657,0.4426765997,-2.3941587534
C,0,-3.9695362509,-0.1590634588,-3.4088484124
C,0,-2.1876249253,1.3751657018,0.8155552209
C,0,-2.0921653445,2.56595846,-0.150756103
C,0,-1.2380733229,1.7542085788,1.9818561709
C,0,-2.018880671,3.7682071722,0.7957492649
C,0,-1.0712455404,3.2962633362,1.9105470719
H,0,-1.3863705666,-1.1216137691,2.2486057159
H,0,-4.2488915782,-1.6078662348,1.2909706139
H,0,-3.7330785883,-0.6320656244,2.672089292
H,0,-0.6886141697,-3.1460656452,1.3721480409
H,0,-1.8573203002,-3.1531815287,0.068802254
H,0,-2.8655672894,-2.6394922847,3.8153740455
H,0,-4.4377468655,-3.1608875495,3.2042939014
H,0,-2.2002269779,-4.5869101419,2.5397635931
H,0,-3.4362805324,-4.2977700341,1.3241642326
H,0,-3.0836648287,-1.7573067201,-1.2422043998
H,0,-4.596687512,0.613155761,-0.2393642966
H,0,-5.1711574801,-0.965821358,-0.7342082902

H,0,-1.883512888,-0.8305314338,-3.0774749513
H,0,-2.2259758593,0.8265949969,-2.5920620484
H,0,-5.9968664648,0.2302832894,-2.6269610237
H,0,-4.8382056841,1.5338703474,-2.3881682156
H,0,-4.2720208705,-1.1826321366,-3.6673926654
H,0,-3.913360913,0.4114644192,-4.3415637274
H,0,-3.2146043009,1.312724708,1.1968879381
H,0,-2.9300246622,2.6171468737,-0.8541900855
H,0,-1.1641626028,2.4949749056,-0.7337340422
H,0,-0.2632558544,1.2670932048,1.8575498107
H,0,-1.6462859088,1.422381133,2.9421210191
H,0,-1.6684174998,4.6787855468,0.2997227282
H,0,-3.0179559179,3.9788184399,1.1996773878
H,0,-0.0386569132,3.5404508008,1.6447097061
H,0,-1.2859843954,3.780098072,2.8685811627
H,0,1.5701501533,0.7222838704,-2.2487509825
H,0,2.8342820735,-0.5227065674,-2.447583678
C,0,4.6870846772,1.309110822,-1.5517724137
C,0,4.4487001073,2.3233744182,-2.6735826969
C,0,5.4681622531,0.0990433306,-2.0697655872
H,0,5.2971526147,1.7946178294,-0.7771237455
H,0,3.9499462864,3.2255415197,-2.3077019271
H,0,5.4000748521,2.6230308483,-3.1244761933
H,0,3.8284501619,1.8900643485,-3.4667097246
H,0,5.6178739483,-0.6589446264,-1.2967584881
H,0,4.9661043562,-0.3747725058,-2.9200387939
H,0,6.453253971,0.4234286101,-2.4203382004
C,0,2.7288035897,2.1275241767,-0.296242701
N,0,2.2718254332,3.0982974961,0.1514986257