Electronic Supplementary Material (ESI) for Dalton Transactions.

C_2-Symmetric Atropisomeric N-Heterocyclic Carbene-Palladium(II) Complexes: Synthesis, Chiral Resolution and Application in enantioselective α-Arylation of Amides

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I General considerations

All reagents were obtained from commercial sources and used as received. Solvents (THF, DCM, toluene and Et_2O) were purified and dried over Braun solvent purification system (MB-SPS-800) or dried by standard procedures prior to use.[1] Anilines have been prepared according to procedures from the literature.[2]

Analytical Thin Layer Chromatography (TLC) was carried out on Merck silica gel60 F_{254}. Products were revealed by ultraviolet light (254 or 366 nm) and stained with dyeing reagents solutions as potassium permanganate solution or *p*-anisaldehyde solution in ethanol followed by gentle heating. Flash chromatography was performed on Combiflash® Companion or with Merck silica gel 60 (230-400 mesh).

^1H, ^{13}C and ^{19}F spectra were recorded in $CDCl_3$ and acetone-d_6 at ambient temperature on Bruker Avance III 300 or 400 spectrometers operating at 300 and 400 MHz respectively for ^1H. ^{13}C nuclei was observed with ^1H decoupling. Solvent residual signals were used as internal standard.[3] Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz respectively. The peaks patterns are indicated as the following format multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; sept: septuplet; m: multiplet; dd: doublet of doublet; dt: doublet of triplet; dm: doublet of multiplet, etc.). The prefix br. indicates a broadened signal and p. for a pseudo multiplicity.

HRMS were recorded on SYNAPT G2 HDMS (Waters) or on QStar Elite (Applied Biosystems SGIEX) equipped with an Atmospheric Pressure Ionization (API) source. Mass spectra were obtained a Time Of Flight (TOF) analyser.

Melting points (uncorrected) were determined with a Büchi Melting Point B-545.

IR spectra were obtained using a Bruker Alpha Platinium ATR.

HRMS were recorded on SYNAPT G2 HDMS (Waters) or on QStar Elite (Applied Biosystems SGIEX) equipped with an Atmospheric Pressure Ionization (API) source. Mass spectra were obtained using a Time Of Flight (TOF) analyser.

Preparative chiral HPLC separations were performed on an Agilent 1260 Infinity unit (pump G1311C, autosampler G1329B, DAD G1365D and fraction collector G1364C), monitored by Agilent OpenLAB CDS Chemstation LC.

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578, 546, 436, 405, 365 and 325 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

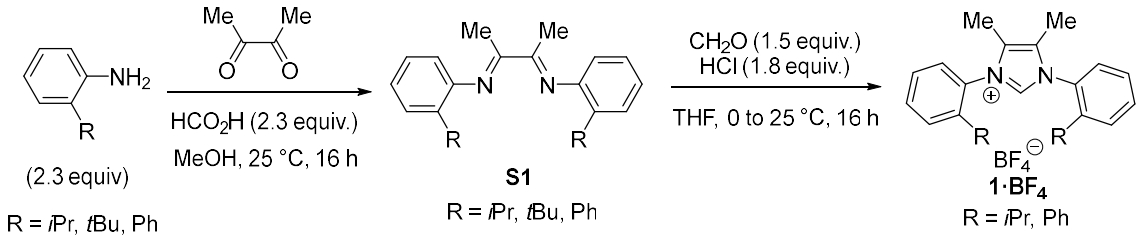
ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical path length was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample. The spectra are presented without smoothing and further data processing.

X-ray Diffraction: Intensity data were collected on an Agilent SuperNova AtlasS2 diffractometer using MoKα radiation (0.71073 Å) at 293(2) K or D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector using MoKα radiation (0.71073 Å) at T = 150 K. Data reduction was performed using the CrysAlisPro software package (version 1.171.37.31) or SHELXT program. The structures were resolved using the software SHELXS-97 by the direct methods and refined using SHELXL-2013-4. The CIF files of imidazolium salts and palladium complexes have been deposited with

CCDC numbers 2049184 ((+)-(R_a,R_a)-**2d**), 2049185 ((+)-(R_a,R_a)-**2f**), 2049186 ((-)-(R_a,R_a)-**2e**), 2250208 (*trans*-**1e·BF$_4$**), 2250209 (*trans*-**1f·BF$_4$**), 2250210 (*meso*-**2a**), 2250211 ((±)-**2c**), 2250212 (*meso*-**2d**), 2250213 (*meso*-**2c**), 2250214 (*meso*-**2f**), 2250215 ((-)-(1S_a,2R_a)-*cis*-**2b**.

Enantiomeric excesses were determined by HPLC analysis (High Performance Liquid Chromatography) on Alliance e2695 Waters® HPLC with a UV/visible detector 2489 Waters®.

II Imidazolium salts synthesis

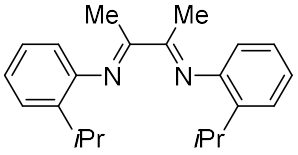


Scheme S1. Preparation of imidazolium via a diimine

General Procedure A: Synthesis of diimines S1

To a solution of the aniline (57.5 mmol, 2.3 equiv.) in methanol (40 mL) at room temperature, biacetyl (25 mmol, 1.0 equiv.) and formic acid (57.5mmol, 2.3 equiv.) were added. The resulting mixture was stirred at room temperature for 16 hours. The yellow solid was collected by filtration, washed with methanol (3 x 5 mL) and dried under vacuum to get the diamine **S1**.

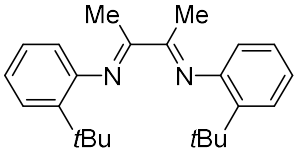
***N*²,*N*³-Bis(2-*iso*propylphenyl)butane-2,3-diimine S1a**[4]



According to the general procedure **A**, from 2-*iso*propylaniline (7.76 g, 57.5 mmol, 2.3 mmol), biacetyl (2.15 g, 25.0 mmol, 1.0 equiv.) and formic acid (2.65 g, 57.5 mmol, 2.3 equiv.), the title product was obtained as a yellow solid (5.20 g, 65% yield).

Rf = 0.85 (PE/Et_2O 20:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.33 (dd, *J*(H, H) = 7.3 and 1.5 Hz, 2H, *H*^{Ar}), 7.22-7.16 (m, 2H, *H*^{Ar}), 7.15-7.09 (m, 2H, *H*^{Ar}), 6.61 (dd, *J*(H, H) = 7.7 and 1.4 Hz, 2H, *H*^{Ar}), 2.97 (hept, *J*(H, H) = 6.9 Hz, 2H, C*H*), 2.17 (s, 6H, CH_3), 1.21 (d, *J*(H, H) = 6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 167.7 (*C*), 148.5 (*C*), 137.9 (*C*), 126.2 (*C*H), 125.9 (*C*H), 124.5 (*C*H), 118.1 (*C*H), 28.7 (*C*H), 22.9 (*C*H_3), 15.8 (*C*H_3).

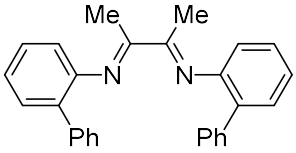
***N*²,*N*³-Bis(2-*tert*butylphenyl)butane-2,3-diimine S1b**[4]



According to the general procedure **A**, from 2-*tert*butylaniline (8.57 g, 57.5 mmol, 2.3 mmol), biacetyl (2.15 g, 25.0 mmol, 1.0 equiv.) and formic acid (2.65 g, 57.5 mmol, 2.3 equiv.), the title was obtained as a yellow solid (7.78 g, 93% yield).

Rf = 0.95 (PE/Et_2O 20 :1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.42 (dd, *J*(H, H) = 7.9 and 1.4 Hz, 2H, *H*^{Ar}), 7.22-7.16 (m, 2H, *H*^{Ar}), 7.11-7.05 (m, 2H, *H*^{Ar}), 6.51 (dd, *J*(H, H) = 7.7 and 1.4 Hz, 2H, *H*^{Ar}), 2.20 (s, 6H, CH_3), 1.35 (s, 18H, C(CH_3)$_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 166.9 (*C*), 149.5 (*C*), 139.5 (*C*), 126.6 (*C*H), 126.5 (*C*H), 124.2 (*C*H), 119.4 (*C*H), 35.3 (*C*), 29.7 (*C*H_3), 16.5 (*C*H_3).

***N*²,*N*³-Di([1,1'-biphenyl]-2-yl)butane-2,3-diimine S1c**



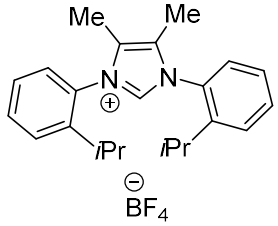
According to the general procedure **A**, from 2-phenylaniline (9.72 g, 57.5 mmol, 2.3 mmol), biacetyl (2.15 g, 25.0 mmol, 1.0 equiv.) and formic acid (2.65 g, 57.5 mmol, 2.3 equiv.), the title compound was obtained as a yellow solid (8.55 g, 88% yield).

Rf = 0.90 (PE/Et_2O 20 :1). **Mp** = 173.3-173.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.38-7.20 (m, 14H, *H*^{Ar}), 7.19-7.11 (m, 2H, *H*^{Ar}), 6.70-6.64 (m, 2H, *H*^{Ar}), 1.80 (s, 6H, C*H*$_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 167.7 (*C*), 148.5 (*C*), 137.9 (*C*), 126.2 (*C*H), 125.9 (*C*H), 124.5 (*C*H), 118.1 (*C*H), 28.7 (*C*H), 22.9 (*C*H$_3$), 15.8 (*C*H$_3$). **HRMS (ESI)**: *m/z*: 389.2012 calcd for $C_{28}H_{25}N_2^+$ $[M+H]^+$: found 389.2013. **IR (ATR):** 3050, 3018, 1631, 1590, 1561, 1498, 1448, 1429, 1356, 1285, 1248, 1195, 1154, 1119, 1071, 1045, 1008, 994, 973, 943, 912, 878, 850, 813, 771, 753, 741, 722, 701, 656, 614, 574, 528 cm^{-1}.

General Procedure B: Preparation of imidazolium salt 1 from diamine S1

To a solution of the diimine **S1** (10 mmol, 1.0 equiv.) in dry THF (100 mL), a mixture of paraformaldehyde (15 mmol, 1.5 equiv.) and HCl (2M in Et_2O, 18 mmol, 1.8 equiv.) was added dropwise at 0 °C under argon atmosphere. The resulting mixture was slowly warmed up to 25 °C and stirred for 16 hours. The solvent was removed under vacuum. Water (100 mL) was added in the residue and sat. $NaHCO_3$ solution was added to adjust the pH to 7. The aqueous phase was extracted by ethyl acetate (2 x 50 mL) and KBF_4 (20 mmol, 2.0 equiv.) was added to the aqueous phase. The mixture was stirred for 1 hour at 25 °C and then extracted by dichloromethane (3 x 100 mL). The combined dichloromethane phase was dried by Na_2SO_4 and filtered. The solvent was removed under vacuum and the residue was purified by silica gel column (DCM/acetone = 9:1) to give the imidazolium salt **1**.

1,3-Bis(2-*iso*propylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate 1a·BF_4

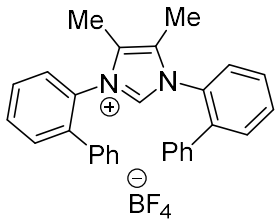


According to the general procedure **B**, from *N*²,*N*³-Bis(2-*iso*propylphenyl)butane-2,3-diimine **S1a** (5.2 g, 16.3 mmol, 1.0 equiv.), paraformaldehyde (0.73 g, 24.3 mmol, 1.5 equiv.), HCl (14.6 mL, 2M in Et_2O, 29.2 mmol, 1.8 equiv.) and KBF_4 (4.11 g, 32.6 mmol, 2.0 equiv.), the title compound was obtained as a white solid (1.8 g, 26% yield).

Rf = 0.45 (DCM/acetone = 9:1). **Mp** = 193.4-193.9 °C In $CDCl_3$ (25 °C) this imidazolium salt exists in two isomeric forms in a 9:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.48 (s, 0.1H, NC*H*N, *min*), 8.29(s, 0.9H, NC*H*N, *maj*), 7.86 (dd, *J*(H,H) = 8.0 and 1.3 Hz, 1.8H, *H*^{Ar}, *maj*), 7.64-7.55 (m, 2.4H, *H*^{Ar}), 7.53-7.44 (m, 4H, *H*^{Ar}), 2.70 (sept, *J*(H,H) = 6.8 Hz, 0.2H, C*H, min*), 2.48 (sept, *J*(H,H) = 6.8 Hz, 0.8H, C*H, maj*), 2.18 (s, 0.6H, C*H*$_3$, *min*), 2.15 (s, 5.4H, C*H*$_3$, *maj*), 1.35-1.29 (m, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, *J*(H,H) = 6.8 Hz, 0.6H, CH(C*H*$_3$)$_2$, *min*), 1.18 (d, *J*(H,H) = 6.8 Hz, 5.4H, CH(C*H*$_3$)$_2$, *maj*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 145.6 (*C*), 147.7 (*C*), 144.0 (*C*H), 133.9 (*C*H), 130.5 (*C*), 130.3 (*C*), 129.4 (*C*), 129.1 (*C*), 128.4 (*C*H), 128.3 (*C*H), 128.0

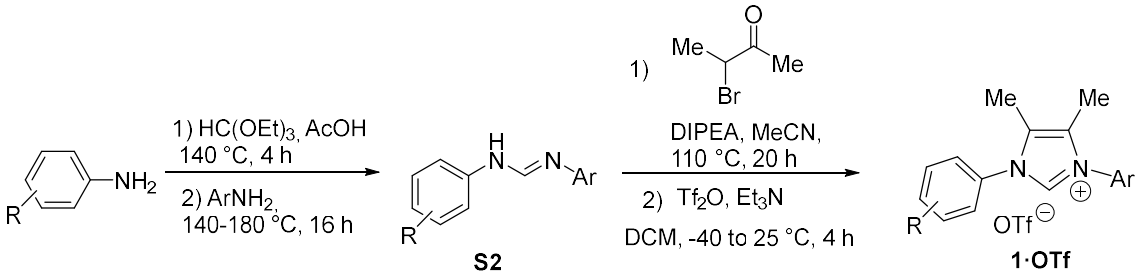
(*C*H), 127.9 (*C*H), 127.8 (*C*H), 127.7 (*C*H), 127.5 (*C*H), 126.9 (*C*H), 28.4 (*C*H), 28.1 (*C*H), 24.7 (CH_3), 24.6 (CH_3), 23.1 (CH_3), 22.8 (CH_3), 8.9 (CH_3), 8.8 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** -152.2 (s, 4F, BF_4). **HRMS (ESI)**: *m/z*: 333.2325 calcd for $C_{23}H_{29}N_2^+$ [C]$^+$: found 333.2314. **IR (ATR):** 3124, 3065, 2961, 2926, 2868, 2358, 2165, 2079, 2029, 2002, 1980, 1637, 1543, 1491, 1451, 1390, 1368, 1353, 1308, 1285, 1253, 1225, 1202, 1167, 1098, 1044, 1026, 884, 842, 773, 755, 721, 671, 660, 627, 601, 573, 553, 520, 507 cm^{-1}.

1,3-Bis(2-phenylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate 1c·BF_4



According to the general procedure B, from *N*^{2},*N*^{3}-Bis(2-phenylphenyl)butane-2,3-diimine (8.5 g, 21.9 mmol, 1.0 equiv.), paraformaldehyde (0.99 g, 32.9 mmol, 1.5 equiv.), HCl (19.7 mL, 2M in Et_2O, 39.4 mmol, 1.8 equiv.) and KBF_4 (5.54 g, 44.0 mmol, 2.0 equiv.), the title compound was isolated as a white solid (2.12 g, 20% yield).

Rf = 0.65 (DCM/acetone = 9:1). **Mp** = 246.1-246.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.59 (s, 1H, NC*H*N), 8.00-7.56 (m, 6H, *H*^{Ar}), 7.55-7.48 (m, 2H, *H*^{Ar}), 7.43-7.31 (m, 6H, *H*^{Ar}), 7.15-6.95 (m, 4H, *H*^{Ar}), 1.76 (s, 6H, CH_3). **^{13}C NMR (101 MHz, CD_3COCD_3):** δ= 139.9 (*C*), 137.3 (*C*), 132.6 (*C*H), 132.5 (*C*H), 131.8 (*C*), 130.2 (*C*H), 130.0 (*C*H), 129.5 (*C*H), 129.3 (*C*H), 8.8 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -153.0 (s, 4F, BF_4). **HRMS (ESI)**: *m/z*: 401.2012 calcd for $C_{29}H_{25}N_2^+$ [C]$^+$: found 401.2019. **IR (ATR):** 3137, 3060, 2362, 1635, 1596, 1541, 1508, 1483, 1435, 1283, 1217, 1180, 1157, 1100, 1048, 1029, 1008, 952, 923, 841, 770, 739, 704, 660, 626, 611, 597, 553, 518 cm^{-1}.

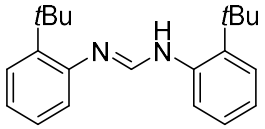


Scheme S2. Preparation of imidazolium via a formamidine

General Procedure C: Preparation of symmetrical formamidines S2

Acetic acid (85 µL, 1.5 mmol, 0.05 equiv.) was added to a round bottom flask charged with the aniline (30 mmol, 1.0 equiv.) and triethyl orthoformate (5 mL, 30 mmol, 0.5 equiv.). The flask was fitted with a distillation head and stirred at 140 °C for 2 h, then at 160 °C for 2 h and finally at 180 °C for 12 h, until ethanol (3.5 mL, 30 mmol) was collected by distillation. After cooling to room temperature, the crude material was triturated with hexane (100 mL)/dichloromethane (20 mL) at -18 °C and filtered to give the expected product.

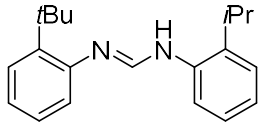
***N'*-(2-*tert*butylphenyl)-*N*-(2-*tert*butylphenyl)formamidine S2b**



According to general procedure **C**, 2-*tert*butylaniline (4.47 g, 30 mmol), triethyl orthoformate (2.5 mL, 15 mmol) and acetic acid (43 µL, 0.75 mmol) were heated at 140 °C for 12 hours. The crude material was triturated with hexane (15 mL) at -18 °C. The resulting solid was recrystallized in acetone to give a white solid (2.7 g, 57%).

Rf = 0.55 (PE/EtOAc = 9:1). In $CDCl_3$ (25 °C) this formamidine exists in two isomeric forms in a 4:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.84 (s, 1H, NC*H*N), 7.41-7.34 (m, 2H, H^{Ar}), 7.20-7.15 (m, 2H, H^{Ar}), 7.10-6.90 (m, 5H, N*H* and H^{Ar}), 1.48 (s, 9H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 147.8 (*C*H), 141.2 (*C*), 138.6 (C), 127.2 (*C*H), 126.6 (*C*H), 123.9 (*C*H), 121.5 (*C*H), 35.2 (*C*), 30.6 (CH_3).

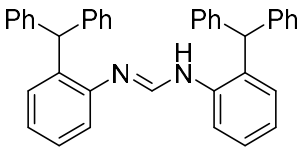
***N*'-(2-(*tert*butyl)phenyl)-*N*-(2-*iso*propylphenyl)formamidine S2b'**



Acetic acid (43 µL, 0.75 mmol, 0.05 equiv.) was added to a round bottom flask charged with 2-*iso*butylaniline (2.05 g, 15 mmol), and triethyl orthoformate (2.5 mL, 15 mmol, 1.0 equiv.). The flask was fitted with a distillation head and was stirred and heated to 140 °C for 12 h and at 160 °C for 2 h. 2-*tert*butylaniline (2.23 g, 15 mmol) was added and the mixture was heated to 140 °C for 12 h and at 160 °C for 2 h, then cooled to room temperature. The crude material was triturated with hexane (15 mL) at -18 °C. The resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate 20:1) to give a white solid (2.24 g, 34%).

Rf = 0.25 (PE/EtOAc = 20:1). **Mp =** 118.5-119.3 °C **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 (s, 1H, NC*H*N), 7.37 (dd, *J*(H,H) = 7.8 and 1.6 Hz, 1H, H^{Ar}), 7.29 (d, *J*(H,H) = 7.3 Hz, 1H, H^{Ar}), 7.22-7.04 (m, 6H, N*H* and H^{Ar}), 6.86 (d, *J*(H,H) = 7.6 Hz, 1H, H^{Ar}), 3.21 (sept, *J*(H,H) = 6.9 Hz, 1H, H^{Ar}), 1.46 (s, 9H, C(CH_3)$_3$), 1.30 (d, *J*(H,H) = 6.9 Hz, 6H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 147.8 (*C*H), 144.2 (*C*H), 142.1 (*C*), 138.2 (C), 127.1 (*C*H), 126.8 (*C*H), 126.4 (*C*H), 126.0 (*C*H), 124.0 (*C*H), 123.9 (*C*H), 121.6 (*C*H), 118.4 (*C*H), 35.5 (*C*), 30.6 (CH_3), 27.8 (CH_3), 23.0 (CH_3). **HRMS (ESI)**: *m/z* 295.2169 calcd for: $C_{20}H_{27}N_2^+$ $[M+H]^+$: found 295.2169. **IR (ATR):** 3191, 3057, 2995, 2955, 2927, 2865, 2359, 2341, 1651, 1636, 1599, 1586, 1568, 1508, 1480, 1449, 1389, 1361, 1348, 1275, 1253, 1201, 1159, 1127, 1085, 1051, 1037, 994, 936, 904, 844, 809, 745, 638, 612 cm^{-1}.

***N*'-(2-benzhydrylphenyl)-N-(2-benzhydrylphenyl) formamidine S2d**

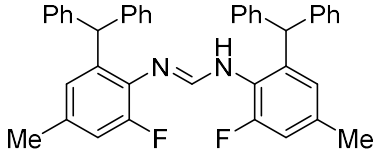


According to the general procedure **C**, from 2-benzhydrylaniline (5.19 g, 20 mmol), triethyl orthoformate (1.66 mL, 10 mmol) and acetic acid (57 µL, 0.5 mmol) a white solid was obtained (4.80 g, 91%).

Rf = 0.32 (PE/ Et_2O 1:1). **Mp** = 199.2-119.9 °C. In $CDCl_3$ (25 °C), this formamidine exists as a mixture of rotamers. ^{1}H NMR chemical shifts cannot be denoted. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.45-6.95 (m,

24.4H, H^{Ar} and N=C*H* and N*H*), 6.90-6.78 (m, 4H, H^{Ar}), 6.70-6.60 (m, 1H, H^{Ar}), 6.48 (s, 0.6H, H^{Ar}), 6.00-5.90 (m, 0.2H, C*H*), 5.85-5.65 (m, 1.6H, C*H*), 5.00 (s, 0.2H, C*H*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 148.7 (*C*H), 143.8 (*C*), 143.2 (*C*), 135.9 (*C*), 130.0 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 129.4 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 128.3 (*C*H), 127.5 (*C*H), 126.6 (*C*H), 123.8 (*C*H), 120.0 (*C*H), 52.0 (*C*H). **HRMS (ESI)**: *m/z*: 529.2638 calcd for: $C_{39}H_{33}N_2^+$ $[M+H]^+$: found 529.2637. **IR (ATR):** 3057, 3024, 2863, 2324, 1668, 1589, 1493, 1478, 1447, 1301, 1206, 1153, 1090, 1075, 1030, 983, 920, 808, 776, 747, 732, 697, 658, 606, 539 cm^{-1}.

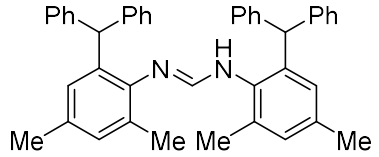
***N*'-(2-benzhydryl-4-fluoro-6-methylphenyl)-N-(2-benzhydryl-4-fluoro-6-methylphenyl) formamidine S2e**



According to the general procedure **C**, from 2-benzhydryl-4-fluoro-6-methylaniline (5.82 g, 20 mmol), triethyl orthoformate (1.66 mL, 10 mmol) and acetic acid (57 µL, 0.1 mmol) a white solid was obtained (4.58 g, 77%).

Rf = 0.33 (PE/ Et_2O 1:1). **Mp** = 196.2-196.8 °C. In $CDCl_3$ (25 °C), this formamidine exists as a mixture of rotamers. ^{1}H NMR chemical shifts cannot be denoted. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-6.65 (m, 24.3H, H^{Ar} and N=C*H* and N*H*), 6.46-6.38 (m, 1.4H, H^{Ar}), 6.27 (s, 0.3H, H^{Ar}), 6.64 (s, 0.2H, H^{Ar}), 5.80-5.65 (m, 1.4H, C*H*), 5.25-5.15 (m, 0.6H, C*H*), 2.30-2.10 (m, 6H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 147.8 (*C*H), 143.6 (*C*), 143.2 (*C*), 141.4 (*C*), 139.4 (*C*), 138.3 (*C*), 134.9 (*C*), 129.7 (*C*H), 129.5 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 126.9 (*C*H), 126.5 (*C*H), 126.1 (*C*H), 125.9 (*C*H), 115.1 (*C*H), 114.8 (*C*H), 51.8 (*C*H), 21.3 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -125.5 (s, *F*), -126.2 (s, *F*). **HRMS (ESI)**: *m/z*: 593.2763 calcd for: $C_{41}H_{35}F_2N_2^+$ $[M+H]^+$: found 593.2768. **IR (ATR):** 3376, 3058, 3025, 2915, 2861, 2325, 1648, 1599, 1580, 1492, 1478, 1447, 1377, 1317, 1294, 1231, 1201, 1154, 1128, 1076, 1030, 1001, 981, 907, 848, 822, 783, 737, 698, 630, 617, 580, 537, 525 cm^{-1}.

***N*'-(2-benzhydryl-4,6-dimethylphenyl)-N-(2-benzhydryl-4,6-dimethylphenyl) formamidine S2f**



According to the general procedure **C**, from 2-benzhydryl-2,6-dimethylaniline (11.7 g, 40 mmol), triethyl orthoformate (3.3 mL, 20 mmol) and acetic acid (115 µL, 2 mmol) a white solid was obtained (8.42 g, 72%).

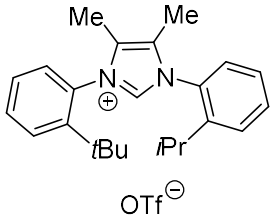
Rf = 0.35 (PE/Et_2O 1:1). **Mp** = 241.6-241.8 °C. In $CDCl_3$ (25 °C), this formamidine exists as a mixture of rotamers. ^{1}H NMR chemical shifts cannot be denoted. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.28-7.13 (m, 13H, H^{Ar} and N=C*H* and N*H)*, 7.04-6.94 (m, 7 H, H^{Ar}), 6.92-6.76 (m, 4H, H^{Ar}), 6.54 (d, *J*(H,H) = 1.9 Hz, 0.4H, H^{Ar}), 6.49 (d, *J*(H,H) = 2.0 Hz, 1.2H, H^{Ar}), 6.40 (d, *J*(H,H) = 1.9 Hz, 0.4H, H^{Ar}), 5.80-5.65 (m, 1.2H, C*H*), 5.49 (s, 0.2H, C*H*), 5.46 (s, 0.2H, C*H*), 5.28 (s, 0.4H, C*H*), 2.28-1.90 (m, 12H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 146.9 (*C*H), 144.9 (*C*), 144.1 (C), 142.6 (*C*), 142.4 (*C*), 141.8 (*C*), 138.4 (*C*), 135.0 (*C*), 134.6 (*C*), 133.4 (*C*), 132.1 (*C*), 132.0 (*C*), 130.9 (*C*H), 130.2 (*C*H), 129.8 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 129.4 (*C*H), 129.1 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 128.1 (*C*), 126.8 (*C*H), 126.6 (*C*H), 126.3 (*C*H), 126.0 (*C*H), 52.4 (*C*H), 51.8 (*C*H), 51.3 (*C*H), 21.2 (CH_3), 21.1 (CH_3), 19.2 (CH_3), 18.6 (CH_3). **HRMS (ESI)**: *m/z*: 585.3264 calcd for: $C_{43}H_{41}N_2^+$ $[M+H]^+$: found 585.3264. **IR**

(ATR): 3023, 2914, 2856, 2522, 2324, 1660, 1599, 1580, 1492, 1466, 1445, 1375, 1307, 1286, 1249, 1228, 1203, 1152, 1138, 1074, 1030, 1001, 968, 918, 895, 850, 823, 780, 742, 700, 631, 616, 599, 570, 558, 533 cm^{-1}.

General Procedure D: Preparation of imidazolium salts from formamidines[5]

To a suspension of formamidine **S2** (1 mmol) in acetonitrile (2 mL), *N,N*-Diisopropylethylamine (0.35 mL, 2 mmol, 2.0 equiv.) and 3-bromo-2-butanone (0.21 mL, 2 mmol, 2.0 equiv.) were added and the resulting mixture was stirred at 110 °C for 20 h. The solvent was removed under vacuo. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 10:1) to give the intermediate. The intermediate was dissolved in dichloromethane (3 mL). Triethylamine (142 μL, 1.1mmol, 1.1 equiv.) was added dropwise at -40 °C. After 5 min, trifluoromethanesulfonic anhydride (188 μL, 1.1 mmol, 1.1 equiv.) was added dropwise. The mixture was slowly warmed up to room temperature and stirred at room temperature for 4 h. The volatiles were removed under vacuo and the residue was purified by silica gel column chromatography (dichloromethane/acetone = 10:1) to give the imidazolium triflate salt **1·OTf**.

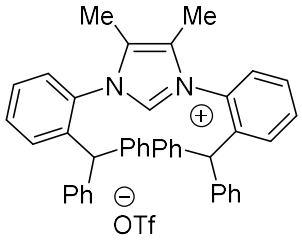
1-(2-*Iso*propylphenyl)-3-(2-*tert*butylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate 1b·OTf



According to the general procedure **D**, from *N*-(2-*iso*propylphenyl)-*N'*-(2-tertbutylphenyl)formimidine **S2b'** (580 mg, 1.97 mmol), *N,N*-diisopropylethylamine (0.70 mL, 4 mmol, 2.0 equiv.), 3-bromo-2-butanone (0.42 mL, 4 mmol, 2.0 equiv.), triethylamine (0.45 mL, 2.89 mmol, 1.1 equiv.) the title compound as a white solid (200 mg, 20% yield).

Mp = 137.1-137.5 °C. In $CDCl_3$ (25 °C) this imidazolium salt exists in two isomeric forms in a 9:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (min). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.94 (s, 0.1H, NC*H*N, *min)*, 8.49 (s, 0.9H, NC*H*N, *maj*), 7.94 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 7.81 (dd, *J*(H,H) = 7.7 and 7.1 Hz, 1H, H^{Ar}), 7.67-7.4 (m, 6H, H^{Ar}), 2.58 (sept, *J*(H,H) = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 2.17 (m, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.35-1.25 (m, 12H, C(CH_3)$_3$ and CH(CH_3)$_2$), 1.18 (d, 3H, CH(CH_3)$_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 145.8 (*C*), 145.0 (*C*), 144.4 (*C*), 135.2 (*C*H), 132.0 (*C*H), 131.6 (*C*H), 131.3 (*C*H), 130.8 (*C*), 130.4 (*C*), 130.2 (*C*), 129.0 (*C*H), 128.7 (*C*H), 128.3 (*C*H), 128.1 (*C*H), 126.8 (*C*H), 120.6 (q, *J*(C,F) = 320.3 Hz, *C*F_3), 36.O (*C*), 31.8 (*C*H), 28.2 (*C*H_3), 27.3 (*C*H_3), 24.9 (*C*H_3), 9.5 (*C*H_3), 9.0 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -78.4 (s, 3F, C*F*$_3$). **HRMS (ESI)**: *m/z*: 347.2482 calcd for $C_{24}H_{31}N_2^+$ [C]$^+$: found 347.2478. **IR (ATR):** 3034, 2964, 1662, 1623, 1536, 1490, 1445, 1388, 1366, 1262, 1223, 1150, 1086, 1051, 1030, 961, 874, 803, 766, 759, 670, 636, 598, 571, 557, 511 cm^{-1}.

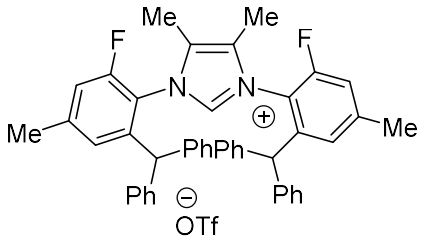
1-(2-Benzhydrylphenyl)-3-(2-benzhydrylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate 1d·OTf



According to the general procedure **D**, from *N*-(2-Benzhydrylphenyl)-*N'*-(2–benzhydrylphenyl)formimidamide **S2d** (1.32 g, 2.5 mmol), *N,N*-di*iso*propylethylamine (0.53 mL, 5 mmol, 2.0 equiv.), 3-bromo-2-butanone (0.88 mL, 5 mmol, 2.0 equiv.), triethylamine (0.35 mL, 2.5 mmol, 1.1 equiv.), trifluoromethanesulfonic anhydride (0.43 mL, 2.5 mmol, 1.1 equiv.) a white solid was obtained (770 mg, 42% yield).

Rf = 0.35 (DCM/acetone 10:1). **Mp** = 288.5-288.8 °C. In CD_3COCD_3 (25 °C), this imidazolium salt exists in two rotamers in a 9:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between rotamers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, CD_3COCD_3):** δ = 9.70 (s, 0.1H, NC*H*N, *min)*, 8.54 (s, 0.9H, NC*H*N, *min)*, 7.75-7.60 (m, 6H, H^{Ar}), 7.45-7.05 (m, 22H, H^{Ar}), 5.54 (s, 1.8H, C*H, maj*), 5.40 (s, 0.2H, C*H, min*), 1.88 (s, 5.4H, CH_3), 1.69 (s, 0.6H, CH_3). **^{13}C NMR (101 MHz, CD_3COCD_3):** δ =142.2 (*C*), 142.1 (*C*), 141.7 (*C*), 136.0 (*C*H), 132.9 (*C*H), 132.2 (*C*H), 131.8(*C*H), 130.1 (*C*H), 129.9 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 129.4 (*C*H), 129.3 (*C*H), 127.9 (*C*H), 127.8 (*C*H), 122.3 (q, *J*(C,F) = 320.8 Hz, *C*F_3), 52.2 (*C*H), 51.9 (*C*H), 8.7 (*C*H_3), 8.4 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -78.3 (s, *F*). **HRMS (ESI)**: *m/z*: 581.2951 calcd for $C_{43}H_{37}N_2^+$ [C]$^+$: found 581.2950. **IR (ATR):** 3144, 3060, 3026, 2926, 2332, 1719, 1623, 1597, 1586, 1536, 1491, 1448, 1389, 1265, 1216, 1182, 1140, 1093, 1078, 1031, 1002, 965, 920, 868, 848, 818, 773, 748, 730, 699, 663, 654, 635, 619, 605, 571, 516 cm^{-1}.

1-(2-Benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate 1e·OTf

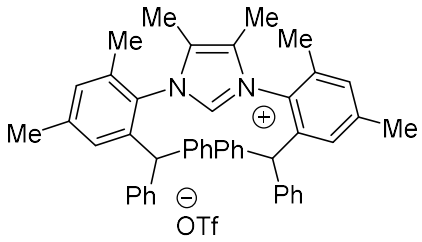


According to the general procedure **D**, from *N*-(2-Benzhydryl-6-fluoro-4-methylphenyl)-*N'*-(2–benzhydryl-4-methyl-6-florophenyl)formimidamide **S2e** (4.58 g, 7.7 mmol), *N,N*-di*iso*propylethylamine (2.56 mL, 15.5 mmol, 2.0 equiv.), 3-bromo-2-butanone (1.65 mL, 15.5 mmol, 2.0 equiv.), triethylamine (0.73 mL, 7.2 mmol, 1.1 equiv.), trifluoromethanesulfonic anhydride (1.2 mL, 7.2 mmol, 1.1 equiv.) a white solid was obtained as a 10:1 mixture of diastereomers which could not be separated by silica gel chromatography (3.98 g, 65% yield). A recrystallization from dichloromethane/ethyl acetate allowed to isolate the pure major diastereomer as a white solid (870 mg).

Rf = 0.40 (DCM/acetone = 10:1). **Mp** = 302.4-302.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 9.81 (s, 0.91H, NC*H*N), 7.34-7.16 (m, 16H, H^{Ar}), 7.08-7.05 (m, 2H, H^{Ar}), 6.95-6.90 (m, 4H, H^{Ar}), 6.67 (s, 2H, H^{Ar}), 5.52 (s, 2H, C*H*), 2.36 (s, 6H, CH_3), 1.23 (s, 6H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =157.4 (d, ^1J(C,F)= 252.6 Hz, *C*), 144.1 (d, ^3J(C,F)= 8.6 Hz, *C*), 143.8 (*C*), 140.1 (d, ^2J(C,F)= 35.2 Hz, *C*), 137.3 (*C*H), 129.8 (*C*H), 129.4 (*C*H), 128.8 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.5 (*C*), 127.7 (*C*H), 127.4 (*C*H,), 127.3 (*C*H), 127.2 (d, ^4J(C,F)=

6.2 Hz, *C*H), 120.8 (q, *J*(C,F) = 320.9 Hz, *C*F_3), 117.4 (d, ^3J(C,F)= 13.1 Hz, *C*), 115.7 (d, ^2J(C,F)= 19.0 Hz, *C*H), 51.8 (*C*H), 22.0 (*C*H_3), 7.6 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -78.5 (s, C*F*$_3$), -121.4 (s, *F*). **HRMS (ESI)**: *m/z*: 645.3076 calcd for $C_{45}H_{39}F_2N_2^+$ [C]$^+$: found 645.3080. **IR (ATR):** 3029, 2928, 2363, 2324, 2271, 1620, 1588, 1542, 1494, 1450, 1391, 1313, 1286, 1254, 1223, 1190, 1151, 1078, 1028, 987, 918, 847, 819, 786, 745, 722, 701, 636, 604, 584, 572, 539, 517 cm^{-1}.

1-(2-Benzhydryl-4,6-dimethylphenyl)-3-(2-benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl imidazolium trifluoromethylsufonate 1f·OTf



According to the general procedure C, from *N*-(2-Benzhydryl-4,6-dimethylphenyl)-*N'*-(2-Benzhydryl-4,6-dimethylphenyl)formimidamide **S2f** (5.8 g, 9.95 mmol), *N,N*-di*iso*propylethylamine (3.3 mL, 19.9 mmol, 2.0 equiv.), 3-bromo-2-butanone (2.12 mL, 19.9 mmol, 2.0 equiv.), triethylamine (1.5 mL, 10.9 mmol, 1.1 equiv.), trifluoromethanesulfonic anhydride (3.7 mL, 10.9 mmol, 1.1 equiv.) a white solid was obtained as a 4:1 mixture of diastereomers. After a meticulous purification by silica gel chromatography (DCM/Acetone 9:1) the pure major diastereomer was isolated as a white solid (5.09 g, 65% - 2 steps). Alternatively, a recrystallization from dichloromethane/ethyl acetate allowed to isolate also the pure major diastereomer.

Rf = 0.45 (DCM/acetone 10:1). **Mp** = 300.0-300.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.75 (s, 1H, NC*H*N), 7.31-7.15 (m, 12H, *H*^{Ar}), 7.11 (s, 2H, *H*^{Ar}), 7.05-6.90 (m, 8H, *H*^{Ar}), 6.74 (s, 2H, *H*^{Ar}), 5.15 (s, 2H, C*H*), 2.30 (s, 6H, C*H*$_3$), 1.96 (s, 6H, C*H*$_3$), 1.55 (s, 6H, C*H*$_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =141.7 (*C*), 141.6 (*C*), 141.2 (*C*), 140.2 (*C*), 135.5 (*C*), 135.2 (*C*), 130.9 (*C*H), 130.1 (*C*H), 129.7 (*C*H), 129.3 (*C*H), 129.2 (*C*), 128.8 (*C*H), 128.7 (*C*H), 128.4 (*C*), 127.4 (*C*H), 127.1(*C*H), 120.8 (q, J^1(C, F) = 321 Hz, *C*F_3), 51.6 (*C*H), 21.5 (*C*H_3), 17.9 (*C*H_3), 8.1 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -78.4 (s, C*F*$_3$). **HRMS (ESI)**: *m/z*: 637.3577 calcd for $C_{47}H_{45}N_2^+$ [C]$^+$: found 637.3574. **IR (ATR):** 3089, 3058, 3028, 2926, 2853, 2360, 2324, 1601, 1540, 1493, 1474, 1448, 1279, 1251, 1223, 1152, 1078, 1028, 1002, 856, 781, 744, 732, 697, 673, 637, 606, 571, 549, 516 cm^{-1}.

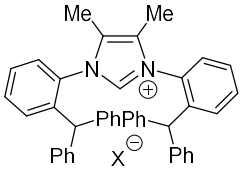
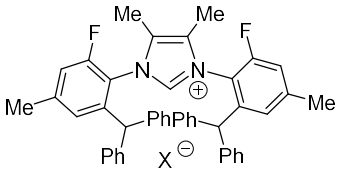
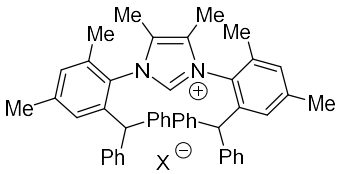
		Isomeric Ratio determined by ^{1}H NMR spectroscopy		
		in $CDCl_3$	in Acetone-d_6	in Methanol-d_4
 **1d•X**	X = OTf	1:1.2	1:9.1	1:4.2
	X = Cl	1:1.2	1:9.0	1:4.2
	X = BF_4	1:1.2	1:8.7	1:4.2
 **1e•X**	X = OTf	1:8.3	1:10.0	1:10.0
	X = Cl	1:9.5	1:10.0	1:8.3
	X = BF_4	1:9.7	1:10.0	1:10.0
 **1f•X**	X = OTf	1:4.3	1:5.3	1:5.6
	X = Cl	1:5.7	1:5.0	1:5.0
	X = BF_4	1:5.0	1:5.0	1:5.0

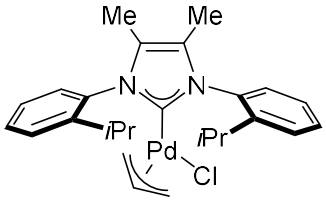
Table S1. Ratios of isomers for imidazolium **1d·X**, **1e·X** and **1f·X** as a function of the NMR solvent and the nature of the counter ion X

III Preparation palladium-NHC complexes and their resolution by chiral HPLC

General Procedure E: Synthesis of the NHC-palladium complexes **2**, **3** and **4**

A mixture of imidazolium tetrafluoroborate **1·BF$_4$** or trifluoromethanesulfonate **1·OTf** (2.3 mmol, 2.3 equiv.), [Pd(allyl)Cl]$_2$ (1.0 mmol, 1.0 equiv.) – or [Pd(cinnamyl)Cl]$_2$ – K_2CO_3 (2.3 mmol, 2.3 equiv.) in acetone was stirred at 60 °C for 5 h. The reaction mixture was filtered through a Celite® pad and the solvent was removed under vacuum. The crude product was purified by silica gel column (PE/Et$_2$O = 1:1) to give the expected NHC-palladium complex.

Chloro[(1,2,3-n)-propenyl][(1,3-bis(2-*iso*propylphenyl)-4,5-dimethyl-1H-imidazol-2-yl)] palladium(II) *meso*-**2a**



According to the general procedure **E**, 1,3-bis(2-*iso*propylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate **1a·BF$_4$** (150 mg, 0.36 mmol, 2.3 equiv.), [Pd(allyl)Cl]$_2$ (59 mg, 0.16 mmol, 1.0 equiv.), K_2CO_3 (100 mg, 0.72 mmol, 4.6 equiv.), afforded a yellow solid (126 mg, 87% yield). Complex **2a** was isolated a single diastereomer.

Rf = 0.54 (PE/Et$_2$O 1:2). **Mp** = 225.6-226.4 °C (decomposition) **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.01 (dd, *J*(H,H) = 7.6 and 1.3 Hz, 1H, H^{Ar}), 7.71 (dd, *J*(H,H) = 7.8 and 1.4 Hz, 1H, H^{Ar}), 7.46-7.27 (m, 6H, H^{Ar}), 4.78-4.62 (m, 1H, H^{allyl}), 3.89 (dd, *J*(H,H) = 7.5 and 2.1 Hz, 1H, H^{allyl}), 2.98 (dd, *J*(H,H) = 6.6 and 1.2 Hz, 1H, H^{allyl}), 2.82-2.62 (m, 3H, H^{allyl} and C*H*(CH$_3$)$_2$), 2.00 (s, 3H, C*H*$_3$), 1.90 (s, 3H, C*H*$_3$), 1.46 (dd, *J*(H,H) = 11.9 and 1.1 Hz, 1H, H^{allyl}), 1.30 (d, *J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.19 (d, *J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.11 (d, *J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, *J*(H,H) = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ = 181.8 (*C*), 145.1 (*C*), 144.9 (*C*), 145.1 (*C*), 136.8 (*C*), 136.0 (*C*), 130.8 (*C*H), 130.7 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 127.0 (*C*), 126.7 (*C*H), 126.6 (*C*H), 126.3 (*C*H), 125.9 (*C*H), 125.7 (*C*H), 113.6 (*C*H), 71.8 (*C*H$_2$), 49.0 (*C*H$_2$), 27.9 (*C*H), 27.8 (*C*H), 24.2 (*C*H$_3$), 24.0 (*C*H$_3$), 23.4 (*C*H$_3$), 23.1 (*C*H$_3$), 9.9 (*C*H$_3$), 9.8 (*C*H$_3$). **HRMS (ESI)**: *m/z*: 539.1259 calcd for $C_{26}H_{33}ClN_2PdNa^+$ [M+Na]$^+$: found 539.1246. **IR (ATR):** 3059, 3029, 2961, 2923, 2867, 2361, 1731, 1652, 1603, 1578, 1491, 1451, 1381, 1347, 1325, 1276, 1235, 1200, 1162, 1094, 1067, 1018, 1006, 955, 928, 919, 895, 799, 784, 759, 733, 691, 659, 627, 572, 552, 512 cm^{-1}.

X-ray diffraction: Crystals of the complex suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S1.

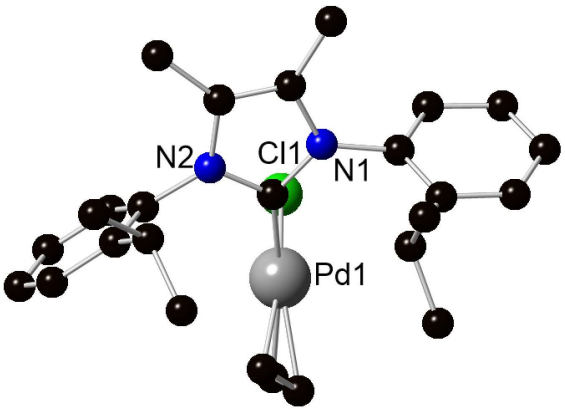
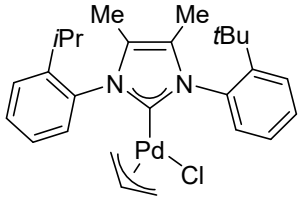


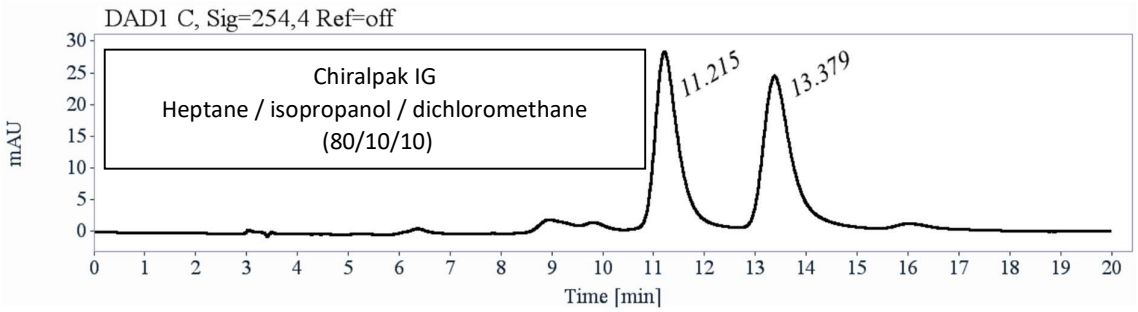
Figure S1. Ball-and-stick representation of palladium complex *meso*-**3a** (hydrogen atoms have been omitted for clarity)

Chloro[(1,2,3-n)-propenyl][(1-(2-isopropylphenyl)-3-(2-*tert*butylphenyl)-4,5-dimethyl-1H-imidazol-2-yl)] palladium(II) 2b



1-(2-*iso*propylphenyl)-3-(2-*tert*butylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1b·OTf** (140 mg, 0.28 mmol, 2.3 equiv.), $[Pd(allyl)Cl]_2$ (47 mg, 0.13 mmol, 1.0 equiv.), KO*t*Bu (33 mg, 0.28 mmol, 2.3 equiv.) were dissolved in dry THF (15 mL) and the resulting mixture was stirred at 25 °C for 16 h. The reaction mixture was filtered through a Celite® pad and the solvent was removed under vacuum. The crude product was purified by silica gel column (PE/Et_2O = 1:1) to give the expected NHC-palladium complex **2b** as a yellow solid (104 mg, 87% yield). Complex **2b** was isolated as the diastereomer (±)-*cis*-**2b** but trace of diastereomer (±)-*trans*-**2b** cannot be ruled out (see cHPLC chromatogram).

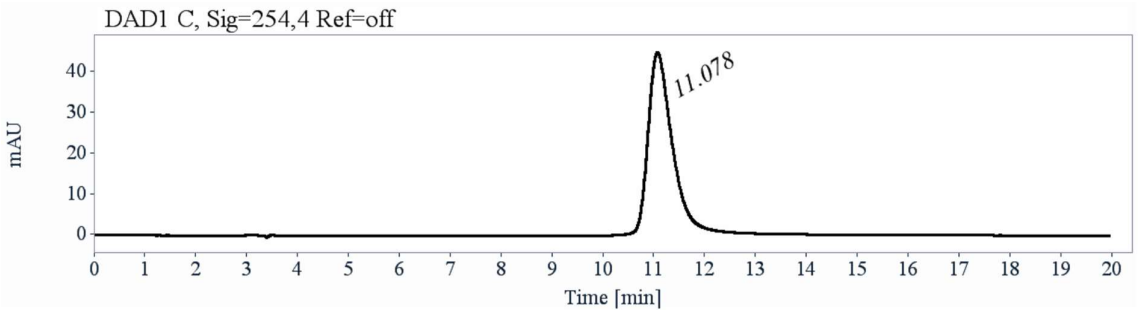
Rf = 0.50 (PE/Et_2O 1:2). **Mp** = 79.5-79.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75-7.05 (m, 8H, H^{Ar}), 4.85-4.45 (m, 1H, H^{allyl}), 3.95-3.75 (m, 1H, H^{allyl}), 3.30-3.00 (m, 1H, H^{allyl}), 2.90-2.60 (m, 2H, H^{allyl} and $CH(CH_3)_2$), 2.02-1.86 (m, 6H, CH_3), 1.55-1.45 (m, 1H, H^{allyl}), 1.35-1.05 (m, 15H, $CH(CH_3)_2$ and $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 181.9 (*C*), 147.1 (*C*), 145.9 (*C*), 145.1 (*C*), 135.3 (*C*), 133.8 (*C*), 133.0 (*C*), 130.9 (*C*H), 130.1 (*C*H), 129.6 (*C*H), 129.3 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 126.6 (*C*H), 126.0 (*C*H), 113.8 (*C*H), 113.4 (*C*H), 71.5 (CH_2), 59.7 (CH_2), 50.7 (CH_2), 50.2 (CH_2), 49.3 (CH_2), 38.3(*C*), 36.8 (*C*), 36.6 (*C*), 33.5 (CH_3), 32.8 (CH_3), 32.2 (CH_3), 32.0 (CH_3), 31.4 (CH_3), 29.8 (CH_2), 27.8 (*C*H), 27.7 (*C*H), 24.5 (CH_3), 24.3 (CH_3), 24.1 (CH_3), 10.4 (CH_3), 9.8 (CH_3). **HRMS (ESI)**: *m/z*: 553.1416 calcd for $C_{27}H_{35}ClN_2PdNa^+$ $[M+Na]^+$: found 553.1417. **IR (ATR):** 2962, 2921, 2869, 2363, 2340, 1490, 1439, 1381, 1324, 1261, 1222, 1149, 1086, 1050, 1030, 916, 797, 784, 756, 725, 695, 635, 517 cm^{-1}. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: heptane/*i*PrOH/DCM 80:10:10; 1st enantiomer: Rt = 11.21 min and 2nd enantiomer: Rt = 13.38 min. (see Figure S2)



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.21	902	49.02	2.80		
13.38	938	50.98	3.54	1.26	2.47
Sum	1840	100.00			

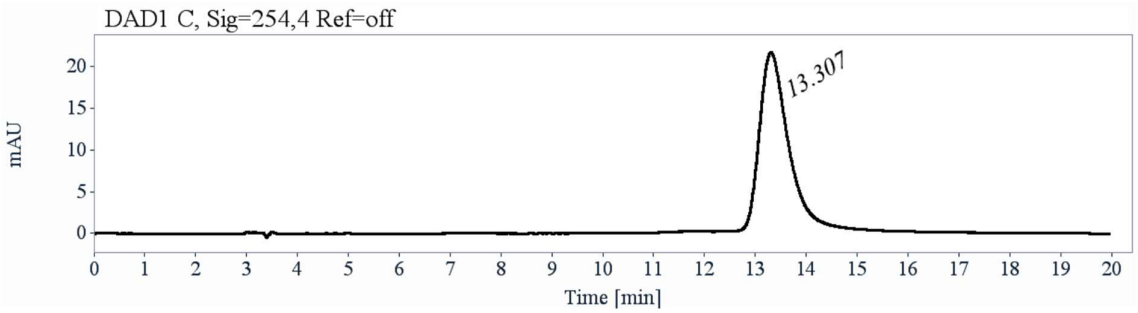
Figure S2. cHPLC analysis of palladium complex (±)-*cis*-**2b**

The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / isopropanol / dichloromethane (85/5/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 280 nm with multiple injections. From 62 mg of racemic mixture, 10 mg of the first eluted enantiomer with ee > 99.5% (Figure S3) and 4 mg of the second eluted enantiomer with ee > 98.5% (Figure S4) were obtained.



RT [min]	Area	Area%
11.08	1508	100.00
Sum	1508	100.00

Figure S3. cHPLC analysis of the first eluted palladium complex *cis*-**2b**

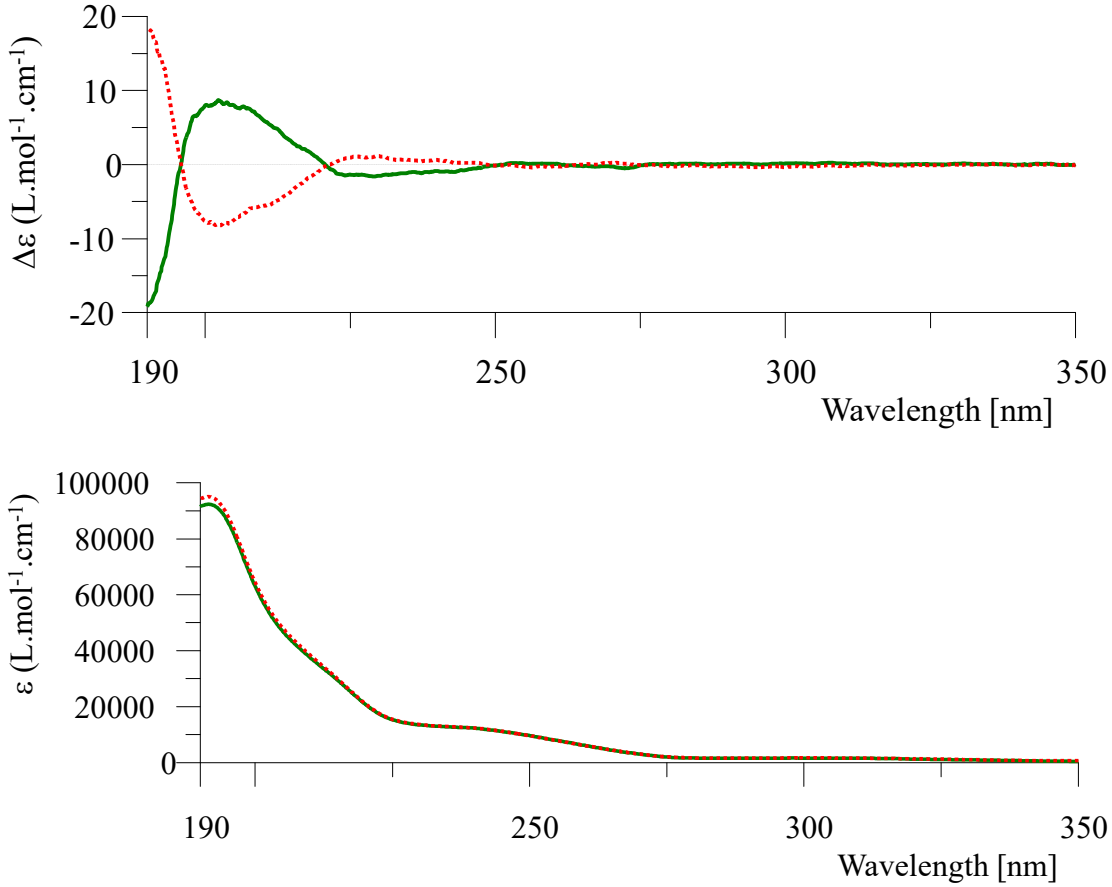


RT [min]	Area	Area%
13.31	864	100.00
Sum	864	100.00

Figure S4. cHPLC analysis of the second eluted palladium complex *cis*-**2b**

λ (nm)	*cis*-**2b** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.54)	*cis*-**2b** second eluted on on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.30)
589	- 6	+ 6
578	- 6	+ 6
546	- 7	+ 7
436	- 13	+ 13
405	- 19	+ 19

Table S2. Optical rotations of complexes **2b**



first eluted enantiomer : green solid line, concentration =0.206 mmol.L^{-1} in acetonitrile.
second eluted enantiomer : red dotted line, concentration = 0.206 mmol.L^{-1} in acetonitrile.

Figure S5. Electronic Circular Dichroism of complexes *cis*-**2c**

X-ray diffraction: Crystals of the first enantiomer of *cis*-**2b** suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S6. The Flack parameter was refined to a value of zero, providing confirmation of the absolute configuration as the ($1S_a$,$2R_a$) enantiomer.

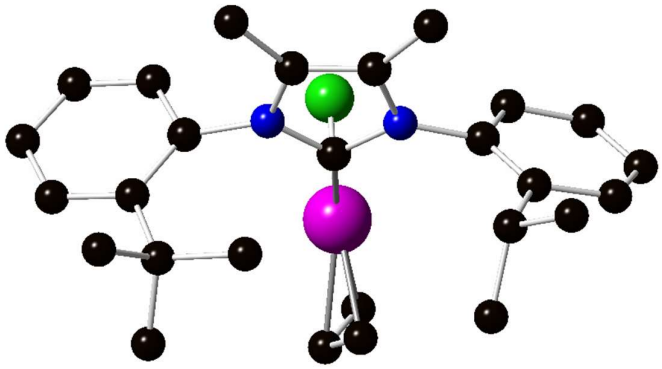
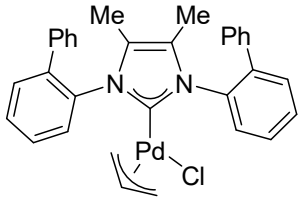


Figure S6. Ball-and-stick representation of the first enantiomer of complex (-)-(1S_a,2R_a)-*cis*-**2b** (hydrogen atoms have been omitted for clarity)

Chloro[(1,2,3-n)-propenyl][(1,3-bis(2-phenylphenyl)-4,5-dimethyl-1H-imidazol-2-yl)] palladium(II) 2c



According to the general procedure **E**, from 1,3-bis(2-phenylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1c·BF$_4$** (350 mg, 0.72 mmol, 2.3 equiv.), [Pd(allyl)Cl]$_2$ (110 mg, 0.30 mmol, 1.0 equiv.), K_2CO_3 (165 mg, 1.2 mmol, 4.6 equiv.), complex **2c** was isolated as two diastereomers after silica gel column (PE/Et_2O = 1:1) 137 mg of *meso*-**2c** complex (white solid) and 185 mg of chiral complex (±)-**2c** (white solid) (overall 99% yield).

Data for *meso*-**2c** are as follow:
Rf = 0.27 (PE/Et_2O 1:2) (*meso* complex). **Mp** = 221.9-222.3 °C (decomposition). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.24-8.19 (m, 1H, H^{Ar}), 7.78-7.72 (m, 1H, H^{Ar}), 7.55-7.25 (m, 14H, H^{Ar}), 7.12-7.08 (m, 2H, H^{Ar}), 4.81 (tt, *J*(H,H) = 13.3 and 7.1 Hz, 1H, H^{allyl}), 3.94 (dd, *J*(H,H) = 7.6 and 2.2 Hz, 1H, H^{allyl}), 2.82 (d, *J*(H,H) = 13.5 Hz, 1H, H^{allyl}), 2.66 (d, *J*(H,H) = 6.4 Hz, 1H, H^{allyl}), 1.68 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.36 (d, *J*(H,H) = 11.8 Hz, 1H, H^{allyl}). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 181.1 (*C*), 139.2 (*C*), 138.8 (*C*), 138.7 (*C*), 137.7 (*C*), 136.5 (*C*), 135.7 (*C*), 132.0 (*C*H), 130.8 (*C*H), 130.6 (*C*H), 129.5 (*C*H), 129.4 (*C*H), 129.3 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 128.1 (*C*H), 127.5 (*C*H), 127.4 (*C*H), 127.3 (*C*), 126.4 (*C*), 113.8 (*C*H), 71.4 (*C*H_2), 46.6 (*C*H_2), 9.8 (*C*H_3), 9.5 (*C*H_3). **HRMS (ESI)**: *m/z*: 607.0947 calcd for $C_{32}H_{29}N_2PdClNa^+$ $[M+Na]^+$: found 607.0952. **IR (ATR):** 3058, 2962, 2922, 2359, 2342, 1653, 1582, 1504, 1483, 1455, 1435, 1376, 1327, 1299, 1260, 1158, 1093, 1020, 1011, 935, 874, 863, 848, 801, 784, 746, 701, 668, 612, 555 cm^{-1}.

X-ray diffraction: Crystals of the complex *meso*-**2c** suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S7.

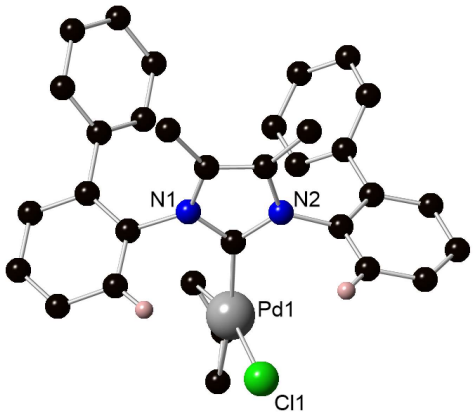
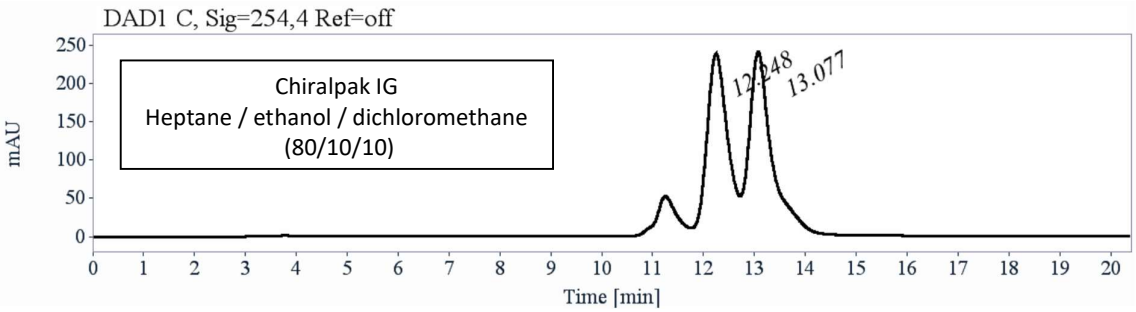


Figure S7. Ball-and-stick representation of complex *meso*-**2c** (most of hydrogen atoms have been omitted for clarity)

Data for (±)-**2c** are as follow:

Rf = 0.28 (PE/Et_2O 1:2) (chiral complex) **Mp** = 200.5-200.9 °C (decomposition). In $CDCl_3$ (25 °C) this complex exists in two conformers in a 3:2 ratio (unassigned). ^{1}H NMR chemical shifts that differ between rotamers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.68 (d, *J*(H,H) = 7.6 Hz, 1H, H^{Ar}), 7.58-7.26 (m, 17H, H^{Ar}), 5.06-4.92 (m, 0.4H, H^{allyl}, *min*), 4.82-4.68 (m, 0.6H, H^{allyl}, *maj*), 3.96 (d, *J*(H,H) = 6.7 Hz, 0.4H, H^{allyl}, *min*), 3.90 (d, *J*(H,H) = 6.7 Hz, 0.6H, H^{allyl}, *maj*), 3.32 (d, *J*(H,H) = 6.6 Hz, 0.4H, H^{allyl}, *min*), 2.87 (d, *J*(H,H) = 13.4 Hz, 0.4H, H^{allyl}, *min*), 2.82 (d, *J*(H,H) = 13.4 Hz, 0.6H, H^{allyl}, *maj*), 2.51 (d, *J*(H,H) = 6.6 Hz, 0.6H, H^{allyl}, *maj*), 1.75 (d, *J*(H,H) = 11.7 Hz, 0.4H, H^{allyl}, *min*), 1.69 (d, *J*(H,H) = 12.1 Hz, 0.6H, H^{allyl}, *maj*), 1.59 (s, 3H, CH_3), 1.35 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 180.8 (*C*), 180.5 (*C*), 139.5 (*C*), 138.7 (*C*), 138.4 (*C*), 138.3 (*C*), 136.5 (*C*), 136.2 (*C*), 130.8 (*C*H), 130.7 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 129.3 (*C*H), 129.2 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 127.8 (*C*H), 127.6 (*C*H), 126.8 (*C*), 126.7 (*C*), 114.3 (*C*H), 113.9 (*C*H), 72.3 (CH_2), 71.9 (CH_2), 50.6 (CH_2), 50.0 (CH_2), 9.6 (CH_3), 9.3 (CH_3). **HRMS (ESI)**: *m/z*: 607.0947 calcd for $C_{32}H_{29}N_2PdClNa^+$ [M+Na]$^+$: found 607.0950. **IR (ATR):** 3057, 3026, 2974, 2945, 2921, 2361, 1734, 1655, 1598, 1582, 1504, 1480, 1453, 1434, 1375, 1321, 1260, 1227, 1202, 1184, 1154, 1106, 1075, 1049, 1008, 930, 882, 848, 799, 783, 744, 718, 701, 626, 559, 534, 513 cm^{-1}. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent : heptane/*i*PrOH/DCM 80:10:10; 1st enantiomer: Rt = 12.25 min and 2nd enantiomer: Rt = 13.08 min (see Figure S8).

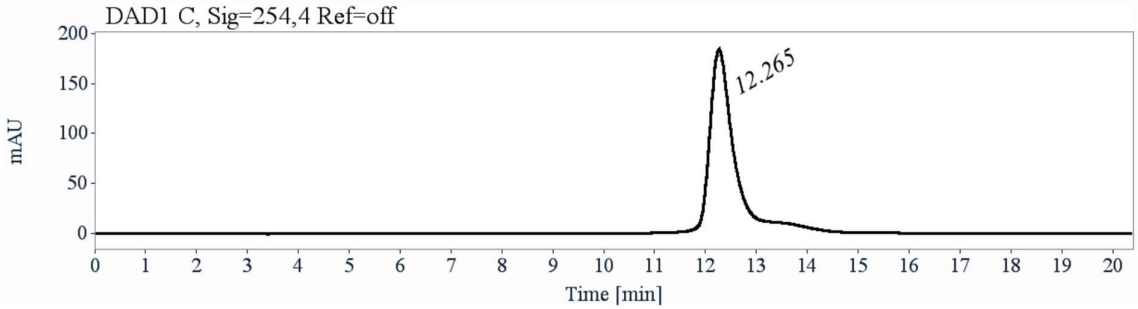


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
12.25	6255	46.78	3.15		
13.08	7116	53.22	3.43	1.09	1.16

Sum	13372	100.00			

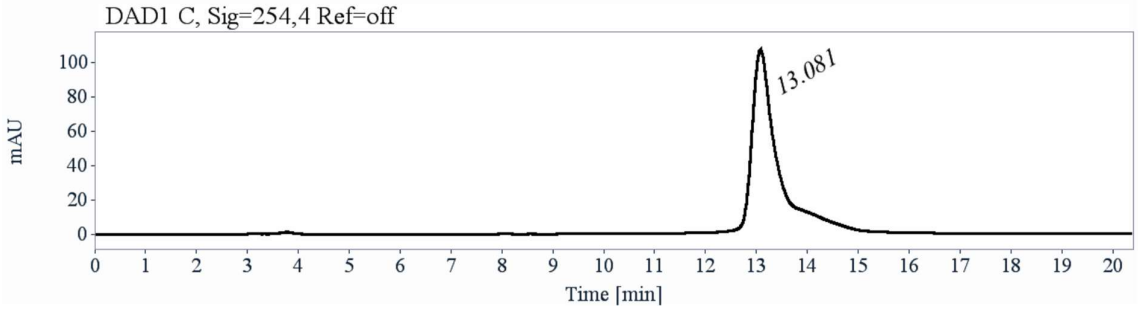
Figure S8. cHPLC analysis of palladium complex (±)-**2c**

The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / isopropanol / dichloromethane (80/10/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 14 mg of racemic mixture, 4 mg of the first eluted enantiomer with ee > 99.5% (Figure S9) and 3 mg of the second eluted enantiomer with ee > 99.5% (Figure S10) were obtained.



RT [min]	Area	Area%
12.27	6163	100.00
Sum	6163	100.00

Figure S9. cHPLC analysis of the first eluted palladium complex **2c**

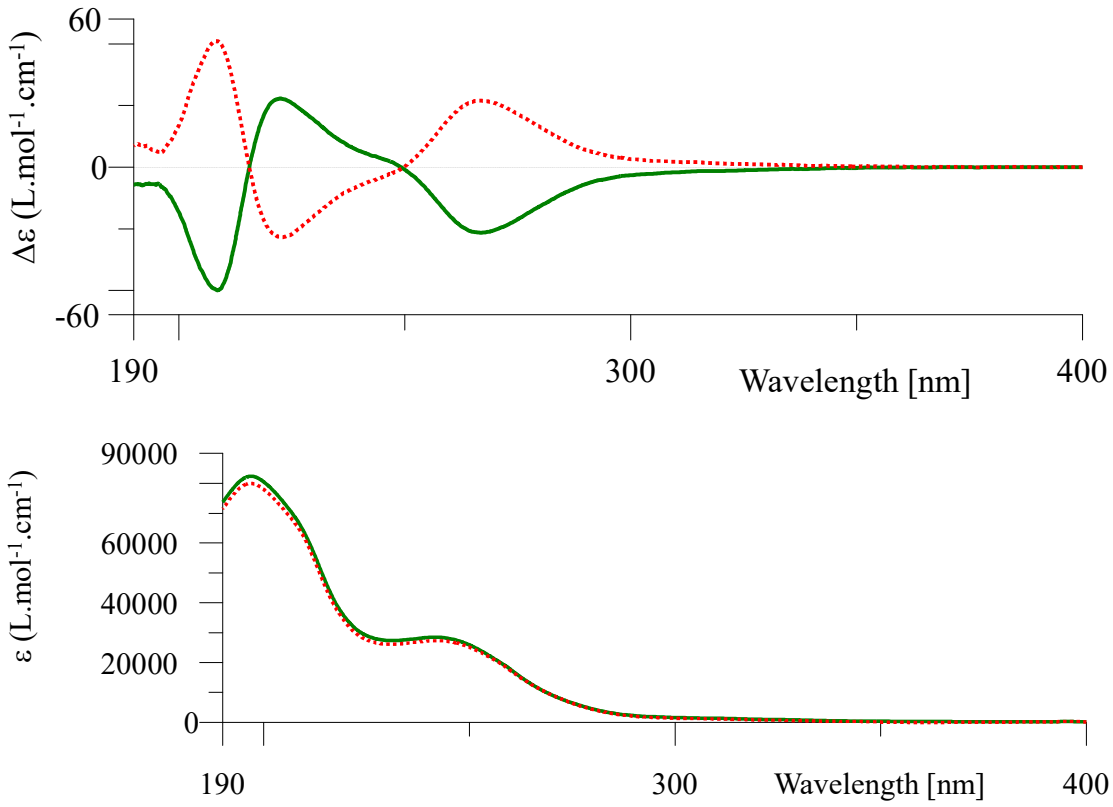


RT [min]	Area	Area%
13.08	3914	100.00
Sum	3914	100.00

Figure S10. cHPLC analysis of the second eluted palladium complex **2c**

λ (nm)	**2c** first eluted on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.21)	**2c** second eluted on on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.095)
589	- 300	+ 300
578	- 315	+ 315
546	- 370	+ 370
436	- 760	+ 760
405	- 1000	+ 1000

Table S3. Optical rotations of enantiomers of complexes **2c**



First eluted enantiomer: green solid line, concentration = 0.228 mmol.L^{-1} in acetonitrile.
second eluted enantiomer: red dotted line, concentration = 0.208 mmol.L^{-1} in acetonitrile.

Figure S11. Electronic Circular Dichroism of complexes **2c**

X-ray diffraction: Crystals of racemic complex (±)-**2c** suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S12.

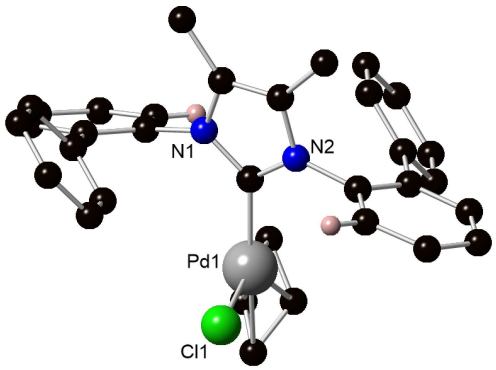
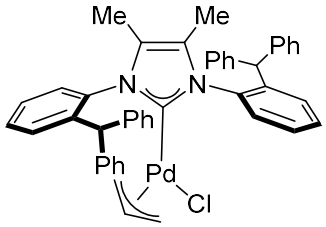


Figure S12. Ball-and-stick representation of complex (±)-**2c** (most of hydrogen atoms have been omitted for clarity)

Chloro(allyl)[(1-(2-benzhydryl)-3-(2-benzhydryl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) 2d



1-(2-benzhydrylphenyl)-3-(2-benzhydrylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1d·OTf** (546 mg, 0.74 mmol) was suspended in MeOH (40 mL) and Dowex-22 Cl (0.82 g)was added in the mixture which was stirred at 25 °C for 14 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL), dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium chloride which is directly used without further purification.

A mixture of the imidazolium chloride and KBF_4 (189 mg, 1.5 mmol, 4.6 equiv.), in a 1:1 mixture of DCM/H_2O (50 mL) was stirred at room temperature for 1 h. The aqueous phase was extracted by DCM (20 mL * 4) and the combined organic phase was dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium tetrafluoroborate **1d·BF_4** which is directly used without further purification.

According to the general procedure **E**, from imidazolium tetrafluoroborate **1d·BF_4**, $[Pd(allyl)Cl]_2$ (117 mg, 0.32 mmol), K_2CO_3 (204 mg, 1.48 mmol, 4.6 equiv.), the silica gel chromatography allowed to separate the chiral complex (white solid, 138 mg, 28% yield) from the *meso* complex (white solid, 308 mg, 62% yield).

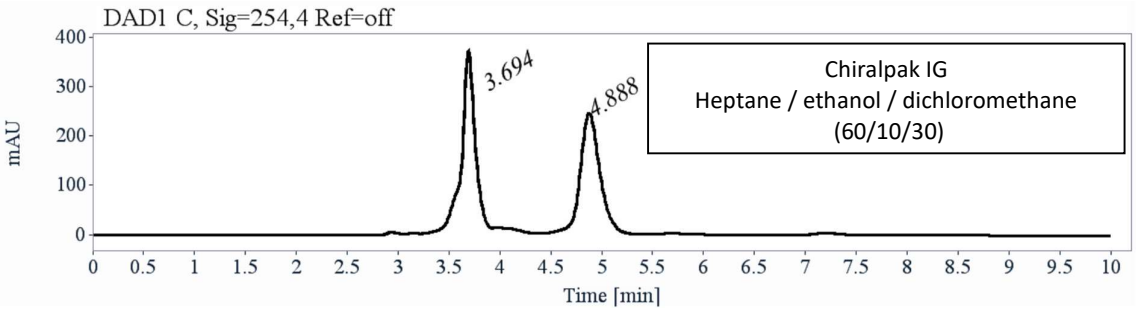
Data for *meso* -**2d** are as follow:

Rf = 0.50 (PE/Et_2O 1:2). **Mp** = 250.3-251.2°C (decomposition). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.07-8.01 (m, 1H, H^{Ar}), 7.74-7.68 (m, 1H, H^{Ar}), 7.45-6.95 (m, 26H, H^{Ar}), 5.64 (s, 1H, C*H*), 5.56 (s, 1H, C*H*), 4.68 (tt, *J*(H, H)= 13.5 and 7.4 Hz, 1H, H^{allyl}), 3.93 (dd, *J*(H, H)= 7.4 and 2.0 Hz, 1H, H^{allyl}), 2.76 (d, *J*(H, H)= 13.5 Hz, 1H, H^{allyl}), 2.46 (d, *J*(H, H)= 6.7 Hz, 1H, H^{allyl}), 1.38 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.25-1.15 (m, 1H, H^{allyl}). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 182.4 (*C*), 143.7 (*C*), 143.2 (*C*), 142.6 (*C*), 142.1 (*C*), 140.9 (*C*), 140.1 (*C*), 138.3 (*C*), 137.5 (*C*), 132.0 (*C*H), 131.7 (*C*H), 130.6 (*C*H), 130.5 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 129.4 (*C*H), 129.3 (*C*H), 129.2 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.2 (*C*H), 127.7 (*C*), 127.5 (*C*H), 127.0 (*C*H), 126.9 (*C*H), 126.8 (*C*H), 126.6 (*C*H), 113.8 (*C*H), 72.1 (*C*H_2), 51.1 (*C*H), 50.7 (*C*H), 49.4 (*C*H_2), 9.4 (*C*H_3), 9.2 (*C*H_3). **HRMS (ESI)**: *m/z*: 785.1898 calcd for $C_{46}H_{41}ClN_2PdNa^+$ $[M+Na]^+$: found 785.1896 (0.3 ppm). **IR (ATR):** 3058, 3024, 2923, 2361, 2334, 1698, 1684, 1652, 1597, 1558, 1541, 1507, 1489, 1449, 1378, 1326, 1268, 1237, 1182, 1075, 1030, 1003, 922, 898, 784, 754, 729, 699, 655, 620, 605, 534 cm^{-1}.

Data for (±)-**2d** are as follow:

Rf = 0.54 (PE/Et_2O 1:2). **Mp** = 224.3-224.6°C (decomposition). In $CDCl_3$ (25 °C), this complex exists in two isomeric forms in a 2.3:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.45-6.95 (m, 29H, H^{Ar} and C*H*), 6.43 (s, 1H, C*H*), 4.95-4.80 (m, 0.7H, H^{allyl}, *maj*), 4.70-4.55 (m, 0.3H, H^{allyl}, *min*), 4.13-4.05 (m, 1H, H^{allyl}), 3.08-2.96 (m, 1.7H, H^{allyl}), 2.87 (d, *J*(H,H)= 5.5 Hz, 0.3H, H^{allyl}, *min*), 1.85 (d, *J*(H,H)= 11.8 Hz, 0.3H, H^{allyl}, *min*), 1.31 (d, *J*(H,H)= 12.0 Hz, 0.7H, H^{allyl}, *maj*), 0.98 (s, 1.8H, CH_3, *min*), 0.94 (s, 4.2H, CH_3, *maj*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 177.1 (*C*), 176.8 (*C*), 143.4 (*C*), 142.4 (*C*), 142.3 (*C*), 142.1 (*C*), 137.9 (*C*), 137.8 (*C*), 130.2 (*C*H), 129.9 (*C*H), 129.8 (*C*H), 129.2 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 126.8 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 114.7 (*C*H), 72.3 (*C*H_2), 71.0 (*C*H_2), 51.3 (*C*H_2), 51.1 (*C*H), 50.2 (*C*H_2), 8.7 (*C*H_3), 8.6 (*C*H_3). **HRMS**

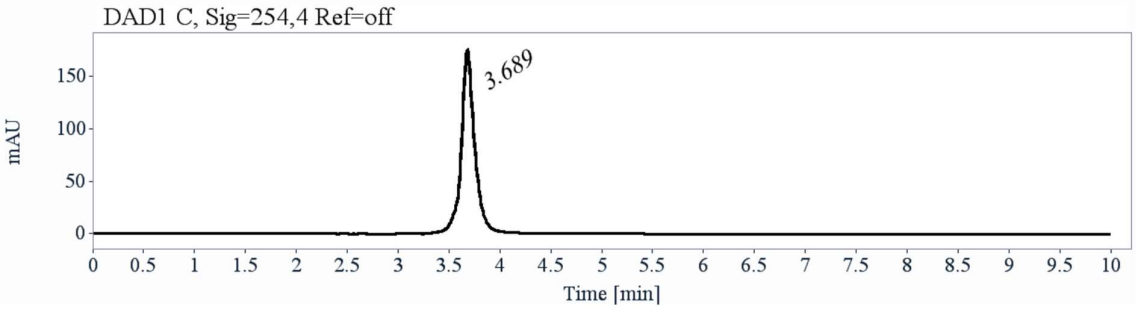
(ESI): *m/z*: 785.1898 calcd for $C_{46}H_{41}ClN_2PdNa^+$ $[M+Na]^+$: found 785.1896 (0.3 ppm). **IR (ATR):** 3049, 2953, 2915, 2859, 2358, 2342, 2119, 1868, 1845, 1678, 1600, 1564, 1541, 1507, 1469, 1451, 1438, 1428, 1364, 1353, 1332, 1311, 1280, 1261, 1223, 1199, 1149, 1118, 1089, 1043, 1032, 1018, 980, 967, 945, 912, 874, 835, 813, 779, 755, 733, 678, 658, 647, 613, 594, 572, 526, 512 cm^{-1}. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane / ethanol / dichloromethane 60:10:30, 1st enantiomer: Rt = 3.69 min and 2nd enantiomer: Rt = 4.89 min. (see Figure S13).



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.69	3769	53.19	0.25		
4.89	3317	46.81	0.66	2.61	4.38
Sum	7086	100.00			

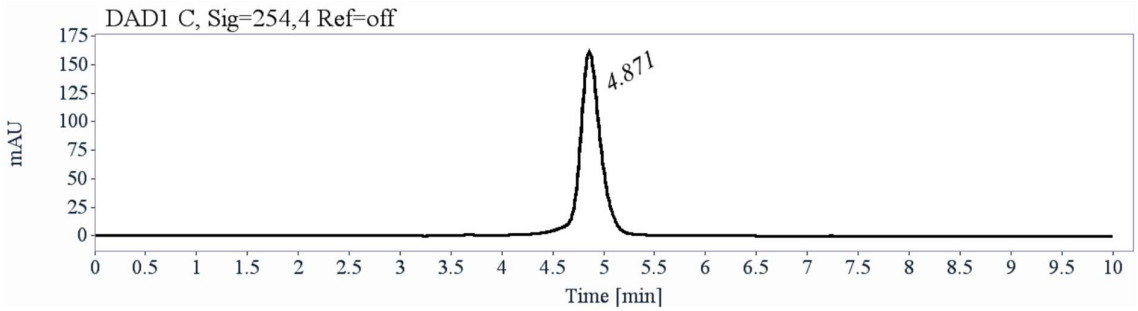
Figure S13. cHPLC analysis of palladium complex (±)-**2d**

The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / ethanol / dichloromethane (60/10/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 59 mg of racemic mixture, 20 mg of the first eluted enantiomer with ee > 99.5% (Figure S14) and 20 mg of the second eluted enantiomer with ee > 99.5% were obtained (Figure S15).



RT [min]	Area	Area%
3.69	1629	100.00
Sum	1629	100.00

Figure S14. cHPLC analysis of the first eluted palladium complex **2d**

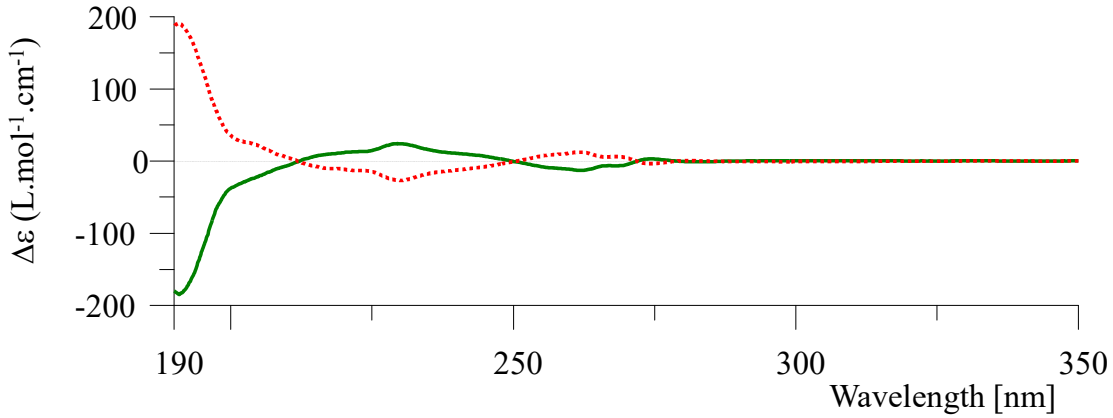


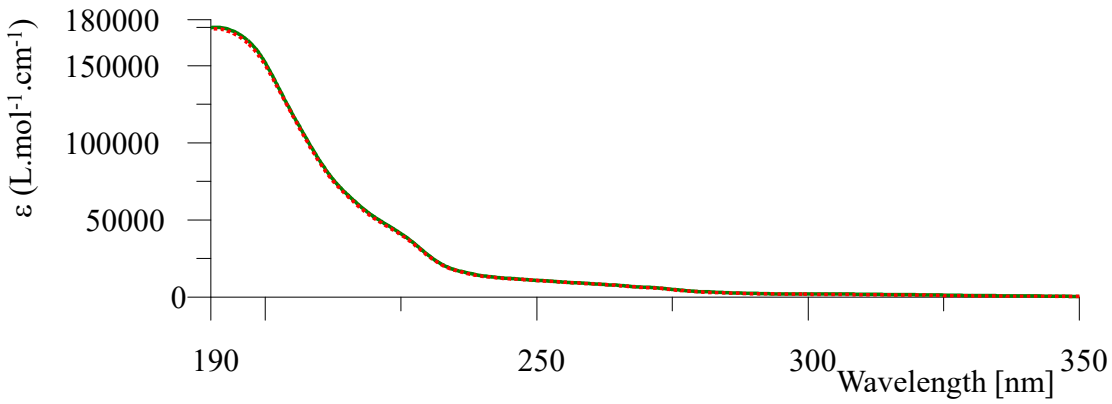
RT [min]	Area	Area%
4.87	2317	100.00
Sum	2317	100.00

Figure S15. cHPLC analysis of the second eluted palladium complex **2d**

λ (nm)	**2d** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.24)	**2d** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.22)
589	- 84	+ 84
578	- 88	+ 88
546	- 102	+ 102
436	- 186	+ 186

Table S4. Optical rotations of complexes **2d**





First eluted enantiomer: green solid line, concentration = 0.113 mmol.L^{-1} in acetonitrile.
second eluted enantiomer: red dotted line, concentration = 0.105 mmol.L^{-1} in acetonitrile.

Figure S16. Electronic Circular Dichroism of complexes **2d**

X-ray diffraction: Crystals of the second enantiomer suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in **Figure S17**. The Flack parameter was refined to a value of zero, providing confirmation of the absolute configuration as the (R_a,R_a) enantiomer.

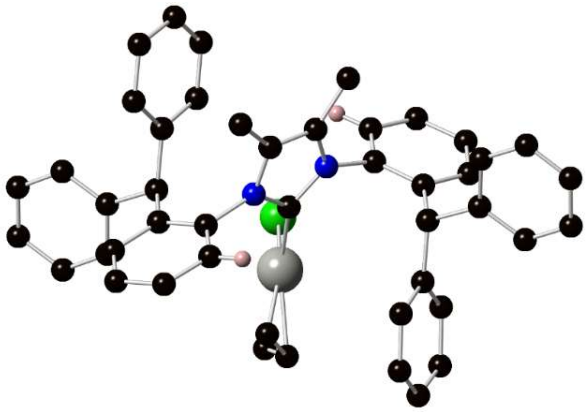
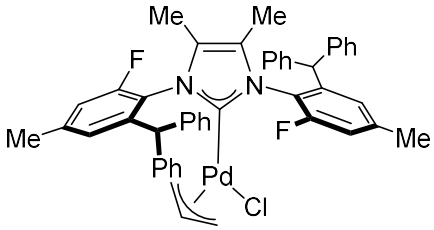


Figure S17. Ball-and-stick representation of the second enantiomer of (+)-(R_a,R_a)-**2d** (most of hydrogen atoms have been omitted for clarity)

Chloro(allyl)[(1-(2-benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) (±)-**2e**



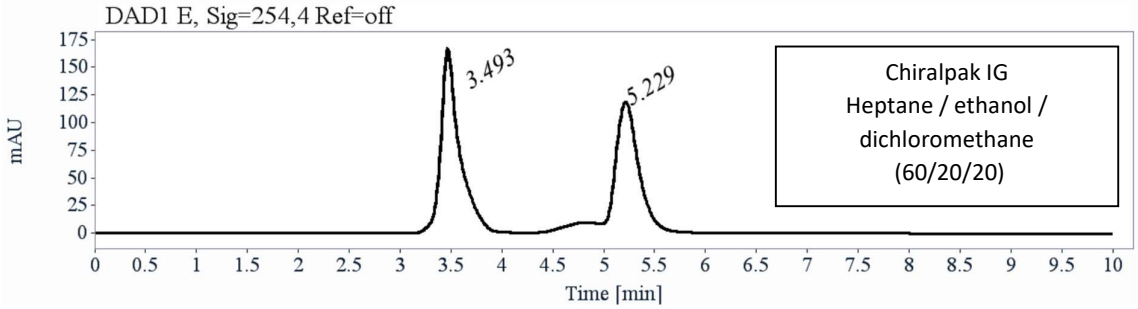
1-(2-benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1e·OTf** (195 mg, 0.25 mmol), was suspended in MeOH (20 mL) and Dowex-22 Cl (0.28 g) was added in the mixture which was stirred at 25 °C for 14 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL), dried by Na_2SO_4 and

filtered. The solvent was removed under vacuum to give the imidazolium chloride which is directly used without further purification.

A mixture of the imidazolium chloride and KBF_4 (63 mg, 0.50 mmol, 4.6 equiv.), in a 1:1 mixture of DCM/H_2O (20 mL) was stirred at room temperature for 1 h. The aqueous phase was extracted by DCM (20 mL * 4) and the combined organic phase was dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium tetrafluoroborate **1e·BF₄** which is directly used without further purification.

According to the general procedure from imidazolium tetrafluoroborate **1e·BF₄**, $[Pd(allyl)Cl]_2$ (39 mg, 0.11 mmol), K_2CO_3 (68 mg, 0.50 mmol, 4.6 equiv.) a white solid was obtained (120 mg, 72% yield).

Rf = 0.54 (PE/Et_2O 1:2). **Mp** >280 °C (decomposition). In $CDCl_3$ (25 °C), this complex exists in two isomeric forms in a 1.1:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-6.90 (m, 23H, H^{Ar} and C*H*), 6.67 (s, 2H, H^{Ar}), 6.35 (s, 1H, C*H*), 5.00-4.85 (m, 0.7H, H^{allyl}, *maj*), 4.78-4.63 (m, 0.3H, H^{allyl}, *min*), 4.17-4.08 (m, 1H, H^{allyl}), 3.23 (d, *J*(H,H)= 6.6 Hz, 0.7H, H^{allyl}, *maj*), 3.14-2.98 (m, 1.3H, H^{allyl}), 2.34 (s, 1.8H, Ar-CH_3, *maj*), 2.31 (s, 4.2H, Ar-CH_3, *min*), 1.98 (d, *J*(H,H)= 11.9 Hz, 0.3H, H^{allyl}, *min*), 1.43 (d, *J*(H,H)= 12.0 Hz, 0.7H, H^{allyl}, *maj*), 0.91 (s, 1.8H, CH_3, *min*), 0.88 (s, 4.2H, CH_3, *maj*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.1 (*C*), 178.4 (*C*), 141.9 (*C*), 141.1 (*C*), 140.9 (*C*), 140.8 (*C*), 130.1 (*C*H), 129.8 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 126.6 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 126.1 (*C*), 123.7 (*C*), 123.6 (*C*), 115.3 (*C*H), 114.7 (*C*H), 72.1 (CH_2), 70.6 (CH_2), 51.4 (CH_2), 51.2 (*C*H), 50.0 (CH_2), 21.9 (CH_3), 7.6 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -117.6 (s, *F*), -117.7 (s, *F*), -121.3 (s, *F*), -123.3 (s, *F*). **HRMS (ESI)**: *m/z*: 849.2024 calcd for $C_{48}H_{43}ClF_2N_2PdNa^+$ $[M+Na]^+$: found 849.2019 (0.6 ppm). **IR (ATR):** 3059, 3026, 2924, 2863, 2358, 2333, 1733, 1716, 1698, 1683, 1663, 1653, 1621, 1588, 1558, 1541, 1493, 1451, 1382, 1307, 1232, 1153, 1118, 1078, 1032, 985, 934, 848, 820, 786, 744, 702, 668, 630, 617, 585, 565, 541, 524 cm^{-1}. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane / ethanol / dichloromethane 60:20:2; 1st enantiomer: Rt = 3.49 min and 2nd enantiomer: Rt = 5.23 min. (see Figure S18).

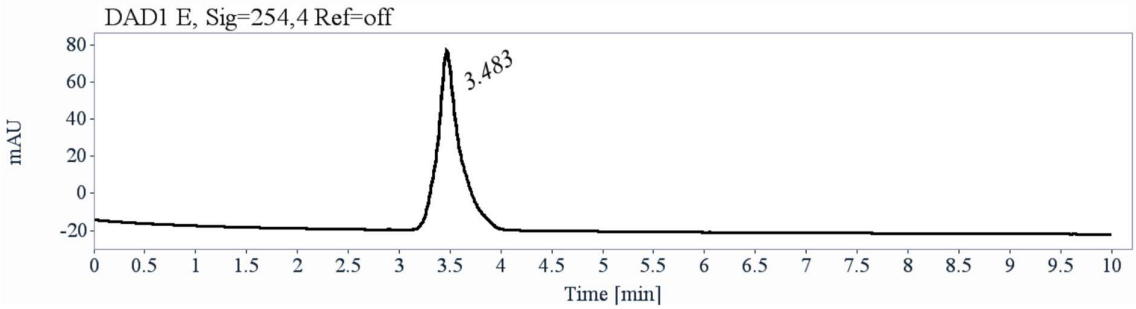


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.49	2125	51.42	0.18		
5.23	2007	48.58	0.77	4.20	5.18
Sum	4132	100.00			

Figure S18. cHPLC analysis of palladium complex (±)-**2e**

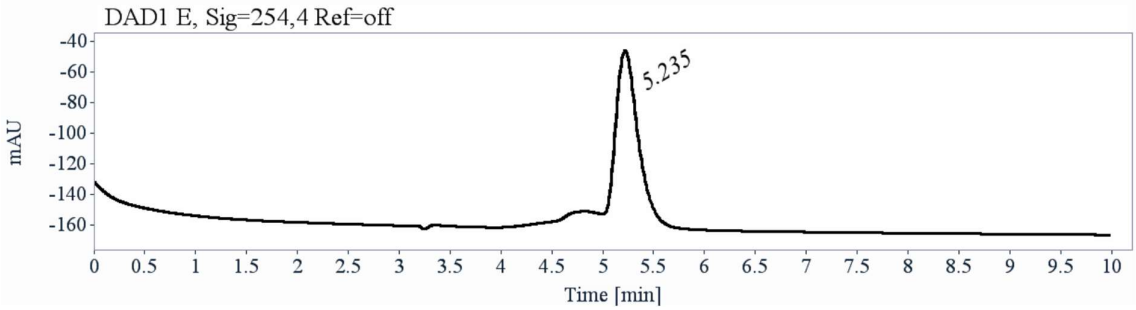
The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 104 mg of racemic mixture, 47 mg of the first eluted

enantiomer with ee > 99.0% (Figure S19) and 45 mg of the second eluted enantiomer with ee > 99.0% were obtained (Figure S20).



RT [min]	Area	Area%
3.48	1476	100.00
Sum	1476	100.00

Figure S19. cHPLC analysis of the first eluted palladium complex **2e**

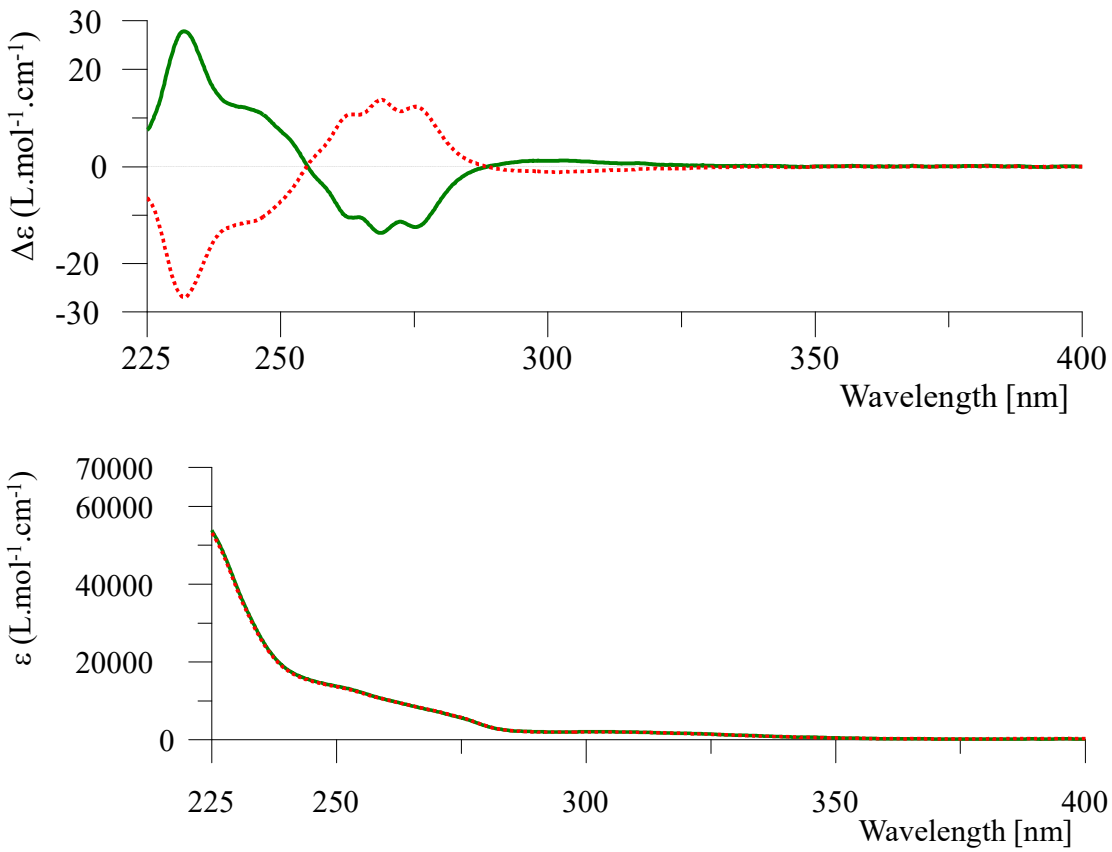


RT [min]	Area	Area%
5.24	1956	100.00
Sum	1956	100.00

Figure S20. cHPLC analysis of the second eluted palladium complex **2e**

λ (nm)	**2e** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.2)	**2e** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.22)
589	- 110	+ 110
578	- 113	+ 113
546	- 132	+ 132
436	- 240	+ 241

Table S5. Optical rotations of complexes **2e**



First eluted enantiomer: green solid line, concentration = 0.249 mmol.L^{-1} in acetonitrile.
second eluted enantiomer: red dotted line, concentration = 0.246 mmol.L^{-1} in acetonitrile.

Figure S21. Electronic Circular Dichroism of complexes **2e**

X-ray diffraction: Crystals of the first enantiomer suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S22. The Flack parameter was refined to a value of zero, providing confirmation of the absolute configuration as the (R_a,R_a) enantiomer.

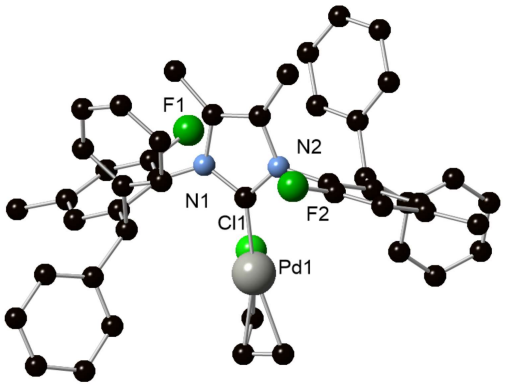
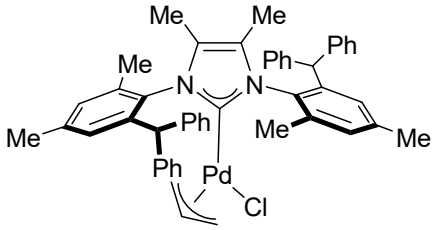


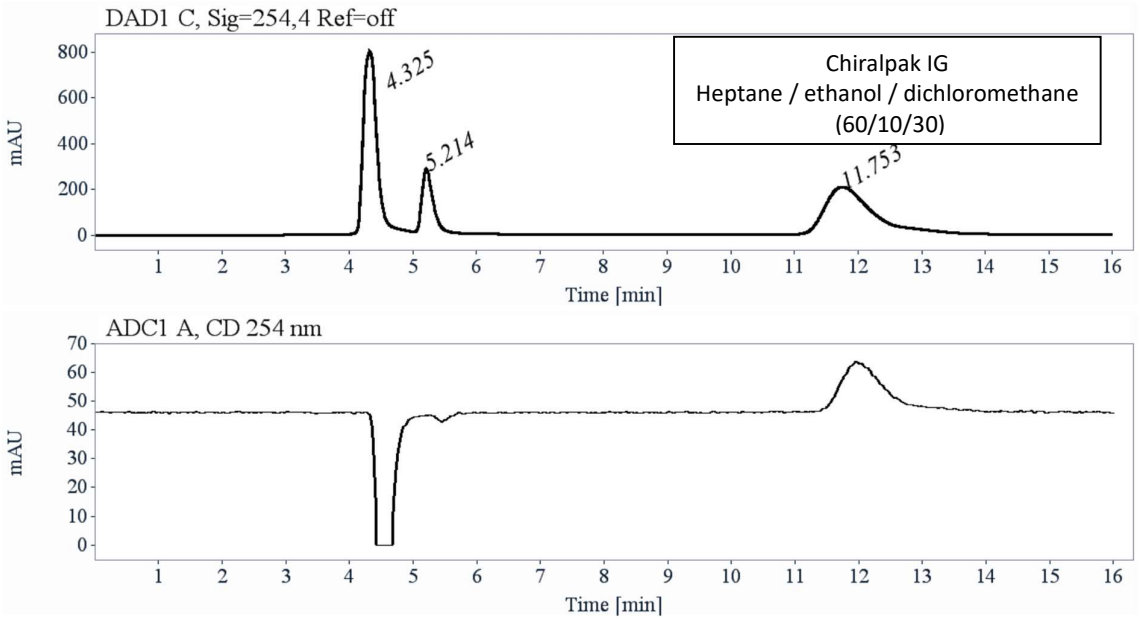
Figure S22. Ball-and-stick representation of the first enantiomer of (-)-(R_a,R_a)-**2e** (hydrogen atoms have been omitted for clarity)

Chloro(allyl)[(1-(2-benzhydryl-4,6-dimethylphenyl)-3-(2-Benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) 2f



According to the general procedure **E**, from 1-(2-benzhydryl-4,6-dimethylphenyl)-3-(2-benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1f·OTf** (100 mg, 0.13 mmol, 2.3 equiv.) $[Pd(allyl)Cl]_2$ (19 mg, 0.053 mmol), K_2CO_3 (36 mg, 0.26 mmol, 4.6 equiv.), two diastereomeric complexes, partially separable by silica gel chromatography were obtained (ratio 5:1) (68 mg, 79% yield, 3 steps).

Chiral HPLC analysis: Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane/ethanol/dichloromethane 60:10:30; 1st enantiomer: Rt = 4.32 min, meso complex: Rt = 5.21 min, and 2nd enantiomer: Rt = 11.75 min. (see Figure S23).

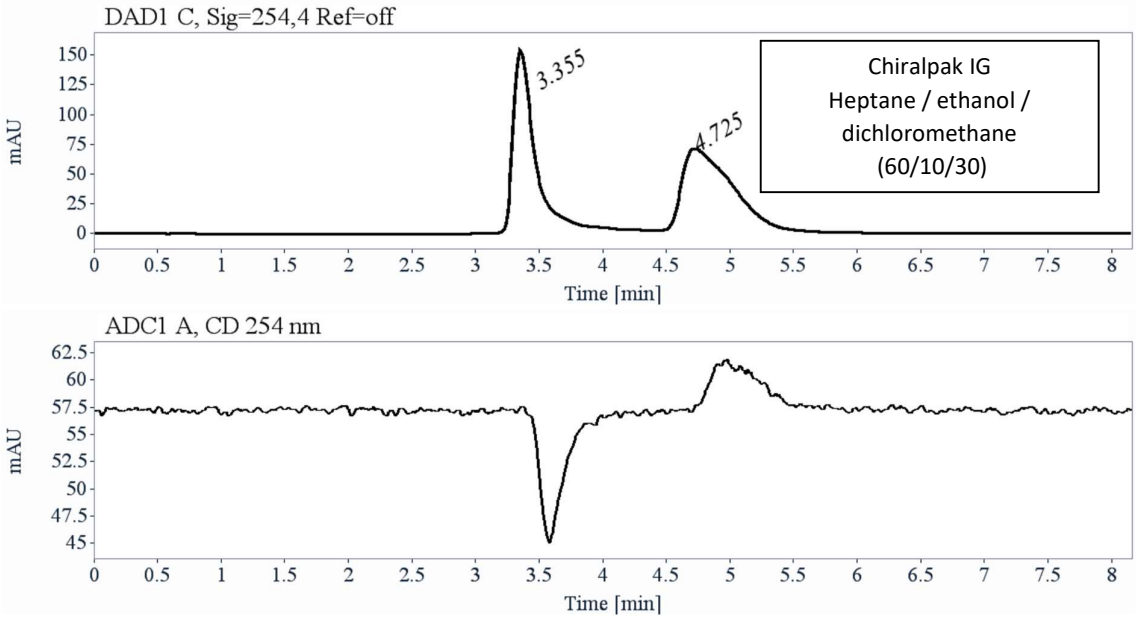


RT [min]	Area	Area%	Capacity Factor
4.33	12278	44.07	0.47
5.21	4009	14.39	0.77
11.75	11571	41.53	2.98
Sum	27858	100.00	

Figure S23. cHPLC analysis of palladium complexes **2f**

According to the general procedure **E**, from diastereomerically pure 1-(2-benzhydryl-4,6-dimethylphenyl)-3-(2-benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate **1f·BF_4** (850 mg, 1.17 mmol, 2.3 equiv.), $[Pd(allyl)Cl]_2$ (205 mg, 0.56 mmol), K_2CO_3 (324 mg, 2.35 mmol, 4.6 equiv.) complex (±)-**2f** was obtained as single diastereomer and as a white solid (850 mg, 92% yield).

Rf = 0.55 (PE/Et_2O 1:2). **Mp** = 261.3-261.5°C (decomposition). In $CDCl_3$ (25 °C), this complex exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.30-7.10 (m, 17H, H^{Ar} and C*H*), 7.05-6.95 (m, 6H, H^{Ar}), 6.75-6.71 (m, 2H, H^{Ar}), 6.10 (s, 1H, C*H*), 4.95-4.80 (m, 0.7H, H^{allyl}, *maj*), 4.68-4.53 (m, 0.3H, H^{allyl}, *min*), 4.14 (dd, *J*(H,H)= 7.6 and 2.2 Hz, 0.7H, H^{allyl}, *maj*), 4.05 (*J*(H,H)= 7.6 and 2.2 Hz, 0.3H, H^{allyl}, *min*), 3.07 (d, *J*(H,H)= 13.7 Hz, 0.7H, H^{allyl}, *maj*), 3.00 (d, *J*(H,H)= 13.7 Hz, 0.3H, H^{allyl}, *min*), 2.94 (d, *J*(H,H)= 6.8 Hz, 0.7H, H^{allyl}, *maj*), 2.62 (d, *J*(H,H)= 6.8 Hz, 0.3H, H^{allyl}, *min*), 2.32-2.18 (m, 12H, Ar-CH_3), 1.69 (d, *J*(H,H)= 11.8 Hz, 0.3H, H^{allyl}, *min*), 1.34 (dd, *J*(H,H)= 11.3 and 1.5 Hz, 0.7H, H^{allyl}, *maj*), 0.99 (s, 2.5H, CH_3, *maj*), 1.88 (s, 3.5H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 178.8 (*C*), 178.4 (*C*), 143.6 (*C*), 142.5 (*C*), 142.3 (*C*), 142.2 (*C*), 138.6 (*C*), 138.5 (*C*), 135.0 (*C*), 134.9 (*C*), 130.2 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 129.9 (*C*H), 129.3 (*C*H), 128.2 (*C*H), 128.0 (*C*H), 127.2 (*C*), 126.6 (*C*H), 126.2 (*C*H), 126.1 (*C*H), 114.8 (*C*H), 114.7 (*C*H), 73.6 (CH_2), 71.6 (CH_2), 70.0 (CH_2), 51.1 (*C*H), 50.9 (*C*H), 50.0 (CH_2), 48.5 (CH_2), 21.6 (CH_3), 19.2(CH_3), 15.4 (CH_3), 8.3 (CH_3), 8.1 (CH_3). **HRMS (ESI)**: *m/z*: 841.2526 calcd for $C_{50}H_{49}ClN_2PdNa^+$ $[M+Na]^+$: found 841.2524 (0.2 ppm). **IR (ATR):** 3056, 3022, 2922, 2856, 2361, 2341, 2218, 1748, 1716, 1698, 1684, 1654, 1599, 1558, 1541, 1507, 1492, 1475, 1447, 1372, 1313, 1296, 1184, 1156, 1076, 1031, 1002, 910, 886, 854, 821, 778, 744, 733, 699, 626, 565 cm^{-1}. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane/ethanol/dichloromethane 60:10:30; 1st enantiomer: Rt = 3.35 min and 2nd enantiomer: Rt = 4.72 min. (see Figure S24).

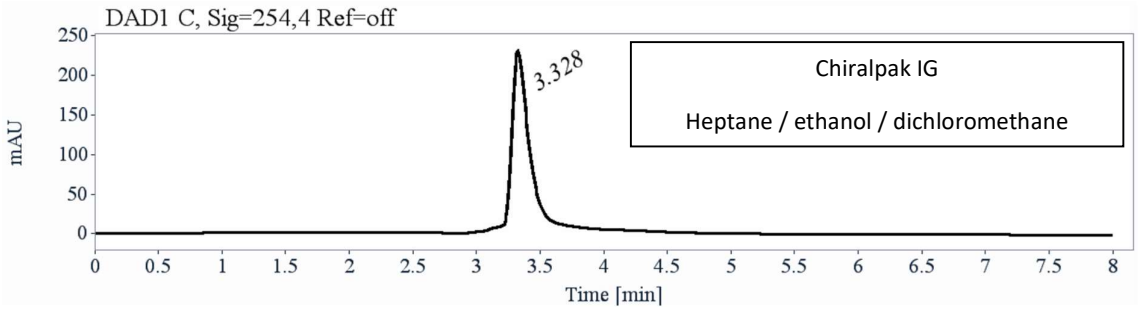


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
3.35	1987	49.81	0.14		
4.73	2002	50.19	0.60	4.39	2.70
Sum	3989	100.00			

Figure S24. cHPLC analysis of palladium complex **2f**

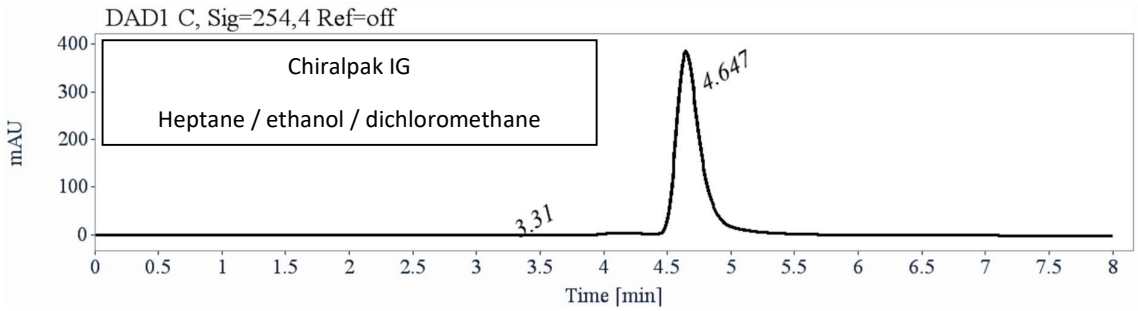
The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane/ethanol/dichloromethane (60/10/30) as mobile phase, flow-rate = 5 mL/min, UV detection at

254 nm with multiple injections (45 injections every 5 min). From 840 mg of racemic mixture, 420 mg of the first eluted enantiomer with ee > 99.5% (Figure S25) and 401 mg of the second eluted enantiomer with ee > 99.5% were obtained Figure S26).



RT [min]	Area	Area%
3.33	2271	100.00
Sum	2271	100.00

Figure S25. cHPLC analysis of the first eluted palladium complex **2f**

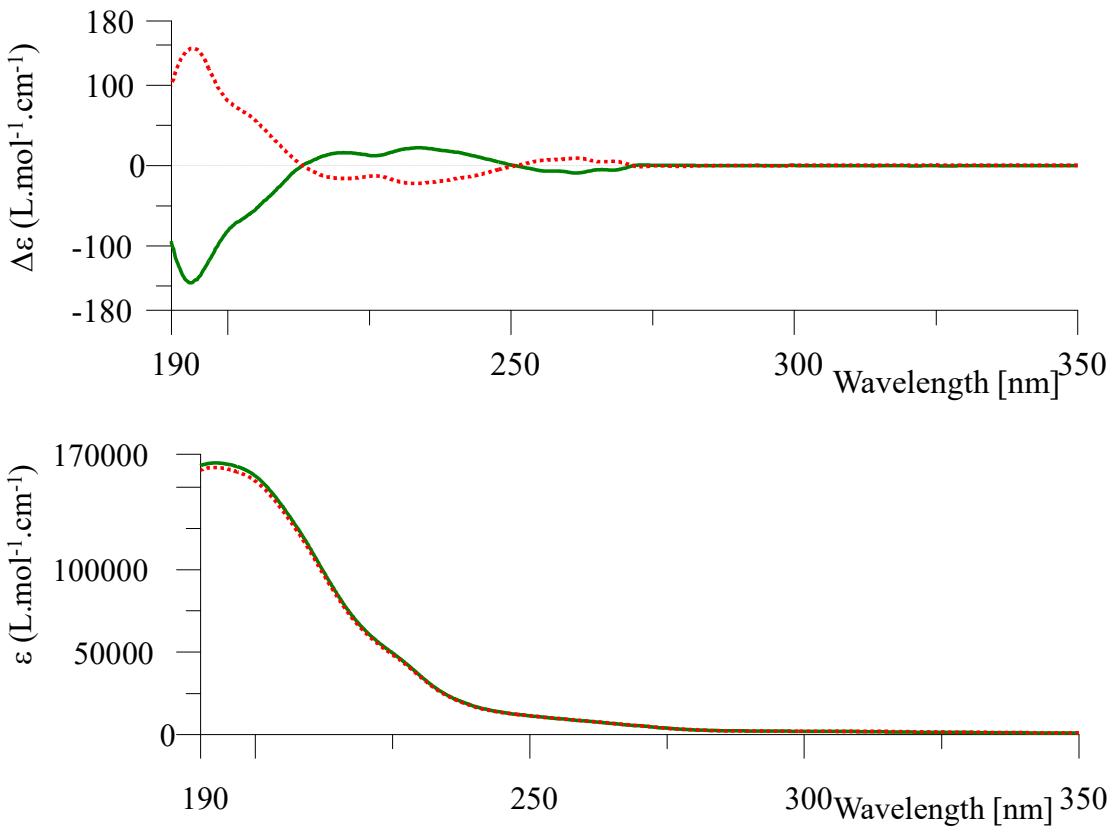


RT [min]	Area	Area%
3.31	13	0.27
4.65	4973	99.73
Sum	4987	100.00

Figure S26. cHPLC analysis of the second eluted palladium complex **2f**

λ (nm)	**2f** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.11)	**2f** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.1)
589	- 116	+ 116
578	- 119	+ 119
546	- 140	+ 140
436	- 270	+ 270
405	- 353	+ 353

Table S6. Optical rotations of complexes **2f**



First eluted enantiomer: green solid line, concentration = 0.110 mmol.L^{-1} in acetonitrile.
second eluted enantiomer: red dotted line, concentration = 0.110 mmol.L^{-1} in acetonitrile.

Figure S27. Electronic Circular Dichroism of complexes **2f**

X-ray diffraction: Crystals of the second enantiomer of complex **2f** suitable for XRD were grown by slow diffusion of octane into dichloromethane. The crystal structure is shown in Figure S28. The Flack parameter was refined to a value of zero, providing confirmation of the absolute configuration as the (R_a,R_a) enantiomer.

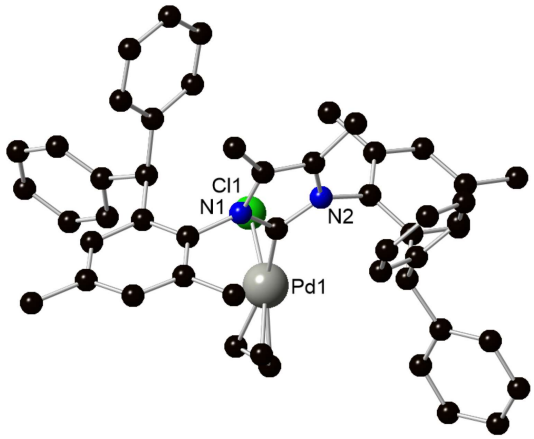
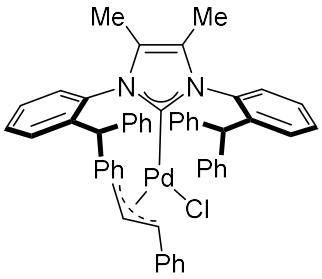


Figure S28. Ball-and-stick representation of the second enantiomer of (+)-(R_a,R_a)-**2f** (hydrogen atoms have been omitted for clarity)

Chloro(cinnamyl)[(1-(2-benzhydrylphenyl)-3-(2-benzhydrylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) *meso*-**3d**



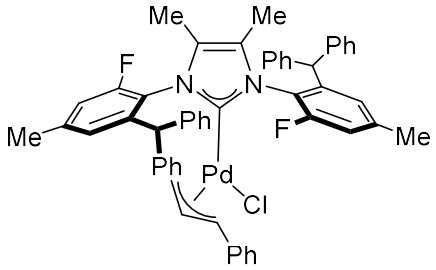
1-(2-benzhydrylphenyl)-3-(2-benzhydrylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1d·OTf** (195 mg, 0.25 mmol) was suspended in MeOH (25 mL) and Dowex-22 Cl (0.33 g) was added in the mixture which was stirred at 25 °C for 14 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL), dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium chloride which is directly used without further purification.

A mixture of the imidazolium chloride and KBF_4 (76 mg, 0.60 mmol, 4.6 equiv.), in a 1:1 mixture of DCM/H_2O (20 mL) was stirred at room temperature for 1 h. The aqueous phase was extracted by DCM (20 mL x 4) and the combined organic phase was dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium tetrafluoroborate which is directly used without further purification.

According to the general procedure **E**, from imidazolium tetrafluoroborate salt, $[Pd(cinamyl)Cl]_2$ (67 mg, 0.13 mmol), K_2CO_3 (83 mg, 0.60 mmol, 4.6 equiv.) a white solid was isolated (162 mg, 78% yield). ^{1}H NMR spectroscopy proves that this compound is the *meso* diastereomer, without any traces of the expected chiral complex.

Rf = 0.55 (PE/Et_2O 1:2). **Mp** = 170.9-171.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.18-8.06 (m, 1H, H^{Ar}), 7.88-7.75 (m, 1H, H^{Ar}), 7.60-7.05 (m, 26H, H^{Ar}), 5.68 (s, 2H, C*H*), 5.08-4.92 (m, 1H, $H^{cinamyl}$), 4.34 (d, *J*(H,H)= 12.5 Hz, 1H, $H^{cinamyl}$), 2.60-2.35 (m, 1H, $H^{cinamyl}$), 1.55-1.25 (m, 7H, CH_3 and $H^{cinamyl}$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 181.6 (*C*), 143.6 (*C*), 143.1 (*C*), 142.5 (*C*), 142.2 (*C*), 140.8 (*C*), 140.4 (*C*), 138.5(*C*), 138.2 (*C*), 137.7 (*C*), 131.9 (*C*H), 130.6 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 129.2 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 127.3 (*C*), 126.9 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 108.9 (*C*H), 88.9 (*C*H), 50.9 (*C*H), 46.8 (CH_2), 29.4(*C*H), 9.3 (CH_3). **HRMS (ESI)**: *m/z*: 861.2213 calcd for $C_{52}H_{45}ClN_2PdNa^+$ $[M+Na]^+$: found 861.2205. **IR (ATR):** 3055, 3024, 2963, 2922, 2362, 2332, 1699, 1653, 1597, 1488, 1447, 1374, 1319, 1281, 1250, 1180, 1155, 1090, 1075, 1049, 1030, 1003, 967, 919, 817, 784, 750, 728, 696, 656, 619, 605, 535, 524 cm^{-1}.

Chloro(cinnamyl)[(1-(2-benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) (±)-**3e**



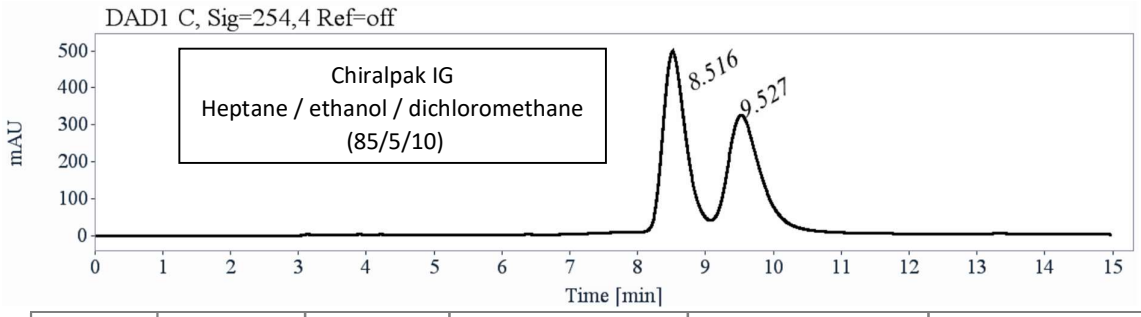
1-(2-benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-imidazolium trifluoromethylsufonate **1e·OTf** (290 mg, 0.36 mmol, 2.3 equiv.) was suspended in MeOH

(25 mL) and Dowex-22 Cl (0.33 g) was added in the mixture which was stirred at 25 °C for 14 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL), dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium chloride which is directly used without further purification.

A mixture of the imidazolium chloride and KBF_4 (76 mg, 0.60 mmol, 4.6 equiv.), in a 1:1 mixture of DCM/H_2O (20 mL) was stirred at room temperature for 1 h. The aqueous phase was extracted by DCM (20 mL x 4) and the combined organic phase was dried by Na_2SO_4 and filtered. The solvent was removed under vacuum to give the imidazolium tetrafluoroborate which is directly used without further purification.

According to the general procedure **E**, from 1-(2-benzhydryl-6-fluoro-4-methylphenyl)-3-(2-benzhydryl-6-fluoro-4-methylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate (290 mg, 0.36 mmol, 2.3 equiv.), $[Pd(cinamyl)Cl]_2$ (82 mg, 0.16 mmol), K_2CO_3 (99 mg, 0.72 mmol, 4.6 equiv.) a white solid was obtained (194 mg, 75% yield).

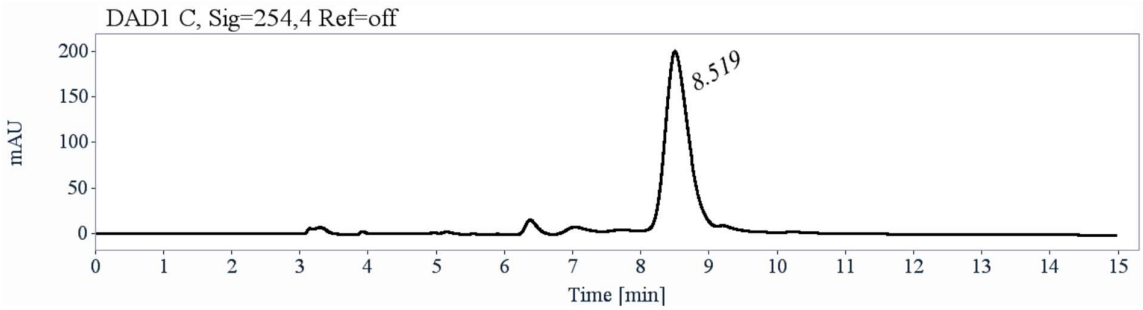
Rf = 0.55 (PE/Et_2O 1:2). **Mp** = 270.8-271.4 °C (decomposition). In $CDCl_3$ (25 °C), this complex exists in two isomeric forms in a 1:1 ratio (unassigned). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.60-6.80 (m, 30H, H^{Ar} and C*H*) , 6.40 (s, 1H, C*H*), 5.55-5.40 (m, 0.5H, $H^{cinamyl}$), 5.25-5.15 (m, 0.5H, $H^{cinamyl}$), 4.86 (d, *J*(H,H)= 13.1 Hz, 0.5H, $H^{cinamyl}$), 4.70 (d, *J*(H,H)= 12.7 Hz, 0.5H, $H^{cinamyl}$), 3.24 (d, *J*(H,H)= 6.7 Hz, 0.5H, $H^{cinamyl}$), 3.14 (d, *J*(H,H)= 6.9 Hz, 0.5H, $H^{cinamyl}$), 2.52-2.41 (m, 6H, Ar-CH_3), 2.13 (d, *J*(H,H)= 11.5 Hz, 0.5H, $H^{cinamyl}$), 1.67(d, *J*(H,H)= 11.5 Hz, 0.5H, $H^{cinamyl}$), 1.06 (s, 6H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 178.3 (*C*), 177.2 (*C*), 159.7 (*C*), 157.2 (*C*), 140.9 (*C*), 140.8 (*C*), 138.2 (*C*), 137.6 (*C*), 130.1 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.2 (*C*H), 127.9 (*C*H), 127.4 (*C*H), 127.3 (*C*H), 127.2 (*C*H), 126.8 (*C*H), 125.6 (*C*H), 123.7 (*C*), 123.6 (*C*), 114.8 (*C*H), 109.2 (*C*H), 108.9 (*C*H), 91.6 (*C*H), 88.5 (*C*H), 51.1 (*C*H), 48.3 (*C*H_2), 46.0 (*C*H_2), 30.5(*C*H_3), 22.0 (*C*H_3), 7.7 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -115.2 (s, *F*), -116.0 (s, *F*), -117.7 (s, *F*), -118.4 (s, *F*), -118.5 (s, *F*), -121.6 (s, *F*), -123.2 (s, *F*). **IR (ATR):** 3058, 3025, 2922, 2358, 2222, 1664, 1619, 1583, 1491, 1449, 1381, 1306, 1177, 1152, 1117, 1076, 1031, 984, 908, 848, 820, 786, 728, 700, 643, 629, 617, 584, 566, 556, 541, 522 cm^{-1}. **HRMS (ESI)**: *m/z*: 925.2339 calcd for $C_{54}H_{47}ClF_2N_2PdNa^+$ $[M+Na]^+$: found 925.2345. **Chiral HPLC analysis:** Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane / ethanol / dichloromethane 85:5:10; 1st enantiomer: Rt = 8.52min and 2nd enantiomer: Rt = 9.53 min. (see Figure S29).



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.52	11632	51.15	1.89		
9.53	11109	48.85	2.23	1.18	1.36
Sum	22740	100.00			

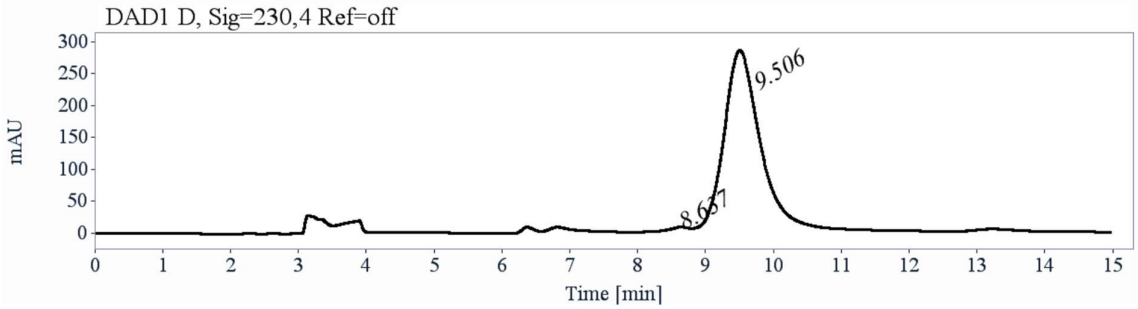
Figure S29. cHPLC analysis of palladium complex (±)-**3e**

The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / ethanol / dichloromethane (85/5/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 160 mg of racemic mixture, 45 mg of the first eluted enantiomer with ee > 99.5% (Figure S30) and 42 mg of the second eluted enantiomer with ee > 97% (Figure S31).



RT [min]	Area	Area%
8.52	4791	100.00
Sum	4791	100.00

Figure S30. cHPLC analysis of the first eluted palladium complex **3e**

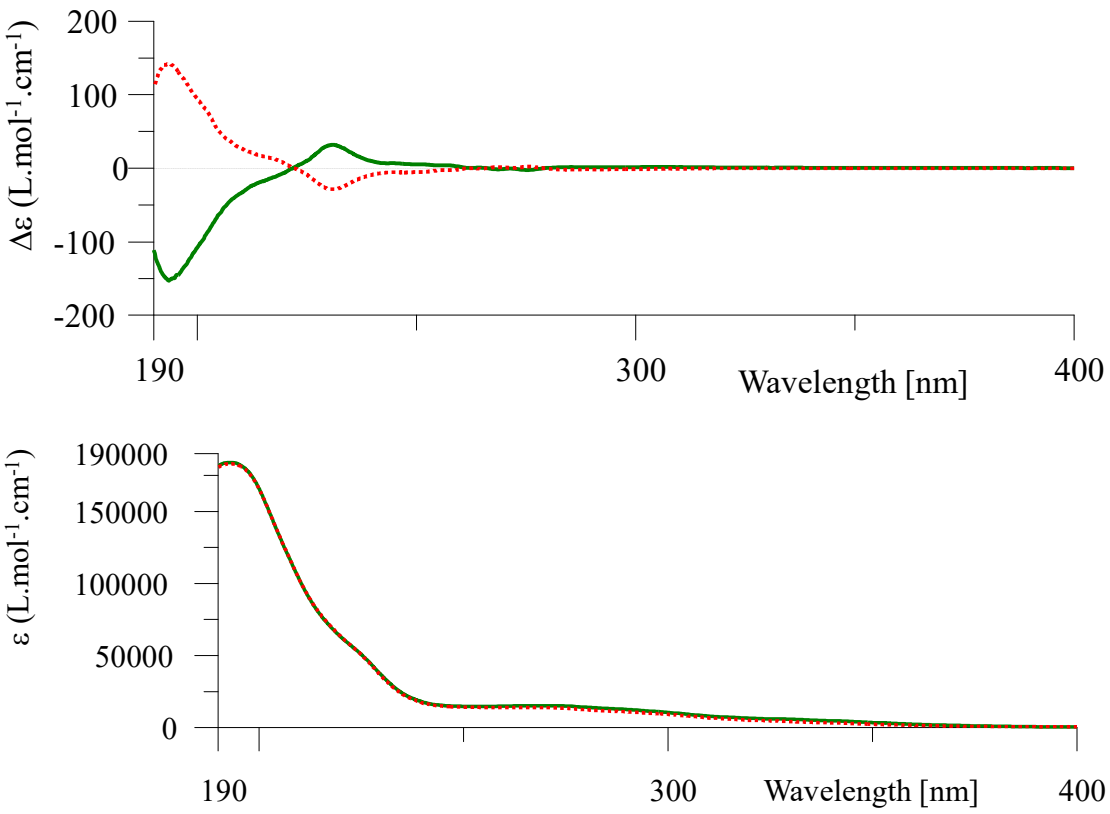


RT [min]	Area	Area%
8.64	158	1.45
9.51	10747	98.55
Sum	10905	100.00

Figure S31. cHPLC analysis of the second eluted palladium complex **3e**

λ (nm)	**3e** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.21)	**3e** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.22)
589	- 60	+ 60
578	- 63	+ 64
546	- 71	+ 72

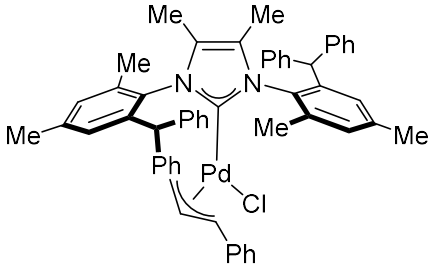
Table S7. Optical rotations of complexes **3e**



First eluted enantiomer: green solid line, concentration = 0.106 mmol.L^{-1} in acetonitrile.
second eluted enantiomer: red dotted line, concentration = 0.102 mmol.L^{-1} in acetonitrile.

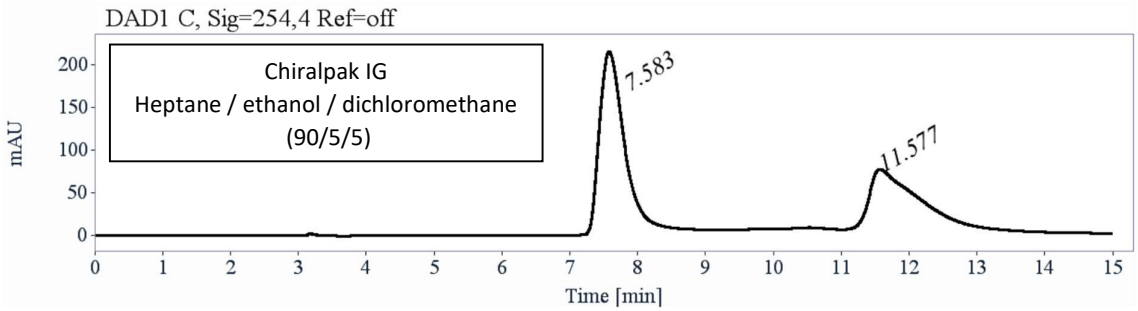
Figure S32. Electronic Circular Dichroism of complexes **3e**

Chloro(cinnamyl)[(1-(2-benzhydryl-4,6-dimethylphenyl)-3-(2-Benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) 3f



According to the general procedure **E**, from 1-(2–benzhydryl-4,6-dimethylphenyl)-3-(2–benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate **1f·BF$_4$** (270 mg, 0.35 mmol, 2.3 equiv.), [Pd(cinamyl)Cl]$_2$ (78 mg, 0.15 mmol), K_2CO_3 (95 mg, 0.70 mmol, 4.6 equiv.) the expected complex **3f** was obtained as inseparable mixture of diastereomer (5:1) and as a white solid (220 mg, 82% yield).

Chiral HPLC analysis: Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane / ethanol / dichloromethane 90:5:5; 1st enantiomer and *meso*-complex: Rt = 7.58 min and 2nd enantiomer: Rt = 11.58 min. (see Figure S33)

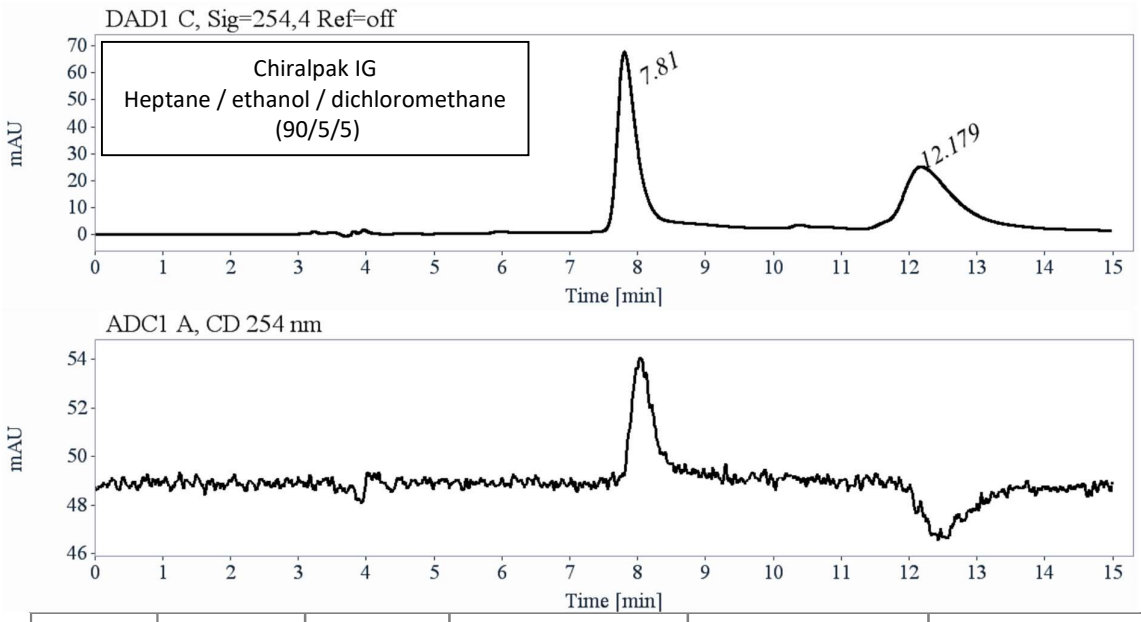


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.58	5555	60.01	1.57		
11.58	3702	39.99	2.92	1.86	4.18
Sum	9257	100.00			

Figure S33: cHPLC analysis of palladium complex **3f**

According to the general procedure **E**, from diastereomerically pure 1-(2–benzhydryl-4,6-dimethylphenyl)-3-(2–benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-imidazolium tetrafluoroborate **1f·BF$_4$** (160 mg, 0.22 mmol, 2.3 equiv.), [Pd(cinamyl)Cl]$_2$ (52 mg, 0.10 mmol), K_2CO_3 (61 mg, 0.44 mmol, 4.6 equiv.) the expected complex **3f** was obtained as a single diastereomer and as a white solid (160 mg, 90% yield).

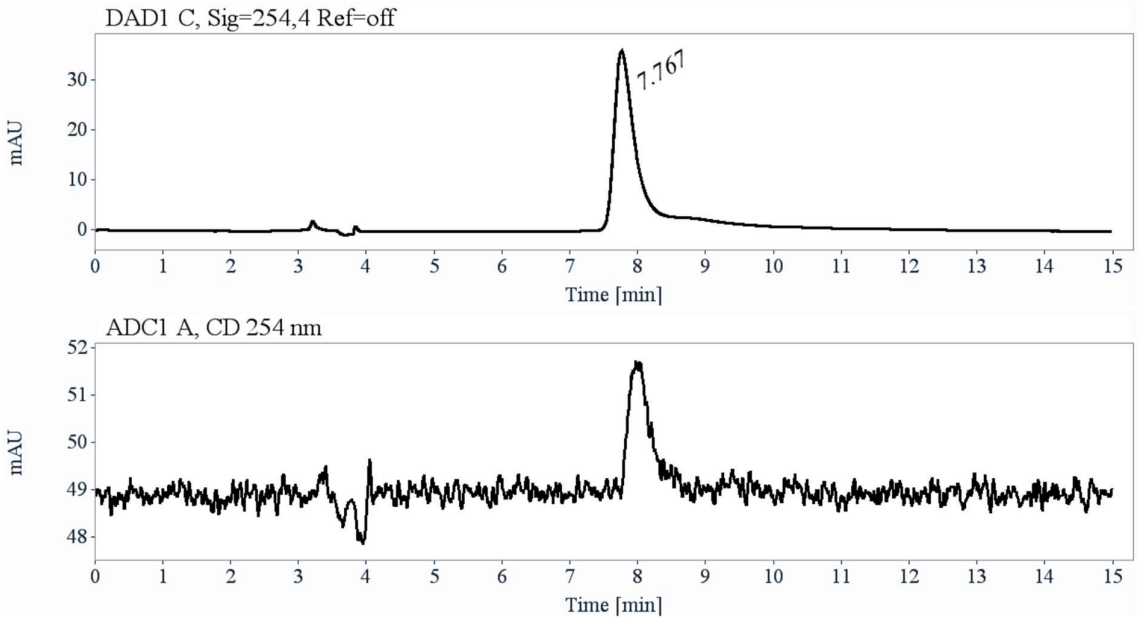
Chiral HPLC analysis: Chiralpak IG column with a UV and CD detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane / ethanol / dichloromethane 90:5:5; 1st enantiomer and *meso*-complex: Rt = 7.81 min and 2nd enantiomer: Rt = 12.18 min. (see Figure S34)



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.81	1516	55.70	1.65		
12.18	1206	44.30	3.13	1.90	4.78
Sum	2723	100.00			

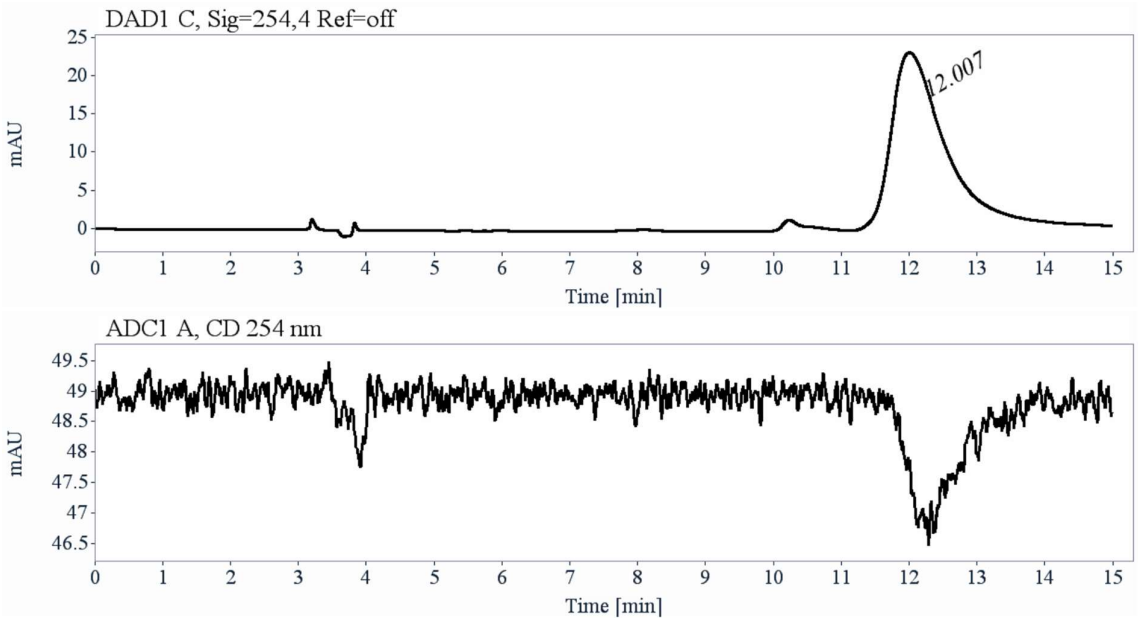
Figure S34. cHPLC analysis of palladium complex **3f**

The preparative chiral HPLC separation was with a Chiralpak IG column (250 x 10 mm, 5 µm) with hexane / ethanol / dichloromethane (90/5/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 150 mg of racemic mixture, 54 mg of the first eluted enantiomer with ee > 99.5% (



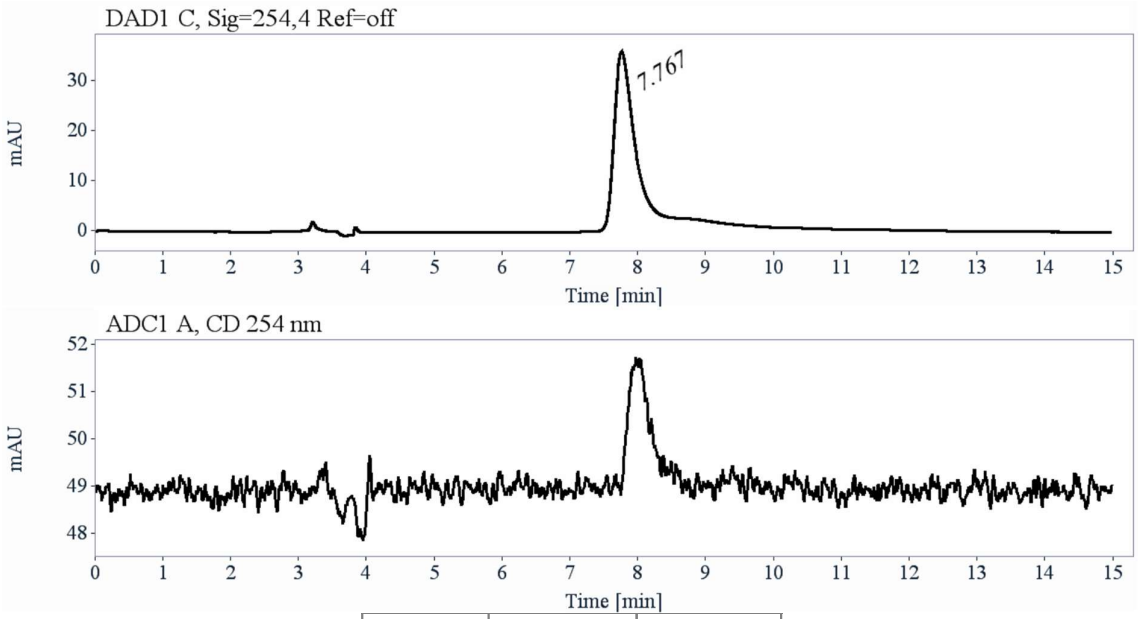
RT [min]	Area	Area%
7.77	981	100.00
Sum	981	100.00

Figure S35) and 49 mg of the second eluted enantiomer with ee > 99.5% (



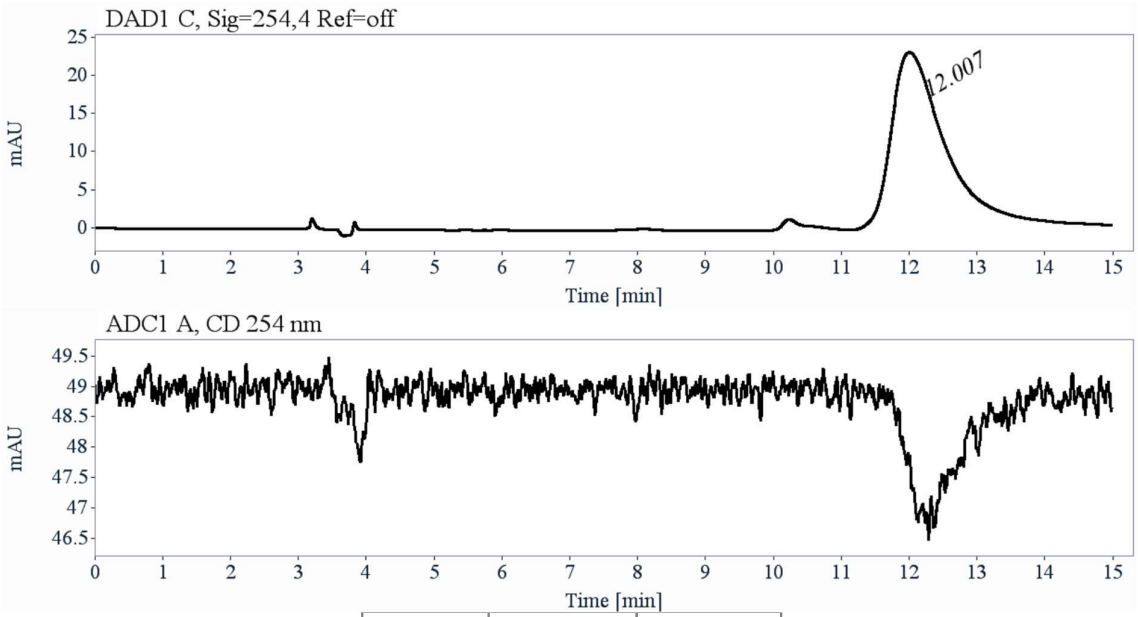
RT [min]	Area	Area%
12.01	1220	100.00
Sum	1220	100.00

Figure S36).



RT [min]	Area	Area%
7.77	981	100.00
Sum	981	100.00

Figure S35. cHPLC analysis of the first eluted complex **3f**



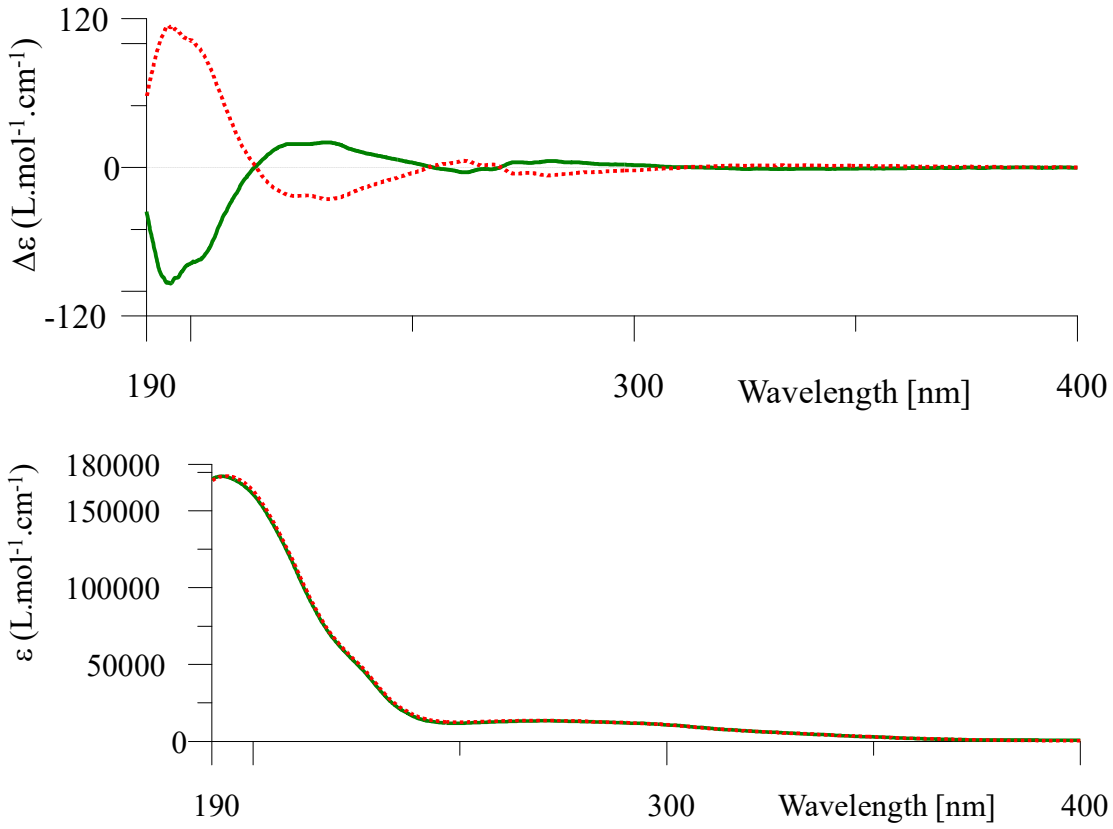
RT [min]	Area	Area%
12.01	1220	100.00
Sum	1220	100.00

Figure S36: cHPLC analysis of the second eluted palladium complex **3f**

λ (nm)	**3f** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =)	**3f** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.186)

589	not determined	+ 77
578	not determined	+ 75
546	not determined	+ 88
436	not determined	+ 177

Table S8. Optical rotations of complexes **3f**



First eluted enantiomer: green solid line, concentration = 0.105 mmol.L^{-1} in acetonitrile.
Second eluted enantiomer: red dotted line, concentration = 0.106 mmol.L^{-1} in acetonitrile.

Figure S37. Electronic Circular Dichroism of complexes **3f**

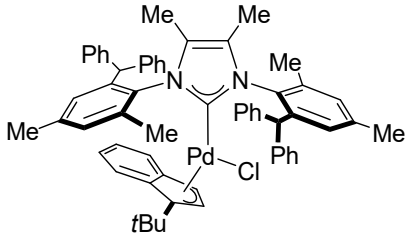
Pure *meso* -**3f** could not be obtained.

Data for (±)-**3f** are as follow:

Rf = 0.53 (PE/Et_2O 1:2). **Mp =** 183.8-185.1 °C (decomposition). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.45-6.95 (m, 28H, H^{Ar} and C*H*), 6.80-6.70 (m, 2H, H^{Ar}), 6.11 (s, 1H, C*H*), 5.24-5.10 (m, 0.52H, $H^{cinamyl}$, *maj*), 5.06-4.94 (m, 0.48H, $H^{cinamyl}$, *min*), 4.65 (d, *J*(H,H)= 13.1 Hz, 0.52H, $H^{cinamyl}$, *maj*), 4.53 (d, *J*(H,H)= 13.1 Hz, 0.48H, $H^{cinamyl}$, *min*), 2.78 (d, *J*(H,H)= 6.9 Hz, 0.52H, $H^{cinamyl}$, *maj*), 2.61 (d, *J*(H,H)= 6.9 Hz, 0.48H, $H^{cinamyl}$, *min*), 2.36-2.16 (m, 12H, Ar-CH_3), 1.72 (d, *J*(H,H)= 11.5 Hz, 0.48H, $H^{cinamyl}$, *min*), 1.28 (d, *J*(H,H)= 11.5 Hz, 0.52H, $H^{cinamyl}$, *maj*), 1.02 (s, 1.44H, CH_3, *min*), 0.99 (s, 1.56H, CH_3, *maj*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 177.6 (*C*), 142.4 (*C*), 142.3 (*C*), 138.6 (*C*), 137.7 (*C*), 134.9 (*C*), 130.1 (*C*H), 130.0 (*C*H), 129.3 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 128.0 (*C*H), 127.6 (*C*H), 127.4 (*C*H), 127.3 (*C*), 127.1 (*C*H), 126.7 (*C*H), 126.5 (*C*H), 126.2 (*C*H), 126.1 (*C*H), 109.0 (*C*H), 108.7 (*C*H), 92.7 (*C*H), 89.6(*C*H), 68.1 (*C*H), 50.9 (*C*H), 46.8 (CH_2), 44.5 (CH_2),

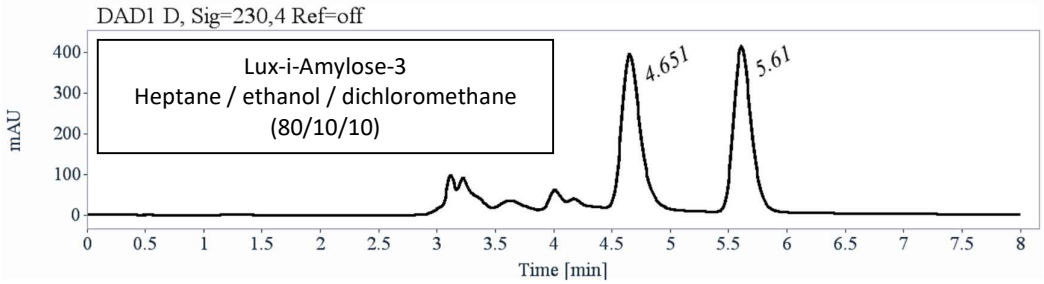
25.8(CH_2), 21.7 (CH_3), 19.2(CH_3), 8.4 (CH_3), 8.3 (CH_3). **HRMS (ESI)**: *m/z*: 917.2841 calcd for $C_{56}H_{53}ClN_2PdNa^+$ $[M+Na]^+$: found 917.2832. **IR(ATR):** 3056, 3022, 2920, 2855, 2358, 1744, 1654, 1598, 1492, 1475, 1447, 1372, 1315, 1178, 1155, 1117, 1076, 1031, 1002, 969, 932, 855, 822, 780, 744, 734, 699, 629, 618, 577, 566, 523 cm^{-1}.

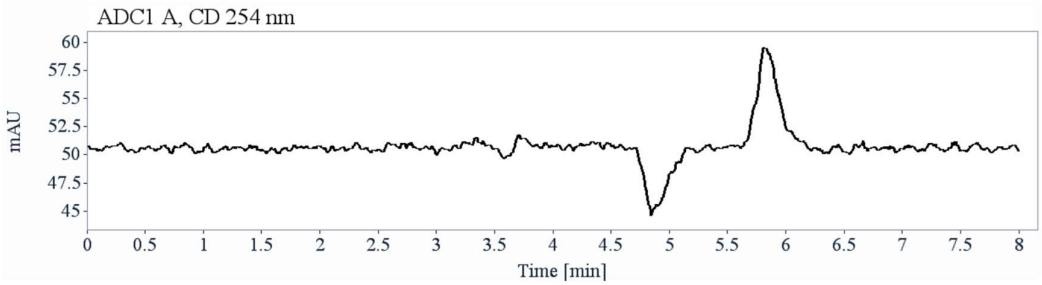
Chloro(η^3-1-^{t}Bu-indenyl)[(1-(2-benzhydryl-4,6-dimethylphenyl)-3-(2-Benzhydryl-4,6-dimethylphenyl)-4,5-dimethyl-2,3-dihydro-1H-imidazol-2-yl)] palladium(II) 4f



A mixture of diastereomerically pure heterochiral imidazolium tetrafluoroborate **1f·BF_4** (100 mg, 0.14 mmol, 2.3 equiv.), [Pd(η^3-1-^{t}Bu-indenyl)]$_2$ (41 mg, 1.0 mmol, 1 equiv.), K_2CO_3 (38 mg, 0.28 mmol, 4.6 equiv.) in acetone was stirred at 60 °C for 4 h. The reaction mixture was filtered through a Celite® pad and the solvent was removed under vacuum. The crude product was purified by silica gel column (PE/Et_2O = 2:1) give the NHC-palladium complex **4f** as orange solid. (71 mg, 57% yield). The product was obtained as a diastereomerically pure complex.

Rf = 0.78 (PE/Et_2O 1:1). **Mp** = 264.2-267.5 °C (decomposition). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.36 (d, J = 7.6 Hz, 3H, H^{Ar} and H^{Ind}), 7.11 (s, 14H, H^{Ar}), 6.97 (s, 6H, H^{Ar} and H^{Ind}), 6.71 (td, J = 7.6, 1.1 Hz, 1H, H^{Ind}), 6.59 (s, 2H, H^{Ar}), 6.50 (s, 1H, C*H*), 6.33 (d, J = 2.8 Hz, 1H, H^{Ar}), 6.18 (td, J = 7.5, 0.9 Hz, 1H, H^{Ind}), 5.89 – 5.82 (m, 1H, H^{Ind}), 5.64 (s, 1H, C*H*), 4.94 (d, J = 2.7 Hz, 1H, H^{Ind}), 2.35 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 1.45 (s, 9H, C(CH_3)$_3$), 0.78 (s, 6H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 169.0($C^{carbene}$), 141.3 (*C*), 139.9 (*C*), 135.3 (*C*), 130.2 (*C*H), 128.0 (*C*H), 124.5 (*C*H), 123.6 (*C*H), 119.3 (*C*H), 118.6 (*C*), 117.2 (*C*H), 109.6 (*C*H), 62.2 (*C*H), 34.4 (*C*), 29.6 (*C*H_3), 21.6 (*C*H_3), 8.4 (*C*H_3). **HRMS (ESI):** *m/z*: 971.3311 calcd for: $C_{60}H_{59}ClN_2PdNa^+$ $[M+Na]^+$: found 971.3326. **IR (ATR):** 3054, 2968, 1706, 1601, 1494, 1449, 1367, 1264, 1199, 1078, 1032, 896, 858, 731, 701, 632, 566, 527 cm^{-1}. **Chiral HPLC analysis:** Lux-i-Amylose-3 column with an UV detector at λ = 230 nm and a circular dichroism detector at λ = 254 nm; flow rate 1 mL/min; eluent: Heptane/ethanol/dichloromethane 80:10:10; 1st enantiomer: Rt = 4.65 min and 2nd enantiomer: Rt = 5.61 min (see Figure S38).

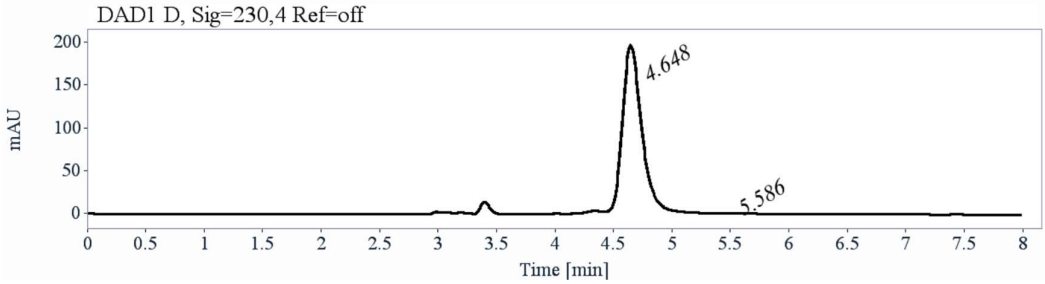




RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.65	4228	49.59	0.58		
5.61	4299	50.41	0.90	1.56	3.41
Sum	8527	100.00			

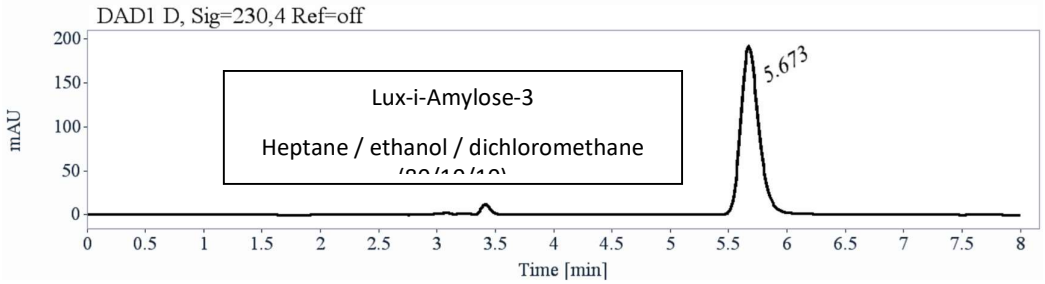
Figure S38. Analysis of complex **4f** by cHPLC

The preparative chiral HPLC separation was done on a Lux-i-Amylose-3 (250 x 10 mm) with hexane / EtOH / dichloromethane (80/10/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm with multiple injections. From 65 mg of complex, 23 mg of the first eluted enantiomer with ee > 99.5% (Figure S39), 20 mg of the second eluted enantiomer with ee > 99.5% (Figure S40) were obtained.



RT [min]	Area	Area%
4.65	2176	99.77
5.59	5	0.23
Sum	2181	100.00

Figure S39. cHPLC analysis of the first eluted palladium complex **4f**



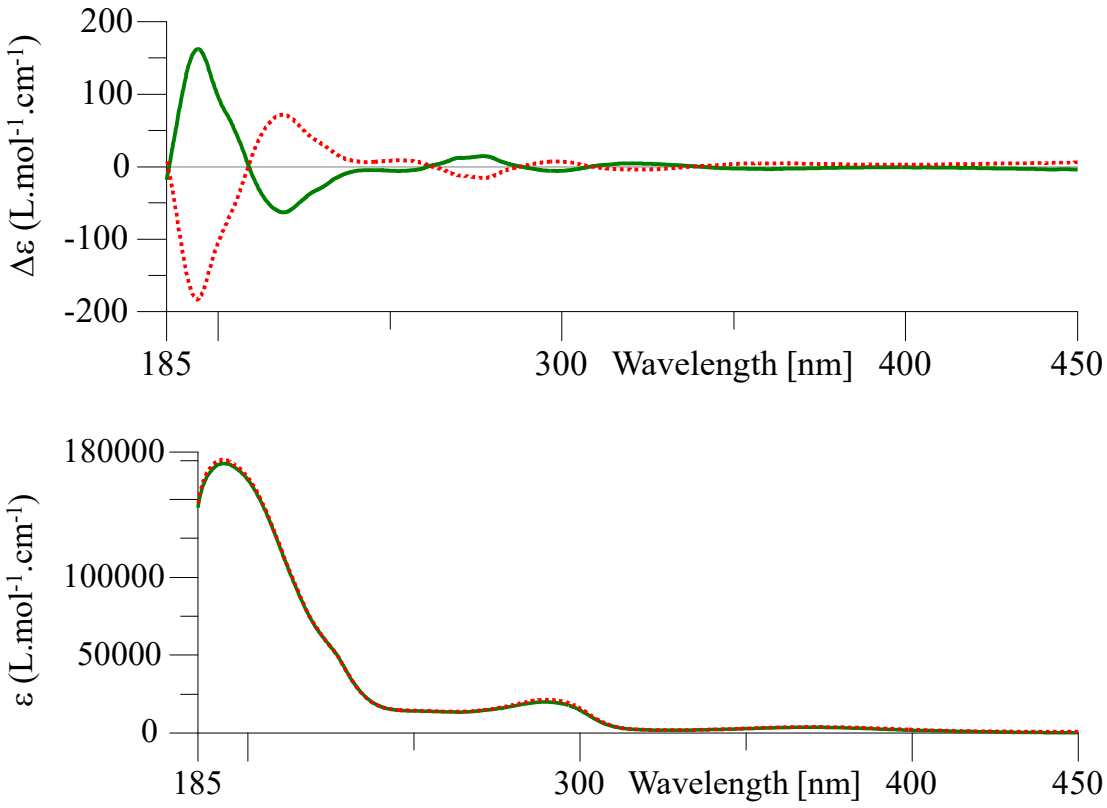
RT [min]	Area	Area%
5.67	2057	100.00

Sum	2057	100.00

Figure S40. cHPLC analysis of the second eluted palladium complex **4f**

λ (nm)	**4f** first eluted on Lux-i-Amylose-3 $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.074)	**4f** second eluted on Lux-i-Amylose-3 $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c = 0.083)
589	- 740	+ 740
578	- 830	+ 830
546	- 1050	+ 1050

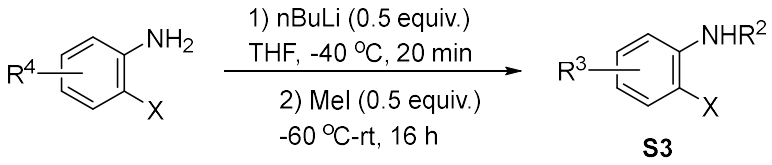
Table S9. Optical rotations of complexes **4f**



first eluted enantiomer : green solid line, concentration = 0.960 mmol.L^{-1} in acetonitrile.
second eluted enantiomer : red dotted line, concentration = 0.957 mmol.L^{-1} in acetonitrile.

Figure S41. Electronic Circular Dichroism of chiral complexes **4f**

IV Substrates syntheses



S3

Scheme S3. Preparation of functionalized bromoanilines

General procedure F: Preparation of functionalized bromoanilines

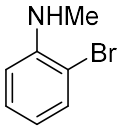
To a solution of aniline (1 mmol) in dry THF (2 mL), *n*BuLi (0.5 mmol, 0.5 equiv., 1.6 M in hexane) was added dropwise at -40 °C under argon atmosphere. The reaction was stirred at -40 °C for 20 minutes before to add dropwise alkylhalide (0.5 mmol, 0.5 equiv.) at -60 °C. The reaction was slowly warmed up to room temperature and stirred for another 16 hours. The reaction was quenched with water (5 mL) and the mixture was extracted by ethyl acetate (3 x 5 mL). The combined organic phases were washed with $NaHCO_3$ (2 x 5 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column (petroleum ether/ether = 20: 1)

2-Chloro-*N*-methylaniline S3[6]

According to the general procedure F, from 2-chloroaniline (2.54 g, 20 mmol), *n*BuLi (6.25 mL, 1.6 M in hexane, 10 mmol, 0.5 equiv.), MeI (0.62 mL, 10 mmol, 0.5 equiv.) the product was obtained as a light yellow liquid. (1.37 g, 97% yield).

Rf = 0.82 (PE/Et_2O 9:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.28-7.12 (m, 2H, H^{Ar}), 6.68-6.59 (m, 2H, H^{Ar}), 4.34 (br, 1H, N*H*), 2.91 (d, *J*(H,H) = 5.1 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =145.1 (*C*), 129.0 (*C*H), 127.9 (*C*H), 119.1 (*C*), 117.1 (*C*H), 127.5 (*C*H), 110.7 (*C*H), 30.4 (*C*H_3).

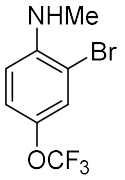
2-Bromo- *N*-methylaniline[6]



According to the general procedure F, from 2-bromoaniline (10.0 g, 58.2 mmol), *n*BuLi (18.2 mL, 1.6 M in hexane, 29.1 mmol, 0.5 equiv.), MeI (1.82 mL, 29.1 mmol, 0.5 equiv.) the product was obtained as a yellow liquid. (3.6 g, 66% yield).

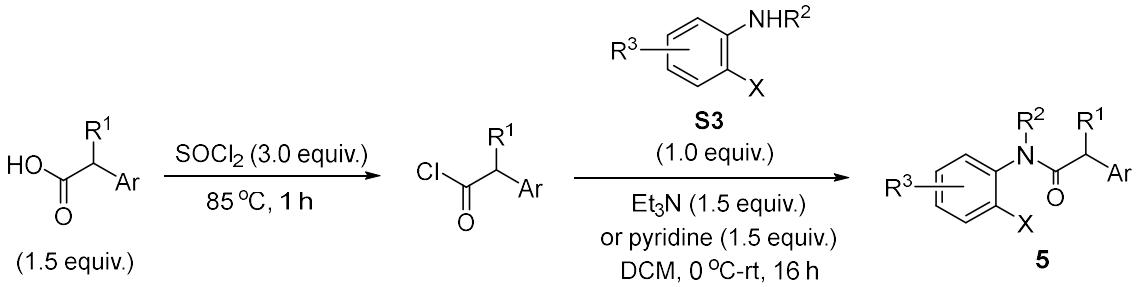
Rf = 0.80 (PE/Et_2O 9:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.44 (dd, *J*(H,H) = 7.9 and 1.5 Hz, 1H, H^{Ar}), 7.25-7.20 (m, 1H, H^{Ar}), 6.65 (dd, *J*(H,H) = 8.2 and 1.5 Hz, 1H, H^{Ar}), 6.62-6.57 (m, 1H, H^{Ar}), 4.37 (br, 1H, N*H*), 2.92 (d, *J*(H,H) = 5.2 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =146.1 (*C*), 132.4 (*C*H), 128.7 (*C*H), 117.7 (*C*H), 110.8(*C*H), 109.7 (*C*), 30.7 (*C*H_3).

2-Bromo-*N*-methyl-4-(trifluoromethoxy)aniline[7]



According to the general procedure F, from 2-bromo-5-trifluoromethoxyaniline (5.0 g, 19.7 mmol), *n*BuLi (6.15 mL, 1.6 M in hexane, 9.85 mmol, 0.5 equiv.), MeI (0.61 mL, 9.85 mmol, 0.5 equiv.) the product was obtained as a yellow liquid. (2.04 g, 77% yield).

Rf = 0.45 (PE/Et_2O 4:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.34 (dd, *J*(H,H) = 2.6 and 1.0 Hz, 1H, H^{Ar}), 7.13-7.07 (m, 1H, H^{Ar}), 6.58 (d, *J*(H,H) = 8.9 Hz, 1H, H^{Ar}), 4.46 (br, 1H, N*H*), 2.89 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =145.2 (*C*), 139.5 (*C*), 125.8 (*C*H), 121.9 (*C*H), 120.8 (q, J^1(C,F) = 256.1 Hz, CF_3), 110.2 (*C*H), 108.7 (*C*), 30.8 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** -58.7 (s, 3F, CF_3).

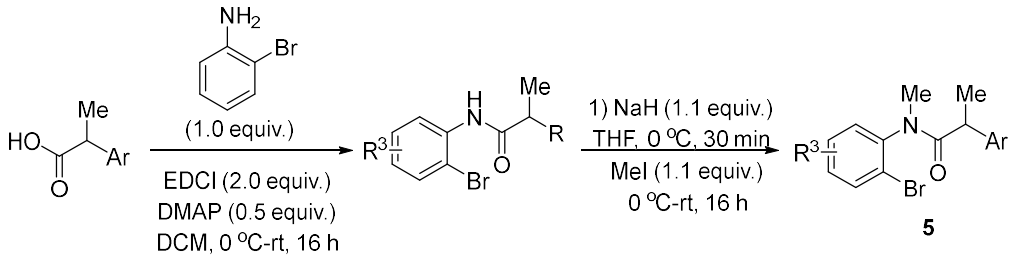


Scheme S4. Synthesis of substrates **5** with acyl chloride reagent

General procedure G: Synthesis of substrates 5 with acyl chloride reagent

A mixture of the carbonyl acid (1.5 mmol, 1.5 equiv.) in $SOCl_2$ (3.0 mmol, 3.0 equiv.) was stirred at 85 °C for 2 hours. The excess $SOCl_2$ was removed under vacuum to give the carbonyl chloride which was used without further treatment.

To a solution of the carbonyl chloride in dry dichloromethane, a solution of triethylamine or pyridine (1.5 mmol, 1.5 equiv.) in dry dichloromethane was added dropwise at 0 °C under argon atmosphere followed a solution of the *N*-methylaniline (1 mmol) in dry dichloromethane (4 mL). The resulting mixture was slowly warmed up to room temperature and stirred for 16 hours. The reaction mixture was diluted with ether (10 mL) and quenched with NH_4Cl (aq. 10 mL). The aqueous phase was extracted by ether (2 x 10 mL). The organic phase was washed with $NaHCO_3$ (3 x 10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column (petroleum ether/ether = 2: 1).



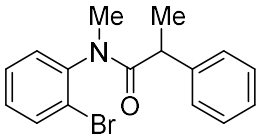
Scheme S5. Synthesis of substrates **5** from carboxylic acid

General procedure H: Synthesis of substrates 5 from carboxylic acid

To a solution of the carboxylic acid (1.0 mmol) and aniline (1.0 mmol 1.0 equiv.) in dry dichloromethane, *N,N*-dimethylaminopyridine (DMAP) (0.5 mmol, 0.5 equiv.) was added in one portion at 0 °C under argon atmosphere. Then *N*-(3-dimethylaminopropyl)-*N′* -ethylcarbodiimide hydrochloride (EDCI) (2.0 mmol, 2.0 equiv.) was added in one portion. The reaction was slowly warmed up to room temperature and stirred for 16 hours. The mixture was quenched by water (20 mL). The aqueous phase was extracted by dichloromethane (2 x 30 mL). The combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column (petroleum ether/dichloromethane = 1: 2) to give the amide.

To suspension of NaH (1.1 mmol, 60% in mineral, 1.1 equiv.) in dry THF (30 mL), a solution of the amide in dry THF was added dropwise at 0 °C under argon atmosphere and the reaction was then stirred at room temperature for 1 hour. MeI (1.1 mmol, 1.1 equiv.) was added dropwise and the reaction was stirred for another 16 hours. The mixture was filtered through a silica/celite® plug and the solvent was removed under vacuum. The residue was purified by silica gel column (petroleum ether/ether = 1: 1).

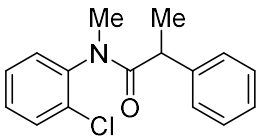
***N*-(2-Bromophenyl)-*N*-methyl-2-phenylpropanamide[6] 5a**



According to the general procedure G, from 2-phenylpropanoic acid (1.95 g, 13.0 mmol, 1.5 equiv.), $SOCl_2$ (1.88 mL, 26.0 mmol, 3.0 equiv.), 2-bromo-*N*-methylaniline (1.6 g, 8.65 mmol, 1.0 equiv.), triethylamine (1.77 mL, 13 mmol, 1.5 equiv.) the product was obtained as a yellow oil. (1.94 g, 71% yield).

Rf = 0.43 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.72 (dd, *J*(H,H) = 7.9 and 1.6 Hz, 0.7H, H^{Ar}, *maj)*, 7.59 (dd, *J*(H,H) = 8.1 and 1.4 Hz, 0.3H, H^{Ar}, *min*), 7.46-7.34 (m, 0.7H, H^{Ar}, *maj*), 7.28-7.14 (m, 4.6H, H^{Ar}), 7.04-6.94 (m, 2H, H^{Ar}), 6.71(dd, *J*(H,H) = 7.7 and 1.7 Hz, 0.7H, H^{Ar}, *maj*), 3.53 (q, *J*(H,H) = 6.9 Hz, 0.3H, C*H*, *min*), 3.35 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.20 (s, 0.9H, NCH_3, *min*), 3.18 (s, 2.1H, NCH_3, *maj*), 1.44 (d, *J*(H,H) = 6.8 Hz, 2.1H, CH_3, *maj*), 1.42 (d, *J*(H,H) = 6.8 Hz, 0.7H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =174.0 (*C*), 173.8 (*C*), 142.6 (*C*), 142.4 (*C*), 141.8 (*C*), 140.8 (*C*), 134.1(*C*H), 133.6 (*C*H), 131.0 (*C*H), 130.2 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 127.6 (*C*H), 126.8 (*C*H), 126.7 (*C*H), 124.3 (*C*), 123.8 (*C*), 44.2 (*C*H), 43.4 (*C*H), 36.3 (*C*H_3), 36.2 (*C*H_3), 20.7 (*C*H_3), 20.2 (*C*H_3).

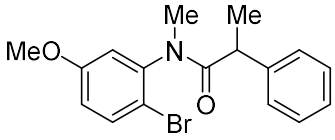
***N*-(2-Chlorophenyl)-*N*-methyl-2-phenylpropanamide[6] 5a(Cl)**



According to the general procedure G, from 2-phenylpropanoic acid (1.13 g, 7.5 mmol, 1.5 equiv.), $SOCl_2$ (1.1 mL, 15.0 mmol, 3.0 equiv.), 2-chloro-*N*-methylaniline (0.71 g, 5 mmol, 1.0 equiv.), triethylamine (1.04 mL, 7.5 mmol, 1.5 equiv.) the product was obtained as a yellow oil. (1.0 g, 73% yield).

Rf = 0.45 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.53 (d, *J*(H,H) = 8.0 Hz, 0.7H, H^{Ar}, *maj)*, 7.39-7.27 (m, 2H, H^{Ar}), 7.22-7.09 (m, 3.6H, H^{Ar}), 7.02-6.92 (m, 2H, H^{Ar}), 6.72 (dd, *J*(H,H) = 7.8 and 1.6 Hz, 0.7H, H^{Ar}, *maj*), 3.55 (q, *J*(H,H) = 6.9 Hz, 0.3H, C*H*, *min*), 3.35 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.19 (s, 3H, NCH_3), 1.42 (d, *J*(H,H) = 6.9 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =174.2 (*C*), 174.1 (*C*), 141.9 (*C*), 141.1 (*C*), 140.9 (*C*), 140.8 (*C*), 134.1 (*C*), 133.2 (*C*), 130.9 (*C*H), 130.5 (*C*H), 130.2 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 128.1 (*C*H), 128.0 (*C*H), 127.9 (*C*H), 127.7 (*C*H), 126.8 (*C*H), 44.0 (*C*H), 43.5 (*C*H), 36.3 (CH_3), 36.2 (CH_3), 20.7 (CH_3), 20.1 (CH_3).

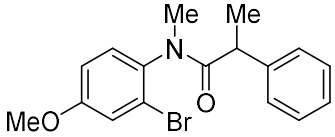
***N*-(2-Bromo-5-methoxyphenyl)-*N*-methyl-2-phenylpropanamide[8] 5b**



According to the general procedure G, from 2-phenylpropanoic acid (0.30 g, 2.0 mmol, 1.0 equiv.), 2-bromo-5-methoxylaniline (0.40 g, 2.0 mmol, 1.0 equiv.), EDCI (0.77 g, 4.0 mmol, 2.0 equiv.), DMAP (0.12 g, 1.0 mmol, 0.5 equiv.), NaH (0.55 g, 60% in mineral oil, 1.1 mmol, 1.1 equiv.), MeI (95 μL, 1.1 mmol, 1.1 equiv.) the product was obtained as a light yellow oil. (340 mg, 49% yield).

Rf = 0.47 (PE/Et_2O 1:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 4:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.62 (d, *J*(H,H) = 8.9 Hz, 0.8H, H^{Ar}, *maj*), 7.58 (d, *J*(H,H) = 8.9 Hz, 0.2H, H^{Ar}, *min*), 7.36-7.20 (m, 2H, H^{Ar}), 7.17-7.12 (m, 0.4H, H^{Ar}, *min*), 7.09-7.02 (m, 1.6H, H^{Ar}, *maj*), 6.98-6.83 (m, 1.2H, H^{Ar}), 6.21 (d, *J*(H,H) = 3.0 Hz, 0.8H, H^{Ar}, *maj*), 3.93 (s, 0.9H, OCH_3, *min*), 3.65 (q, *J*(H,H) = 7.0 Hz, 0.2H, C*H*, *min*), 3.44 (q, *J*(H,H) = 6.9 Hz, 0.8H, C*H*, *maj*), 3.47 (s, 2.1H, OCH_3, *maj*), 3.25 (s, 3H, NCH_3), 1.50 (d, *J*(H,H) = 7.0 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =174.0 (*C*), 173.6 (*C*), 159.9 (*C*), 159.5 (*C*), 143.3 (*C*), 142.8 (*C*), 142.2 (*C*), 140.8 (*C*), 134.3 (*C*H), 133.7 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 127.6 (*C*H), 126.8 (*C*H), 126.7 (*C*H), 117.0 (*C*), 115.9 (*C*H), 115.5 (*C*H), 115.4 (*C*H), 114.4 (*C*), 113.6 (*C*), 55.9 (CH_3), 55.4 (CH_3), 44.4 (*C*H), 43.3 (*C*H), 36.2 (CH_3), 36.1 (CH_3), 20.8 (CH_3), 20.3 (CH_3).

***N*-(2-Bromo-4-methoxyphenyl)-*N*-methyl-2-phenylpropanamide 5c**

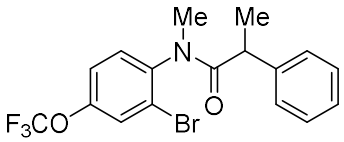


According to the general procedure H, from 2-phenylpropanoic acid (0.30 g, 2.0 mmol, 1.0 equiv.), 2-bromo-4-methoxylaniline (0.40 g, 2.0 mmol, 1.0 equiv.), EDCI (0.77 g, 4.0 mmol, 2.0 equiv.), DMAP (0.12 g, 1.0 mmol, 0.5 equiv.), NaH (0.55 g, 60% in mineral oil, 1.1 mmol, 1.1 equiv.), MeI (95 μL, 1.1 mmol, 1.1 equiv.) the product was obtained as a light yellow oil. (560 mg, 80% yield).

Rf = 0.47 (PE/Et_2O 1:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.36-6.98 (m, 6.6H, H^{Ar}), 6.78-6.72 (m, 0.7H, H^{Ar}, *maj*), 6.69-6.64 (m, 0.7H, H^{Ar}, *maj*), 3.93 (s, 0.9H, OCH_3, *min*), 3.91 (s, 2.1H, OCH_3, *maj*), 3.62 (q, *J*(H,H) = 6.9 Hz, 0.3H, C*H*, *min*), 3.46 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.24 (s, 0.9H, NCH_3, *min*), 3.21 (s, 2.1H, NCH_3, *maj*), 1.50 (d, *J*(H,H) = 7.0 Hz, 2.1H, CH_3, *maj*), 1.48 (d, *J*(H,H) = 7.2 Hz, 0.7H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):**

δ =174.5 (*C*), 174.3 (*C*), 159.8 (*C*), 159.7 (*C*), 142.0 (*C*), 140.9 (*C*), 135.5 (*C*), 135.2 (*C*), 131.2 (*C*H), 130.4 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 127.6 (*C*H), 126.8 (*C*H), 126.7 (*C*H), 124.7 (*C*), 124.1 (*C*), 118.8 (*C*H), 118.5 (*C*H), 114.6 (*C*H), 114.2 (*C*H), 55.9 (CH_3), 44.0 (*C*H), 43.2 (*C*H), 36.5 (CH_3), 20.7 (CH_3), 20.3 (CH_3). **HRMS (ESI)**: *m/z*: 348.0594 calcd for: $C_{17}H_{19}NO_2Br^+$ $[M+H]^+$: found 348.0589. **IR (ATR):** 3058, 3027, 2969, 2931, 2839, 2358, 2117, 1892, 1657, 1599, 1562, 1492, 1453, 1439, 1419, 1375, 1319, 1284, 1256, 1222, 1181, 1127, 1066, 1031, 910, 846, 820, 776, 732, 697, 676, 602, 578, 525, 508 cm^{-1}.

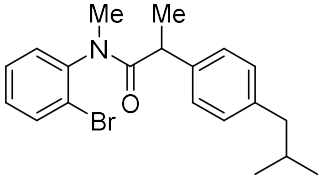
***N*-(2-Bromo-4-(trifluoromethoxy)phenyl)-*N*-methyl-2-phenylpropanamide 5d**



According to the general procedure G, from 2-phenylpropanoic acid (0.45 g, 3.0 mmol, 1.5 equiv.), $SOCl_2$ (0.44 mL, 6.0 mmol, 3.0 equiv.), 2-Bromo-*N*-methyl-4-(trifluoromethoxy)aniline (0.54 g, 2.0 mmol, 1.0 equiv.), pyridine (0.25 mL, 3 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (700 mg, 87% yield).

Rf = 0.35 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.58 (d, *J*(H,H) = 2.6 Hz, 0.7H, H^{Ar}, *maj)*, 7.43-7.36 (m, 0.7H, H^{Ar}, *maj*), 7.32-7.14 (m, 3.3H, H^{Ar}), 7.00-6.86 (m, 2.6H, H^{Ar}), 6.63 (d, *J*(H,H) = 8.7 Hz, 0.7H, H^{Ar}, *maj*), 3.50 (q, *J*(H,H) = 6.9 Hz, 0.3H, C*H*, *min*), 3.30 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.18 (s, 0.9H, NCH_3, *min*), 3.16 (s, 2.1H, NCH_3, *maj*), 1.43 (d, *J*(H,H) = 6.8 Hz, 2.1H, CH_3, *maj*), 1.42 (d, *J*(H,H) = 6.8 Hz, 0.7H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =173.8 (*C*), 173.6 (*C*), 148.8 (*C*), 148.7 (*C*), 141.7 (*C*), 141.4 (*C*), 141.1 (*C*), 140.4 (*C*), 131.9 (*C*H), 131.1 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 128.0 (*C*H), 127.4 (*C*H), 127.1 (*C*H), 127.0 (*C*H), 126.5 (*C*H), 126.0 (*C*H), 125.4 (*C*), 124.5 (*C*), 121.1 (*C*H), 120.8 (*C*H), 120.4 (q, J^1(C,F) = 259.0 Hz, *C*F_3), 44.7 (*C*H), 43.9 (*C*H), 38.4 (*C*H_3), 36.3 (*C*H_3), 20.8 (*C*H_3), 20.4 (*C*H_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -58.0 (s, 3F, C*F*$_3$). **HRMS (ESI)**: *m/z*: 402.0311 calcd for: $C_{17}H_{16}BrF_3NO_2^+$ $[M+H]^+$: found 402.0310. **IR (ATR):** 3373, 3063, 3028, 2974, 2933, 2361, 1667, 1599, 1573, 1488, 1453, 1420, 1375, 1248, 1213, 1165, 1124, 1067, 1043, 1018, 942, 906, 879, 827, 806, 778, 749, 698, 678, 649, 594, 569, 545, 506 cm^{-1}.

***N*-(2-Bromophenyl)-2-(4-*iso*butylphenyl)-*N*-methylpropanamide[9] 5e**

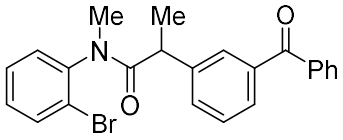


According to the general procedure G, from 2-(4-*iso*butylphenyl)propanoic acid (0.5 g, 2.43 mmol, 1.5 equiv.), $SOCl_2$ (0.35 mL, 4.86 mmol, 3.0 equiv.), 2-bromo-*N*-methylaniline (0.30 g, 1.62 mmol, 1.0 equiv.), pyridine (0.20 mL, 2.43 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (600 mg, 98% yield).

Rf = 0.55 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.70 (dd, *J*(H,H) = 7.9 and 1.6 Hz, 0.7H, H^{Ar}, *maj)*, 7.55 (dd, *J*(H,H) = 8.0 and 1.5 Hz, 0.3H, H^{Ar}, *min*), 7.45-7.39 (m, 0.3H, H^{Ar}, *min*), 7.36-7.32 (m, 0.3H, H^{Ar}, *min*), 7.26-7.10 (m, 1.7H, H^{Ar}), 6.98-6.93 (m, 2H, H^{Ar}), 6.89-6.81 (m, 2H, H^{Ar}), 6.69 (dd, *J*(H,H) = 7.7 and 1.8 Hz, 0.7H, H^{Ar},

maj), 3.50 (q, *J*(H,H) = 7.0 Hz, 0.3H, C*H*, *min*), 3.31 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.18 (s, 0.9H, NCH_3, *min*), 3.16 (s, 2.1H, NCH_3, *maj*), 2.44-2.36 (m, 2H, CH_2), 1.88-1.74 (m, 1H, CH_2CH), 1.41 (d, *J*(H,H) = 6.8 Hz, 2.1H, CH_3, *maj*), 1.39 (d, *J*(H,H) = 6.8 Hz, 0.7H, NCH_3, *min*), 0.89 (d, *J*(H,H) = 6.7 Hz, 3H, CH(CH_3)$_2$), 0.88 (d, *J*(H,H) = 6.7 Hz, 3H, CH(CH_3)$_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =174.2 (*C*), 174.1 (*C*), 142.7 (*C*), 142.5 (*C*), 140.2 (*C*), 140.1 (*C*), 139.1 (*C*), 138.0 (*C*), 134.1 (*C*H), 133.6 (*C*H), 131.1 (*C*H), 130.3 (*C*H), 129.7 (*C*H), 129.2 (*C*H), 129.1 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 127.8 (*C*H), 127.3 (*C*H), 124.4 (*C*), 123.8 (*C*H), 45.2 (*C*H_2), 45.1 (*C*H_2), 43.9 (*C*H), 43.1 (*C*H), 36.3 (*C*H_3), 36.2 (*C*H_3), 30.3 (*C*H), 25.5 (*C*H_3), 25.4 (*C*H_3), 20.7 (*C*H_3), 20.3 (*C*H_3).

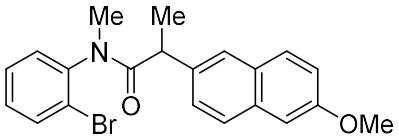
2-(3-Benzoylphenyl)-*N*-(2-bromophenyl)-*N*-methylpropanamide 5f



According to the general procedure G, from ketoprofen (0.62 g, 2.43 mmol, 1.5 equiv.), $SOCl_2$ (0.35 mL, 4.86 mmol, 3.0 equiv.), 2-bromo-N-methylaniline (0.30 g, 1.62 mmol, 1.0 equiv.), pyridine (0.20 mL, 2.43 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (663 mg, 97% yield).

Rf = 0.25 (PE/Et_2O 1:2). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75-7.05 (m, 12.3H, H^{Ar}), 6.69 (dd, *J*(H,H) = 7.4 and 2.1 Hz, 0.7H, H^{Ar}, *maj*), 3.54 (q, *J*(H,H) = 7.0 Hz, 0.3H, C*H*, *min*), 3.38 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H*, *maj*), 3.12 (s, 0.9H, NCH_3, *min*), 3.11 (s, 2.1H, NCH_3, *maj*), 1.40 (d, *J*(H,H) = 6.9 Hz, 2.1H, CH_3, *maj*), 1.36 (d, *J*(H,H) = 6.8 Hz, 0.7H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =196.7 (*C*), 196.5 (*C*), 173.6 (*C*), 173.4 (*C*), 142.4 (*C*), 142.3 (*C*), 142.1 (*C*), 141.1 (*C*), 137.8 (*C*), 137.7 (*C*), 137.6 (*C*), 134.2 (*C*H), 133.9 (*C*H), 132.6 (*C*H), 132.4 (*C*H), 132.2 (*C*H), 131.4 (*C*H), 130.8 (*C*H), 130.2 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 129.4 (*C*H), 129.0 (*C*H), 128.8 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 124.2 (*C*), 123.8(*C*), 44.0 (*C*H), 43.3 (*C*H), 36.4 (*C*H_3), 36.3 (*C*H_3), 20.5 (*C*H_3), 20.1 (*C*H_3). **HRMS (ESI)**: *m/z*: 424.0733 calcd for: $C_{23}H_{21}NO_2Br^+$ $[M+H]^+$: found 424.0723. **IR (ATR):** 3058, 2974, 2931, 2361, 1966, 1813, 1654, 1596, 1580, 1475, 1445, 1434, 1376, 1316, 1278, 1243, 1196, 1177, 1130, 1072, 1046, 1027, 998, 953, 927, 904, 821, 790, 764, 717, 698, 643, 606, 576, 561, 512 cm^{-1}.

***N*-(2-Bromophenyl)-2-(6-methoxynaphthalen-2-yl)-*N*-methylpropanamide 5g**

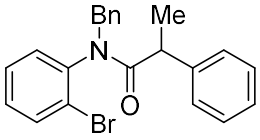


According to the general procedure H, from 2-(6-methoxynaphthalen-2-yl)propanoic acid (0.25 g, 1.5 mmol, 1.0 equiv.), 2-bromo-5-methoxylaniline (0.35 g, 1.5 mmol, 1.0 equiv.), EDCI (0.57 g, 3.0 mmol, 2.0 equiv.), DMAP (0.09 g, 0.75 mmol, 0.5 equiv.), NaH (0.58 g, 60% in mineral oil, 1.65 mmol, 1.1 equiv.), MeI (129 μL, 1.65 mmol, 1.1 equiv.) afforded a light yellow oil. (340 mg, 49% yield).

Rf = 0.23 (PE/Et_2O 2:1). **Mp** = 119.9-112.0 °C. In $CDCl_3$ (25 °C), this f amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.91 (dd, *J*(H,H) = 8.0 and 1.5 Hz, 0.7H, H^{Ar}, *maj)*, 7.79-7.71 (m, 2H, H^{Ar}), 7.70-7.55 (m, 0.7H, H^{Ar}, *maj*), 7.48-7.34 (m, 2.5H, H^{Ar}), 7.30-7.22 (m, 3.4H, H^{Ar}), 6.81 (dd, *J*(H,H) = 7.8 and 1.7 Hz, 0.7H, H^{Ar}, *maj*), 4.08 (s, 2.1H, OCH_3, *maj*), 4.07 (s, 0.9H, OCH_3, *min*), 3.85

(q, *J*(H,H) = 7.0 Hz, 0.3H, C*H, min*), 3.65 (q, *J*(H,H) = 6.9 Hz, 0.7H, C*H, maj)*, 3.37 (s, 0.9H, NCH_3, *min*), 3.36 (s, 2.1H, NCH_3, *maj*), 1.67 (d, *J*(H,H) = 6.9 Hz, 2.1H, CH_3, *maj*), 1.66 (d, *J*(H,H) = 6.9 Hz, 0.9H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =174.1 (*C*), 173.9 (*C*), 157.6 (*C*), 157.4 (*C*), 142.7 (*C*), 142.4 (*C*), 136.9 (*C*), 135.8 (*C*), 134.0 (*C*H), 133.4 (*C*H), 133.6 (*C*H), 133.5 (*C*), 131.1 (*C*H), 130.2 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 129.3 (*C*H), 129.2 (*C*H), 129.0 (*C*), 128.8 (*C*H), 128.4 (*C*H), 127.0 (*C*H), 126.8 (*C*H), 126.7 (*C*H), 126.4 (*C*H), 126.0 (*C*H), 124.5 (*C*), 123.8 (*C*), 118.8 (*C*H), 118.6 (*C*H), 105.7 (*C*H), 105.6 (*C*H), 55.4 (*C*H_3), 55.3 (*C*H_3), 44.2 (*C*H), 43.3 (*C*H), 36.3 (*C*H_3), 36.2 (*C*H_3), 20.7 (*C*H_3), 20.2 (*C*H_3). **HRMS (ESI)**: *m/z*: 400.0732 calcd for: $C_{21}H_{21}NO_2Br^+$ $[M+H]^+$: found 400.0728. **IR (ATR):** 3305, 3053, 3004, 2966, 2924, 2841, 2361, 2333, 2117, 1657, 1603, 1581, 1504, 1475, 1453, 1434, 1415, 1388, 1374, 1315, 1280, 1265, 1227, 1198, 1172, 1154, 1130, 1119, 1102, 1073, 1047, 1027, 956, 926, 878, 853, 831, 810, 792, 774, 733, 679, 658, 637, 603, 575, 519 cm^{-1}.

***N*-Benzyl-*N*-(2-bromophenyl)-2-phenylpropanamide[10] 5h**



A mixture of 2-phenylpropanoic acid (0.45 g, 3.0 mmol, 1.5 equiv.) in $SOCl_2$ (0.44 mL, 6.0 mmol, 3.0 equiv.) was stirred at 85 °C for 2 hours. The excess $SOCl_2$ was removed under vacuum to give the carbonyl chloride which was used without further treatment.

To a solution of the carbonyl chloride in dry dichloromethane (10 mL), a solution of pyridine (0.25 mL, 3.0 mmol, 1.5 equiv.) in dry dichloromethane (5 mL) was added dropwise at 0 °C under argon atmosphere followed by a solution of 2-bromoaniline (0.35 g, 2.0 mmol, 1.0 equiv.) in dry dichloromethane (5 mL). The resulting mixture was slowly warmed up to room temperature and stirred for 16 hours.

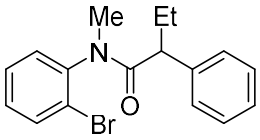
The reaction mixture was diluted with ether (10 mL) and quenched with NH_4Cl (aq. 10 mL). The aqueous phase was extracted by diethyl ether (2 x 10 mL). The organic phase was washed with $NaHCO_3$ (3 x 10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column (petroleum ether/ether = 9: 1) to give the amide.

To suspension of NaH (0.09 g, 60% in mineral, 2.2 mmol, 1.1 equiv.) in dry THF (30 mL), a solution of the amide in dry THF (10 mL) was added dropwise at 0 °C under argon atmosphere and the reaction was then stirred at room temperature for 1 hour. Benzyl bromide (0.38 g, 2.2 mmol, 1.1 equiv.) was added dropwise and the reaction was stirred for another 16 hours. The mixture was filtered through silica/celite® plug and the volatiles were removed under vacuum. The residue was purified by silica gel column (petroleum ether/ether = 9: 1) to give a light yellow oil. (676 mg, 86% yield).

Rf = 0.25 (PE/Et_2O 9:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.69 (dd, *J*(H,H) = 8.1 and 1.3 Hz, 0.7H, H^{Ar}, *maj)*, 7.62-7.56 (m, 0.3H, H^{Ar}, *min*), 7.30-7.00 (m, 10H, H^{Ar}), 6.97-6.88 (m, 2H, H^{Ar}), 6.84-6.80 (m, 0.3H, H^{Ar}, *min*), 6.15 (dd, *J*(H,H) = 7.9 and 1.6 Hz, 0.7H, H^{Ar}, *maj*), 5.71 (d, *J*(H,H) = 14.4 Hz, 0.3H, CH_2, *min*), 5.60 (d, *J*(H,H) = 14.4 Hz, 0.7H, CH_2, *maj*), 4.02 (d, *J*(H,H) = 14.4 Hz, 0.7H, CH_2, *maj*), 3.92 (d, *J*(H,H) = 14.4 Hz, 0.3H, CH_2, *min*), 3.47 (q, *J*(H,H) = 7.0 Hz, 0.3H, C*H, min*), 3.34 (q, *J*(H,H) = 6.8 Hz, 0.7H, C*H, maj)*, 1.46 (d, *J*(H,H) = 6.8 Hz, 2.1H, CH_3, *maj*), 1.41 (d, *J*(H,H) = 7.0 Hz, 0.9H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =173.9 (*C*), 173.7 (*C*), 141.8 (*C*), 140.6 (*C*), 140.5 (*C*), 140.4 (*C*), 137.3 (*C*), 137.1 (*C*), 134.0 (*C*), 133.5 (*C*H), 132.3 (*C*H), 132.0 (*C*), 129.8 (*C*H), 129.7 (*C*H), 129.4 (*C*H), 129.1 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.3 (*C*), 128.2 (*C*H), 128.0

(*C*H), 127.8 (*C*H), 127.6 (*C*H), 127.5 (*C*H), 127.4 (*C*H), 126.9 (*C*H), 126.8 (*C*H), 124.6 (*C*), 124.2 (*C*), 51.8 (CH_2), 51.5 (CH_2), 44.6 (*C*H), 43.6 (*C*H), 20.8 (CH_3), 20.4 (CH_3).

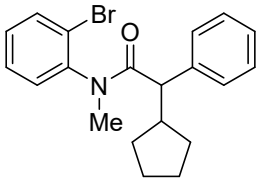
***N*-(2-Bromophenyl)-*N*-methyl-2-phenylbutanamide[8] 5i**



According to the general procedure G, from 2-phenylbutanoic acid (0.50 g, 3.0 mmol, 1.5 equiv.), $SOCl_2$ (0.44 mL, 6.0 mmol, 3.0 equiv.), 2-bromo-*N*-methylaniline (0.37 g, 2.0 mmol, 1.0 equiv.), pyridine (0.25 mL, 3.0 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (550 mg, 82% yield).

Rf = 0.53 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.64 (dd, *J*(H,H) = 7.9 and 1.5 Hz, 0.7H, H^{Ar}, *maj)*, 7.50 (dd, *J*(H,H) = 8.0 and 1.4 Hz, 0.3H, H^{Ar}, *min*), 7.40-7.00 (m, 4.6H, H^{Ar}), 6.95-6.80 (m, 1.7H, H^{Ar}), 6.53 (d, *J*(H,H) = 7.9 Hz, 0.7H, H^{Ar}, *maj*), 3.17 (t, *J*(H,H) = 7.5 Hz, 0.3H, C*H*, *min*), 3.12 (s, 0.9H, NCH_3, *min*), 3.09 (s, 2.1H, NCH_3, *maj*), 2.95 (t, *J*(H,H) = 7.5 Hz, 0.7H, C*H*, *maj*), 2.10-1.95 (m, 1H, CH_2), 1.70-1.50 (m, 1H, CH_2),0.90-0.66 (m, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =173.3 (*C*), 173.1 (*C*), 142.7 (*C*), 142.3 (*C*), 140.4 (*C*), 139.3 (*C*), 134.1(*C*H), 133.7 (*C*H), 131.3 (*C*H), 130.6 (*C*H), 129.8 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 128.2 (*C*H), 128.1 (*C*H), 126.9 (*C*H), 126.8 (*C*H), 124.6 (*C*), 123.6 (*C*), 52.2 (*C*H), 51.2 (*C*H), 36.2 (CH_3), 36.1 (CH_3), 28.6 (CH_2), 28.3 (CH_2), 12.7 (CH_3), 12.5 (CH_3).

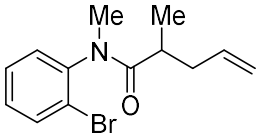
***N*-(2-Bromophenyl)-2-cyclopentyl-*N*-methyl-2-phenylacetamide[11] 5j**



According to the general procedure G, from 2-cyclopentyl-2-phenylacetic acid (0.50 g, 2.43 mmol, 1.5 equiv.), $SOCl_2$ (0.35 mL, 4.86 mmol, 3.0 equiv.), 2-bromo-*N*-methylaniline (0.30 g, 1.62 mmol, 1.0 equiv.), pyridine (0.20 mL, 2.43 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (480 mg, 80% yield).

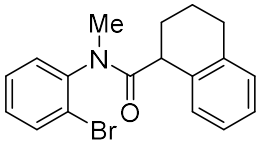
Rf = 0.40 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 7:3 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.71 (dd, *J*(H,H) = 7.9 and 1.4 Hz, 0.7H, H^{Ar}, *maj)*, 7.56 (dd, *J*(H,H) = 7.9 and 1.4 Hz, 0.3H, H^{Ar}, *min*), 7.48-7.39 (m, 0.3H, H^{Ar}, *min*), 7.35-7.28 (m, 0.3H, H^{Ar}, *min*), 7.26-7.06 (m, 4.7H, H^{Ar}), 6.96-6.88 (m, 2H, H^{Ar}), 6.50 (dd, *J*(H,H) = 7.8 and 1.6 Hz, 0.7H, H^{Ar}, *maj*), 3.19 (s, 0.9H, NCH_3, *min*), 3.15 (s, 2.1H, NCH_3, *maj*), 3.05 (d, *J*(H,H) = 10.7 Hz, 0.3H, COC*H*, *min*), 2.81 (d, *J*(H,H) = 10.5 Hz, 0.7H, COC*H*, *maj*), 2.70-2.48 (m, 1H, C*H*), 2.06-1.92 (m, 1H, CH_2), 1.65-1.10 (m, 6H, CH_2), 0.95-0.70 (m, 1H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =173.2 *C*), 173.1 (*C*), 142.7 (*C*), 142.1 (*C*), 140.1 (*C*), 139.2 (*C*), 134.1 (*C*), 133.7 (*C*H), 131.7 (*C*H), 130.9 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 128.1 (*C*H), 126.8 (*C*H), 126.7 (*C*H), 124.8 (*C*), 123.3 (*C*), 56.4 (*C*H), 55.2 (*C*H), 45.1 (*C*H), 44.9 (*C*H), 36.2 (CH_3), 36.1 (CH_3), 32.2 (CH_2), 30.6 (CH_2), 25.2 (CH_2), 24.7 (CH_2).

***N*-(2-Bromophenyl)-*N*-2-dimethylpent-4-enamide 5k**



According to the general procedure H, from 2-methylpent-4-enoic acid (0.28 g, 2.43 mmol, 1.5 equiv.), $SOCl_2$ (0.20 mL, 4.86 mmol, 3.0 equiv.), 2-bromo-*N*-methylaniline (0.30 g, 1.62 mmol, 1.0 equiv.), pyridine (0.20 mL, 2.43 mmol, 1.5 equiv.) the product was obtained as a brown oil. (663 mg, 97% yield).
Rf = 0.31 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 1.3:1 ratio (unassigned). ^{1}H NMR chemical shifts that differ between isomers will be denoted by (*maj*) and (*min*). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.72-7.65 (m, 1H, H^{Ar}*)*, 7.41-7.34 (m, 2H, H^{Ar}), 7.27-7.20 (m, 2H, H^{Ar}), 5.75-5.50 (m, 1H, C*H*=CH_2), 5.05-4.90 (m, 2H, CH=CH_2) 3.19 (s, 3H, NCH_3), 2.50-1.95 (m, 3H, C*H* and CH_2), 1.09 (d, *J*(H,H) = 6.5 Hz, 1.7H, CH_3, *maj*), 1.01 (d, *J*(H,H) = 6.5 Hz, 1.3H, CH_3, *min*). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 176.4 (*C*), 176.1 (*C*), 142.9 (*C*), 136.5 (*C*H), 136.1 (*C*H), 134.1 (*C*H), 134.0 (*C*H), 130.6 (*C*H), 129.9 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 128.9 (*C*H), 128.8 (*C*H), 123.7 (*C*), 123.6 (*C*H), 116.8 (*C*H_2), 116.6 (*C*H_2), 39.0 (*C*H_2), 38.2 (*C*H_2), 37.3 (*C*H), 37.2 (*C*H_2), 36.1 (*C*H_3), 36.0 (*C*H_3), 17.5 (*C*H_3). **HRMS (ESI)**: *m/z*: 282.0488 calcd for: $C_{13}H_{17}NOBr^+$ $[M+H]^+$: found 282.0486. **IR (ATR):** 3074, 2973, 2933, 2361, 1657, 1583, 1475, 1460, 1434, 1419, 1382, 1328, 1280, 1248, 1225, 1116, 1048, 1026, 993, 912, 764, 728, 681, 662, 643, 572 cm^{-1}.

***N*-(2-Bromophenyl)-*N*-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxamide[8] 5l**



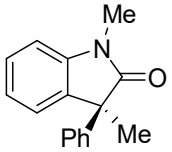
According to the general procedure G, from 1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (0.43 g, 2.43 mmol, 1.5 equiv.), $SOCl_2$ (0.35 mL, 4.86 mmol, 3.0 equiv.), 2-bromo-N-methylaniline (0.30 g, 1.62 mmol, 1.0 equiv.) pyridine (0.20 mL, 2.43 mmol, 1.5 equiv.) the product was obtained as a light yellow oil. (480 mg, 80% yield).
Rf = 0.35 (PE/Et_2O 2:1). In $CDCl_3$ (25 °C), this amide exists in two isomeric forms in a 1:1 ratio (unassigned). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.72 (d, *J*(H,H) = 7.9 Hz, 1H, H^{Ar}*)*, 7.52-7.20 (m, 4H, H^{Ar}), 7.14-7.00 (m, 3H, H^{Ar}), 3.60-3.50 (m, 1H, C*H*), 3.32 (s, 1.5H, NCH_3), 3.28 (s, 1.5H, NCH_3,), 2.95-2.75 (m, 1H, CH_2), 2.70-2.60 (m, 1H, CH_2), 2.10-1.80 (m, 3H, CH_2), 1.60-1.40 (m, 1H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =175.9 (*C*), 175.6 (*C*), 143.2 (*C*), 142.9 (*C*), 137.8 (*C*), 137.5 (*C*), 135.7 (*C*), 135.1 (*C*), 134.3 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 129.9 (*C*H), 129.6 (*C*H), 129.5 (*C*H), 129.3 (*C*H), 129.2 (*C*H), 128.9 (*C*H), 127.8 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 125.9 (*C*H), 125.8 (*C*H), 123.6 (*C*), 123.5 (*C*), 43.5 (*C*H), 43.3 (*C*H), 36.4 (*C*H), 36.3 (*C*H), 29.4 (*C*H_2), 29.2 (*C*H_2), 28.1 (*C*H_2), 27.6 (*C*H_2), 21.5 (*C*H_2), 21.4 (*C*H_2).

V Asymmetric catalysis

Procedure I : intermolecular α-arylation of amides

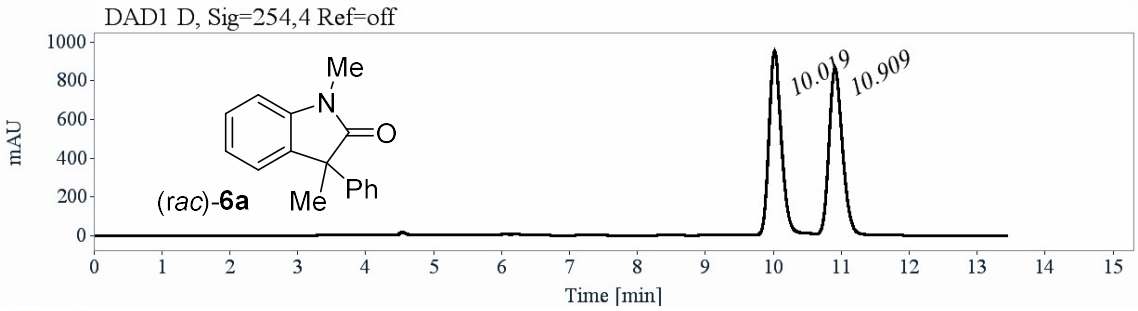
A mixture of the amide or ketone substrate (0.1 mmol, 1.0 equiv.), catalyst (0.005 mmol, 5 mol%) and potassium tert-butoxide (*t*BuOK) (0.15 mmol, 1.5 equiv.) in dry 1,2-Dimethoxyethane (DME) (2 mL) was stirred at 40 °C for 20 hours under argon. The solvent was removed under reduced pressure and the residue was purified by silica gel column (petroleum ether/ether = 2: 1)

(-)-(*S*)-1,3-Dimethyl-3-phenylindolin-2-one[10] (-)-(*S*)-6a



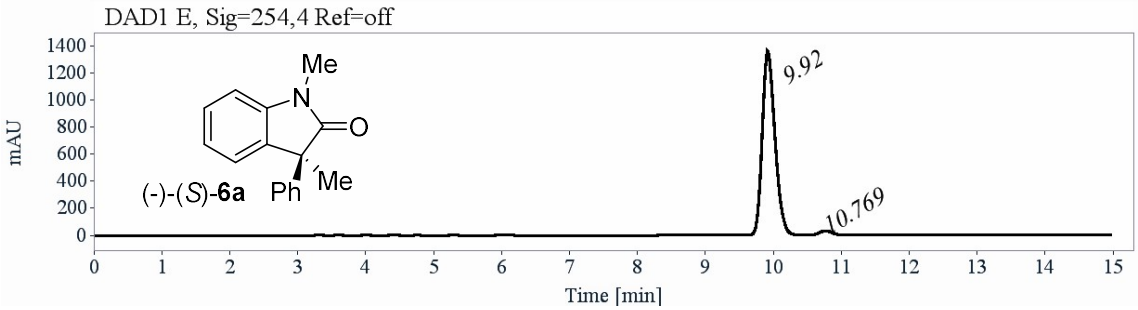
According to the general procedure I, *N*-(2-bromophenyl)-*N*-methyl-2-phenylpropanamide **5a** (63 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a, R_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.3 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (39.4 mg, 84% yield).

Rf = 0.44 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.26 (m, 5H, H^{Ar}), 7.26-7.17 (m, 2H, H^{Ar}), 7.12-7.07 (m, 1H, H^{Ar}), 6.92 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.25 (s, 3H, NCH_3), 1.79 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.5 (*C*), 143.3 (*C*), 140.1 (*C*), 134.9 (*C*), 128.6 (*C*H), 128.2 (*C*H), 127.3 (*C*H), 126.7 (*C*H), 124.3 (*C*H), 122.8 (*C*H), 108.4 (*C*H), 52.2 (C), 26.6 (CH_3), 23.9 (CH_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = -75, $[\alpha]_{578}$ = -79, $[\alpha]_{546}$ = -93 (*c* = 1.71 in CH_2Cl_2), 95% *ee*. **cHPLC analysis:** [Chiracel IE column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 9.92 min (major) and 10.77 min];



Signal: DAD1 D, Sig=254,4 Ref=off

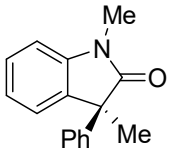
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
10.02	12223	50.47	2.40		
10.91	11995	49.53	2.70	1.13	2.58
Sum	24218	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

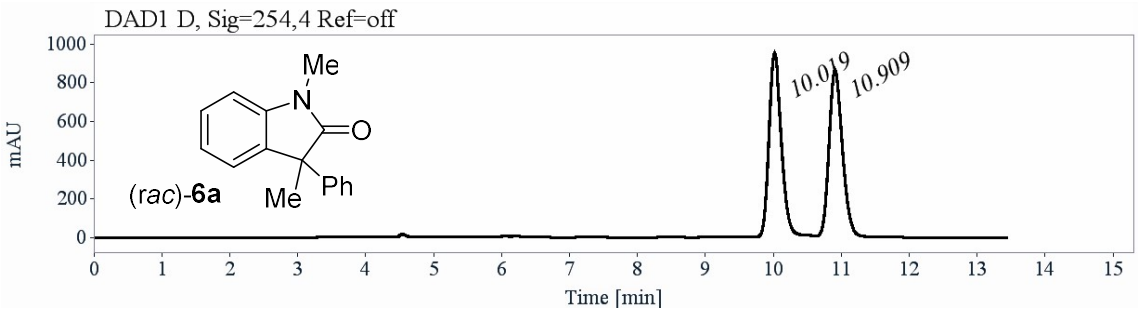
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.92	17789	97.48	2.36		
10.77	461	2.52	2.65	1.12	2.41
Sum	18250	100.00			

(-)-(*S*)-1,3-Dimethyl-3-phenylindolin-2-one [10] **(-)-(*S*)-6a(Cl)**



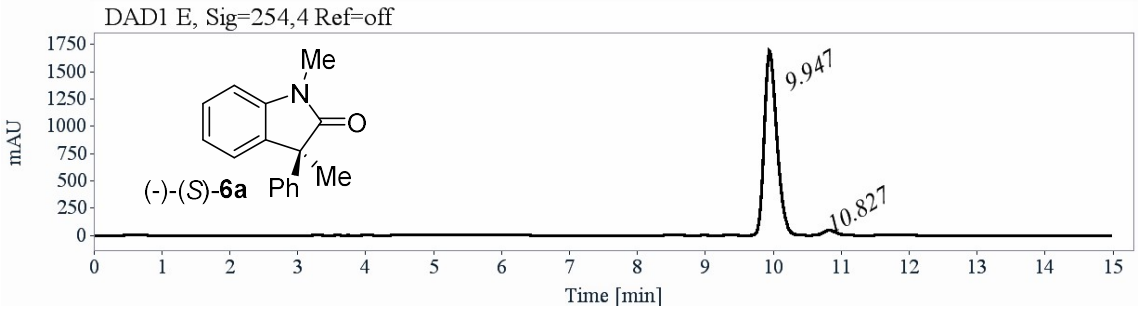
According to the general procedure I, *N*-(2-chlorophenyl)-*N*-methyl-2-phenylpropanamide **5a(Cl)** (55 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a, R_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.3 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (40.3 mg, 86% yield).

Rf = 0.44 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.26 (m, 5H, H^{Ar}), 7.26-7.17 (m, 2H, H^{Ar}), 7.12-7.07 (m, 1H, H^{Ar}), 6.92 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.25 (s, 3H, NCH_3), 1.79 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.5 (*C*), 143.3 (*C*), 140.1 (*C*), 134.9 (*C*), 128.6 (*C*H), 128.2 (*C*H), 127.3 (*C*H), 126.7 (*C*H), 124.3 (*C*H), 122.8 (*C*H), 108.4 (*C*H), 52.2 (C), 26.6 (*C*H_3), 23.9 (*C*H_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = -75, $[\alpha]_{578}$ = -79, $[\alpha]_{546}$ = -93 (*c* = 1.71 in CH_2Cl_2), 95% *ee*. **cHPLC analysis:** [Chiracel IE column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 9.95 min (major) and 10.83 min].



Signal: DAD1 D, Sig=254,4 Ref=off

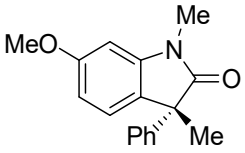
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
10.02	12223	50.47	2.40		
10.91	11995	49.53	2.70	1.13	2.58
Sum	24218	100.00			



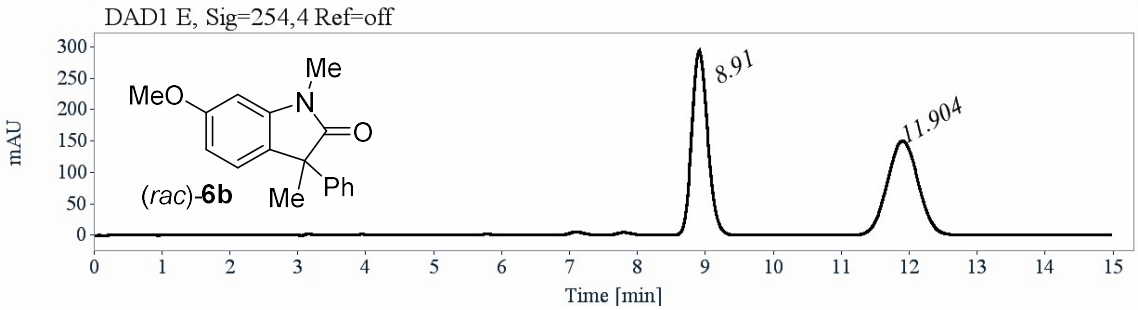
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.95	21877	97.23	2.37		
10.83	622	2.77	2.67	1.13	2.54
Sum	22499	100.00			

(+)-(*R*)-6-Methoxy-1,3-dimethyl-3-phenylindolin-2-one[8] **(+)-(*R*)-6b**

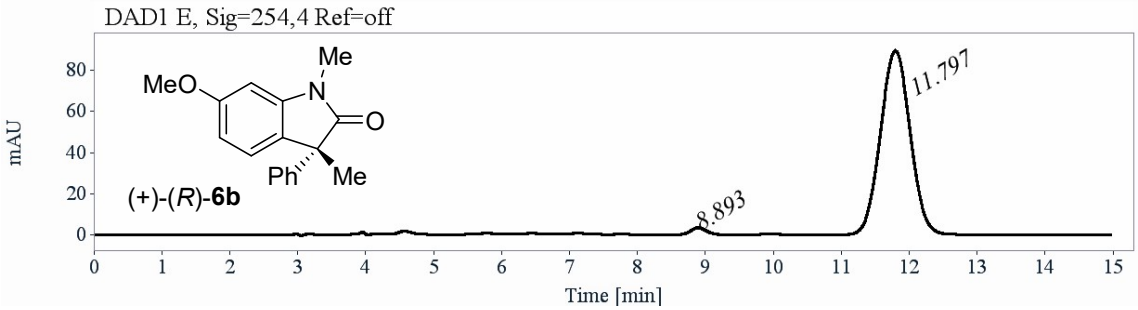


According to the general procedure I, *N*-(2-bromo-5-methoxyphenyl)-*N*-methyl-2-phenylpropanamide **5b** (35 mg, 0.1 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (4.1 mg, 0.005 mmol, 5 mol%), *t*BuOK (17 mg, 0.15 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (25.0 mg, 91% yield).
Rf = 0.46 (PE/Et_2O 1:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.30-7.15 (m, 5H, H^{Ar}), 7.04 (d, *J*(H,H) = 8.2 Hz, 1H, H^{Ar}), 6.56 (dd, *J*(H,H) = 8.2 and 2.3 Hz, 1H, H^{Ar}), 6.46 (d, *J*(H,H) = 2.3 Hz, 1H, H^{Ar}), 3.81 (s, 3H, OCH_3), 3.17 (s, 3H, NCH_3), 1.72 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ= 180.1 (*C*), 160.3 (*C*), 144.6 (*C*), 141.3 (*C*), 128.6 (*C*H), 127.3 (*C*H), 126.9 (*C*), 124.7 (*C*H), 106.7 (*C*H), 96.4 (*C*H), 55.7 (CH_3), 51.8 (*C*), 26.6 (CH_3), 24.2 (CH_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +86, $[\alpha]_{578}$ = +90, $[\alpha]_{546}$ = +106, $[\alpha]_{436}$ = +204 (*c* = 0.84 in CH_2Cl_2), 97% *ee*. **cHPLC analysis:** [Chiracel IG column, n-heptane/*iso*propanol = 80:20, 1.0 mL/min, 254 nm; Rt = 8.89 min and 11.80 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

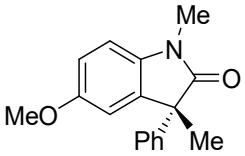
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.91	4745	49.92	2.02		
11.90	4760	50.08	3.04	1.50	4.71
Sum	9504	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

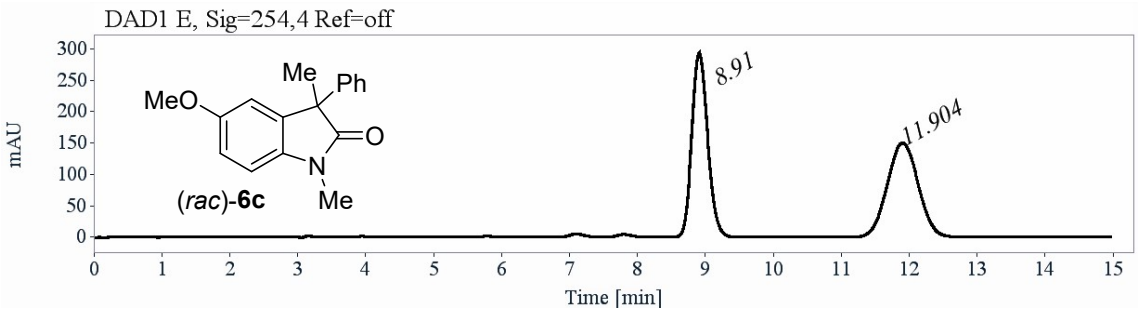
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.89	54	1.94	2.01		
11.80	2712	98.06	3.00	1.49	4.73
Sum	2765	100.00			

(+)-(*R*)-5-Methoxy-1,3-dimethyl-3-phenylindolin-2-one (+)-(*R*)-6c



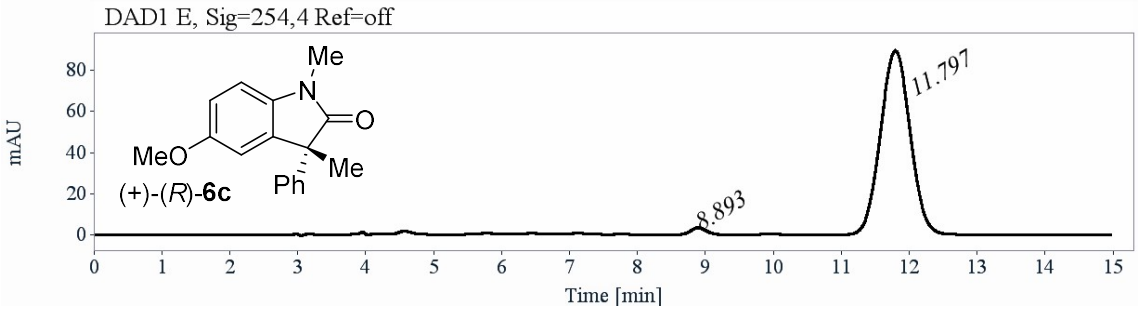
According to the general procedure I, *N*-(2-bromo-4-methoxyphenyl)-*N*-methyl-2-phenylpropanamide **5c** (35 mg, 0.1 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (4.1 mg, 0.005 mmol, 5 mol%), *t*BuOK (17 mg, 0.15 mmol, 1.5 equiv.) were stirred at 40 °C for 60 hours to afford a light yellow oil. (23.0 mg, 86% yield).

Rf = 0.46 (PE/Et_2O 1:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.32-7.28 (m, 4H, H^{Ar}), 7.24-7.18 (m, 1H, H^{Ar}), 6.85-6.79 (m, 3H, H^{Ar}), 3.78 (s, 3H, OCH_3), 3.22 (s, 3H, NCH_3), 1.79 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =179.3 (*C*), 156.3 (*C*), 140.9 (*C*), 136.9 (*C*), 136.3 (*C*), 128.7 (*C*H), 127.4 (*C*H), 126.8 (*C*H), 112.5 (*C*H), 111.8 (*C*H), 108.7 (*C*H), 56.0 (CH_3), 52.7 (*C*), 26.6 (CH_3), 23.9 (CH_3). **HRMS (ESI)**: *m/z*: 268.1332 calcd for: $C_{17}H_{18}NO_2^+$ $[M+H]^+$: found 268.1333. **IR (ATR):** 3057, 3025, 2932, 2833, 2360, 1703, 1653, 1598, 1495, 1467, 1432, 1371, 1349, 1286, 1241, 1166, 1148, 1107, 1076, 1030, 914, 894, 872, 838, 802, 722, 697, 641, 619, 574, 556, 508 cm^{-1}. **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +108, $[\alpha]_{578}$ = +114, $[\alpha]_{546}$ = +133 (*c* = 0.57 in CH_2Cl_2), 91% *ee*. **cHPLC analysis:** [Chiracel IG column, n-heptane/*iso*propanol = 80:20, 1.0 mL/min, 254 nm; Rt = 8.89 min and 11.80 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

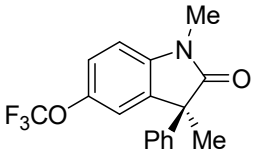
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.91	4745	49.92	2.02		
11.90	4760	50.08	3.04	1.50	4.71
Sum	9504	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

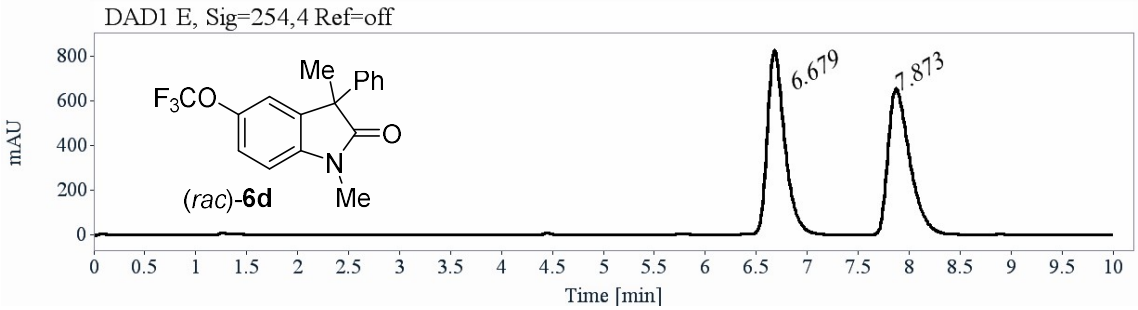
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.89	54	1.94	2.01		
11.80	2712	98.06	3.00	1.49	4.73
Sum	2765	100.00			

(-)-(*S*)-1,3-Dimethyl-3-phenyl-5-(trifluoromethoxy)indolin-2-one (-)-(*S*)-6d



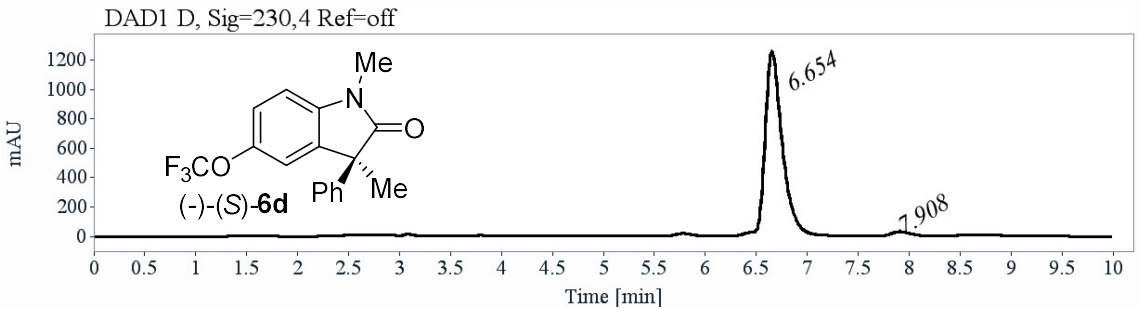
According to the general procedure I, *N*-(2-Bromo-4-(trifluoromethoxy)phenyl)-*N*-methyl-2-phenylpropanamide **5d** (81 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a,R_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.3 mmol, 1.5 equiv.) were stirred at 60 °C for 20 hours to afford a light yellow oil. (57.0 mg, 89% yield).

Rf = 0.34 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.17 (m, 6H, H^{Ar}), 7.08 (s, 1H, H^{Ar}), 6.90 (d, *J*(H,H) = 8.5 Hz, 1H, H^{Ar}), 3.25 (s, 3H, NCH_3), 1.80 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.2 (*C*), 145.1 (q, J^3(C,F) = 2.0 Hz, *C*), 142.0 (*C*), 140.1 (*C*), 136.4 (*C*), 128.8 (*C*H), 127.7 (*C*H), 126.6 (*C*H), 112.3 (*C*H), 118.3 (*C*H), 120.7 (q, J^1(C,F) = 256.6 Hz, CF_3), 108.8 (*C*H), 52.7 (*C*), 26.7 (CH_3), 23.8 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$):** δ = -58.4 (s, 3F, CF_3). **HRMS (ESI)**: *m/z*: 322.1049 calcd for: $C_{17}H_{15}NO_2F_3^+$ [M+H]$^+$: found 322.1050. **IR (ATR):** 3056, 2983, 2937, 2475, 2359, 2341, 2117, 1715, 1669, 1618, 1558, 1491, 1454, 1371, 1290, 1247, 1206, 1158, 1101, 1077, 1047, 1027, 1020, 973, 953, 893, 878, 848, 829, 810, 791, 765, 730, 698, 657, 635, 617, 597, 570, 548, 507 cm^{-1}. **Specific rotations at 25 °C:** $[\alpha]_{589}$ = -82, $[\alpha]_{578}$ = -86, $[\alpha]_{546}$ = -100, $[\alpha]_{436}$ = -188 (*c* = 0.97 in CH_2Cl_2), 95% *ee*. **cHPLC analysis:** [Chiracel OD-3 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 6.65 min (major) and 7.91 min].



Signal: DAD1 E, Sig=254,4 Ref=off

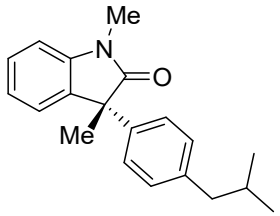
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.68	9803	50.31	1.26		
7.87	9683	49.69	1.67	1.32	3.47
Sum	19485	100.00			



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.65	14708	97.42	1.26		
7.91	390	2.58	1.68	1.34	3.95
Sum	15097	100.00			

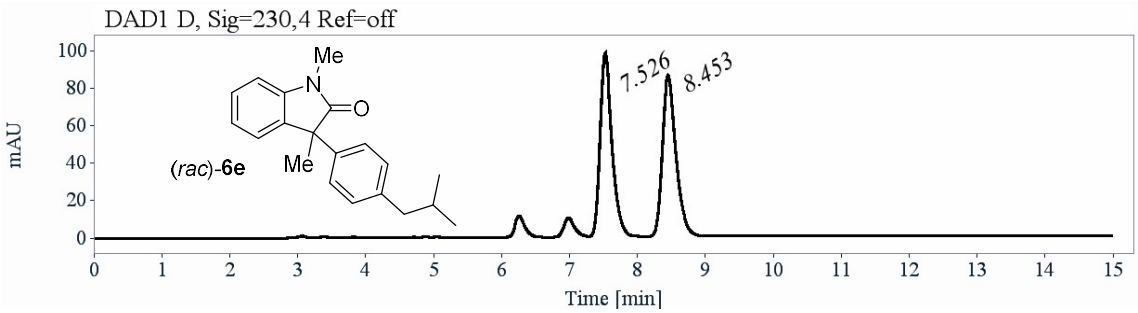
(+)-(*R*)-3-(4-*Iso*butylphenyl)-1,3-dimethylindolin-2-one[9] **(+)-(*R*)-6e**



According to the general procedure I, *N*-(2-bromophenyl)-2-(4-*iso*butylphenyl)-*N*-methylpropanamide **5e** (38 mg, 0.1 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (4.1 mg, 0.005 mmol, 5 mol%), *t*BuOK (17 mg, 0.15 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (27.0 mg, 93% yield).

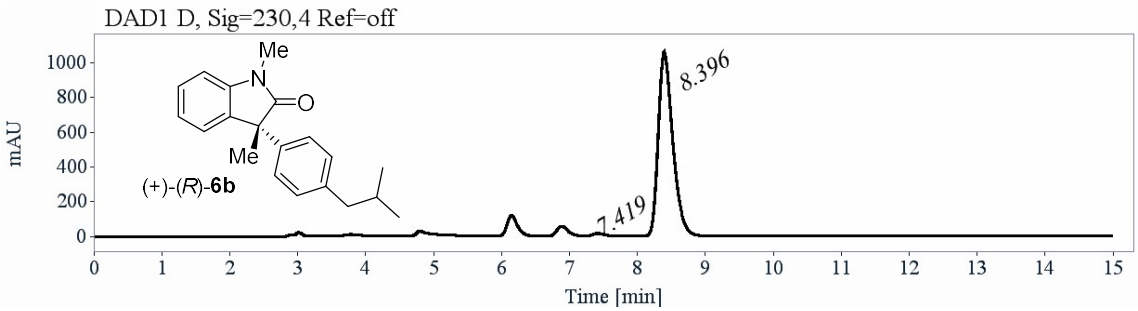
Rf = 0.54 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.35-7.28 (m, 1H, H^{Ar}), 7.24-7.17 (m, 3H, H^{Ar}), 7.13-7.03 (m, 3H, H^{Ar}), 6.91 (d, *J*(H,H) = 7.1 Hz, 1H, H^{Ar}), 3.24 (s, 3H, NCH_3), 2.41 (d, *J*(H,H) = 7.2 Hz, 2H, CH_2), 1.87-1.75 (m, 4H, CH_3 and CH), 0.87 (s, 6H, $CH(CH_3)_2$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.8 (*C*), 143.4 (*C*), 140.8 (*C*), 138.2 (*C*), 135.2 (*C*), 129.4 (*C*H), 128.1 (*C*H), 126.5 (*C*H), 124.3 (*C*H), 122.8 (*C*H), 108.3 (*C*H), 52.0 (C), 45.1 (CH_2), 30.2 (*C*H), 26.6 (CH_3), 24.0 (CH_3), 22.5 (CH_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +12, $[\alpha]_{578}$ = +13, $[\alpha]_{546}$ = +15, $[\alpha]_{436}$ = +30 (*c* = 1.66 in CH_2Cl_2), 98% *ee*. **cHPLC analysis:** [Chiracel

Lux-Cellulose-2 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 230 nm; Rt = 7.42 min and 8.40 min (major)].



Signal: DAD1 D, Sig=230,4 Ref=off

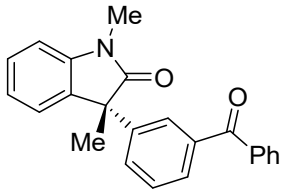
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.53	1188	49.92	1.55		
8.45	1192	50.08	1.87	1.20	2.77
Sum	2380	100.00			



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.42	176	1.10	1.51		
8.40	15802	98.90	1.85	1.22	2.82
Sum	15978	100.00			

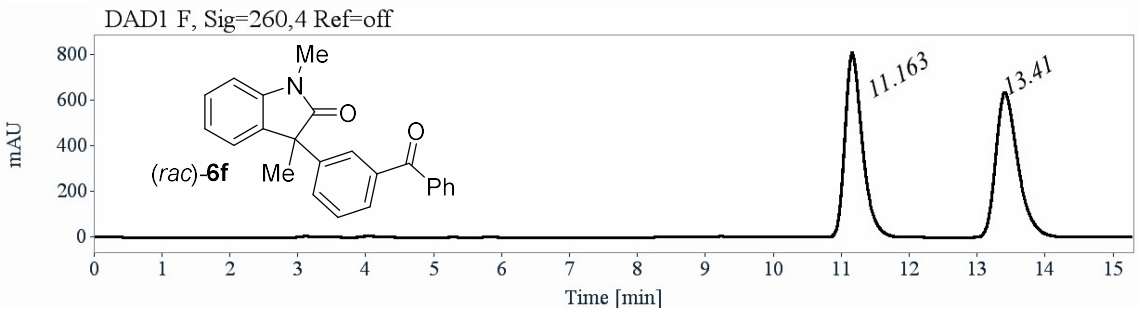
(+)-(*R*)-3-(3-Benzoylphenyl)-1,3-dimethylindolin-2-one (+)-(*R*)-6f



According to the general procedure I, 2-(3-benzoylphenyl)-*N*-(2-bromophenyl)-*N*-methylpropanamide **5f** (86 mg, 0.2 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (66.0 mg, 95% yield).

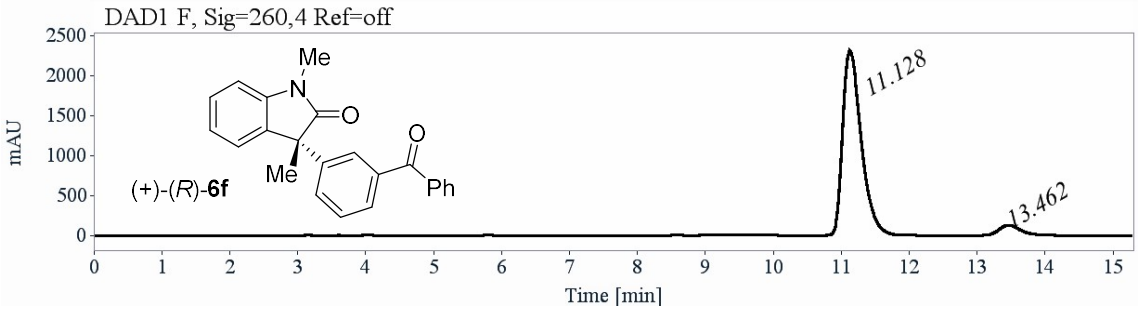
Rf = 0.23 (PE/Et_2O 1:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.82-7.75 (m, 3H, H^{Ar}), 7.70-7.25 (m, 7H, H^{Ar}), 7.22-7.17 (m, 1H, H^{Ar}), 7.13-7.06 (m, 1H, H^{Ar}), 6.92 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.25 (s, 3H, NCH_3), 1.82 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 196.4 (*C*), 179.1 (*C*), 143.3 (*C*), 141.4 (*C*), 137.8 (*C*), 137.5 (*C*), 134.4 (*C*), 132.5 (*C*H), 130.9 (*C*H), 130.2 (*C*H), 129.2 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 124.2

(*C*H), 123.1 (*C*H), 108.6 (*C*H), 52.2 (C), 26.6 (CH_3), 23.9 (CH_3). **HRMS (ESI)**: *m/z*: 342.1489 calcd for: $C_{23}H_{20}NO_2^+$ $[M+H]^+$: found 342.1489. **IR (ATR):** 3056, 2968, 2928, 1708, 1655, 1609, 1595, 1577, 1491, 1469, 1446, 1421, 1372, 1343, 1315, 1277, 1237, 1176, 1157, 1137, 1115, 1101, 1073, 1055, 1023, 999, 969, 955, 929, 899, 812, 783, 754, 743, 730, 712, 692, 664, 641, 627, 572, 541, 510 cm^{-1}. **Specific rotations at 25 °C:**$[\alpha]_{589}$ = +49, $[\alpha]_{578}$ = +51, $[\alpha]_{546}$ = +60 (*c* = 2.13 in CH_2Cl_2), 88% *ee*. **cHPLC analysis:** [Chiracel Lux-Cellulose-4 column, n-heptane/*iso*propanol = 70:30, 1.0 mL/min, 260 nm; Rt = 11.16 min (major) and 13.41 min].



Signal: DAD1 F, Sig=260,4 Ref=off

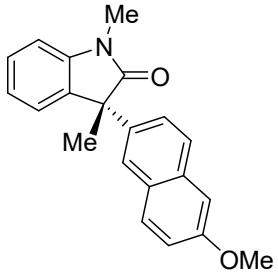
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.16	14357	49.93	2.78		
13.41	14396	50.07	3.55	1.27	4.32
Sum	28753	100.00			



Signal: DAD1 F, Sig=260,4 Ref=off

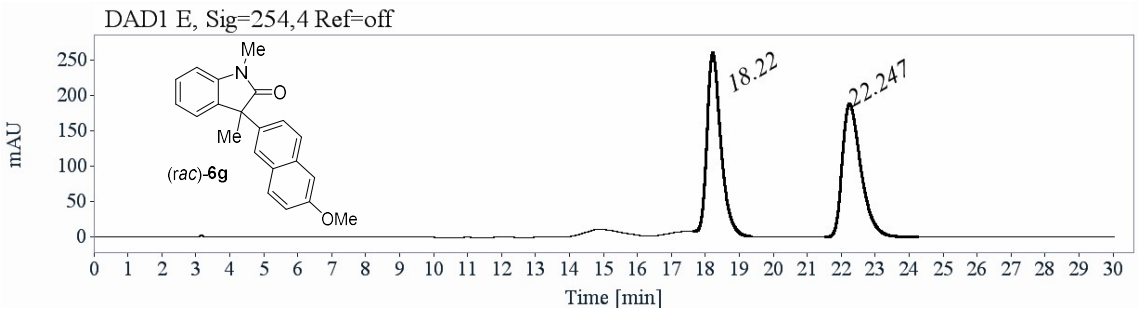
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.13	43985	93.88	2.77		
13.46	2865	6.12	3.56	1.29	4.43
Sum	46850	100.00			

(+)-(*R*)-3-(6-Methoxynaphthalen-2-yl)-1,3-dimethylindolin-2-one (+)-(*R*)-6g



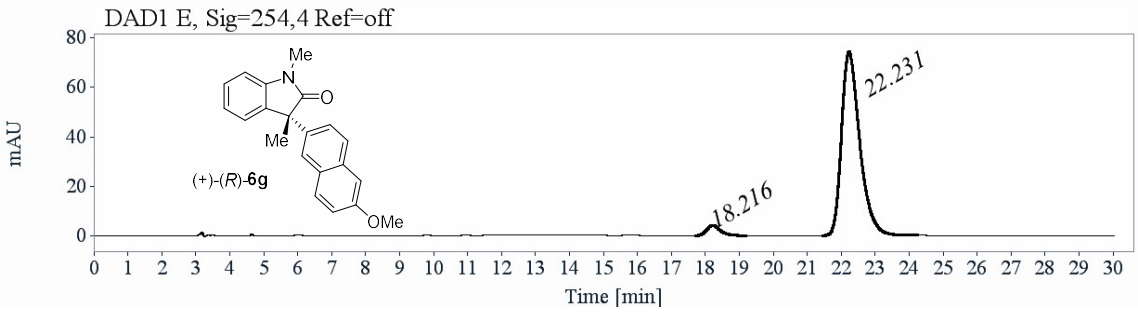
According to the general procedure I, *N*-(2-bromophenyl)-2-(6-methoxynaphthalen-2-yl)-*N*-methylpropanamide **5g** (80 mg, 0.2 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a white solid. (61.0 mg, 96% yield).

Rf = 0.23 (PE/Et_2O 1:1). **Mp:** 201.6-202.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.82-7.75 (m, 3H, H^{Ar}), 7.38-7.70 (m, 2H, H^{Ar}), 7.24-7.20 (m, 1H, H^{Ar}), 7.14-7.06 (m, 3H, H^{Ar}), 6.95 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.90 (s, 3H, OCH_3), 3.27 (s, 3H, NCH_3), 1.88 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 179.9 (*C*), 157.9 (*C*), 136.0 (*C*), 135.1 (*C*), 133.8 (*C*), 129.7 (*C*H), 128.8 (*C*), 128.3 (*C*H), 127.3 (*C*H), 125.5 (*C*H), 125.2 (*C*H), 124.4 (*C*H), 122.9 (*C*H), 119.0 (*C*H), 108.5 (*C*H), 105.6 (*C*H), 55.4 (*C*H_3), 52.3 (C), 26.6 (*C*H_3), 23.8 (*C*H_3). **HRMS (ESI)**: *m/z*: 318.1489 calcd for: $C_{21}H_{20}NO_2^+$ [M+H]$^+$: found 318.1487. **IR (ATR):** 3055, 3028, 2960, 2930, 2361, 2341, 1706, 1628, 1602, 1558, 1541, 1502, 1489, 1468, 1419, 1389, 1374, 1345, 1302, 1260, 1235, 1220, 1194, 1182, 1159, 1133, 1117, 1098, 1053, 1024, 958, 930, 906, 895, 852, 837, 827, 807, 764, 751, 738, 701, 685, 674, 650, 629, 586, 541, 531, 522 cm^{-1}. **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +62, $[\alpha]_{578}$ = +65, $[\alpha]_{546}$ = +78 (*c* = 2.22 in CH_2Cl_2), 92% *ee*. **cHPLC analysis:** [Chiracel Lux-Cellulose-4 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 18.22 min and 22.23 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

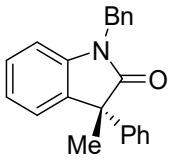
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
18.22	7119	49.70	5.18		
22.25	7204	50.30	6.54	1.26	4.72
Sum	14324	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

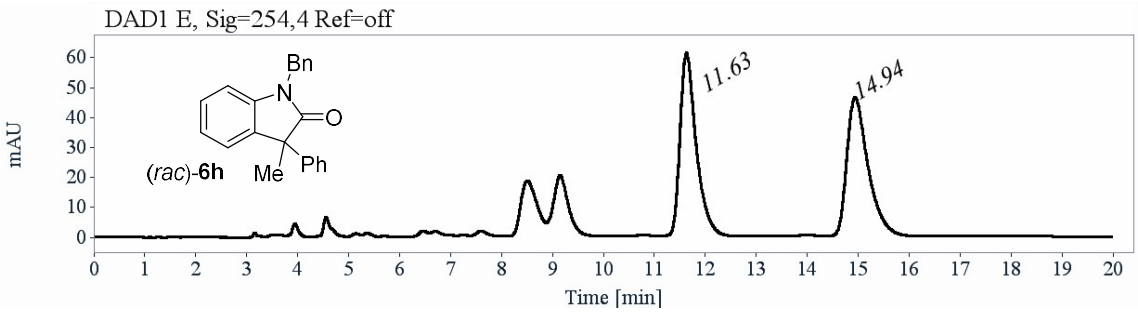
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
18.22	117	4.05	5.18		
22.23	2766	95.95	6.54	1.26	4.84
Sum	2883	100.00			

(+)-(*R*)-1-Benzyl-3-methyl-3-phenylindolin-2-one[10] (+)-(*R*)-6h



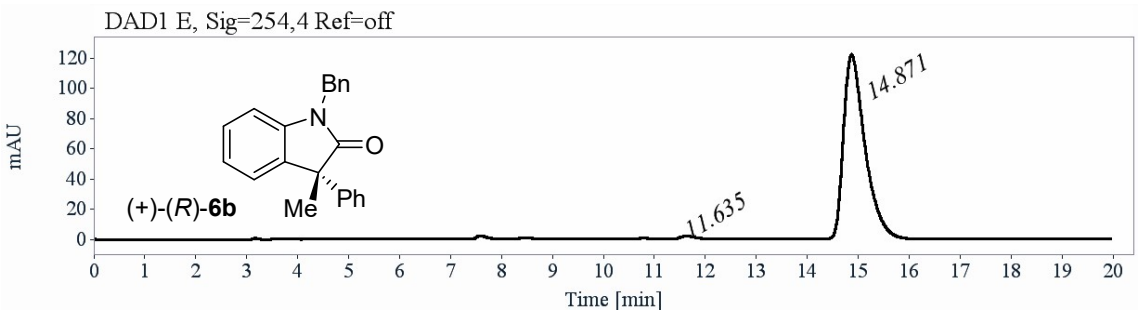
According to the general procedure I, *N*-benzyl-*N*-(2-bromophenyl)-2-phenylpropanamide **5h** (80 mg, 0.2 mmol, 1.0 equiv.), (-)-(S_a,S_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 40 °C for 60 hours to afford a light yellow oil. (60.0 mg, 95% yield).

Rf = 0.23 (PE/Et_2O 9:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.34-7.12 (m, 12H, H^{Ar}), 7.08-6.96 (m, 1H, H^{Ar}), 6.77 (d, *J*(H,H) = 7.5 Hz, 1H, H^{Ar}), 5.00-4.85 (m, 2H, CH_2), 1.83 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ= 179.7 (*C*), 142.4 (*C*), 140.9 (*C*), 136.1 (*C*), 135.1 (*C*), 128.9 (*C*H), 128.7 (*C*H), 128.1 (*C*H), 127.7 (*C*H), 127.4 (*C*H), 127.3 (*C*H), 126.8 (*C*H), 124.3 (*C*H), 122.9 (*C*H), 109.5 (*C*H), 52.3 (C), 44.0 (CH_2), 23.9 (CH_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +56, $[\alpha]_{578}$ = +59, $[\alpha]_{546}$ = +70 (*c* = 1.36 in CH_2Cl_2), 98% *ee*. **cHPLC analysis:** [Chiracel IF column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 11.63 min and 14.87 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

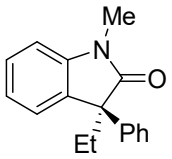
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.63	1347	50.11	2.94		
14.94	1342	49.89	4.06	1.38	5.12
Sum	2689	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

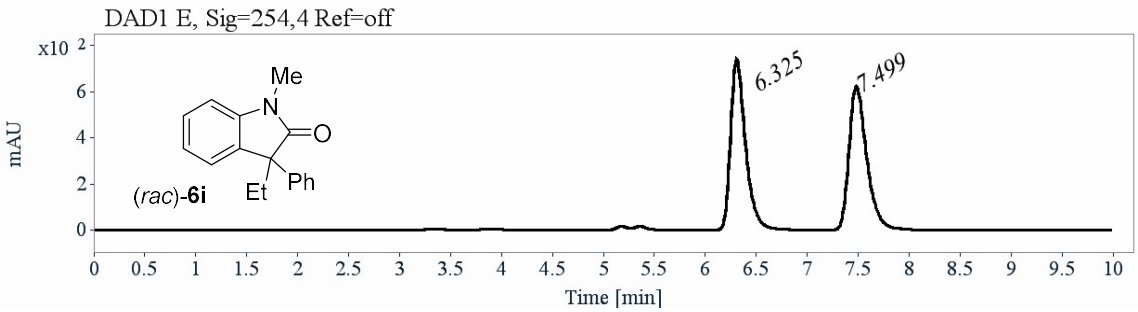
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.63	45	1.24	2.94		
14.87	3578	98.76	4.04	1.37	5.04
Sum	3623	100.00			

(-)-(*S*)-3-Ethyl-1-methyl-3-phenylindolin-2-one[8] (-)-(*S*)-6i



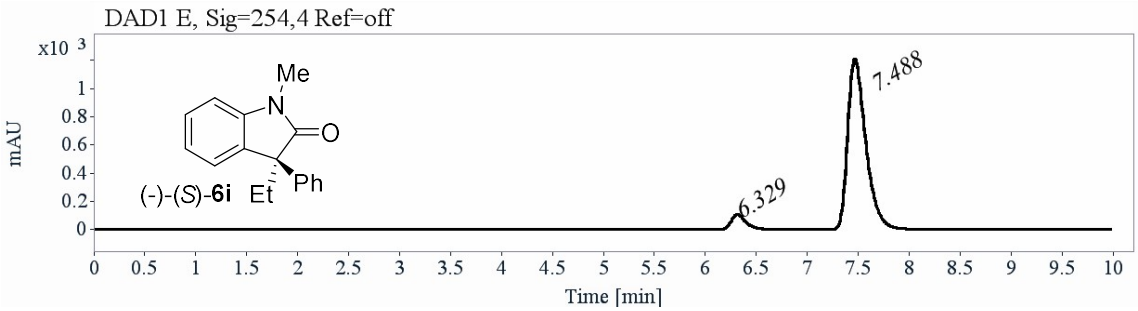
According to the general procedure I, *N*-(2-bromophenyl)-*N*-methyl-2-phenylbutanamide **5i** (67 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a,R_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 60 °C for 20 hours to afford a brown oil. (48.0 mg, 96% yield).

Rf = 0.51 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.20 (m, 7H, H^{Ar}), 7.16-7.08 (m, 1H, H^{Ar}), 6.91(d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.23 (s, 3H, NCH_3), 2.50-2.36 (m, 1H, CH_2), 2.30-2.14 (m, 1H, CH_2), 0.63 (t, *J*(H,H) = 7.3 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 178.7 (*C*), 144.3 (*C*), 140.4 (*C*), 132.2 (*C*), 128.6 (*C*H), 128.2 (*C*H), 127.3 (*C*H), 127.1 (*C*H), 124.9 (*C*H), 122.7 (*C*H), 108.3 (*C*H), 57.5 (C), 31.0 (CH_2), 26.5 (CH_3), 9.2 (CH_3). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = -98, $[\alpha]_{578}$ = -102, $[\alpha]_{546}$ = -120 (*c* = 1.62 in CH_2Cl_2), 87% *ee*. **cHPLC analysis:** [Chiracel OD-3 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 6.33 min and 7.49 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

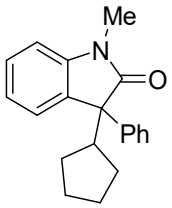
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.32	7544	49.96	1.14		
7.50	7557	50.04	1.54	1.35	4.13
Sum	15101	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

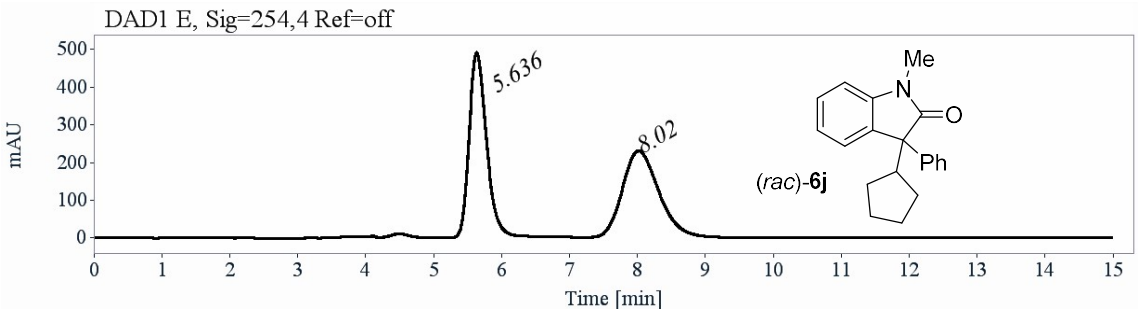
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.33	1079	6.71	1.15		
7.49	14986	93.29	1.54	1.34	4.06
Sum	16065	100.00			

(+)-3-Cyclopentyl-1-methyl-3-phenylindolin-2-one[11] (+)-6j



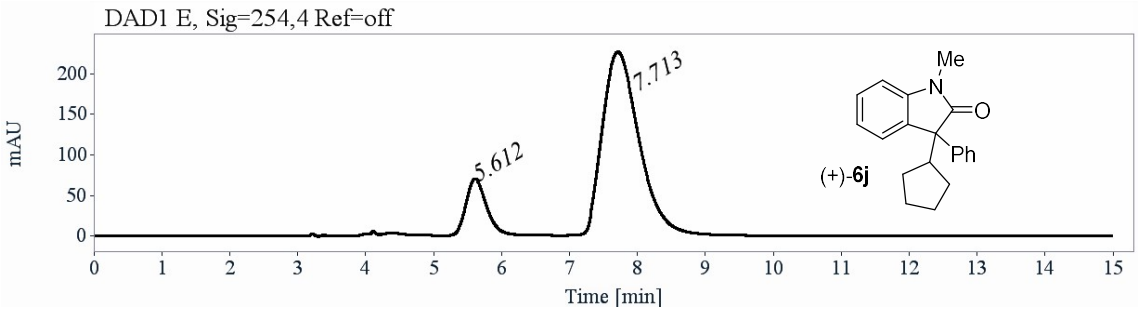
According to the general procedure I, *N*-(2-bromophenyl)-2-cyclopentyl-*N*-methyl-2-phenylacetamide **5j** (78 mg, 0.2 mmol, 1.0 equiv.), (-)-(R_a,R_a)-**2e** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 80 °C for 20 hours to afford a brown oil. (60.0 mg, 90% yield).

Rf = 0.38 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.48-7.42 (m, 2H, H^{Ar}), 7.37-7.17 (m, 5H, H^{Ar}), 7.15-7.07 (m, 1H, H^{Ar}), 6.90 (d, *J*(H,H) = 7.7 Hz, 1H, H^{Ar}), 3.20 (s, 3H, CH_3), 3.15-3.05 (m, 1H, C*H*), 1.65-1.35 (m, 7H, CH_2), 0.95-0.80 (m, 1H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 178.5 (*C*), 144.5 (*C*), 139.9 (*C*), 131.1 (*C*), 128.5 (*C*H), 128.3 (*C*H), 127.6 (*C*H), 127.2 (*C*H), 126.0 (*C*H), 122.3 (*C*H), 108.2 (*C*H), 58.9 (C), 47.5 (*C*H), 28.1 (CH_2), 27.5 (CH_2), 26.4 (CH_3), 25.5 (CH_2), 25.4 (CH_2). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +132, $[\alpha]_{578}$ = +139, $[\alpha]_{546}$ = +163, $[\alpha]_{436}$ = +314, $[\alpha]_{405}$ = +408 (*c* = 0.90 in CH_2Cl_2), 72% *ee*. **cHPLC analysis:** [Chiracel Lux-Cellulose-3 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 5.61 min and 7.71 min (major)].



Signal: DAD1 E, Sig=254,4 Ref=off

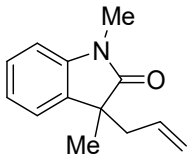
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.64	8525	49.93	0.91		
8.02	8549	50.07	1.72	1.89	3.32
Sum	17074	100.00			



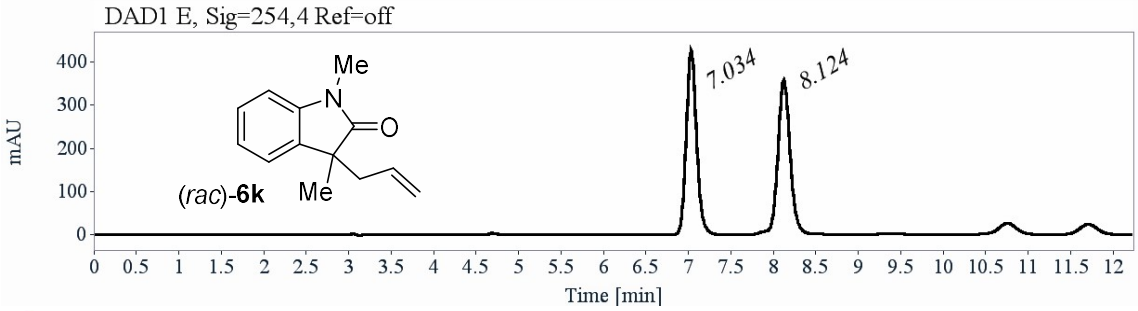
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.61	1434	14.43	0.90		
7.71	8503	85.57	1.61	1.79	2.76
Sum	9937	100.00			

3-Allyl-1,3-dimethylindolin-2-one 6k

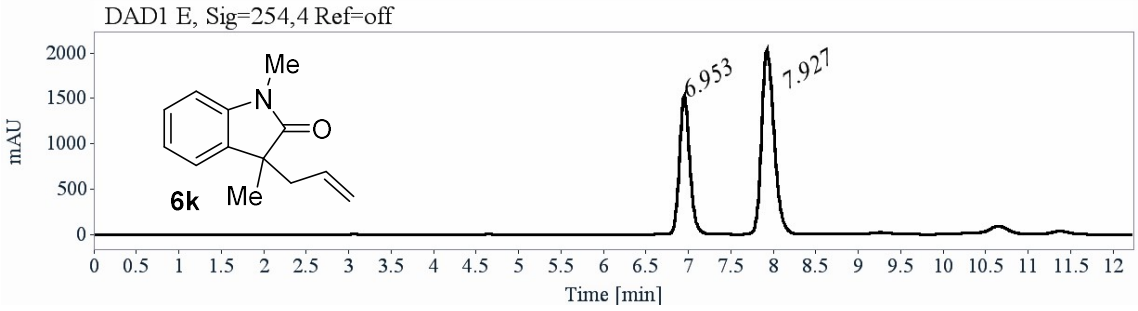


According to the general procedure I, *N*-(2-bromophenyl)-*N*-2-dimethylpent-4-enamide **5k** (57 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a,R_a)-**2f** (8.1 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 60 °C for 20 hour **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.29-7.23 (m, 1H, H^{Ar}), 7.21-7.18 (m, 1H, H^{Ar}), 7.08-7.04 (m, 1H, H^{Ar}), 6.83 (d, *J*(H,H) = 7.7 Hz, 1H, H^{Ar}), 5.55-5.40 (m, 1H, CH_2=C*H*), 5.00-4.85 (m, 2H, CH_2=CH), 3.20(s, 3H, NCH_3), 2.52 (ddt, *J*(H,H) = 7.1, 3.8 and 1.1 Hz, 2H, CH_2), 1.37 (s, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$):** δ =180.3 (*C*), 143.3 (*C*), 133.8 (*C*), 132.7 (*C*H), 127.9 (*C*H), 124.0 (*C*H), 122.5 (*C*H), 118.7 (CH_2), 108.0 (*C*H), 48.4 (*C*), 42.6 (CH_2), 26.3 (CH_3), 22.9 (CH_3).s to afford a brown oil. (30.0 mg, 75% yield). **Rf =** 0.35 (PE/Et_2O 2:1). **HRMS (ESI)**: *m/z*: 202.1226 calcd for: $C_{13}H_{16}NO^+$ $[M+H]^+$: found 202.1225. **IR (ATR):** 3056, 2968, 2927, 2359, 1707, 1660, 1612, 1492, 1469, 1450, 1418, 1375, 1348, 1317, 1306, 1248, 1158, 1121, 1083, 1051, 1026, 994, 964, 915, 874, 752, 740, 700, 688, 655, 629, 567, 541 cm^{-1}. **cHPLC analysis:** [Chiracel Lux-Amylose-2 column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 254 nm; Rt = 6.95 min and 7.93 min (major)]: 24% *ee*.



Signal: DAD1 E, Sig=254,4 Ref=off

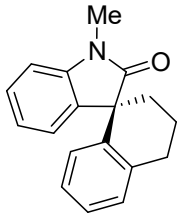
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.03	3597	49.85	1.38		
8.12	3619	50.15	1.75	1.27	4.58
Sum	7216	100.00			



Signal: DAD1 E, Sig=254,4 Ref=off

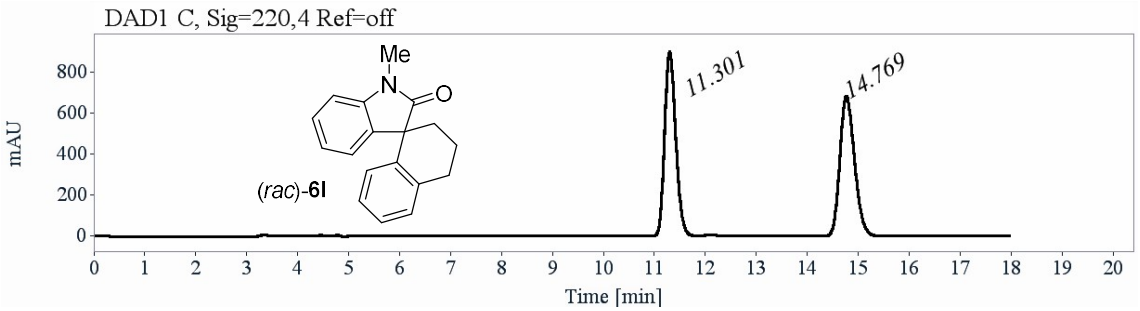
RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.95	12958	38.33	1.36		
7.93	20849	61.67	1.69	1.24	4.00
Sum	33806	100.00			

(-)-(*S*)-1-Methyl-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one[8] (-)-(*S*)-6l



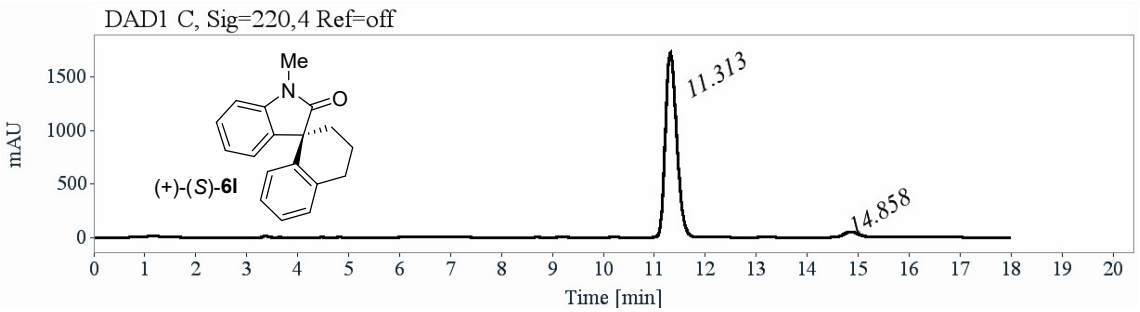
According to the general procedure I, *N*-(2-bromophenyl)-*N*-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxamide **5l** (69 mg, 0.2 mmol, 1.0 equiv.), (+)-(R_a,R_a)-**2f** (8.2 mg, 0.01 mmol, 5 mol%), *t*BuOK (34 mg, 0.30 mmol, 1.5 equiv.) were stirred at 40 °C for 20 hours to afford a light yellow oil. (50.0 mg, 93% yield).

Rf = 0.40 (PE/Et_2O 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.34-7.24 (m, 1H, H^{Ar}), 7.20-6.88 (m, 6H, H^{Ar}), 6.47 (d, *J*(H,H) = 7.8 Hz, 1H, H^{Ar}), 3.29 (s, 3H, CH_3), 3.00 (q, *J*(H,H) = 6.6 Hz, 2H, Ar- CH_2), 2.45-2.35 (m, 1H, CCH_2), 2.25-2.10 (m, 1H, CCH_2), 2.10-1.90 (m, 2H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 180.5 (*C*), 145.2 (*C*), 137.9 (*C*), 137.5 (*C*), 135.3 (*C*), 129.7 (*C*H), 128.1 (*C*H), 127.9 (*C*H), 127.1 (*C*H), 126.4 (*C*H), 124.1 (*C*H), 122.9 (*C*H), 108.1 (*C*H), 52.3 (C), 34.2 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 18.9 (CH_2). **Specific rotations at 25 °C:** $[\alpha]_{589}$ = +8.2, $[\alpha]_{578}$ = +7.7, $[\alpha]_{546}$ = +7.1 (*c* = 1.93 in CH_2Cl_2), 92% *ee*. **cHPLC analysis:** [Chiracel IE column, n-heptane/*iso*propanol = 90:10, 1.0 mL/min, 220 nm; Rt = 11.31 min and 14.86 min (major)].



Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.30	13571	49.80	2.83		
14.77	13679	50.20	4.01	1.42	7.47
Sum	27250	100.00			



Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.31	26788	96.06	2.83		
14.86	1099	3.94	4.04	1.42	7.59
Sum	27888	100.00			

VI Theoretical calculations

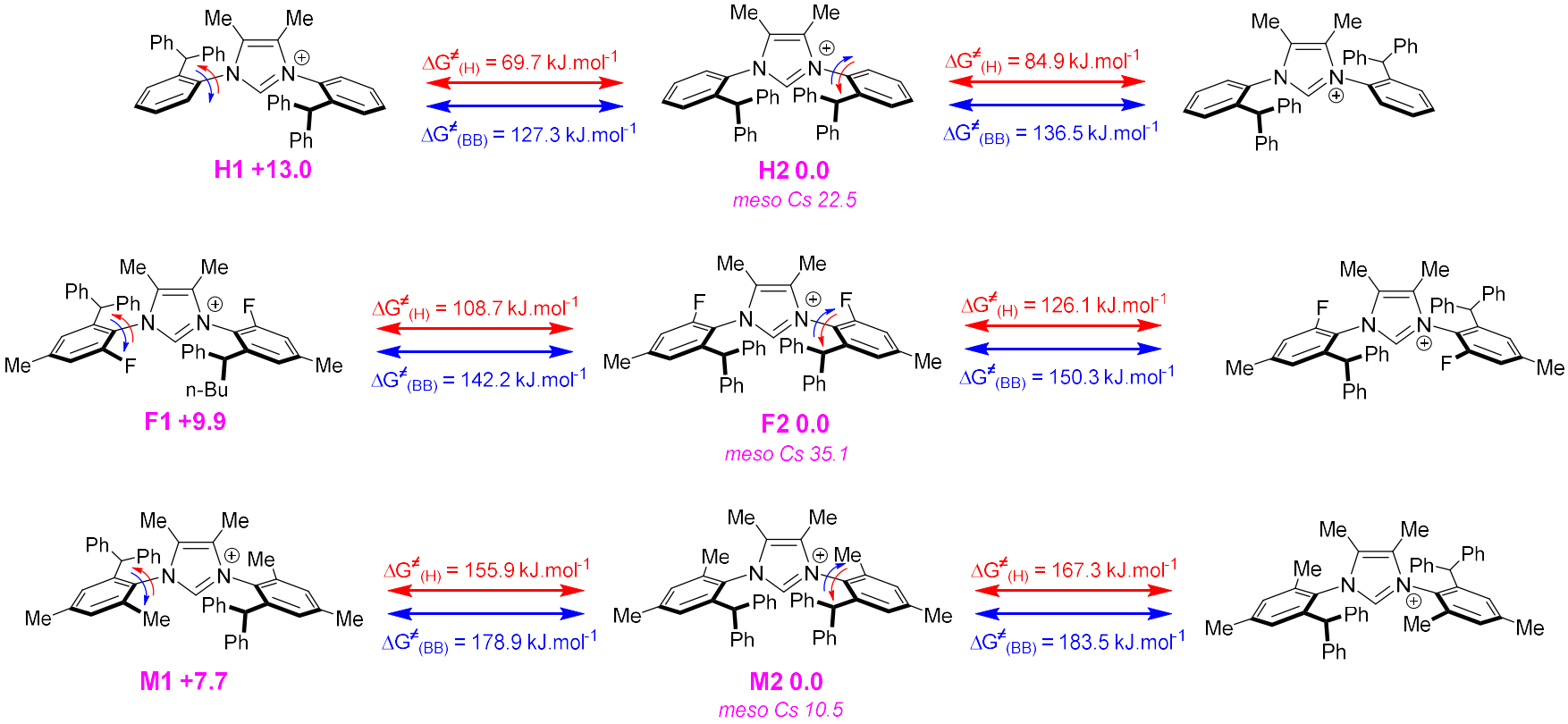
Computations were all done with Gaussian G09RevD.01.[12-15]
PBE0 calculations were done in gaussian at the dual level :
RPBE1PBE/Def2SVP // PBE1PBE/Def2TZVP.
PBE1PBE/**Def2TZVP** are noted LB

Thermal corrections to Gibbs Free Energy were evaluated in the small basis set (Def2SVP) computation ($Corr^{SB}$), and added to the Large basis set electronic energy : $\Delta G^{LB} = \Delta E^{LB} + Corr^{SB}$

transition states for a rotation on backbone side are noted BB
transition states for a rotation on Hydrogen side noted H

There are two BackBone side transition states (**BB1** and **BB2**) of similar energies, depending on the orientation of the other N-substituent :
The same notation is used for the Hydrogen side transition states (**H1** and **H2**).

system	G^{SB}	E^{SB}	$Corr^{SB}$	E^{LB}	$G^{LB} = E^{LB} + Corr^{SB}$	ΔG^{LB}
1d·X	-1766.32334	-1766.93927	0.6159	-1768.760542	-1768.1446	0.0
BB1	-1766.26953	-1766.88877	0.6192	-1768.711844	-1768.0926	136.5
BB2	-1766.27211	-1766.88959	0.6175	-1768.713597	-1768.0961	127.3
H1	-1766.29026	-1766.91158	0.6213	-1768.733587	-1768.1123	84.9
H2	-1766.29558	-1766.91330	0.6177	-1768.735797	-1768.1181	69.7
1e·X	-2042.92124	-2043.56736	0.6461	-2045.711753	-2045.0656	0.0
BB1	-2042.86313	-2043.51119	0.6481	-2045.656429	-2045.0084	150.3
BB2	-2042.86584	-2043.51277	0.6469	-2045.658394	-2045.0115	142.2
H1	-2042.87387	-2043.52523	0.6514	-2045.66897	-2045.0176	126.1
H2	-2042.87988	-2043.52761	0.6477	-2045.671964	-2045.0242	108.7
1f·X	-1923.20357	-1923.92067	0.7171	-1925.903453	-1925.1864	0.0
BB1	-1923.13130	-1923.85138	0.7201	-1925.836564	-1925.1165	183.5
BB2	-1923.13296	-1923.85154	0.7186	-1925.836809	-1925.1182	178.9
H1	-1923.13830	-1923.85959	0.7213	-1925.843934	-1925.1226	167.3
H2	-1923.14274	-1923.86296	0.7202	-1925.8472	-1925.1270	155.9



Scheme S6. DFT Calculations on symmetric imidazolium salts **1·X**

Same template than previously when multiple with | |:
filename E1 |E2 | zpc | entro | G

1a·X

1a

H2_x_GB.log -1768.7605421
H2.log -1766.9392748 | | 0.687408 |230.622| -1766.323341
State 1-A
NImag 0
PG C01 [X(C43H37N2)]
HF -1766.9392748
Low frequencies --- -4.7689 -0.0007

C	-0.034687	-1.784912	-1.209313
C	-0.850589	-2.788462	0.597214
C	0.518922	-2.820123	0.679837
C	-1.902212	-3.285518	1.515996
C	1.419427	-3.374744	1.716654
C	-2.494941	-1.937105	-1.086683
C	2.382327	-2.027317	-0.803824
C	-3.092155	-2.978648	-1.795985
C	-4.395148	-2.829848	-2.259730
C	-5.082640	-1.645712	-1.997574
C	-4.473062	-0.616772	-1.283306
C	-3.161778	-0.734967	-0.811684
C	-2.455601	0.398048	-0.090924
H	-2.582951	-2.472859	1.812665
H	2.028938	-2.579159	2.171254
H	-1.447926	-3.703419	2.422229
H	0.832345	-3.854345	2.508621
H	-2.515318	-4.066722	1.041939
H	2.104427	-4.123066	1.291529
H	-2.531099	-3.898049	-1.978311
H	-4.871502	-3.637501	-2.818970
H	-6.108452	-1.520975	-2.351358
H	-5.024685	0.302720	-1.077015
N	-1.161202	-2.140091	-0.592852
N	0.995049	-2.185444	-0.462510
C	-3.407139	1.228070	0.753214
H	-1.754163	-0.073134	0.619590
C	-1.605627	1.240709	-1.035080
C	-3.730787	0.799255	2.045090
C	-4.633294	1.514018	2.829240
C	-5.226092	2.672520	2.327651
C	-4.000699	2.395184	0.261509
C	-4.906461	3.111073	1.043682
H	-3.265639	-0.107527	2.445385
H	-4.871910	1.168639	3.837923
H	-5.932162	3.237051	2.940870
H	-3.742735	2.754315	-0.738221
H	-5.361524	4.021960	0.647603
C	-1.624865	1.078142	-2.423632
C	-0.824786	1.878022	-3.245263
C	0.000341	2.850466	-2.688787
C	-0.775778	2.231285	-0.487954
C	0.021333	3.027121	-1.303766
H	-2.282974	0.333438	-2.878031
H	-0.860406	1.743293	-4.329166
H	0.627797	3.475108	-3.328177
H	-0.771492	2.394245	0.593279
H	0.672706	3.782105	-0.857449
C	3.034316	-3.127070	-1.361066
C	4.389881	-3.043903	-1.660011
C	5.073608	-1.858970	-1.394413
C	4.406149	-0.765467	-0.848042
C	3.041277	-0.816448	-0.540262
C	2.314553	0.349434	0.112356
H	2.471474	-4.043028	-1.555173
H	4.907059	-3.899727	-2.098120
H	6.139732	-1.781369	-1.619041
H	4.951335	0.162117	-0.661289
C	2.912563	1.709684	-0.219354
H	1.293195	0.383112	-0.304910
C	2.160764	0.084013	1.600699
C	3.170927	2.038121	-1.557729
C	3.640035	3.300392	-1.906532
C	3.848413	4.267237	-0.921067
C	3.125889	2.683379	0.759269
C	3.588023	3.954378	0.410483
H	2.995049	1.295555	-2.340688
H	3.839372	3.534613	-2.955172
H	4.214868	5.259892	-1.192533
H	2.923652	2.454667	1.807498
H	3.747475	4.702455	1.190634
C	3.267751	-0.243004	2.394234
C	3.116238	-0.495149	3.756448
C	1.852721	-0.431075	4.346970
C	0.903416	0.157911	2.206384
C	0.745239	-0.100954	3.567831
H	4.260001	-0.304968	1.940095
H	3.990585	-0.746065	4.361608
H	1.735009	-0.631737	5.414323
H	0.035443	0.429582	1.601363
H	-0.247190	-0.035299	4.020930
H	0.030077	-1.250953	-2.154858

BB1

H12Bdn_x_GB.log -1768.7118443
H12Bdn.log -1766.8887698 | | 0.688614 |223.280| -1766.269532
State 1-A
NImag 1
PG C01 [X(C43H37N2)]
HF -1766.8887698
Low frequencies --- -95.0897 -4.2765

C	-0.752948	-1.755382	0.429922
C	0.508148	-1.166905	-1.277814
C	-0.733359	-1.524752	-1.748669
C	1.553843	-0.709858	-2.228317
C	-1.254299	-1.564482	-3.138855
C	1.422766	-1.083143	1.257548
C	-2.899914	-2.170647	-0.642069
C	0.877564	-1.325396	2.537613
C	1.604666	-1.215716	3.710831
C	2.941923	-0.848260	3.653434
C	3.484907	-0.576591	2.411783
C	2.773775	-0.662521	1.199831
C	3.546367	-0.159009	-0.006579
H	1.916940	0.300178	-2.006031
H	-2.346452	-1.667438	-3.134372
H	1.089135	-0.664538	-3.219835
H	-1.013754	-0.634887	-3.670670
H	2.398400	-1.408349	-2.314096

H	-0.831827	-2.411828	-3.701145
H	-0.159023	-1.607551	2.680059
H	1.112672	-1.423077	4.663111
H	3.548365	-0.761047	4.556803
H	4.528710	-0.266127	2.349469
N	0.483016	-1.309116	0.133100
N	-1.494465	-1.875346	-0.657507
C	5.026895	-0.520640	0.053574
H	3.184075	-0.689786	-0.883672
C	3.302754	1.325583	-0.248105
C	5.397369	-1.854676	-0.157730
C	6.732535	-2.242973	-0.096062
C	7.722065	-1.298139	0.178626
C	6.025182	0.419375	0.325166
C	7.364419	0.031580	0.388363
H	4.625454	-2.602828	-0.364228
H	7.003987	-3.287626	-0.265709
H	8.771011	-1.599465	0.225609
H	5.757016	1.465914	0.487977
H	8.132934	0.778254	0.601883
C	2.689996	2.161156	0.690594
C	2.506400	3.520522	0.425238
C	2.920971	4.062905	-0.788207
C	3.725193	1.887089	-1.463888
C	3.531845	3.238206	-1.735298
H	2.355443	1.756422	1.647819
H	2.033382	4.157213	1.176749
H	2.775864	5.125588	-0.995345
H	4.231810	1.255426	-2.199706
H	3.870639	3.653853	-2.687283
C	-3.321453	-3.395666	-1.152682
C	-4.681675	-3.687942	-1.196784
C	-5.595144	-2.747424	-0.727921
C	-5.156780	-1.529260	-0.209096
C	-3.798539	-1.204377	-0.149898
C	-3.302979	0.128089	0.411463
H	-2.579953	-4.112114	-1.513279
H	-5.022212	-4.645711	-1.594956
H	-6.665544	-2.962399	-0.760892
H	-5.884034	-0.805471	0.163753
C	-4.398598	0.923372	1.105856
H	-2.581213	-0.113980	1.209274
C	-2.531038	0.919977	-0.628897
C	-4.773983	0.553624	2.404090
C	-5.793202	1.225295	3.073120
C	-6.454043	2.285206	2.451463
C	-5.061610	1.990883	0.494833
C	-6.083605	2.665793	1.163957
H	-4.263013	-0.279434	2.897136
H	-6.070430	0.923721	4.085980
H	-7.252154	2.817318	2.974146
H	-4.774227	2.312231	-0.508150
H	-6.589247	3.500854	0.673388
C	-3.003476	1.046294	-1.940548
C	-2.288526	1.781572	-2.885698
C	-1.078210	2.380769	-2.537822
C	-1.326035	1.543213	-0.286047
C	-0.596176	2.258669	-1.234075
H	-3.941419	0.561167	-2.225965
H	-2.678130	1.881981	-3.901918
H	-0.511913	2.949922	-3.278834
H	-0.947349	1.463893	0.737878
H	0.351087	2.724104	-0.951526
H	-1.138819	-2.025629	1.399948

BB2

H12Bup_x_GB.log -1768.7135973
H12Bup.log -1766.88959 | | 0.687961 |226.319| -1766.272114
State 1-A
NImag 1
PG C01 [X(C43H37N2)]
HF -1766.88959
Low frequencies --- -65.0503 -4.5266 -0.0009

C	-0.676867	1.075241	1.181769
C	0.358401	1.278047	-0.754161
C	-0.908288	1.798505	-0.874500
C	1.314206	1.366112	-1.888714
C	-1.574091	2.451169	-2.032755
C	1.536435	0.122905	1.371396
C	-2.883673	1.968992	0.683795
C	1.125495	-0.273480	2.663232
C	2.001794	-0.760453	3.616093
C	3.351574	-0.884181	3.305496
C	3.745417	-0.601913	2.011990
C	2.875000	-0.140604	1.005807
C	3.505093	-0.071136	-0.375611
H	2.268969	1.828185	-1.610318
H	-1.078144	3.397901	-2.297117
H	0.859598	2.011921	-2.649800
H	-1.562628	1.803782	-2.921481
H	1.506416	0.397549	-2.373011
H	-2.620609	2.681598	-1.791043
H	0.081359	-0.258422	2.956729
H	1.617054	-1.048147	4.596539
H	4.074931	-1.238138	4.042335
H	4.784394	-0.774336	1.726670
N	0.490096	0.797174	0.573362
N	-1.522629	1.658105	0.348484
C	4.280021	-1.354986	-0.662966
H	2.691687	-0.098213	-1.100704
C	4.293510	1.201593	-0.633771
C	3.554765	-2.518524	-0.947423
C	4.204315	-3.725560	-1.188864
C	5.597621	-3.787051	-1.148763
C	5.675721	-1.425775	-0.628800
C	6.329288	-2.634965	-0.868987
H	2.460858	-2.476800	-0.971708
H	3.622532	-4.622906	-1.413044
H	6.111604	-4.731770	-1.340067
H	6.260396	-0.526176	-0.420879
H	7.420808	-2.673383	-0.839735
C	4.436585	2.209452	0.323928
C	5.133456	3.382865	0.026058
C	5.694574	3.565263	-1.234234
C	4.862885	1.397792	-1.902429
C	5.555825	2.566271	-2.200374
H	4.003928	2.080589	1.318620
H	5.239019	4.156600	0.790260
H	6.241946	4.481755	-1.466063
H	4.767846	0.615420	-2.660753
H	5.994823	2.698335	-3.192175
C	-3.144818	3.129180	1.406582
C	-4.457936	3.428666	1.762281
C	-5.482209	2.565030	1.382806

C -5.203734 1.409927 0.651334
C -3.896969 1.079750 0.284439
C -3.551517 -0.184021 -0.493535
H -2.320733 3.791036 1.682316
H -4.676247 4.335452 2.329711
H -6.515295 2.791361 1.655918
H -6.016341 0.744194 0.353657
C -4.773090 -0.859415 -1.095970
H -2.936941 0.135047 -1.352125
C -2.680363 -1.122911 0.323570
C -5.320381 -0.332640 -2.272860
C -6.461121 -0.891518 -2.842261
C -7.072681 -1.992080 -2.241024
C -5.389450 -1.965066 -0.504059
C -6.533046 -2.526670 -1.073453
H -4.847219 0.531911 -2.749095
H -6.872716 -0.469736 -3.762246
H -7.965733 -2.435552 -2.687220
H -4.971028 -2.403560 0.404500
H -7.001108 -3.393414 -0.600913
C -2.894580 -1.314513 1.694295
C -2.089248 -2.190008 2.424048
C -1.053173 -2.880247 1.794621
C -1.643648 -1.826881 -0.299027
C -0.833184 -2.696370 0.429811
H -3.701435 -0.772519 2.195857
H -2.277097 -2.337953 3.490579
H -0.418202 -3.561068 2.365793
H -1.473759 -1.694841 -1.371651
H -0.026449 -3.237903 -0.070489
H -0.946210 0.870487 2.206377

H1

H12Fdn_x_GB.log -1768.7335865
H12Fdn.log -1766.9115809 | | 0.688856 |218.965|
-1766.290255
State 1-A
NImag 1
PG C01 [X(C43H37N2)]
HF -1766.9115809
Low frequencies --- -63.2232 -0.0008
C -0.367306 1.100809 0.956205
C 1.086826 2.756165 1.046476
C 0.002279 3.191387 0.331658
C 2.356315 3.460332 1.358162
C -0.034809 4.528046 -0.323144
C 1.728077 0.619666 2.166858
C -2.247887 2.111627 -0.312618
C -2.683459 3.302260 -0.909628
C -3.898450 3.405371 -1.572714
C -4.725146 2.295768 -1.651926
C -4.325871 1.123756 -1.024706
C -3.114651 0.982841 -0.332427
C -2.863651 -0.377220 0.319507
C -1.841649 -1.217574 -0.433049
C -4.148815 -1.157961 0.573815
H 2.176398 4.357404 1.968912
H 2.862392 3.760155 0.429195
H 3.041268 2.803134 1.907172
H -0.191719 4.456237 -1.408645
H 0.943781 5.000003 -0.172355
H -0.788397 5.205717 0.104564
H -2.075249 4.192350 -0.861012
H -4.184493 4.359103 -2.020446
H -5.681089 2.337946 -2.177453
H -4.992396 0.261492 -1.054339
H -2.481623 -0.186154 1.336967
N 0.826321 1.453296 1.420099
N -0.928425 2.128108 0.295217
H -0.774121 0.108814 1.080569
C 2.524387 -0.332992 1.506763
C 3.495774 -0.974073 2.284058
C 3.636758 -0.714579 3.646175
C 1.844996 0.876834 3.532013
C 2.798876 0.197396 4.282771
C 2.339598 -0.610842 0.018624
H 4.153917 -1.701712 1.806561
H 4.409181 -1.237118 4.214902
H 2.894369 0.391938 5.352752
H 1.194378 1.623548 3.993060
C 2.973743 -1.910488 -0.465343
H 1.255857 -0.753470 -0.144824
C 2.747023 0.599534 -0.803044
C -4.576939 -2.185851 -0.272197
C -5.773574 -2.856807 -0.019532
C -6.553370 -2.512045 1.082676
C -4.937099 -0.821427 1.680335
C -6.130681 -1.491637 1.934803
H -3.970151 -2.467852 -1.136037
H -6.095320 -3.657835 -0.689205
H -7.488117 -3.041271 1.281355
H -4.614916 -0.018014 2.349978
H -6.732462 -1.219068 2.804961
C -1.450918 -0.927480 -1.742848
C -0.551418 -1.758268 -2.417721
C -0.040611 -2.892576 -1.794366
C -1.318203 -2.361938 0.188002
C -0.434523 -3.195502 -0.489169
H -1.861892 -0.050909 -2.249887
H -0.254198 -1.516418 -3.440894
H 0.670232 -3.538234 -2.314708
H -1.637156 -2.615766 1.203501
H -0.046931 -4.090427 0.000870
C 4.001176 1.195836 -0.626498
C 4.384039 2.287397 -1.403888
C 3.509778 2.809060 -2.359014
C 1.882419 1.121617 -1.769927
C 2.256815 2.223138 -2.539641
H 4.688948 0.793041 0.122281
H 5.371133 2.734589 -1.263310
H 3.810363 3.664222 -2.969065
H 0.907094 0.650384 -1.922370
H 1.571537 2.617219 -3.294580
C 2.713388 -3.107850 0.217694
C 3.208818 -4.322071 -0.246639
C 3.968335 -4.367022 -1.417257
C 3.734730 -1.968800 -1.635689
C 4.226502 -3.187183 -2.108809
H 2.107537 -3.088948 1.126965
H 2.997960 -5.241176 0.305777
H 4.357698 -5.319147 -1.784948
H 3.942518 -1.055392 -2.195578
H 4.818678 -3.208151 -3.026721

H2

H12Fup_x_GB.log -1768.7357967

H12Fup.log -1766.9133046 | | 0.688176 |226.199| -1766.295582
State 1-A
NImag 1
PG C01 [X(C43H37N2)]
HF -1766.9133046
Low frequencies --- -63.1234 -5.3100
C -0.113237 -1.225283 -0.105832
C 1.335241 -2.757453 -0.750531
C 0.229781 -2.863930 -1.555753
C 2.611202 -3.512859 -0.704364
C 0.093953 -3.866047 -2.648409
C 1.948646 -1.299661 1.201768
C -2.057490 -1.642780 -1.564986
C -2.523919 -2.421611 -2.631774
C -3.842122 -2.379971 -3.065080
C -4.742588 -1.546191 -2.420429
C -4.276914 -0.725476 -1.402273
C -2.946264 -0.708694 -0.959472
C -2.602353 0.333061 0.109574
C -2.413590 -0.264599 1.496549
C -3.578208 1.505569 0.116358
H 3.470530 -2.844951 -0.870419
H 2.638098 -4.298733 -1.467115
H 2.750798 -3.983269 0.280642
H -0.738507 -4.564675 -2.483157
H 1.013206 -4.462908 -2.679092
H -0.019694 -3.404027 -3.639807
H -1.855256 -3.088691 -3.154643
H -4.151650 -3.011265 -3.900289
H -5.793047 -1.511349 -2.715614
H -4.973688 -0.034823 -0.926051
H -1.647913 0.802429 -0.192028
N 1.083403 -1.734639 0.142690
N -0.694210 -1.876551 -1.121990
H -0.532147 -0.429831 0.489249
C 2.920314 -0.325837 0.931584
C 3.755032 0.048214 1.987948
C 3.610391 -0.515152 3.255564
C 1.785067 -1.867441 2.462709
C 2.623066 -1.467693 3.500227
C 2.974782 0.336371 -0.434432
H 4.528870 0.797338 1.806599
H 4.276636 -0.201344 4.062327
H 2.505166 -1.902749 4.494615
H 0.999378 -2.608975 2.623536
C 4.326210 0.971887 -0.723905
H 2.842857 -0.457538 -1.189305
C 1.808344 1.295354 -0.615618
C -4.475536 1.732727 1.162399
C -5.354515 2.817258 1.119019
C -5.346627 3.685933 0.031219
C -3.581509 2.383305 -0.976381
C -4.456168 3.463943 -1.021129
H -4.491662 1.059800 2.022404
H -6.049744 2.980834 1.945769
H -6.033629 4.534675 -0.000073
H -2.897001 2.203098 -1.809481
H -4.445869 4.137493 -1.881589
C -2.931694 -1.514005 1.847275
C -2.718477 -2.037579 3.124348
C -1.980834 -1.319747 4.063385
C -1.682929 0.455883 2.453301
C -1.463567 -0.067854 3.724017
H -3.509914 -2.084910 1.116500
H -3.136456 -3.012782 3.385481
H -1.814589 -1.730325 5.062115
H -1.281117 1.438107 2.189166
H -0.888520 0.504848 4.455447
C 1.303728 2.050132 0.450202
C 0.282432 2.978163 0.243376
C -0.254409 3.159179 -1.030231
C 1.250931 1.473234 -1.887560
C 0.226289 2.395296 -2.094575
H 1.719891 1.919199 1.452334
H -0.090999 3.572381 1.081114
H -1.048079 3.891637 -1.188742
H 1.639556 0.894129 -2.730403
H -0.190274 2.527209 -3.096310
C 5.412692 0.138066 -1.017871
C 6.676126 0.669315 -1.258238
C 6.872590 2.050299 -1.209034
C 4.531531 2.353036 -0.680509
C 5.798278 2.888074 -0.921000
H 5.267007 -0.946202 -1.054652
H 7.511587 0.004265 -1.489281
H 7.862370 2.471004 -1.400441
H 3.695405 3.022063 -0.465641
H 5.941998 3.970573 -0.886701

1e·X

1e

F2_x_GB.log -2045.7117533
F2.log -2043.5673648 | | 0.725713 |259.614| -2042.921244
State 1-A
NImag 0
PG C01 [X(C45H39F2N2)]
HF -2043.5673648
Low frequencies --- -5.1327 -2.1409
C -0.039339 -1.616740 -0.715800
C -0.784459 -2.392200 1.230220
C 0.584981 -2.400040 1.271190
C -1.801409 -2.808230 2.223720
C 1.530501 -2.818770 2.329720
C -2.482149 -1.782610 -0.493300
C 2.383211 -1.783990 -0.353680
C -3.102249 -2.945100 -0.952300
C -4.408719 -2.933550 -1.407770
C -5.128029 -1.733110 -1.394970
C -4.501509 -0.572490 -0.920260
C -3.184269 -0.569910 -0.461580
C -2.492650 0.694750 0.012200
H -2.546939 -2.014720 2.384490
H 2.189251 -1.984880 2.615980
H -1.323469 -3.033700 3.184550
H 0.980741 -3.145930 3.220070
H -2.338489 -3.708110 1.885830
H 2.157131 -3.655480 1.985830
F -2.405929 -4.076440 -0.934390
H -4.850539 -3.866520 -1.763320
C -6.556889 -1.697340 -1.845740

H	-5.061850	0.364430	-0.897070
N	-1.140479	-1.892200	-0.018050
N	1.016731	-1.905570	0.044400
C	-3.457730	1.661760	0.675920
H	-1.783500	0.383610	0.799640
C	-1.655050	1.342680	-1.083330
C	-3.797890	1.474660	2.020180
C	-4.713790	2.315910	2.647230
C	-5.304090	3.358770	1.933300
C	-4.049100	2.713750	-0.030420
C	-4.968790	3.555520	0.594740
H	-3.337490	0.657480	2.585010
H	-4.965460	2.160460	3.698990
H	-6.020590	4.022130	2.423090
H	-3.778840	2.882710	-1.076010
H	-5.421900	4.374940	0.031750
C	-1.703540	0.932120	-2.418970
C	-0.910360	1.558030	-3.385420
C	-0.063680	2.603180	-3.028000
C	-0.805970	2.405620	-0.738880
C	-0.015930	3.029210	-1.698930
H	-2.376980	0.125020	-2.718040
H	-0.967090	1.228910	-4.425940
H	0.558890	3.092160	-3.780430
H	-0.779050	2.761750	0.294720
H	0.650610	3.844910	-1.409220
C	3.054831	-2.955070	-0.708060
C	4.391951	-2.944330	-1.060620
C	5.090361	-1.731589	-1.053660
C	4.409711	-0.560110	-0.697430
C	3.059291	-0.555020	-0.341970
C	2.342900	0.701420	0.126470
F	2.375751	-4.097230	-0.687110
H	4.872011	-3.885490	-1.335920
C	6.549131	-1.697909	-1.396690
H	4.949430	0.389080	-0.701330
C	2.932830	1.993970	-0.417350
H	1.316330	0.670000	-0.277450
C	2.206700	0.659880	1.639620
C	3.160360	2.117860	-1.795560
C	3.614760	3.314420	-2.340450
C	3.839730	4.418670	-1.516100
C	3.162950	3.103780	0.399090
C	3.611000	4.308610	-0.147150
H	2.969750	1.265760	-2.453610
H	3.788950	3.389090	-3.416700
H	4.194080	5.360280	-1.941740
H	2.983770	3.035290	1.473880
H	3.783490	5.165770	0.507960
C	3.322070	0.449430	2.460210
C	3.185090	0.402870	3.846280
C	1.928370	0.558740	4.434120
C	0.955810	0.824260	2.240370
C	0.812560	0.772090	3.626760
H	4.308250	0.317770	2.007490
H	4.065520	0.241990	4.472910
H	1.822320	0.519930	5.520690
H	0.081810	1.002730	1.609450
H	-0.174370	0.907430	4.076360
H	-0.012949	-1.211890	-1.725130
H	6.876931	-0.686489	-1.672080
H	7.153251	-2.020919	-0.532910
H	6.782051	-2.378619	-2.228050
H	-6.822139	-0.716910	-2.264880
H	-6.764899	-2.468640	-2.600060
H	-7.229239	-1.881041	-0.991370

BB1

F12Bdn_x_GB.log -2045.6564286
F12Bdn.log -2043.5111861 | | 0.726166 |253.956|
-2042.863127
State 1-A
NImag 1
PG C01 [X(C45H39F2N2)]
HF -2043.5111861
Low frequencies --- -43.8959 -4.1897

C	-0.741917	0.772545	-1.063974
C	-0.714071	2.040486	0.727152
C	0.551287	1.538728	0.556014
C	-1.242646	2.973203	1.752522
C	1.673538	2.028803	1.398108
C	-2.895270	1.718513	-0.471366
C	1.479077	-0.176856	-1.265690
C	1.014018	-0.997248	-2.331375
C	1.833559	-1.636698	-3.236849
C	3.218858	-1.551852	-3.115347
C	3.686115	-0.912394	-1.975080
C	2.873211	-0.283558	-1.021321
C	3.607959	0.045875	0.272595
C	4.510018	1.265105	0.206389
C	4.310850	-1.220723	0.763190
H	-2.326416	2.837276	1.864926
H	-1.061599	4.022036	1.469509
H	-0.782381	2.780911	2.729364
H	1.973607	1.324761	2.187619
H	1.328119	2.940270	1.900819
H	2.555300	2.311544	0.812409
F	-0.297904	-1.244304	-2.515261
H	1.349437	-2.217740	-4.024337
H	4.756453	-0.944974	-1.762867
H	2.854707	0.234207	1.039226
N	-1.490762	1.545558	-0.296924
N	0.511428	0.678037	-0.575973
H	-1.118337	0.313639	-1.963804
C	-3.792692	0.643588	-0.312842
C	-5.149804	0.917799	-0.465425
C	-5.633881	2.202904	-0.759401
C	-3.369365	2.995702	-0.761878
C	-4.723266	3.251293	-0.907120
C	-3.274405	-0.756262	0.012928
H	-5.860923	0.098104	-0.346036
C	-7.104656	2.430526	-0.934333
H	-5.045611	4.269250	-1.134089
F	-2.486403	3.981284	-0.887598
C	-4.371244	-1.809527	0.016060
H	-2.604475	-1.044494	-0.813745
C	-2.425720	-0.767363	1.272689
C	5.692736	-1.409543	0.670260
C	6.274174	-2.602188	1.102117
C	5.483973	-3.619637	1.632468
C	3.526508	-2.249282	1.298533
C	4.103826	-3.439534	1.730734
H	6.325025	-0.614911	0.266584
H	7.356197	-2.733192	1.025568

H	5.942234	-4.551062	1.972626
H	2.442768	-2.113906	1.367134
H	3.476044	-4.230513	2.148176
C	4.663636	2.034250	-0.950476
C	5.468652	3.175822	-0.946947
C	6.129650	3.564481	0.214138
C	5.180467	1.668456	1.371981
C	5.981471	2.805320	1.376994
H	4.148725	1.745789	-1.869435
H	5.577622	3.762142	-1.862396
H	6.760534	4.456247	0.216561
H	5.076075	1.074571	2.284350
H	6.496628	3.101350	2.293905
C	-2.789703	-0.032484	2.406726
C	-2.003852	-0.063172	3.558604
C	-0.837031	-0.825476	3.589848
C	-1.258703	-1.538239	1.317969
C	-0.469087	-1.566100	2.466174
H	-3.700150	0.573623	2.387142
H	-2.307698	0.509823	4.438181
H	-0.221892	-0.853597	4.492301
H	-0.967770	-2.126295	0.442040
H	0.433717	-2.181315	2.491026
C	-4.733581	-2.409287	-1.196109
C	-5.758942	-3.350335	-1.249130
C	-6.437945	-3.707748	-0.084506
C	-5.053436	-2.178984	1.179068
C	-6.080677	-3.121129	1.128069
H	-4.205522	-2.133156	-2.114035
H	-6.025581	-3.810769	-2.203380
H	-7.239868	-4.448631	-0.121508
H	-4.775345	-1.739845	2.139374
H	-6.600795	-3.402799	2.046668
C	4.139256	-2.163904	-4.122783
H	3.732842	-3.104611	-4.520986
H	4.279228	-1.481184	-4.977156
H	5.129763	-2.365679	-3.692936
H	-7.365258	3.495450	-0.870544
H	-7.432385	2.063892	-1.920900
H	-7.684589	1.882549	-0.177632

BB2

F12Bup_x_GB.log -2045.6583939
F12Bup.log -2043.5127712 | | 0.726293 |256.791|
-2042.865842
State 1-A
NImag 1
PG C01 [X(C45H39F2N2)]
HF -2043.5127712
Low frequencies --- -62.5378 -3.8390

C	0.603052	-1.458902	-0.039656
C	0.905726	-0.504658	-1.990892
C	-0.400140	-0.294390	-1.625441
C	1.643072	-0.087474	-3.212309
C	-1.278483	0.542163	-2.483464
C	2.871933	-1.600622	-0.861519
C	-1.700006	-1.032841	0.597804
C	-1.497818	-1.805906	1.776410
C	-2.331297	-1.790332	2.874679
C	-3.490168	-1.019877	2.872598
C	-3.783840	-0.380349	1.676965
C	-2.968007	-0.396909	0.535940
C	-3.650797	0.204599	-0.685797
C	-3.660092	1.723757	-0.712882
C	-5.036325	-0.418582	-0.856345
H	2.668809	-0.480182	-3.187272
H	1.701777	1.008607	-3.296464
H	1.158595	-0.470823	-4.122066
H	-2.054406	-0.029205	-3.013264
H	-0.642377	0.990645	-3.256096
H	-1.745658	1.371330	-1.939862
F	-0.465742	-2.655706	1.906056
H	-2.045751	-2.418722	3.720653
H	-4.739077	0.139952	1.589395
H	-3.108078	-0.135182	-1.567132
N	1.500805	-1.222130	-0.979652
N	-0.595715	-0.938447	-0.368462
H	0.856571	-1.963540	0.877767
C	3.849903	-0.674021	-0.454316
C	5.157586	-1.133393	-0.329479
C	5.513862	-2.466985	-0.593673
C	3.216243	-2.923344	-1.125130
C	4.524693	-3.365713	-0.997167
C	3.447970	0.768824	-0.171475
H	5.929853	-0.427936	-0.015841
C	6.941250	-2.901542	-0.452568
H	4.749493	-4.411467	-1.214937
F	2.259040	-3.762976	-1.499273
C	4.639970	1.686289	0.045397
H	2.956152	1.132413	-1.089518
C	2.402323	0.856001	0.926736
C	-6.217295	0.266253	-0.554803
C	-7.455862	-0.358379	-0.704365
C	-7.530345	-1.673114	-1.158929
C	-5.122443	-1.738593	-1.314744
C	-6.357204	-2.363231	-1.465635
H	-6.172871	1.301907	-0.208611
H	-8.369608	0.191521	-0.466656
H	-8.501167	-2.159312	-1.278953
H	-4.206269	-2.289025	-1.551389
H	-6.405220	-3.392915	-1.827822
C	-3.153108	2.505025	0.328655
C	-3.147859	3.899195	0.241029
C	-3.649963	4.532310	-0.891957
C	-4.168497	2.374585	-1.848426
C	-4.162711	3.762608	-1.938562
H	-2.759690	2.020534	1.224134
H	-2.751556	4.491767	1.069466
H	-3.648029	5.622486	-0.960759
H	-4.581631	1.780087	-2.668248
H	-4.564837	4.249223	-2.830305
C	2.469247	0.054627	2.073429
C	1.477817	0.130738	3.052205
C	0.407574	1.012566	2.899233
C	1.332586	1.746714	0.791030
C	0.341790	1.825466	1.767916
H	3.297902	-0.649568	2.192220
H	1.541376	-0.504760	3.938829
H	-0.372105	1.067748	3.662447
H	1.273053	2.387288	-0.093643
H	-0.484991	2.527101	1.639621
C	5.313361	2.193714	-1.072818
C	6.434737	3.005479	-0.923417
C	6.899534	3.324292	0.352712
C	5.109736	2.015999	1.319753

C 6.233383 2.828897 1.471608
H 4.955476 1.945959 -2.077041
H 6.945544 3.395762 -1.806852
H 7.776582 3.964219 0.473645
H 4.589893 1.646901 2.206289
H 6.585644 3.081061 2.474594
C -4.382325 -0.931609 4.070047
H -4.513573 -1.915256 4.544287
H -3.945693 -0.261377 4.828527
H -5.373252 -0.538409 3.806359
H 7.055379 -3.986011 -0.579945
H 7.571848 -2.401967 -1.205126
H 7.339990 -2.624672 0.535037

H1

F12Fdn_x_GB.log -2045.6689696
F12Fdn.log -2043.5252257 | | 0.726790 |247.401| -2042.873868
State 1-A
NImag 1
PG C01 [X(C45H39F2N2)]
HF -2043.5252257
C 0.317113 0.841322 -0.849934
C -0.852803 2.680923 -1.153406
C 0.336461 3.043609 -0.573939
C -1.999676 3.503398 -1.609384
C 0.573598 4.436668 -0.102816
C -1.936600 0.534093 -1.779479
C 2.434941 1.602221 0.097005
C 3.255042 2.658260 0.541850
C 4.426282 2.484782 1.257958
C 4.904448 1.208236 1.522309
C 4.205495 0.157299 0.930954
C 3.027509 0.303876 0.192416
C 2.560155 -0.975417 -0.514392
C 1.540541 -1.777702 0.278188
C 3.742551 -1.837518 -0.951934
H -2.936768 2.937599 -1.531032
H -1.867850 3.804816 -2.660363
H -2.104124 4.407578 -0.998549
H 0.907945 4.468069 0.939695
H -0.389532 4.957325 -0.150044
H 1.289310 4.993988 -0.718293
F 2.961665 3.918489 0.248277
H 4.956604 3.386790 1.569844
H 4.625234 -0.846886 1.004608
H 2.100550 -0.675419 -1.470261
N -0.838652 1.308677 -1.295955
N 1.102194 1.850604 -0.428994
H 0.517625 -0.216105 -0.761007
C -2.771171 -0.218362 -0.929482
C -3.909414 -0.784772 -1.503865
C -4.223083 -0.655846 -2.865269
C -2.241629 0.661544 -3.134348
C -3.362541 0.070707 -3.690964
C -2.419014 -0.388589 0.548703
H -4.587509 -1.350638 -0.863470
C -5.447209 -1.314684 -3.425426
H -3.555785 0.203694 -4.757085
F -1.435361 1.401711 -3.889390
C -3.329240 -1.354994 1.299545
H -1.421404 -0.864031 0.571485
C -2.278865 0.957016 1.236121
C 4.081597 -3.029625 -0.305385
C 5.184935 -3.773185 -0.726205
C 5.958305 -3.336633 -1.799085
C 4.523618 -1.408661 -2.032300
C 5.623015 -2.150475 -2.453765
H 3.480528 -3.385076 0.534711
H 5.437496 -4.702989 -0.211127
H 6.819489 -3.921519 -2.130116
H 4.270362 -0.475875 -2.545404
H 6.220022 -1.803678 -3.300504
C 1.357321 -1.603836 1.653215
C 0.457428 -2.405975 2.358973
C -0.264933 -3.395385 1.698395
C 0.797838 -2.769142 -0.380708
C -0.090984 -3.574680 0.324327
H 1.932659 -0.841057 2.183239
H 0.324464 -2.256743 3.432918
H -0.971187 -4.019962 2.248691
H 0.944656 -2.927873 -1.453189
H -0.648501 -4.353879 -0.200854
C -3.265202 1.940064 1.098156
C -3.135470 3.172567 1.736825
C -2.011345 3.441992 2.517657
C -1.166019 1.229021 2.037793
C -1.027679 2.464665 2.669022
H -4.149298 1.733479 0.487850
H -3.918758 3.926612 1.626366
H -1.908392 4.408076 3.017502
H -0.400249 0.459066 2.165621
H -0.150131 2.661876 3.290106
C -3.393048 -2.694662 0.886725
C -4.183678 -3.618766 1.561976
C -4.923936 -3.222866 2.677405
C -4.071568 -0.972727 2.419634
C -4.862440 -1.899455 3.102526
H -2.816124 -3.014349 0.015874
H -4.221472 -4.655489 1.218130
H -5.544172 -3.946007 3.211922
H -4.030805 0.057649 2.776523
H -5.432947 -1.577775 3.976992
C 6.127497 0.972759 2.351078
H 6.826273 1.818824 2.292071
H 5.852142 0.848053 3.411538
H 6.654702 0.060497 2.038911
H -5.227854 -2.360988 -3.695442
H -6.264179 -1.332726 -2.690418
H -5.803420 -0.808092 -4.332794

H2

F12Fup_x_GB.log -2045.6719636
F12Fup.log -2043.5276052 | | 0.726060 |254.753| -2042.879879
State 1-A
NImag 1
PG C01 [X(C45H39F2N2)]
HF -2043.5276052
Low frequencies --- -69.8664 -1.9770
C 0.198938 1.013729 0.534400
C -1.125780 2.763810 0.636946
C 0.093479 3.196952 0.180023
C -2.377302 3.517046 0.912561
C 0.341169 4.642463 -0.080242
C -2.007096 0.526441 1.391316

C	2.353458	1.870325	-0.185970
C	3.153354	2.956371	-0.583144
C	4.536039	2.924501	-0.641529
C	5.220891	1.755056	-0.341268
C	4.438024	0.625446	-0.102338
C	3.041050	0.619711	-0.065021
C	2.409243	-0.778999	0.006916
C	2.003686	-1.205160	1.410344
C	3.276389	-1.822513	-0.692436
H	-3.144255	2.842045	1.316458
H	-2.778186	3.982922	-0.000056
H	-2.210339	4.312727	1.653652
H	1.180803	5.041414	0.500740
H	-0.561696	5.184042	0.226695
H	0.521317	4.864590	-1.138697
F	2.598710	4.101263	-0.964716
H	5.044474	3.842894	-0.941481
C	6.715541	1.691187	-0.314234
H	4.941982	-0.334926	0.017919
H	1.497006	-0.754897	-0.615813
N	-1.023796	1.404934	0.848482
N	0.938867	2.048529	0.109630
H	0.524373	0.000779	0.709339
C	-3.023895	-0.009617	0.587349
C	-3.937867	-0.872186	1.187547
C	-3.854259	-1.219928	2.545556
C	-1.913006	0.184377	2.738242
C	-2.822195	-0.684671	3.321170
C	-3.039639	0.312410	-0.898000
H	-4.740325	-1.290067	0.575381
C	-4.874792	-2.134446	3.153069
H	-2.710454	-0.929068	4.379127
F	-0.924727	0.702815	3.455754
C	-4.395444	0.056697	-1.536998
H	-2.858793	1.396039	-0.994770
C	-1.886756	-0.378013	-1.608455
C	3.881164	-2.880436	-0.010371
C	4.666360	-3.809679	-0.697011
C	4.855156	-3.691858	-2.070964
C	3.474535	-1.711063	-2.075776
C	4.255973	-2.635309	-2.760600
H	3.741465	-2.984229	1.067721
H	5.132781	-4.631117	-0.148059
H	5.468602	-4.419853	-2.606711
H	3.018461	-0.877078	-2.616184
H	4.400977	-2.532783	-3.838889
C	2.541344	-0.614012	2.557199
C	2.114367	-1.010245	3.825347
C	1.143546	-1.999537	3.962392
C	1.034994	-2.208920	1.559320
C	0.605311	-2.601367	2.823915
H	3.296241	0.169910	2.459364
H	2.541946	-0.536590	4.712011
H	0.806723	-2.303506	4.956139
H	0.613612	-2.679537	0.667278
H	-0.153514	-3.381379	2.921291
C	-1.498999	-1.682158	-1.277188
C	-0.481774	-2.322663	-1.984868
C	0.170631	-1.663740	-3.026426
C	-1.216421	0.278857	-2.646572
C	-0.193200	-0.356298	-3.349033
H	-2.005239	-2.205095	-0.461359
H	-0.198101	-3.346276	-1.727429
H	0.962201	-2.170976	-3.581227
H	-1.511770	1.296499	-2.918548
H	0.313687	0.169024	-4.162269
C	-5.436290	0.958526	-1.279607
C	-6.706407	0.753054	-1.809480
C	-6.955711	-0.362186	-2.610800
C	-4.652589	-1.053588	-2.344666
C	-5.926252	-1.261243	-2.877336
H	-5.248411	1.834137	-0.650212
H	-7.505550	1.468349	-1.600961
H	-7.950710	-0.524815	-3.031346
H	-3.852029	-1.760951	-2.571508
H	-6.110373	-2.132408	-3.510478
H	7.081750	0.727021	-0.694727
H	7.167857	2.497023	-0.908244
H	7.083087	1.795875	0.719993
H	-4.526122	-2.565839	4.101040
H	-5.805969	-1.582011	3.360245
H	-5.132654	-2.955555	2.468789

1f·X

1f

M2_x_GB.log -1925.9034525
M2.log -1923.9206662 | | 0.797152 |263.881| -1923.203572
State 1-A
NImag 0
PG C01 [X(C47H45N2)]
HF -1923.9206662
Low frequencies --- -4.2439 -0.0008

C	0.035527	1.697882	-0.635931
C	0.790220	2.211298	1.387814
C	-0.581037	2.221876	1.434742
C	1.811805	2.447907	2.434992
C	-1.515011	2.494427	2.551550
C	2.490467	1.838243	-0.406027
C	-2.396017	1.827048	-0.249028
C	3.068426	3.041112	-0.836875
C	4.395416	2.996261	-1.267081
C	5.134013	1.808357	-1.264285
C	4.509705	0.633413	-0.831319
C	3.184637	0.621001	-0.397682
C	2.477492	-0.664615	-0.007197
H	2.447978	1.559710	2.570591
H	-2.038855	1.576591	2.857924
H	1.329397	2.675374	3.393045
H	-0.966574	2.885698	3.416797
H	2.476732	3.284024	2.170261
H	-2.278124	3.231274	2.261187
C	2.283195	4.320692	-0.847830
H	4.867522	3.920060	-1.612295
C	6.571862	1.794196	-1.688894
H	5.071139	-0.303488	-0.827284
N	1.141210	1.883006	0.083728
N	-1.019082	1.893484	0.156234
C	3.418472	-1.685403	0.608296
H	1.756573	-0.400207	0.786138
C	1.654016	-1.237012	-1.156173
C	3.708489	-1.619492	1.975341

C	4.597618	-2.517970	2.560832
C	5.211327	-3.498390	1.781682
C	4.032951	-2.676957	-0.163391
C	4.925721	-3.575715	0.419452
H	3.227676	-0.854212	2.593253
H	4.809164	-2.456285	3.630973
H	5.906591	-4.206529	2.238291
H	3.800492	-2.753407	-1.228761
H	5.396753	-4.346213	-0.195530
C	1.718233	-0.734717	-2.459615
C	0.938470	-1.293027	-3.477030
C	0.089365	-2.361406	-3.204419
C	0.803997	-2.323294	-0.898605
C	0.026781	-2.879482	-1.909247
H	2.394299	0.091564	-2.692978
H	1.007950	-0.892520	-4.491503
H	-0.523271	-2.797065	-3.996701
H	0.766322	-2.751663	0.106799
H	-0.642129	-3.713615	-1.684607
C	-3.029126	3.032285	-0.590906
C	-4.385520	2.978742	-0.910959
C	-5.101093	1.776605	-0.893767
C	-4.419330	0.599038	-0.573689
C	-3.060495	0.592369	-0.251889
C	-2.330838	-0.689827	0.120270
C	-2.266798	4.325325	-0.630547
H	-4.898535	3.904522	-1.185258
C	-6.569335	1.753661	-1.197511
H	-4.956681	-0.351993	-0.591069
C	-2.894159	-1.934481	-0.552370
H	-1.300698	-0.608518	-0.267092
C	-2.207602	-0.806746	1.629613
C	-3.138293	-1.919789	-1.933107
C	-3.564885	-3.065831	-2.596268
C	-3.744327	-4.257608	-1.891501
C	-3.079167	-3.131265	0.144049
C	-3.498735	-4.285427	-0.521218
H	-2.983960	-0.997459	-2.499192
H	-3.752850	-3.031732	-3.672280
H	-4.077119	-5.159505	-2.410365
H	-2.886991	-3.170421	1.218085
H	-3.636178	-5.211705	0.041655
C	-3.329104	-0.690852	2.460357
C	-3.201522	-0.793515	3.844542
C	-1.948449	-1.008822	4.421288
C	-0.960560	-1.034617	2.218487
C	-0.826581	-1.132045	3.603209
H	-4.312597	-0.512323	2.018463
H	-4.086619	-0.702407	4.478589
H	-1.849806	-1.086574	5.506477
H	-0.081096	-1.140861	1.579181
H	0.157784	-1.313327	4.042201
H	0.003626	1.416026	-1.686061
H	-6.884679	0.779835	-1.597231
H	-7.154330	1.938462	-0.281227
H	-6.845019	2.532804	-1.922192
H	-2.925064	5.160981	-0.900110
H	-1.802851	4.563361	0.339792
H	-1.453296	4.289318	-1.373437
H	2.903552	5.159936	-1.187068
H	1.414601	4.254269	-1.523186
H	1.892559	4.573724	0.150804
H	6.835910	0.850287	-2.186435
H	6.803713	2.623995	-2.370823
H	7.230785	1.894201	-0.810485

BB1

M12Bdn_x_GB.log -1925.8365635
M12Bdn.log -1923.851383 | | 0.798097 |256.159| -1923.131301
State 1-A
NImag 1
PG C01 [X(C47H45N2)]
HF -1923.851383
Low frequencies --- -37.2376 -3.4350

C	-0.531936	-1.625900	-0.262420
C	0.590848	-0.442418	-1.743561
C	-0.727427	-0.494768	-2.128434
C	1.604828	0.145986	-2.655403
C	-1.405473	0.102814	-3.305210
C	1.777612	-1.469765	0.424033
C	-2.805652	-1.506170	-1.119050
C	1.434541	-2.160761	1.624408
C	2.433468	-2.868087	2.301084
C	3.764630	-2.855871	1.907310
C	4.094807	-1.916290	0.932558
C	3.156553	-1.159341	0.228324
C	3.689348	0.091007	-0.476522
H	2.030894	1.084313	-2.281356
H	-2.476253	-0.137536	-3.288110
H	1.092261	0.384251	-3.594806
H	-1.312245	1.199010	-3.289760
H	2.403458	-0.565161	-2.904407
H	-0.982296	-0.273996	-4.248673
C	0.125349	-2.083856	2.389326
H	2.145397	-3.425207	3.197087
C	4.803949	-3.711107	2.559951
H	5.149549	-1.716099	0.742221
N	0.694827	-1.127687	-0.504094
N	-1.397086	-1.237598	-1.185311
C	5.207919	0.202157	-0.455779
H	3.443641	0.042376	-1.536071
C	3.061325	1.371613	0.068909
C	5.952759	-0.346156	-1.505498
C	7.344787	-0.273640	-1.507540
C	8.011330	0.352468	-0.455270
C	5.886340	0.835716	0.591678
C	7.277897	0.907351	0.593264
H	5.436899	-0.843179	-2.332946
H	7.910756	-0.703625	-2.337306
H	9.102026	0.414269	-0.455790
H	5.318675	1.280907	1.412497
H	7.793260	1.406326	1.417406
C	2.412108	1.451386	1.305008
C	1.902168	2.667039	1.768041
C	2.039057	3.824534	1.006565
C	3.211281	2.550165	-0.677986
C	2.704136	3.762265	-0.219648
H	2.314332	0.561538	1.929456
H	1.403838	2.707890	2.739779
H	1.641598	4.774455	1.371191
H	3.762712	2.519915	-1.622946
H	2.838184	4.666791	-0.818042
C	-3.332159	-2.537044	-1.906609
C	-4.709652	-2.759491	-1.832638

C -5.538924 -1.995166 -1.007526
C -4.963486 -0.978869 -0.234227
C -3.596824 -0.710875 -0.272330
C -2.976194 0.433368 0.520052
C -2.453601 -3.359484 -2.803312
H -5.145363 -3.559218 -2.437462
C -7.010661 -2.268705 -0.921113
H -5.595949 -0.378599 0.424528
C -3.806677 0.827766 1.731969
H -2.022633 0.064404 0.931797
C -2.613888 1.587253 -0.398857
C -3.898262 -0.078013 2.798238
C -4.651268 0.221448 3.928791
C -5.327304 1.440092 4.013716
C -4.480415 2.046764 1.829533
C -5.237524 2.349265 2.963498
H -3.377806 -1.039118 2.734657
H -4.710941 -0.497083 4.749832
H -5.918788 1.679580 4.900364
H -4.410280 2.774800 1.018878
H -5.757352 3.308368 3.023788
C -3.512634 2.055599 -1.365150
C -3.173307 3.124689 -2.193104
C -1.921141 3.729468 -2.078870
C -1.364825 2.206798 -0.286757
C -1.015689 3.265125 -1.124311
H -4.489330 1.575936 -1.471804
H -3.889520 3.483700 -2.936124
H -1.653070 4.563958 -2.731187
H -0.646043 1.860447 0.462284
H -0.030766 3.725746 -1.020639
H -0.806029 -2.303528 0.529012
H -2.992357 -4.236541 -3.184249
H -2.113137 -2.776505 -3.674908
H -1.551930 -3.715326 -2.281757
H -7.245165 -2.820814 0.003759
H -7.590089 -1.334370 -0.893840
H -7.364959 -2.872085 -1.767901
H 0.361926 -2.109958 3.461517
H -0.422816 -1.147291 2.211310
H -0.562482 -2.929282 2.213462
H 5.767696 -3.187323 2.635382
H 4.498037 -4.029084 3.566540
H 4.975577 -4.623216 1.964373

BB2

M12Bup_x_GB.log -1925.8368089
M12Bup.log -1923.8515367 | | 0.797707 |259.041|
-1923.132957
State 1-A
NImag 1
PG C01 [X(C47H45N2)]
HF -1923.8515367
Low frequencies --- -41.4575 -3.5759
C -0.574352 0.685396 0.779230
C 0.408262 0.911977 -1.179556
C -0.853388 1.450000 -1.254795
C 1.208311 0.718339 -2.416085
C -1.570942 2.072142 -2.398430
C 1.655817 -0.232589 0.884068
C -2.794720 1.588870 0.345682
C 1.454355 -0.491438 2.270206
C 2.190138 -1.513807 2.877816
C 3.166828 -2.237550 2.208685
C 3.542728 -1.734012 0.964160
C 2.877473 -0.696030 0.308708
C 3.656386 0.008689 -0.807694
H 2.102372 1.349948 -2.466440
H -2.509512 2.526371 -2.051893
H 0.569982 0.996949 -3.263257
H -0.965044 2.857886 -2.870850
H 1.478902 -0.335802 -2.562147
H -1.825444 1.329708 -3.171704
C 0.621378 0.316602 3.244955
H 1.991901 -1.726601 3.932071
C 3.859301 -3.413816 2.821788
H 4.447083 -2.127716 0.499098
N 0.600708 0.479008 0.159133
N -1.440002 1.285801 -0.020298
C 5.007706 -0.629772 -1.100565
H 3.114723 -0.087910 -1.747779
C 3.830132 1.500777 -0.540443
C 5.103037 -1.615911 -2.088391
C 6.322152 -2.230643 -2.369665
C 7.466634 -1.862450 -1.664004
C 6.164356 -0.260884 -0.404591
C 7.383857 -0.875021 -0.682272
H 4.207807 -1.912477 -2.643893
H 6.379125 -2.996088 -3.147243
H 8.424655 -2.338841 -1.884681
H 6.110257 0.519614 0.358320
H 8.278686 -0.574625 -0.131953
C 3.738514 2.073399 0.732185
C 3.959936 3.439917 0.917631
C 4.278148 4.255762 -0.164525
C 4.180328 2.329543 -1.616936
C 4.393995 3.692529 -1.436217
H 3.509358 1.447857 1.596952
H 3.891259 3.865460 1.921884
H 4.450276 5.324526 -0.018017
H 4.314586 1.891124 -2.610986
H 4.663982 4.317533 -2.290823
C -3.049497 2.786434 1.022169
C -4.375396 3.051990 1.378625
C -5.412199 2.166960 1.076091
C -5.106430 0.981477 0.392587
C -3.804253 0.668218 0.014146
C -3.448254 -0.631633 -0.699366
C -1.940856 3.741645 1.356630
H -4.601085 3.982590 1.906039
C -6.830909 2.469179 1.455522
H -5.907670 0.282084 0.142503
C -4.660329 -1.337922 -1.283521
H -2.821549 -0.355888 -1.563970
C -2.580063 -1.511146 0.183566
C -5.230794 -0.825327 -2.456085
C -6.362322 -1.410983 -3.015542
C -6.942301 -2.526032 -2.408869
C -5.244576 -2.457604 -0.686637
C -6.379610 -3.046919 -1.246370
H -4.783620 0.052042 -2.933964
H -6.792348 -0.999135 -3.931656
H -7.828516 -2.990855 -2.846953
H -4.807932 -2.884104 0.219005
H -6.822541 -3.924459 -0.769456

C -2.833989 -1.644250 1.554156
C -1.997364 -2.417837 2.359656
C -0.890770 -3.062876 1.806517
C -1.480811 -2.182350 -0.364181
C -0.636640 -2.946095 0.440241
H -3.687894 -1.124424 1.997404
H -2.212768 -2.517810 3.426553
H -0.226768 -3.656781 2.438157
H -1.278217 -2.094299 -1.435782
H 0.229949 -3.446171 0.001175
H -0.855990 0.326129 1.755189
H -2.340370 4.688777 1.741102
H -1.272094 3.327363 2.129120
H -1.315538 3.967709 0.479001
H -7.267476 1.643944 2.038688
H -6.909428 3.388851 2.050590
H -7.455704 2.591477 0.556581
H 1.144457 0.322416 4.210780
H 0.502058 1.366230 2.940998
H -0.377136 -0.111602 3.440508
H 4.929090 -3.428965 2.567609
H 3.760451 -3.420903 3.916319
H 3.424710 -4.354493 2.444283

H1

M12Fdn_x_GB.log -1925.843934
M12Fdn.log -1923.8595906 | | 0.798262 |253.754|
-1923.138295
State 1-A
NImag 1
PG C01 [X(C47H45N2)]
HF -1923.8595906
Low frequencies --- -52.2838 -3.5762
C -0.284038 0.620325 0.910533
C 0.803494 2.303627 1.806736
C -0.355673 2.799068 1.262987
C 1.908733 3.020707 2.491407
C -0.576895 4.263480 1.143361
C 1.919381 0.061908 1.835904
C -2.296360 1.565202 -0.047296
C -3.067349 2.662244 -0.513171
C -3.895203 2.456067 -1.622511
C -4.104394 1.212028 -2.208014
C -3.595553 0.124030 -1.502860
C -2.738062 0.258197 -0.410843
C -2.536085 -1.019457 0.419401
C -1.535143 -2.022305 -0.135137
C -3.900081 -1.653707 0.684876
H 2.762257 2.349665 2.651775
H 1.588663 3.416785 3.467102
H 2.260340 3.862485 1.878783
H -0.835434 4.545605 0.118157
H 0.376729 4.753278 1.373225
H -1.326394 4.669430 1.833319
C -3.294886 3.977628 0.189971
H -4.453897 3.318283 -1.998786
H -3.928228 -0.882098 -1.769253
H -2.176644 -0.719389 1.417441
N 0.821548 0.946510 1.561031
N -1.072881 1.698221 0.736678
H -0.438646 -0.370789 0.502208
C 2.753716 -0.364745 0.782099
C 3.881634 -1.103286 1.132475
C 4.172642 -1.446862 2.459416
C 2.146953 -0.291653 3.172212
C 3.282646 -1.054833 3.458546
C 2.392028 -0.096665 -0.681105
H 4.554414 -1.436747 0.340228
C 5.413751 -2.225101 2.779137
H 3.473664 -1.345468 4.495051
C 1.213720 0.135256 4.268248
C 3.329716 -0.781738 -1.669268
H 1.416076 -0.589496 -0.838571
C 2.188143 1.373624 -0.986602
C -4.307460 -2.846126 0.080853
C -5.577575 -3.367598 0.331928
C -6.451263 -2.706674 1.191570
C -4.784747 -0.997320 1.549912
C -6.049528 -1.517995 1.803428
H -3.627430 -3.378016 -0.588696
H -5.881990 -4.301040 -0.147355
H -7.443728 -3.117851 1.389707
H -4.478452 -0.059652 2.023783
H -6.726663 -0.995775 2.483547
C -1.126955 -2.034308 -1.473897
C -0.260545 -3.022671 -1.944867
C 0.214112 -4.007453 -1.081790
C -1.028851 -3.004735 0.728973
C -0.161921 -3.988047 0.262346
H -1.494539 -1.270571 -2.162582
H 0.045580 -3.018718 -2.993464
H 0.883243 -4.787144 -1.453461
H -1.338794 -3.007861 1.778145
H 0.214885 -4.749792 0.948769
C 3.107072 2.340055 -0.562206
C 2.925329 3.684569 -0.885540
C 1.811325 4.083904 -1.624307
C 1.081360 1.783807 -1.737491
C 0.887197 3.128643 -2.048223
H 3.976447 2.032138 0.025943
H 3.661239 4.425251 -0.561986
H 1.670021 5.137213 -1.878287
H 0.361112 1.036968 -2.085380
H 0.014243 3.428467 -2.633717
C 3.245477 -2.173933 -1.811377
C 4.079282 -2.857528 -2.690634
C 5.015736 -2.156748 -3.452121
C 4.267323 -0.089635 -2.439640
C 5.104771 -0.773506 -3.323283
H 2.517437 -2.726022 -1.212584
H 3.996925 -3.943250 -2.785194
H 5.670267 -2.688507 -4.146555
H 4.343686 0.996567 -2.366206
H 5.829436 -0.213920 -3.919478
C -4.926810 1.036523 -3.445793
H -5.613968 1.879857 -3.601570
H -4.275475 0.975404 -4.333587
H -5.516273 0.108970 -3.410005
H 5.416508 -2.583277 3.817471
H 5.520064 -3.094155 2.112735
H 6.309922 -1.599769 2.636745
H 1.319312 -0.518633 5.143970
H 1.427187 1.163162 4.604063
H 0.161481 0.109628 3.948719
H -4.371141 4.192865 0.132980

H -3.046079 3.931774 1.253638
H -2.779012 4.833461 -0.264801

H2

M12Fup_x_GB.log -1925.8471999
M12Fup.log -1923.86296 | | 0.798059 |256.091| -1923.142738
State 1-A
NImag 1
PG C01 [X(C47H45N2)]
HF -1923.86296
Low frequencies --- -78.1197 -5.3997
C 0.286427 0.973725 0.909975
C -1.139390 2.635352 0.990806
C 0.071722 3.143004 0.585239
C -2.425608 3.324669 1.277991
C 0.259117 4.611229 0.442658
C -1.943331 0.303774 1.580681
C 2.415321 1.894658 0.242635
C 3.307212 2.982632 0.052005
C 4.675938 2.761329 0.243104
C 5.227312 1.513526 0.505387
C 4.353561 0.437574 0.389056
C 2.974809 0.578035 0.220152
C 2.259891 -0.736087 -0.138342
C 1.886912 -1.602937 1.060825
C 3.069745 -1.495040 -1.189323
H -3.161561 2.602810 1.657277
H -2.846155 3.801711 0.380117
H -2.296585 4.102460 2.045581
H 1.073539 4.990014 1.069664
H -0.663054 5.090996 0.791890
H 0.420034 4.946061 -0.588486
C 2.991533 4.338414 -0.526099
H 5.343591 3.619852 0.127676
C 6.684146 1.321435 0.788209
H 4.762968 -0.575428 0.367299
H 1.321712 -0.487309 -0.664817
N -0.971459 1.280265 1.175371
N 0.979532 2.050996 0.507807
H 0.674872 -0.014440 1.112602
C -2.920664 -0.097777 0.653831
C -3.820114 -1.083186 1.052760
C -3.757479 -1.669013 2.323839
C -1.841633 -0.249053 2.863028
C -2.765630 -1.239966 3.207731
C -2.935926 0.480199 -0.755148
H -4.595889 -1.398296 0.350407
C -4.757749 -2.711806 2.724786
H -2.705280 -1.686512 4.203844
C -0.764309 0.163498 3.822800
C -4.313301 0.424255 -1.403376
H -2.699480 1.552144 -0.675589
C -1.824688 -0.127550 -1.592187
C 3.458910 -2.825976 -1.028297
C 4.164651 -3.486043 -2.037685
C 4.491640 -2.823526 -3.216741
C 3.408655 -0.834705 -2.379212
C 4.112002 -1.489414 -3.383674
H 3.211512 -3.360027 -0.108780
H 4.461520 -4.527650 -1.893940
H 5.044643 -3.340691 -4.004197
H 3.119479 0.211489 -2.511981
H 4.368027 -0.958059 -4.303648
C 2.591951 -1.571415 2.269892
C 2.207287 -2.380751 3.340232
C 1.105126 -3.225714 3.224241
C 0.780948 -2.460140 0.956981
C 0.389525 -3.260347 2.027045
H 3.445942 -0.902003 2.387569
H 2.773410 -2.344161 4.274012
H 0.802450 -3.853649 4.065421
H 0.214995 -2.484885 0.022952
H -0.481494 -3.911742 1.925231
C -1.650691 -1.514533 -1.674953
C -0.658894 -2.060070 -2.489157
C 0.186663 -1.227013 -3.221532
C -0.969700 0.699010 -2.329381
C 0.031125 0.155708 -3.135191
H -2.305617 -2.173963 -1.099150
H -0.540289 -3.144584 -2.550542
H 0.971777 -1.654889 -3.847674
H -1.099918 1.784638 -2.281596
H 0.688369 0.816577 -3.705648
C -5.358006 1.143539 -0.804876
C -6.635619 1.140721 -1.354012
C -6.892483 0.416978 -2.520197
C -4.578814 -0.290112 -2.573123
C -5.861514 -0.294339 -3.126406
H -5.167042 1.707577 0.113233
H -7.436203 1.707468 -0.872589
H -7.894538 0.413174 -2.955145
H -3.779129 -0.844753 -3.067531
H -6.050235 -0.858278 -4.042957
H 7.065993 0.401099 0.322948
H 7.284367 2.168630 0.428393
H 6.856076 1.233819 1.873853
H 3.851781 4.648262 -1.134441
H 2.131208 4.312200 -1.200572
H 2.840969 5.126700 0.222570
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H 0.169009 -0.390389 3.624754
H -0.535467 1.237452 3.757769
H -4.441992 -3.257064 3.624631
H -5.733281 -2.246665 2.941481
H -4.922443 -3.440128 1.917018

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VIII NMR Spectra of new compounds

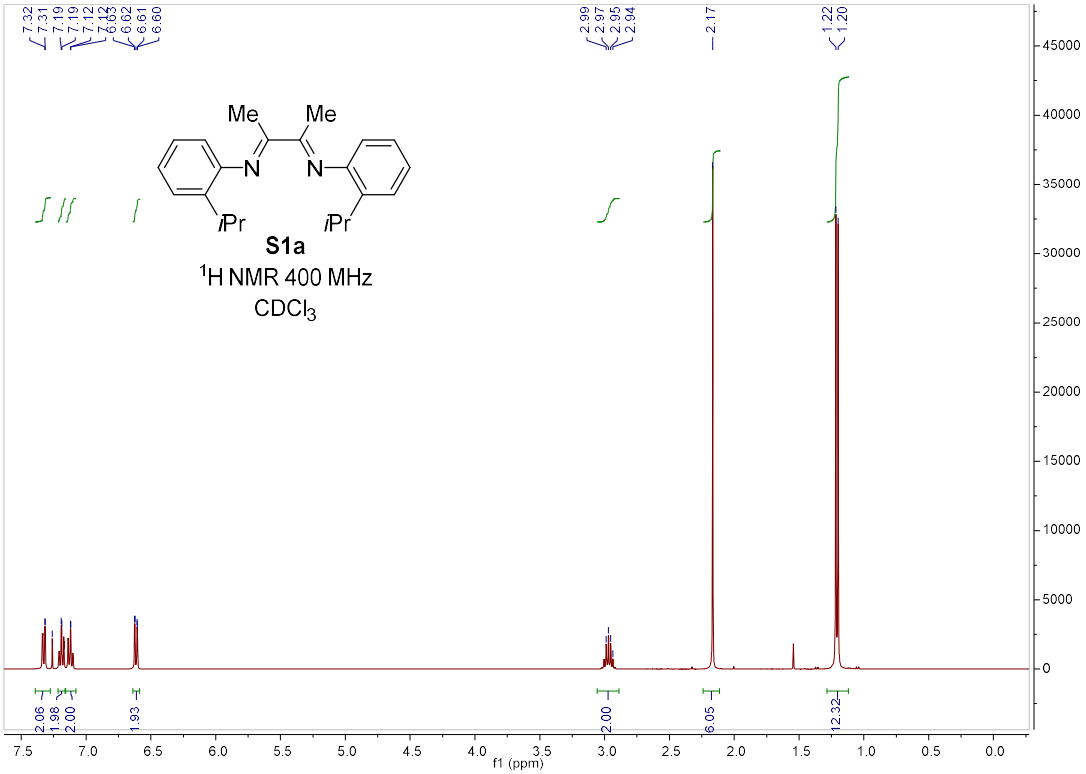

Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of diimine **S1a**

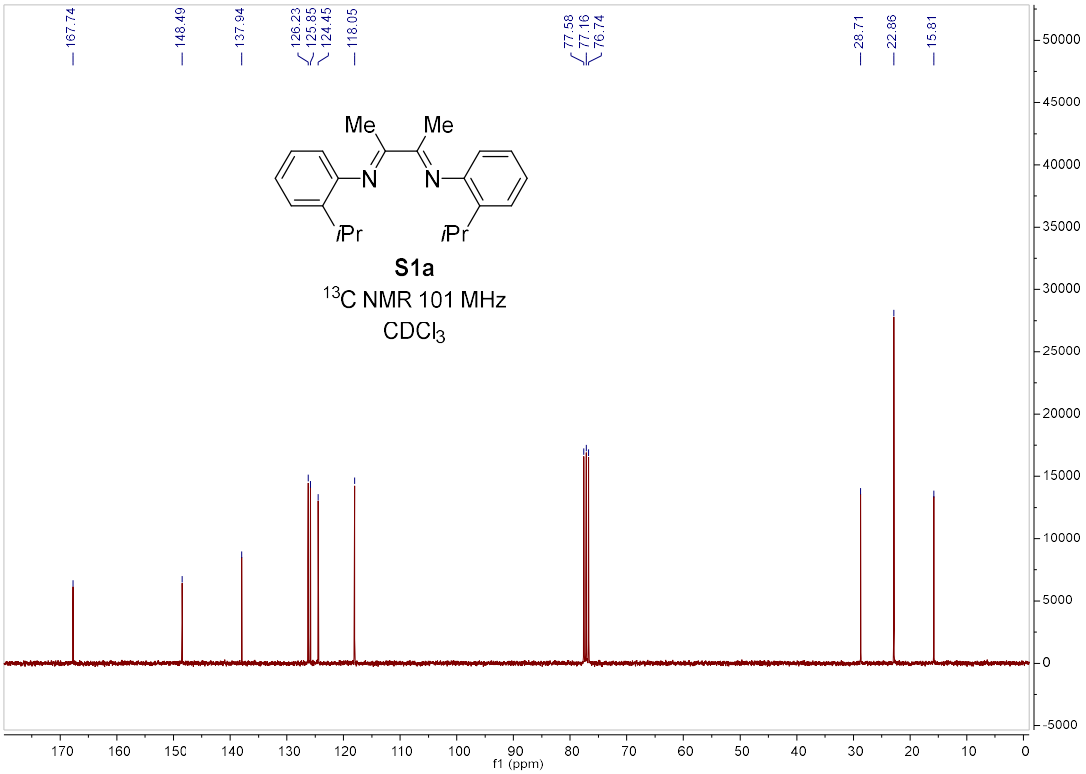

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of diimine **S1a**

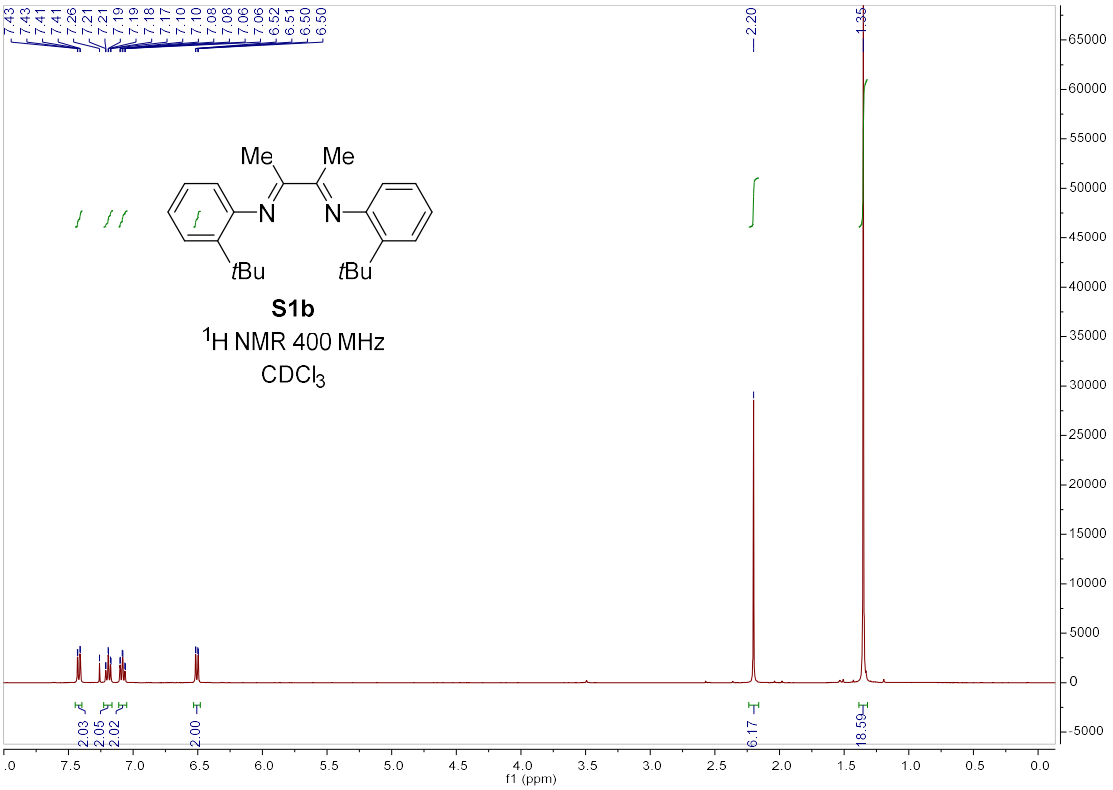

Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of diimine **S1b**

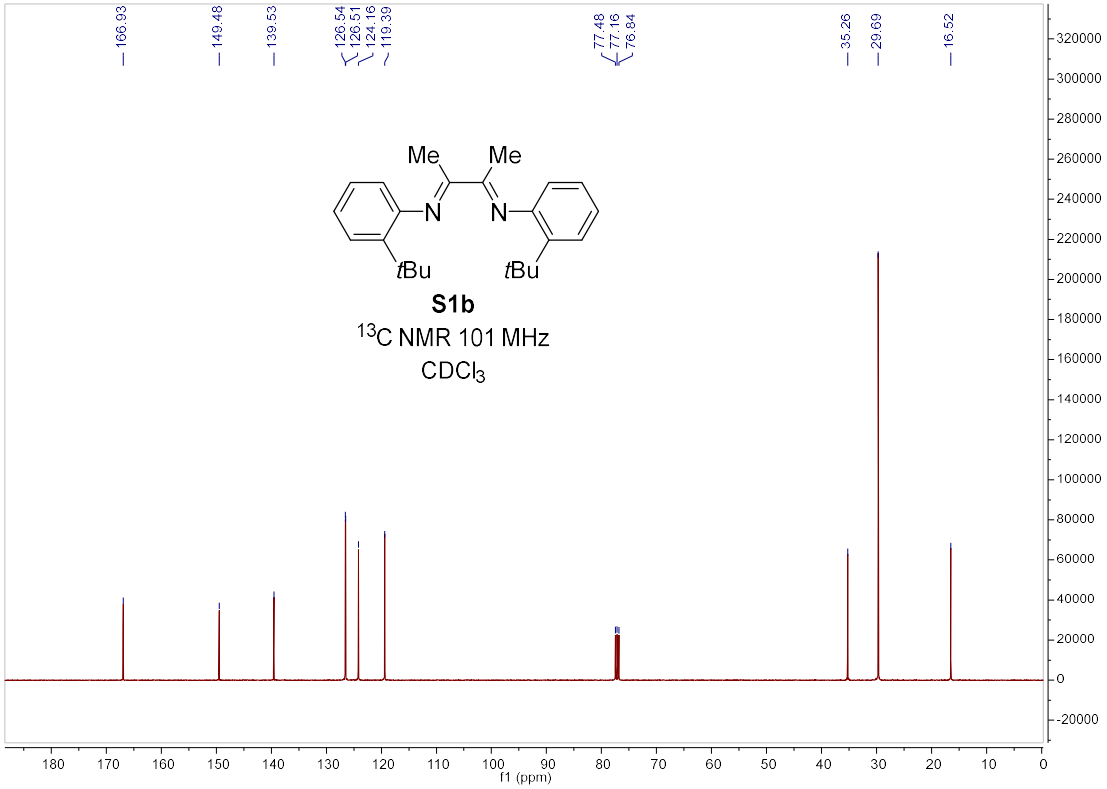

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of diamine **S1b**

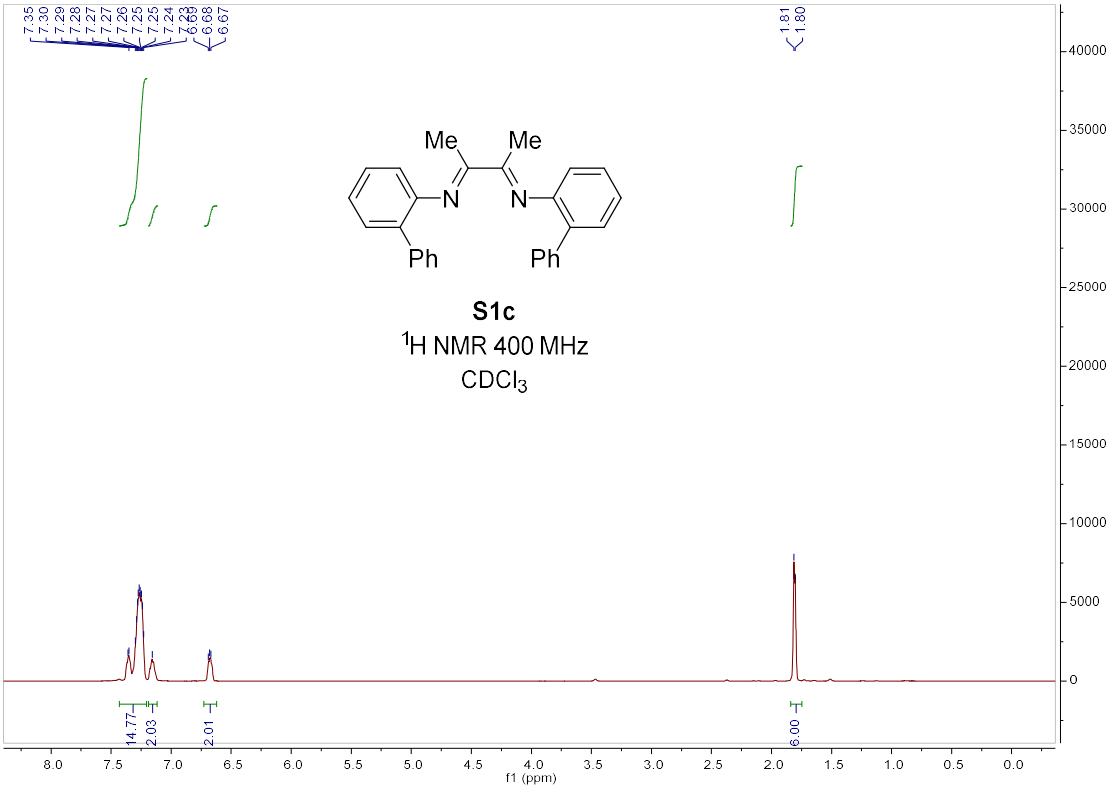

Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of diimine **S1c**

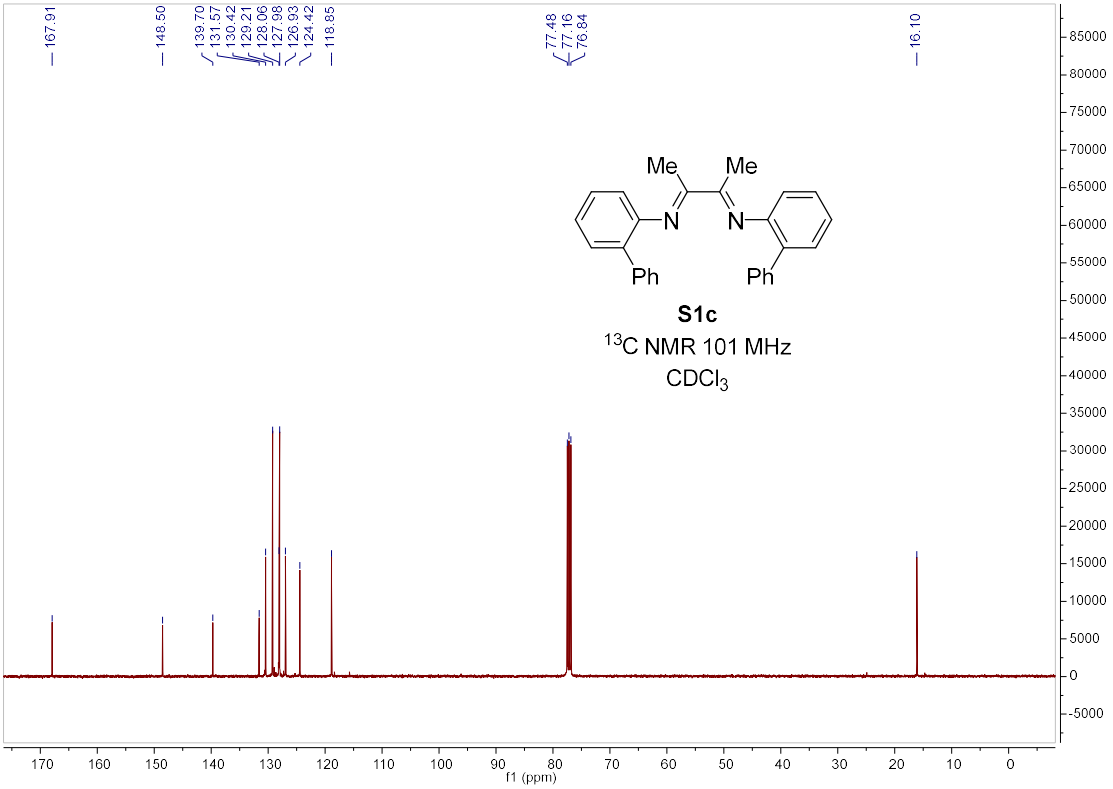

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of diimine **S1c**

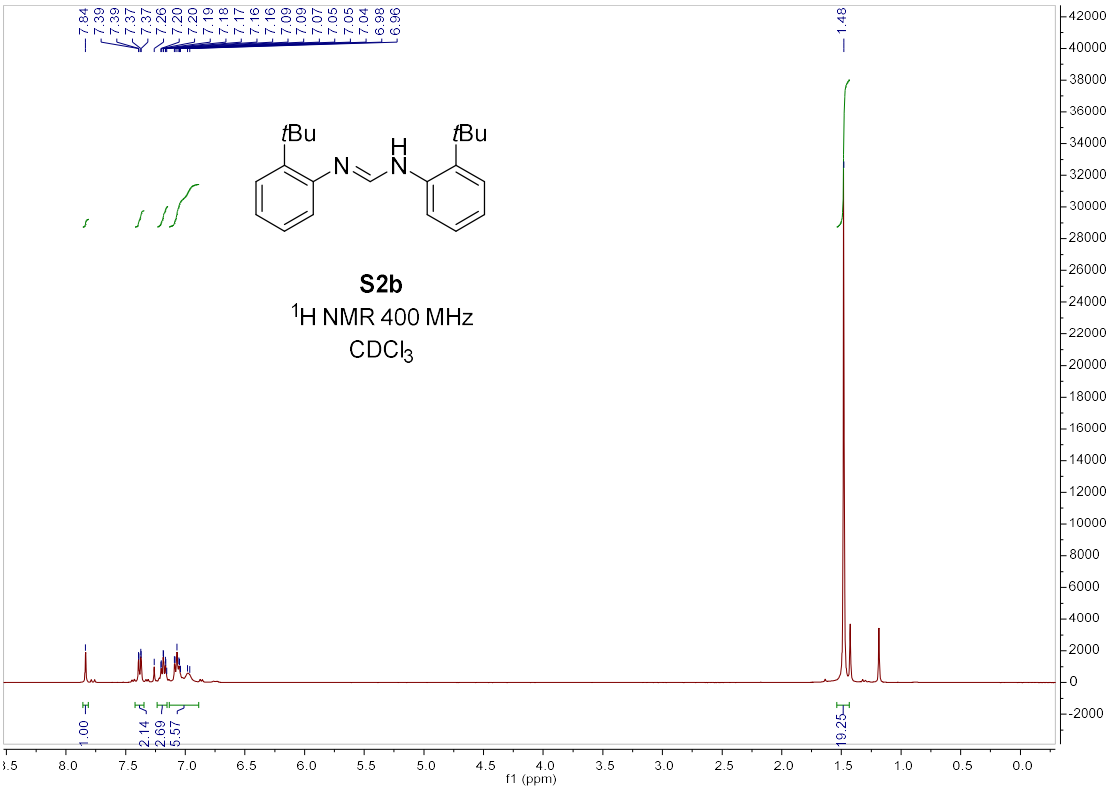

Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of formamidine **S2b**

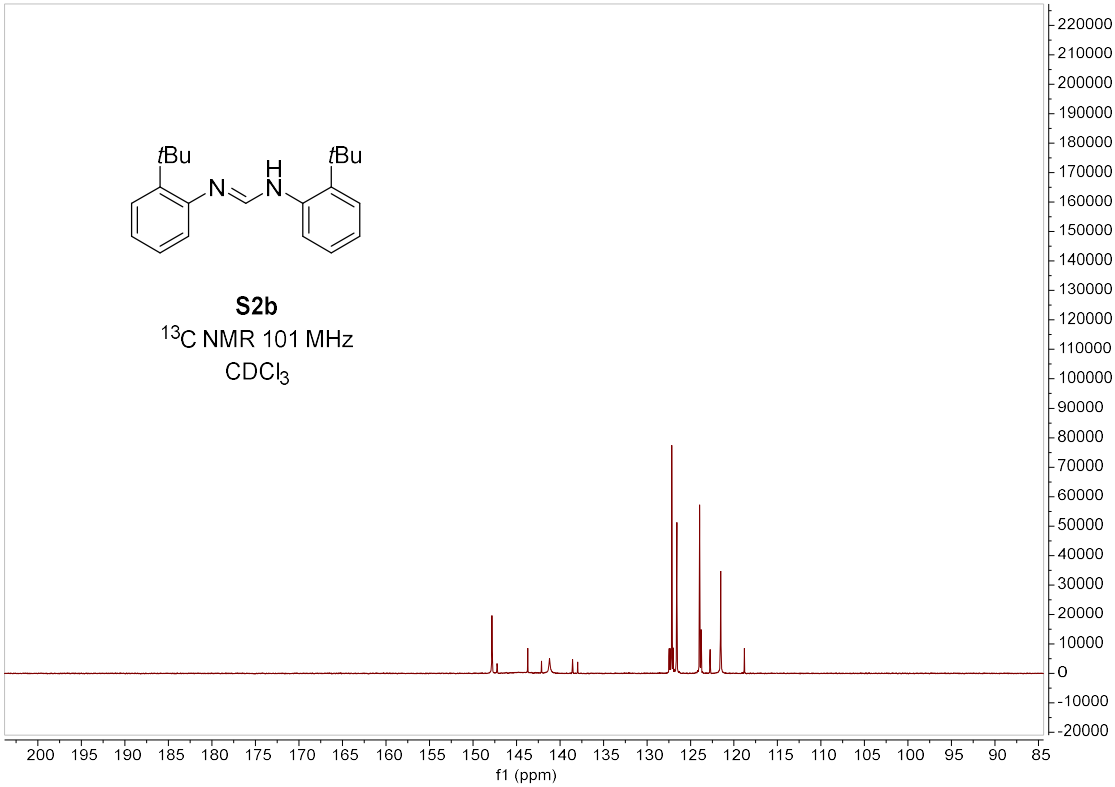

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of formamidine **S2b**

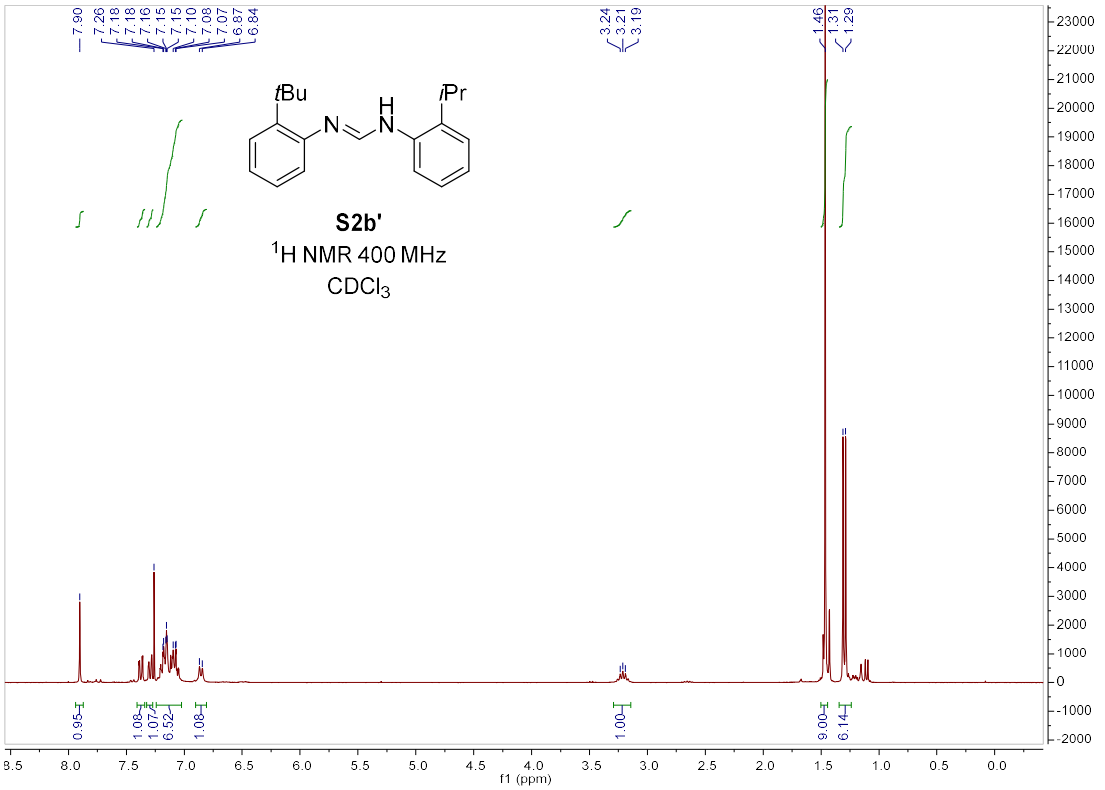

Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of formamidine **S2b'**

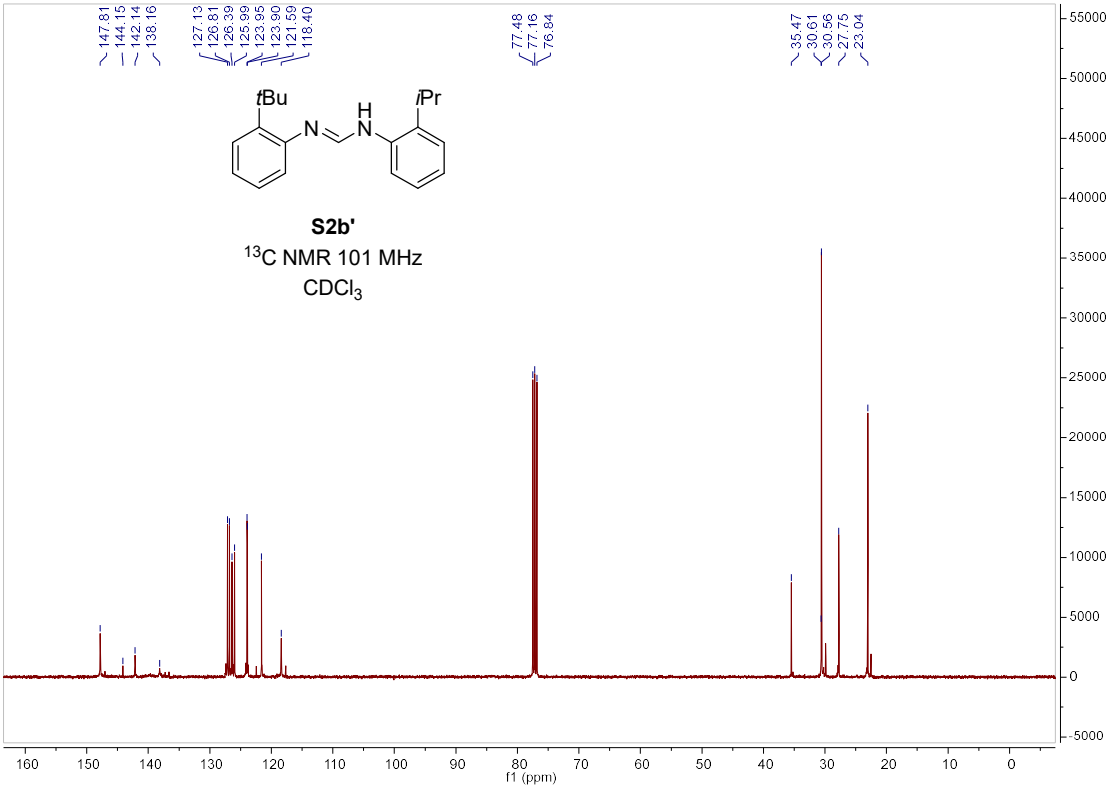

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of formamidine **S2b'**

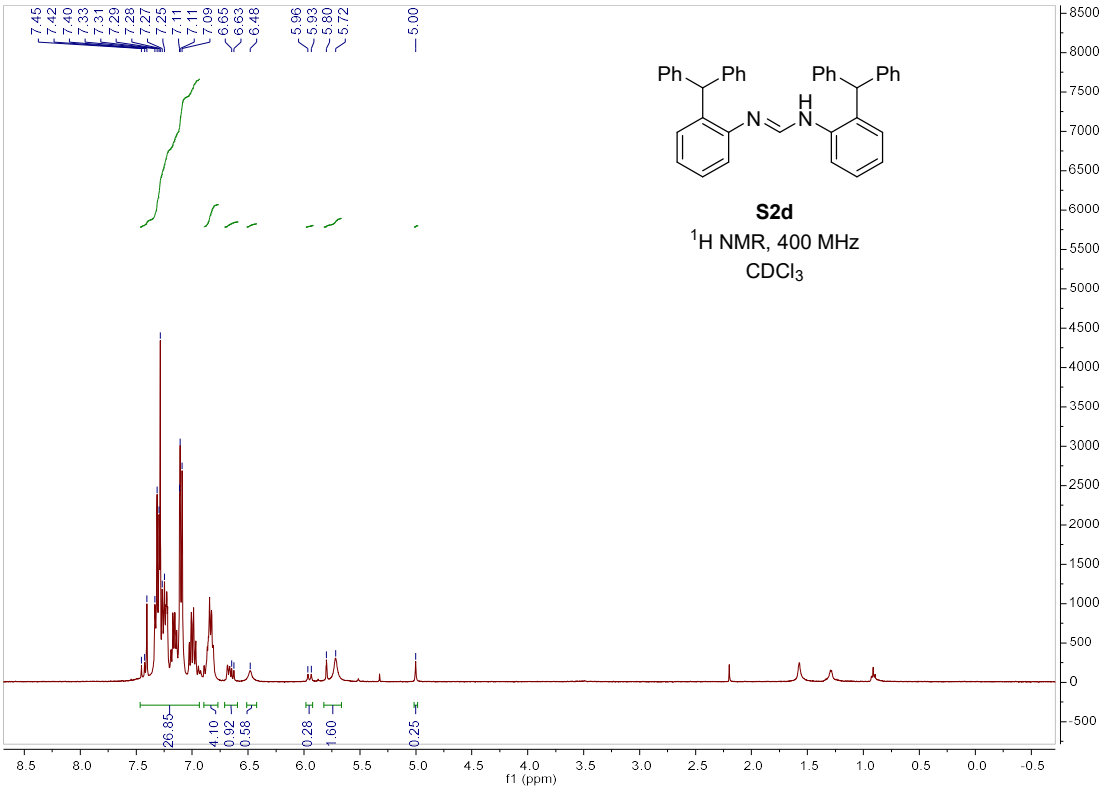

Figure S52. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of formamidine **S2d**

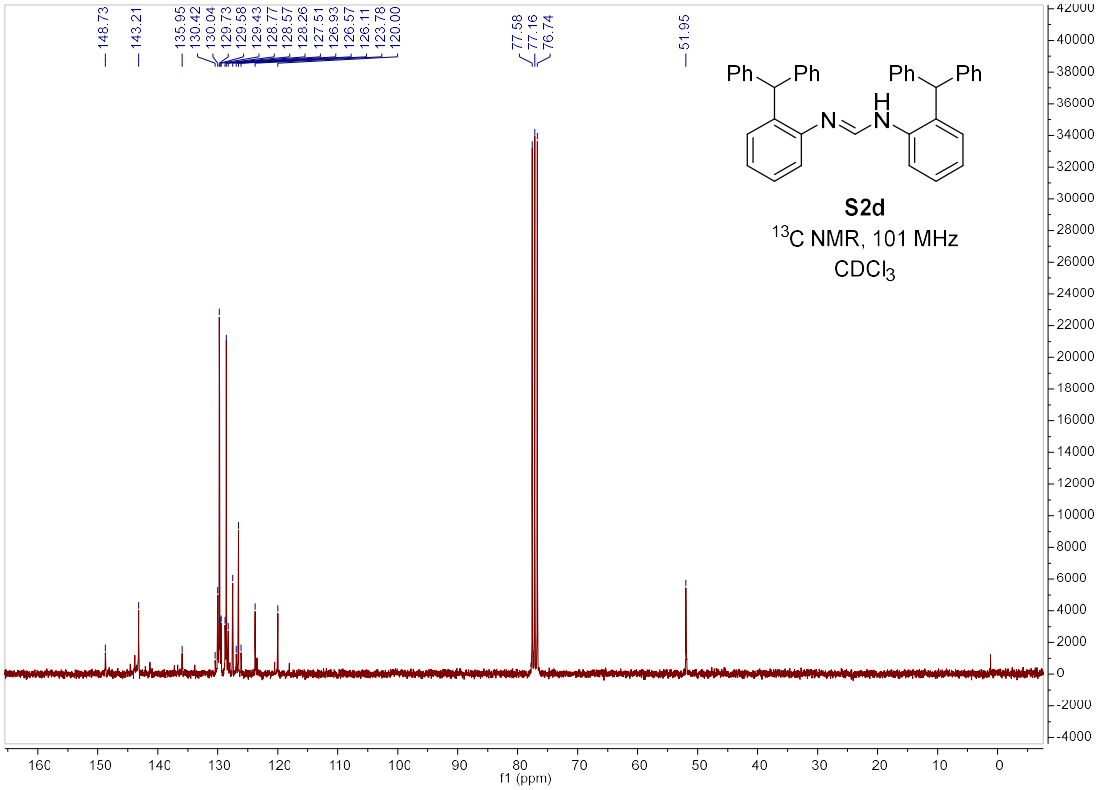

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of formamidine **S2d**

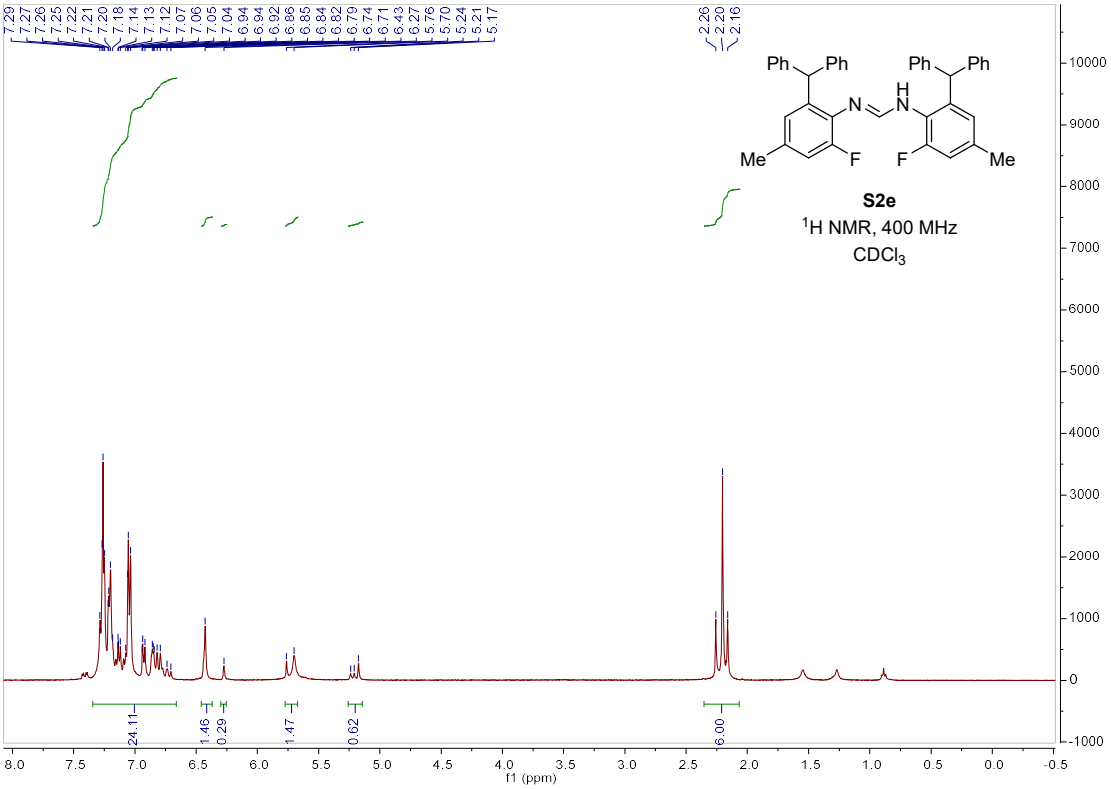

Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of formamidine **S2e**

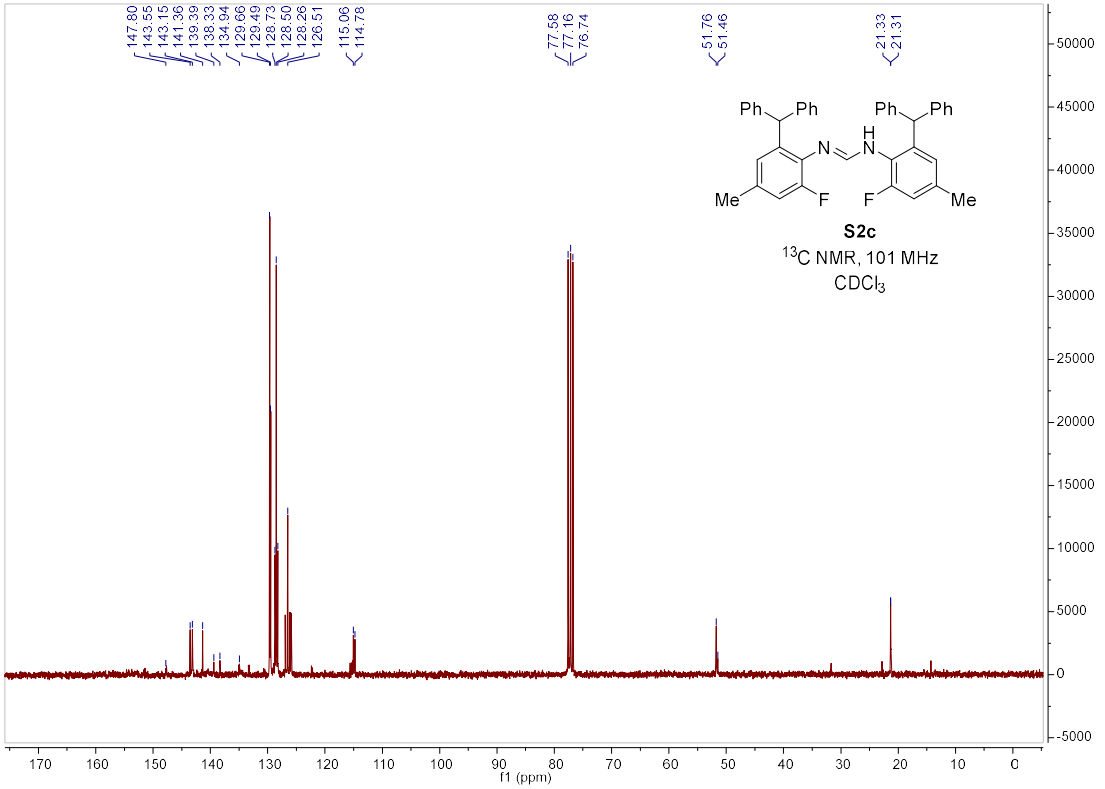

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of formamidine **S2e**

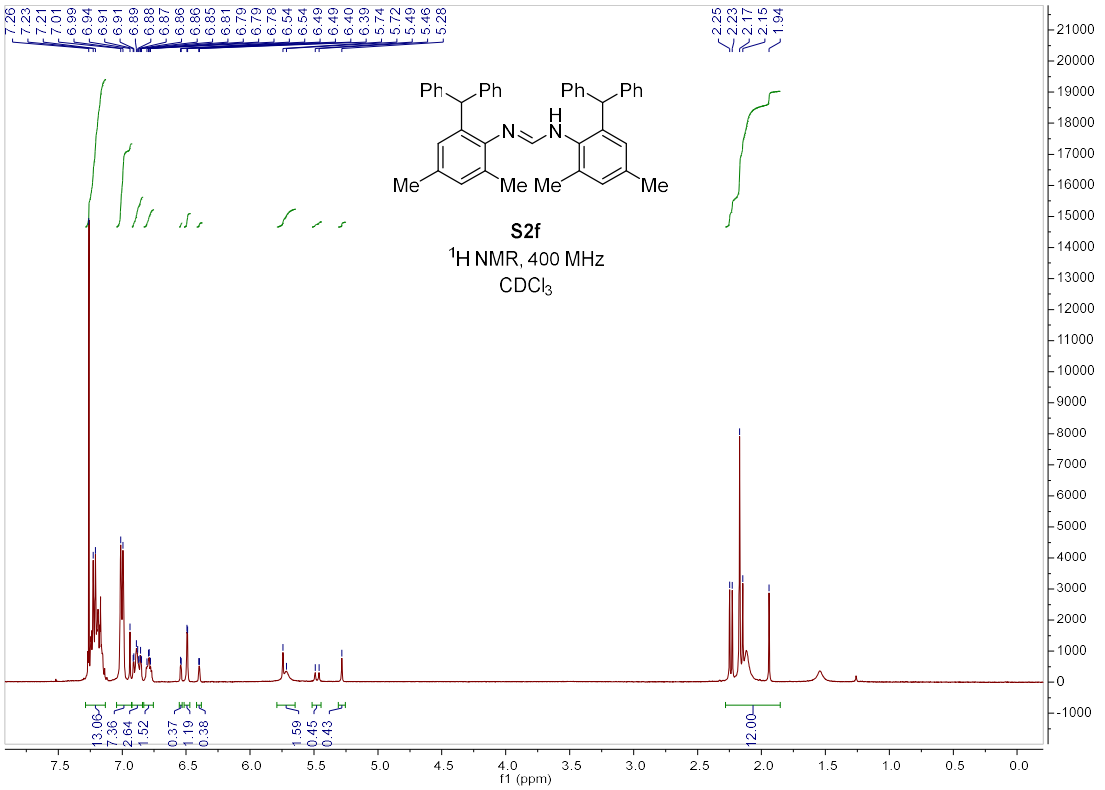

Figure S56. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of formamidine **S2f**

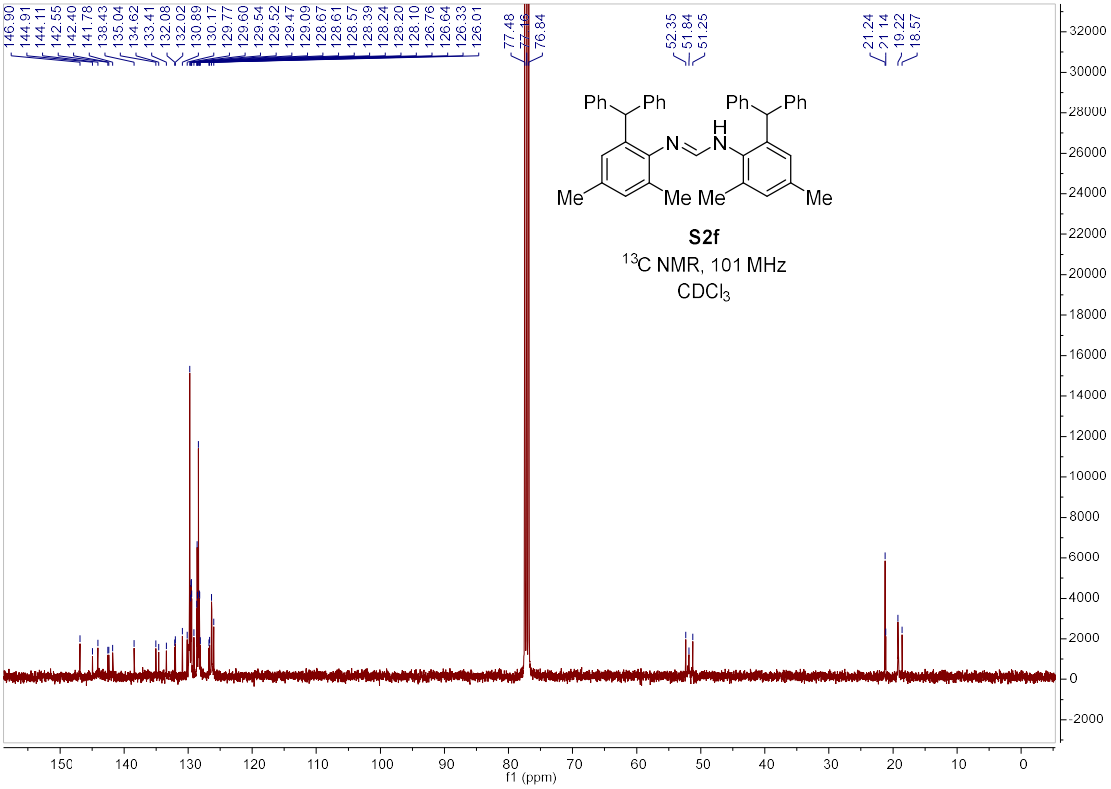

Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of formamidine **S2f**

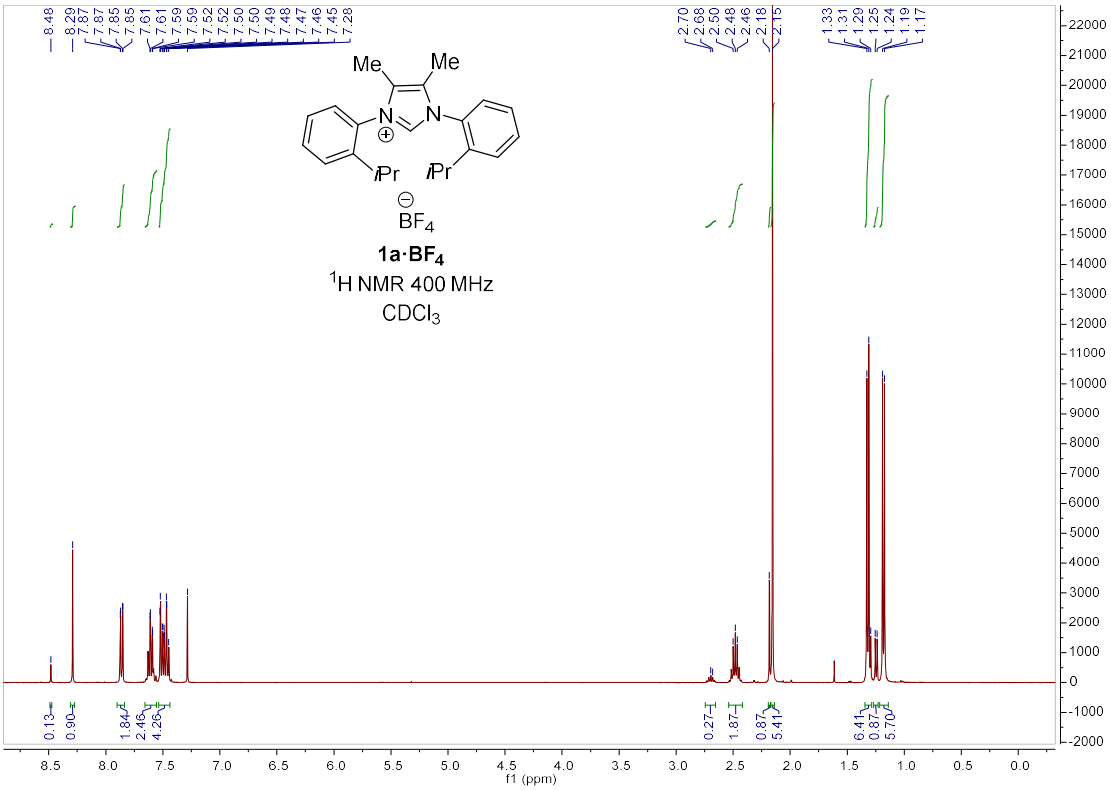

Figure S58. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1a·BF_4**

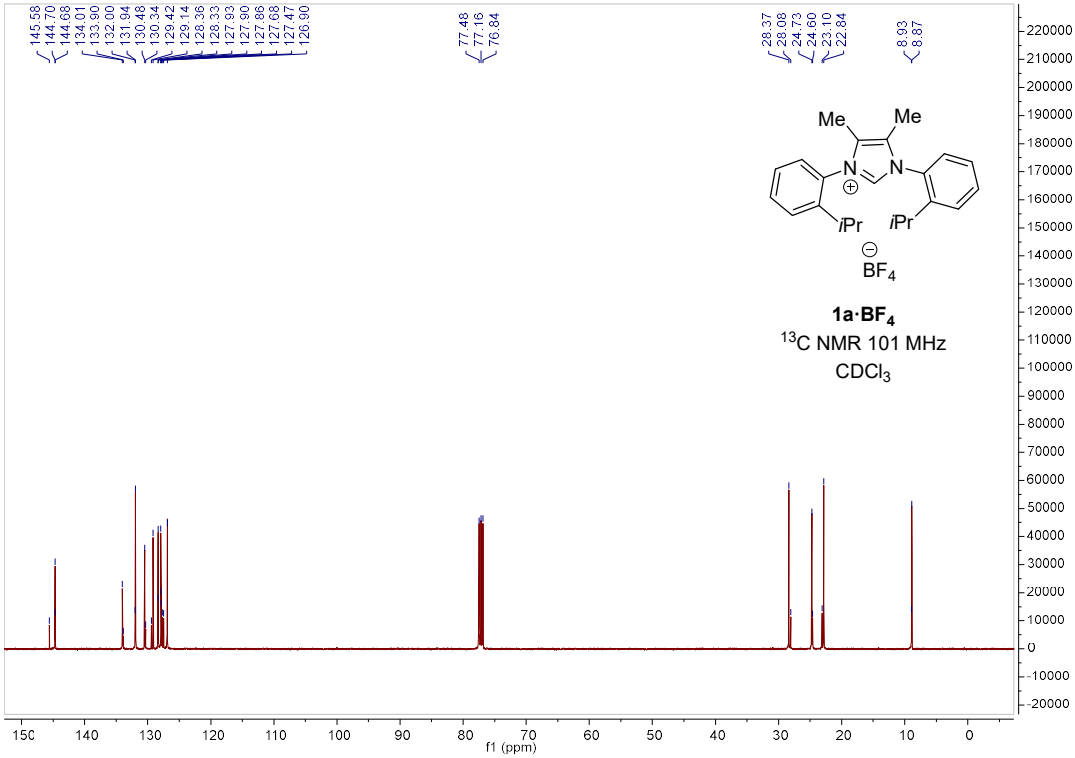

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1a·BF_4**

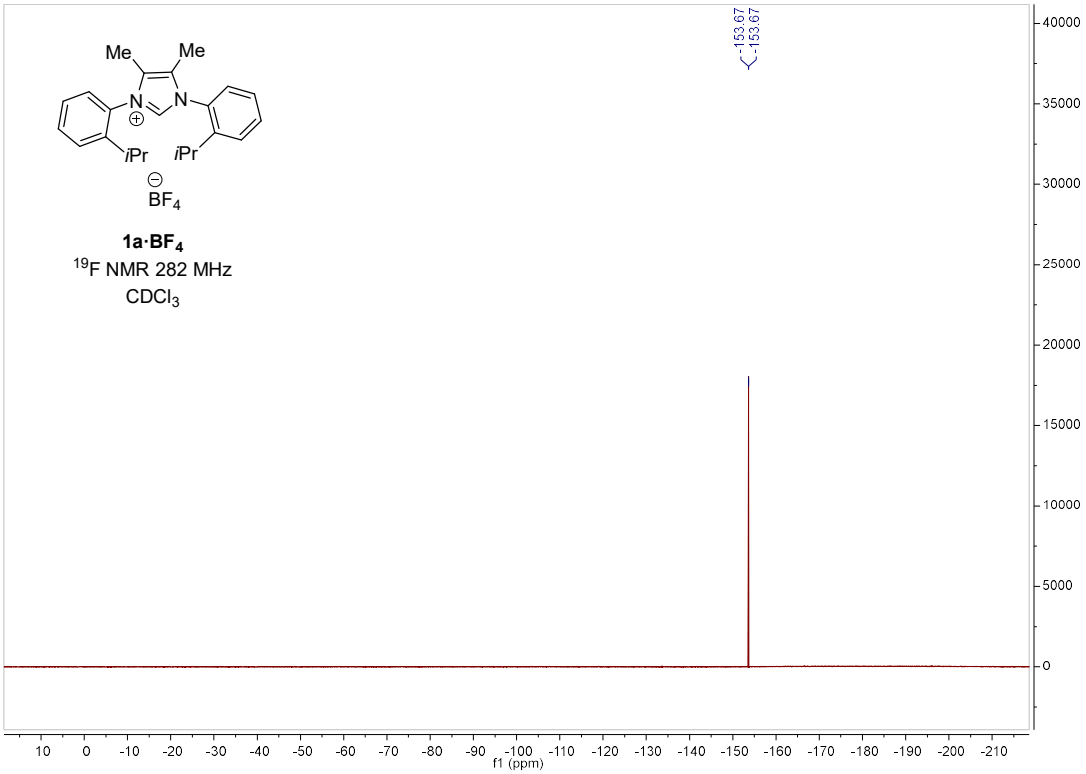

Figure S60. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1a·BF$_4$**

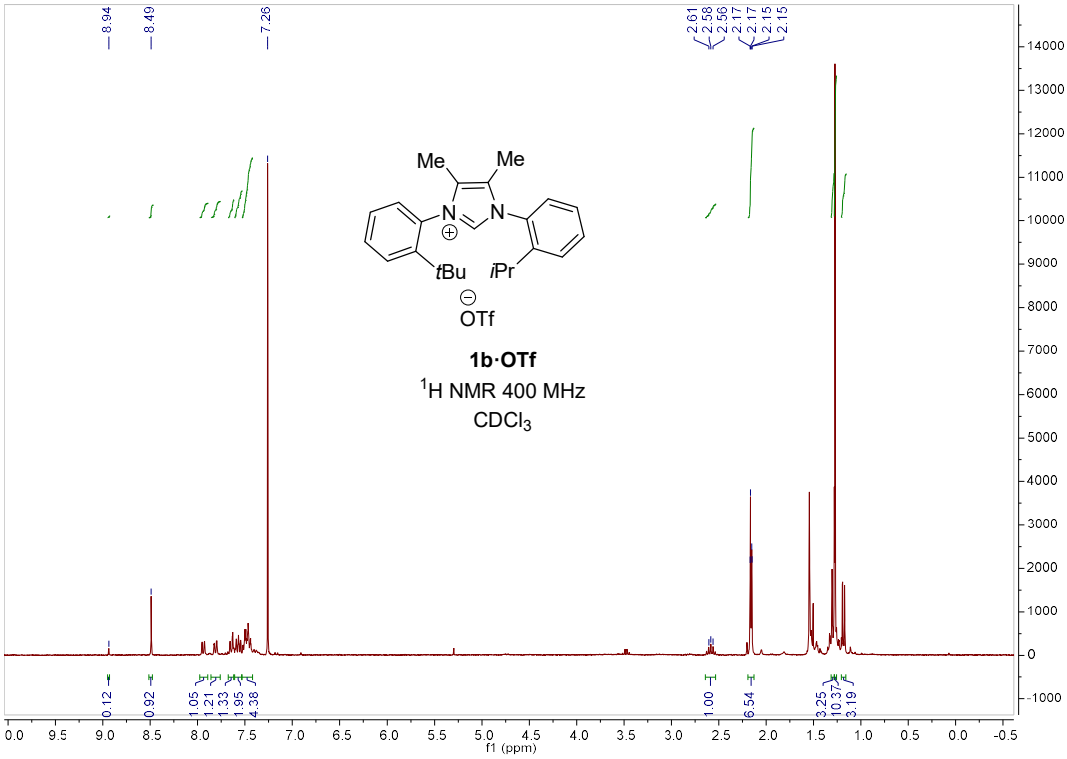

Figure S61. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1b·OTf**

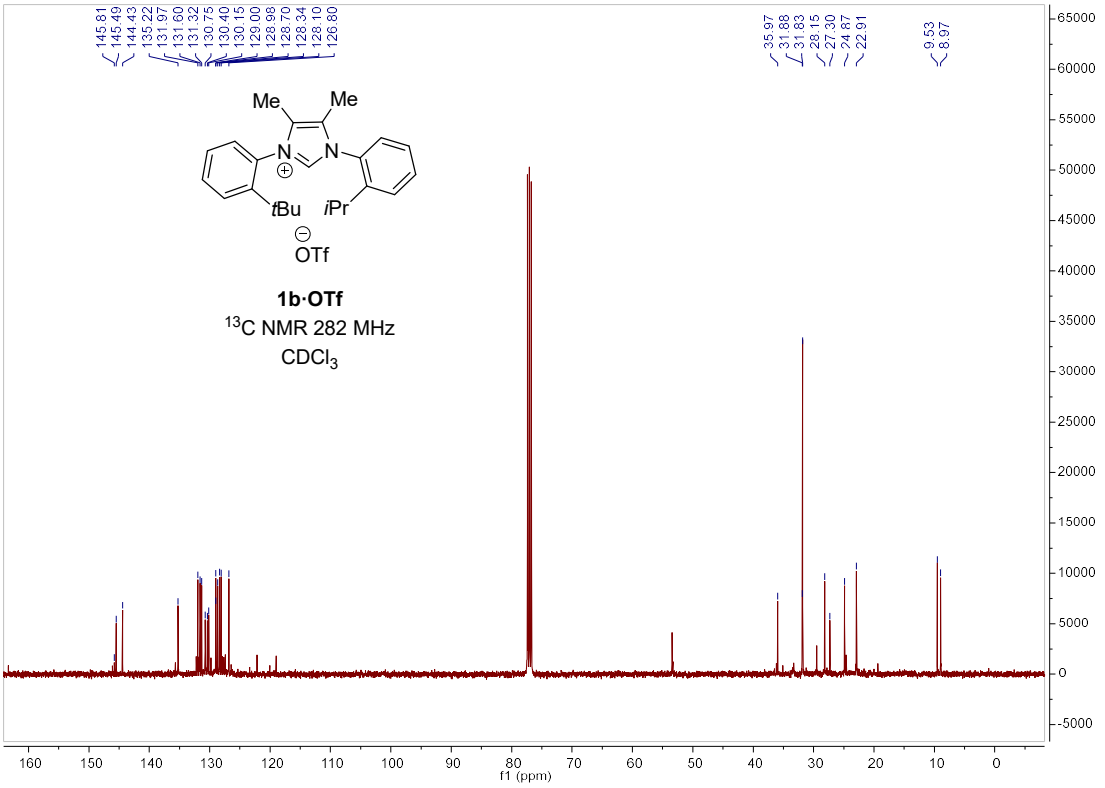

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1b·OTf**

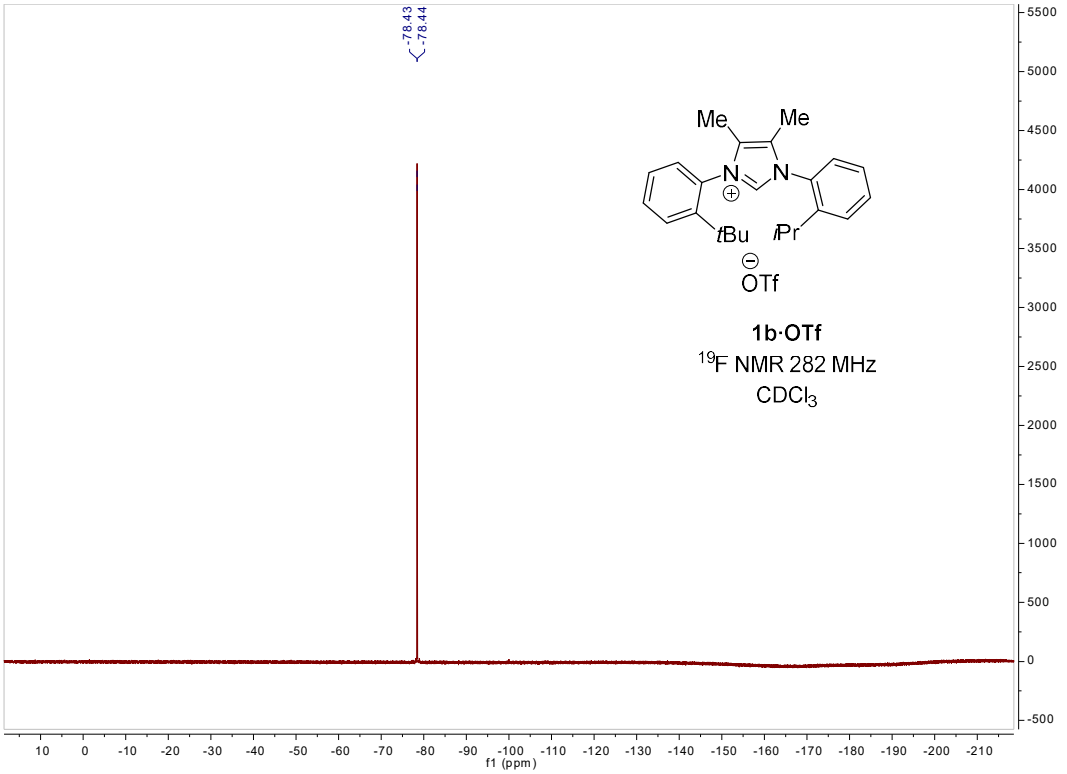

Figure S63. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1b·OTf**

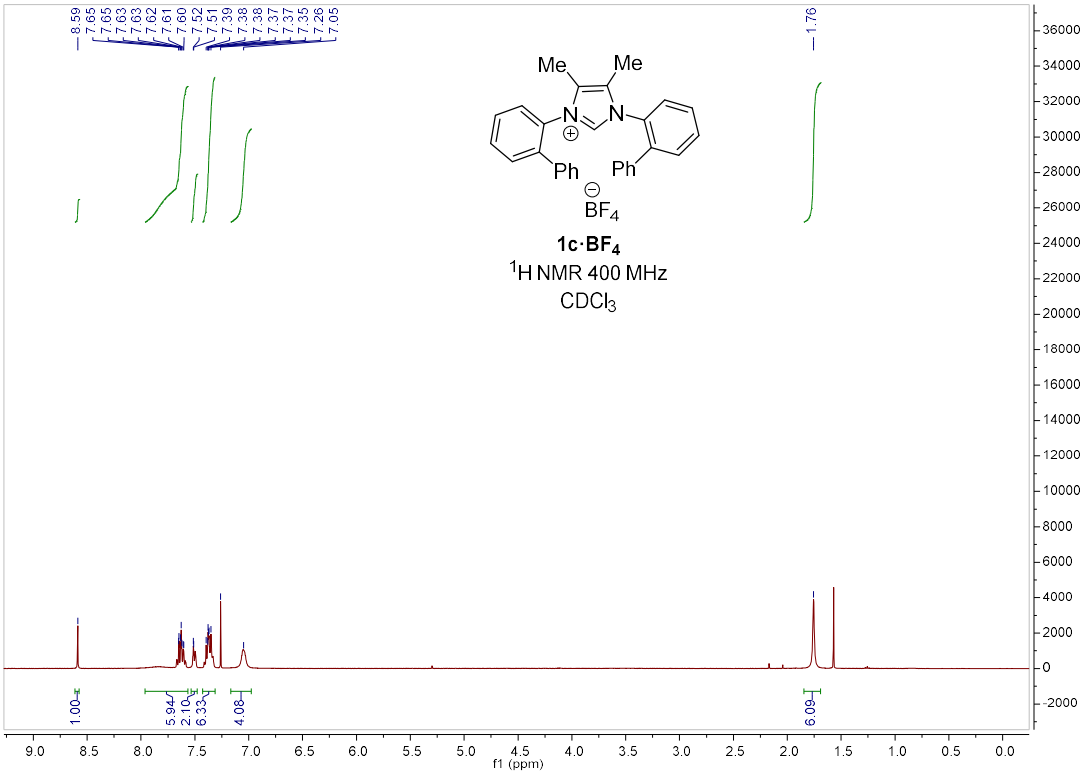

Figure S64. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1c·BF$_4$**

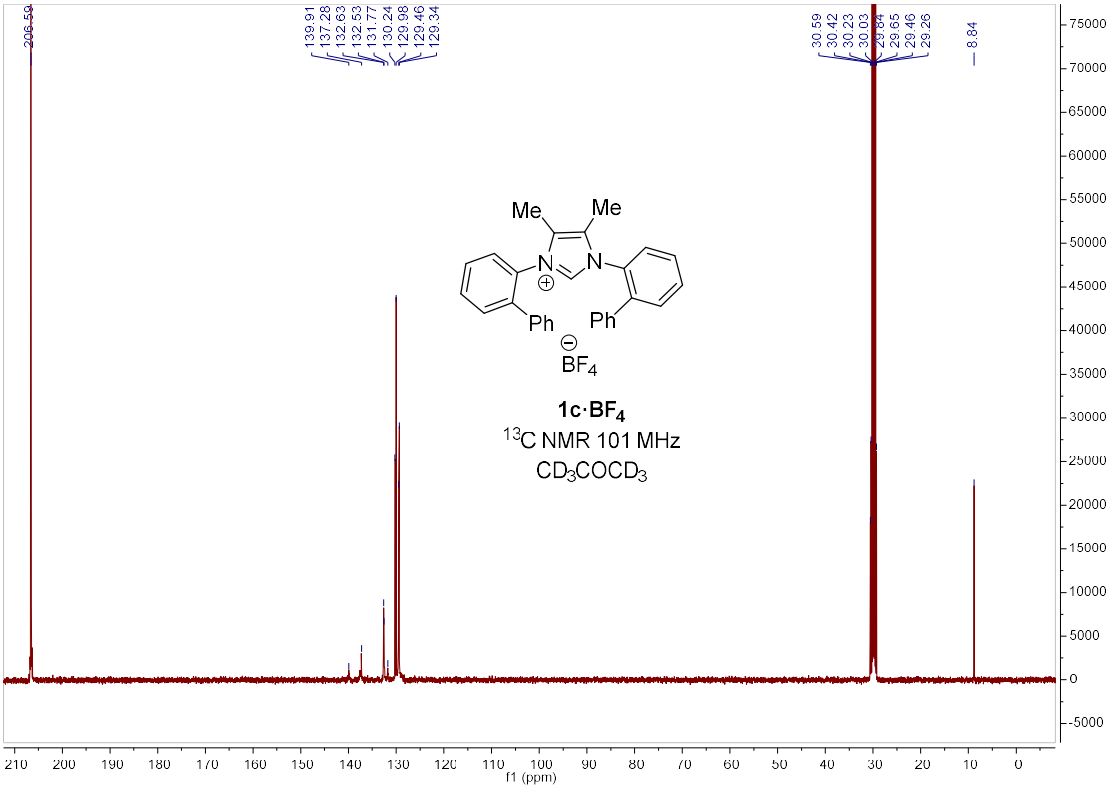

Figure S65. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1c·BF$_4$**

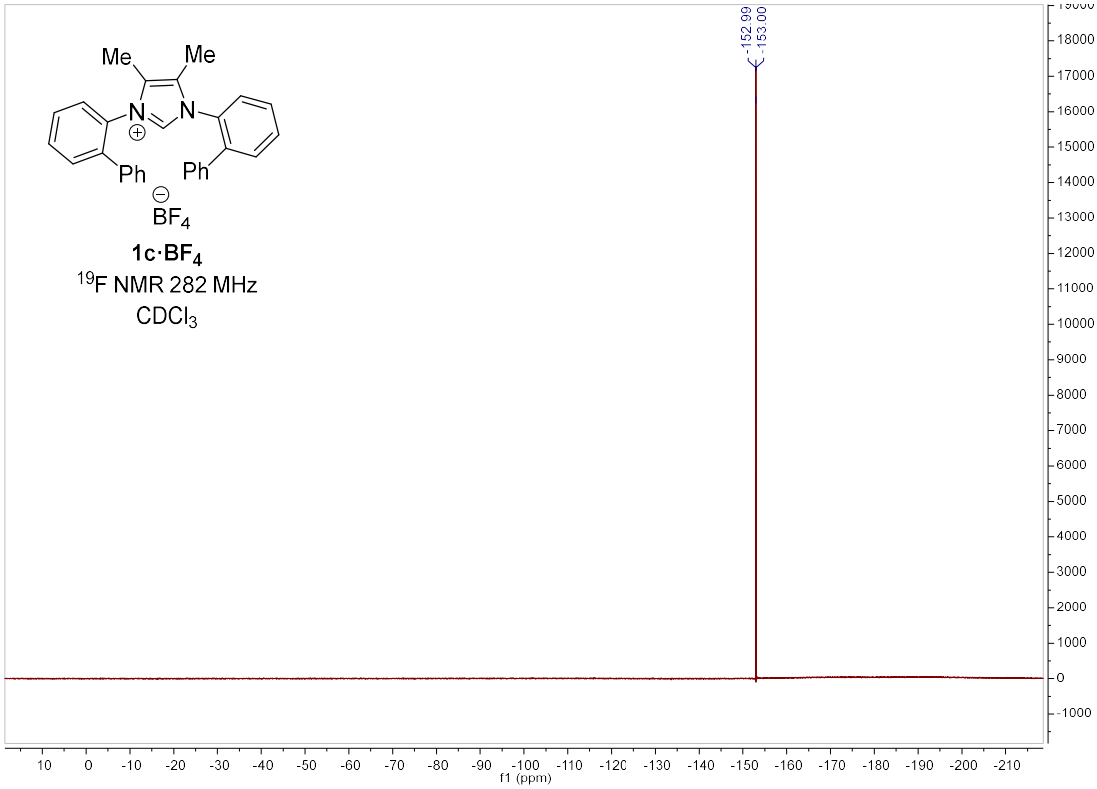

Figure S66. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1c·BF₄**

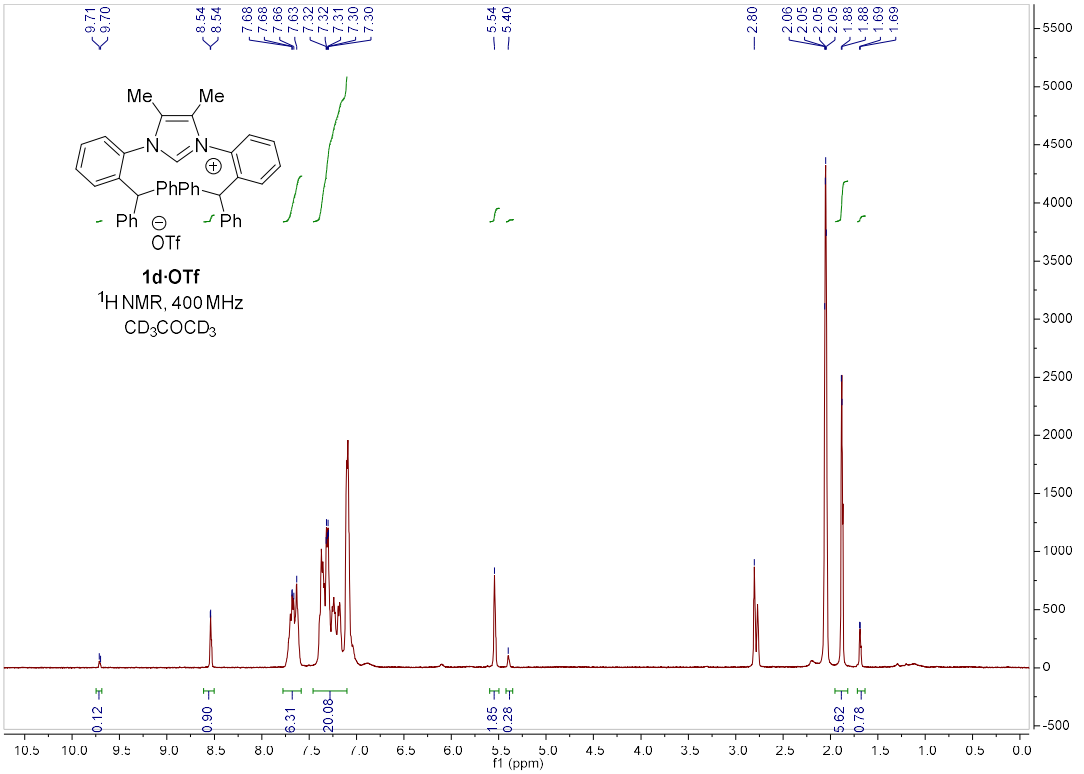

Figure S67. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1d·OTf**

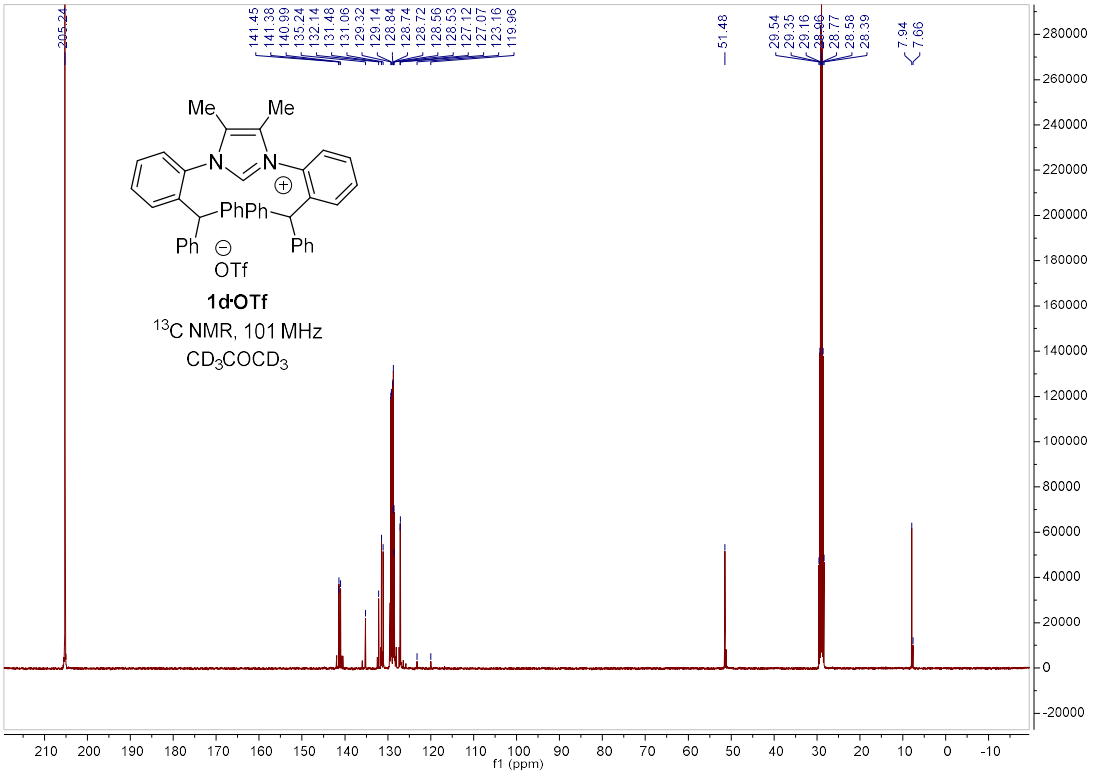

Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1d·OTf**

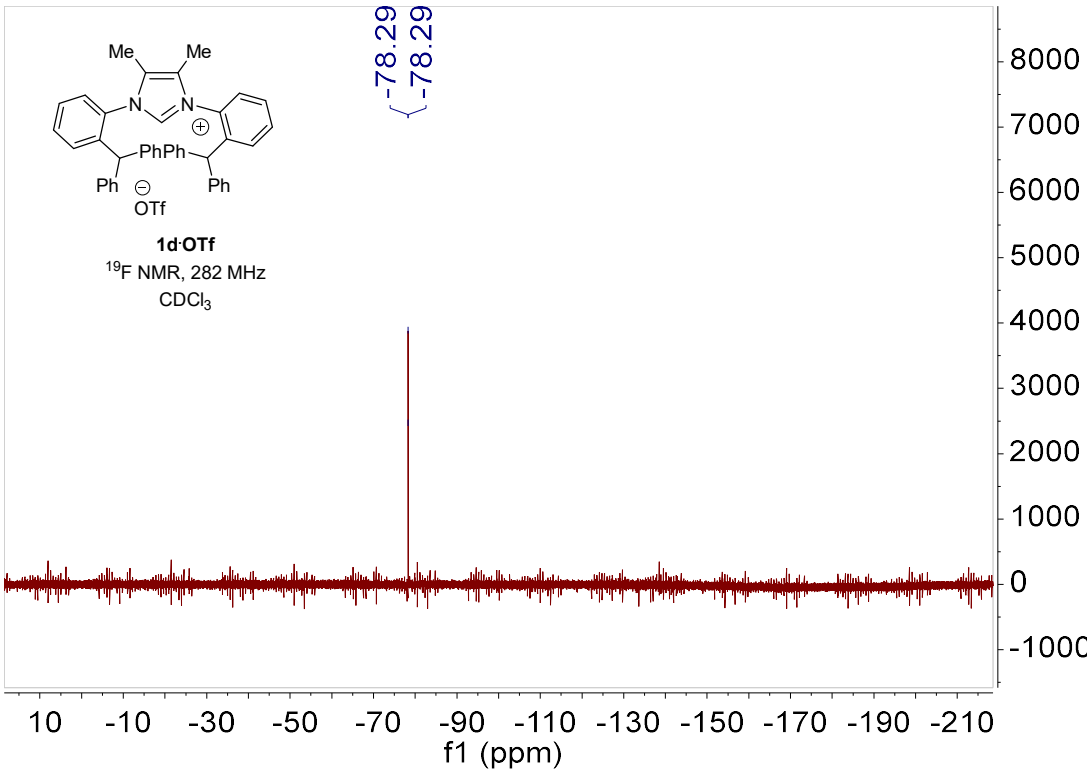

Figure S69. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1d·OTf**

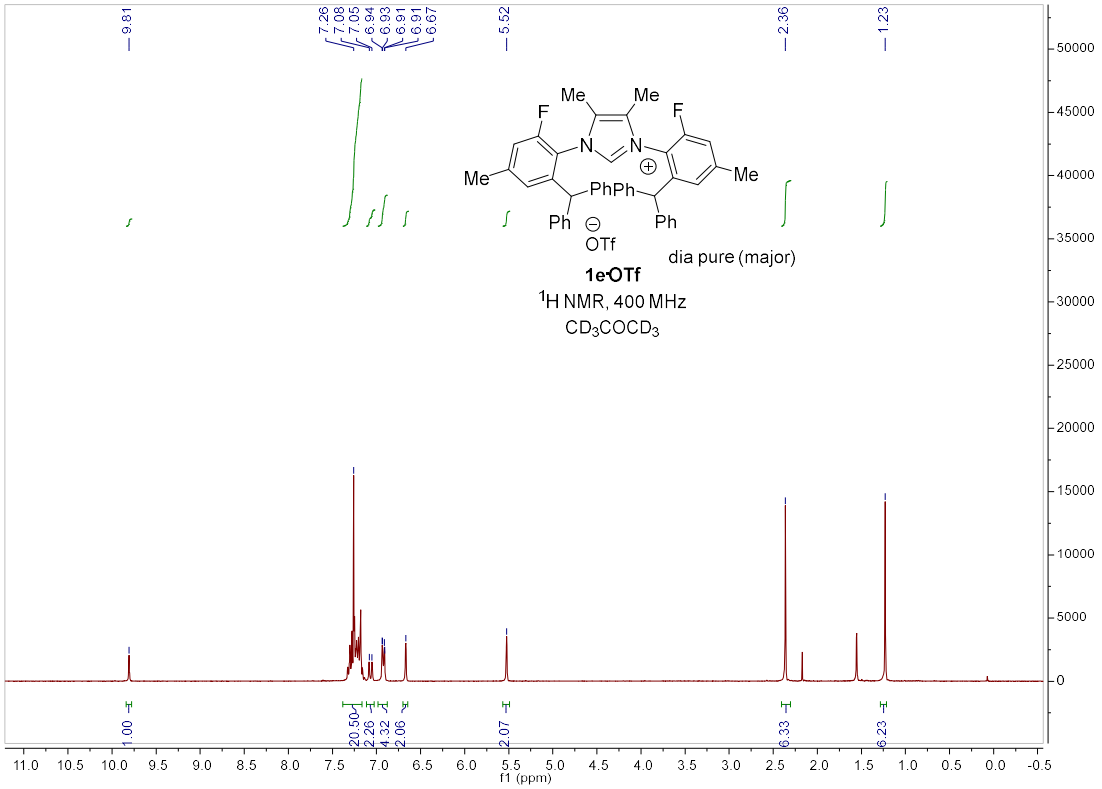

Figure S70. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1e·OTf**

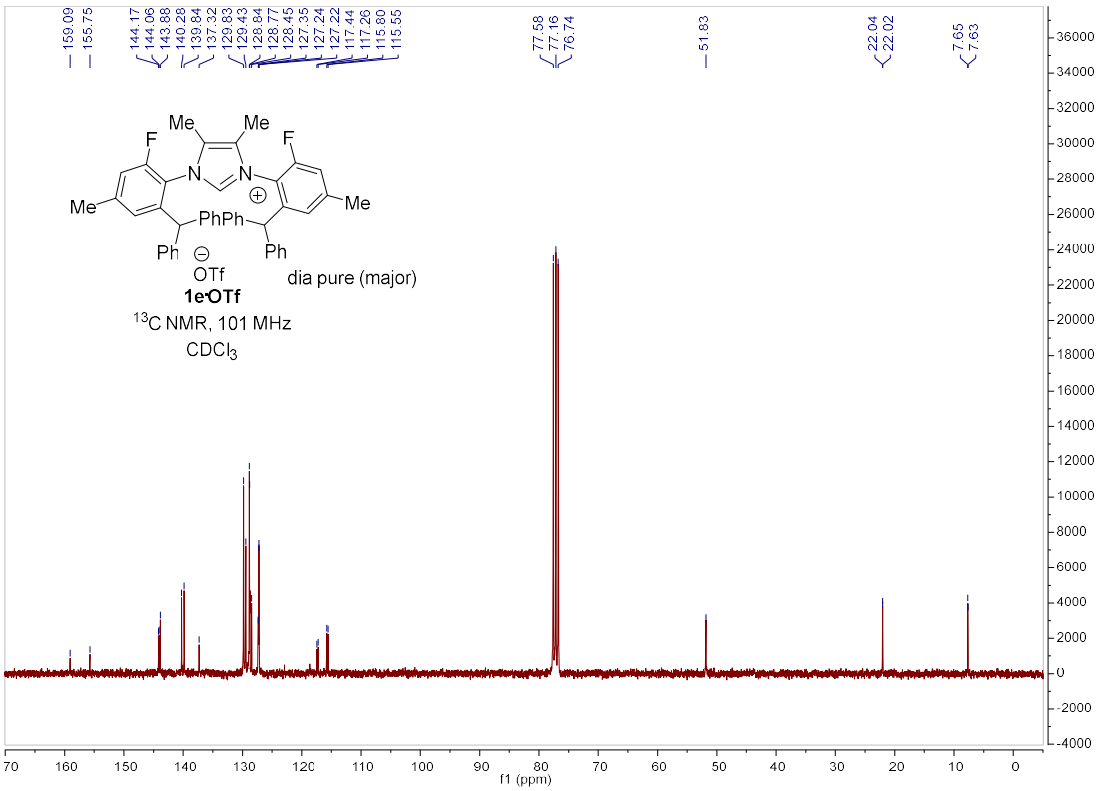

Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1e·OTf**

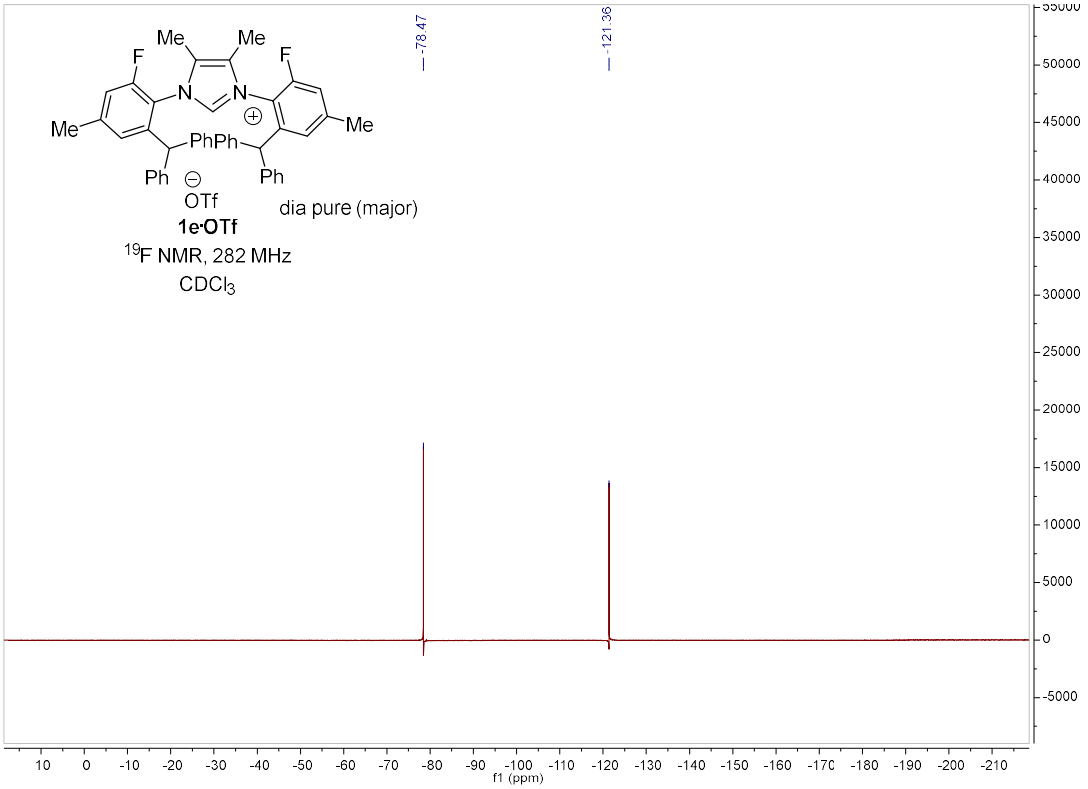

Figure S72. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1e·OTf**

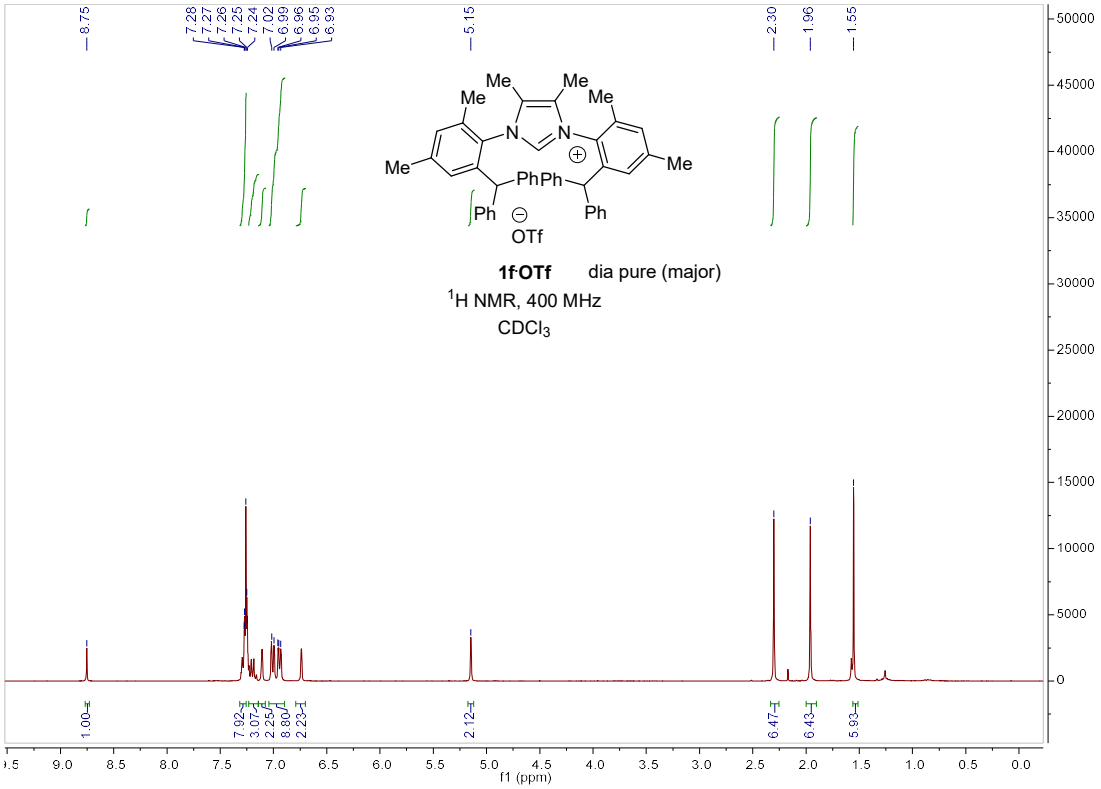

Figure S73. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of imidazolium salt **1f·OTf**

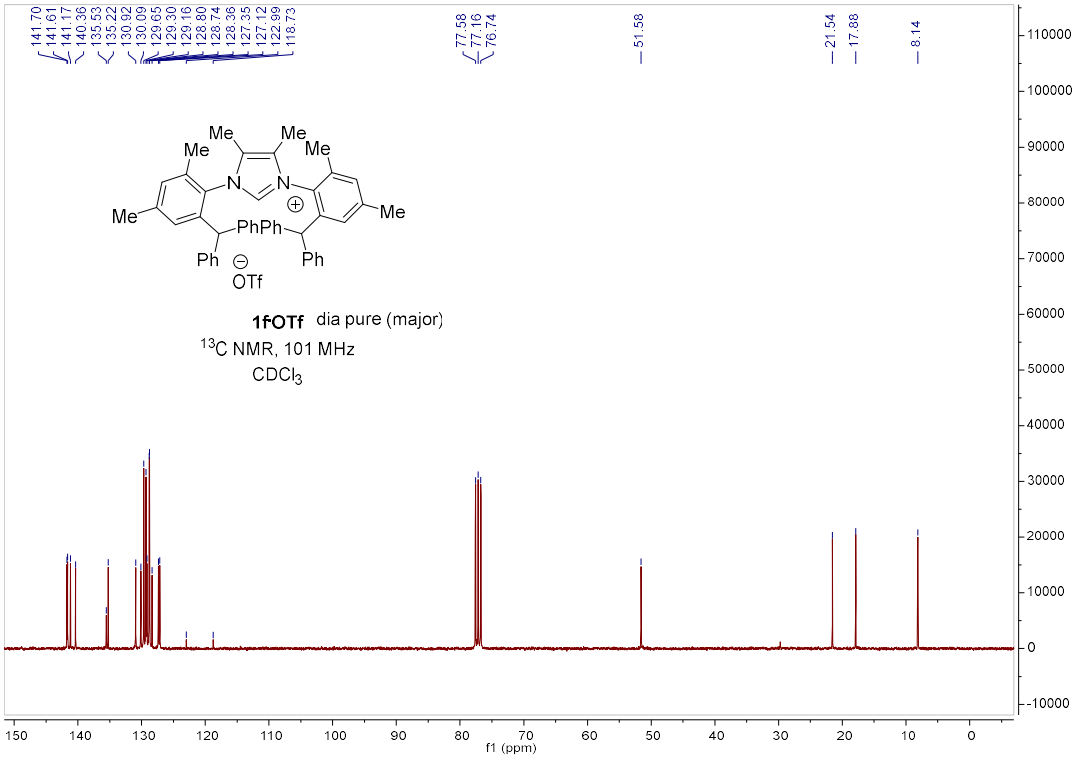

Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of imidazolium salt **1f·OTf**

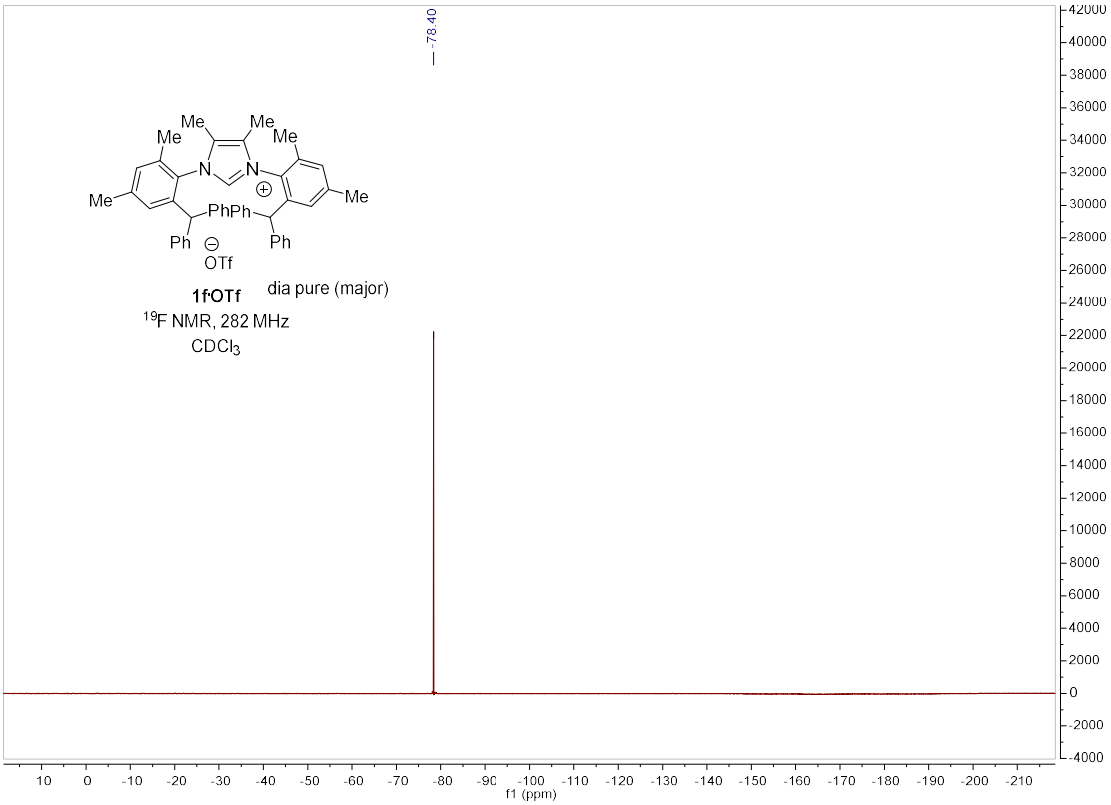

Figure S75. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of imidazolium salt **1f·OTf**

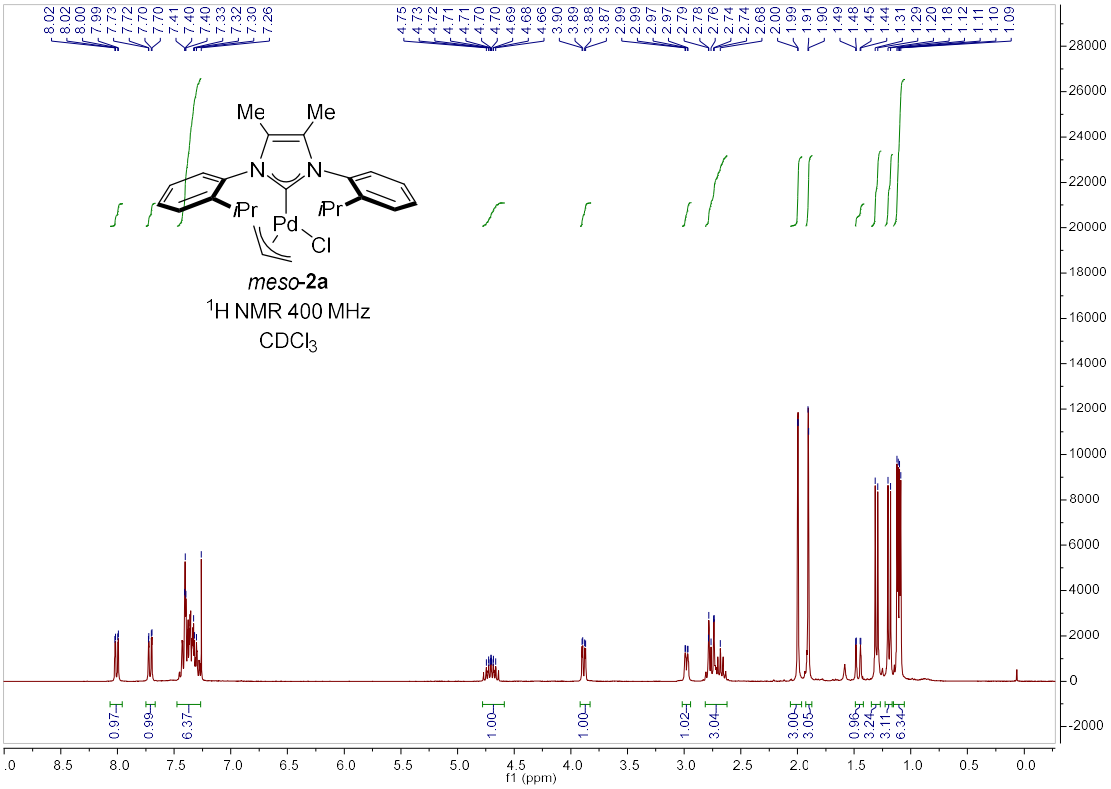

Figure S76. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex *meso*-**2a**

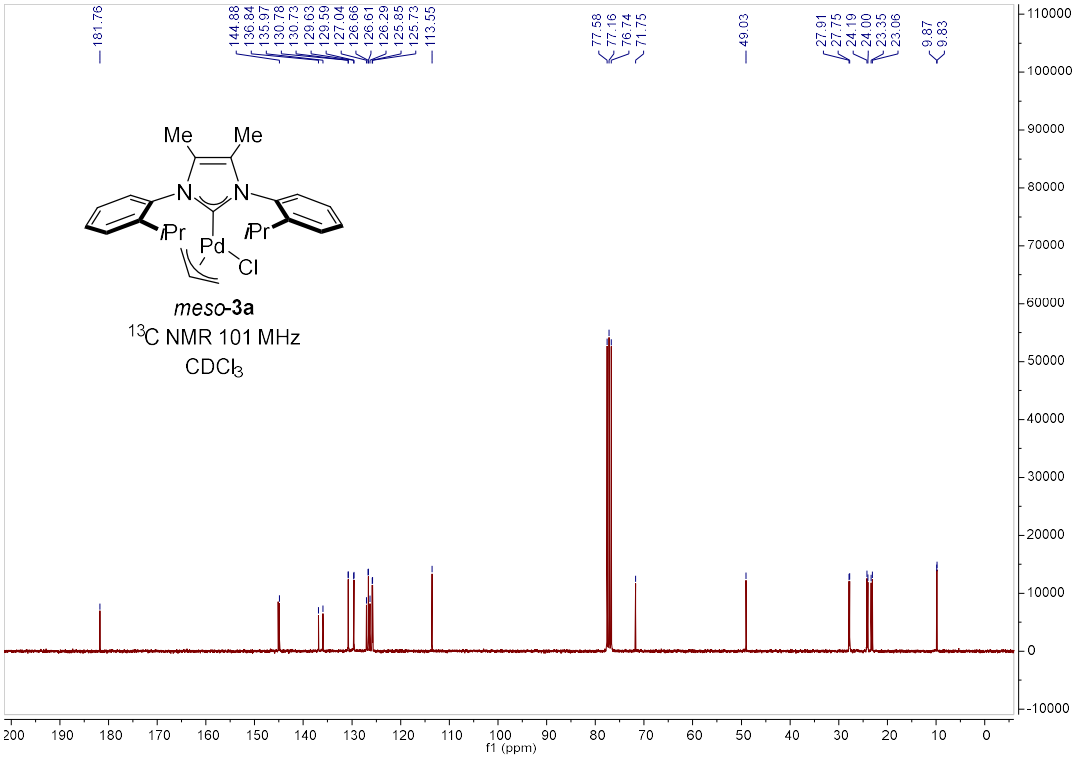

Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex *meso*-**2a**

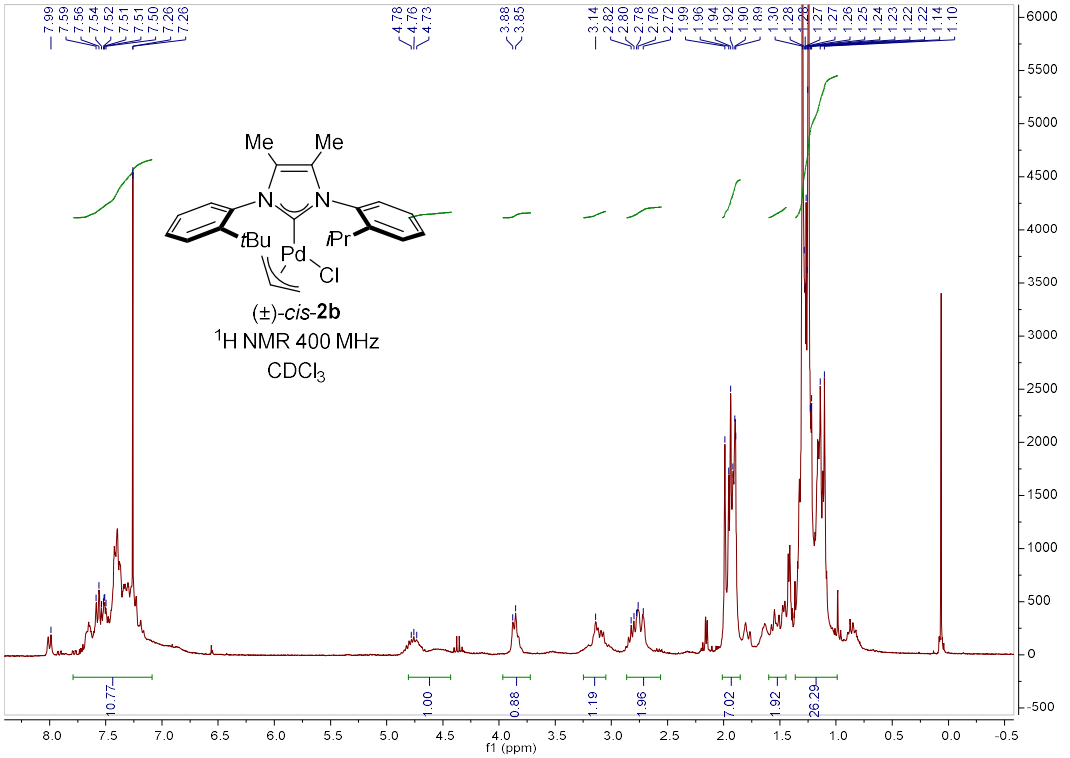

Figure S78. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-*cis*-**2b**

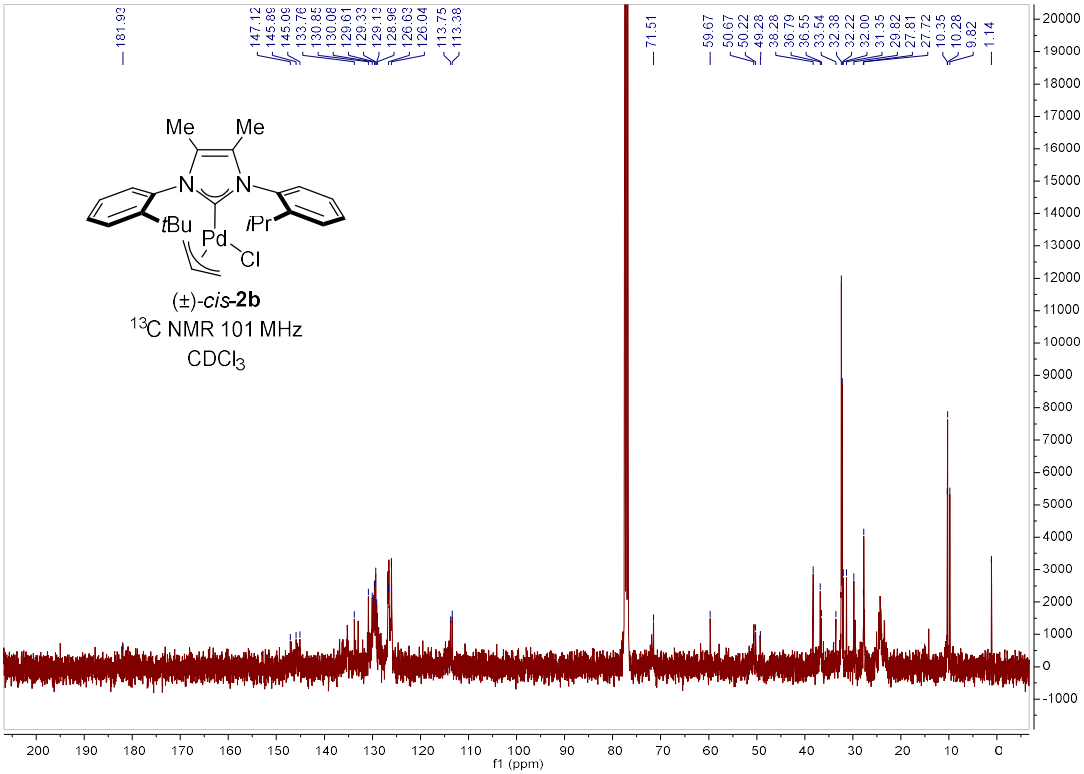

Figure S79. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-*cis*-**2b**

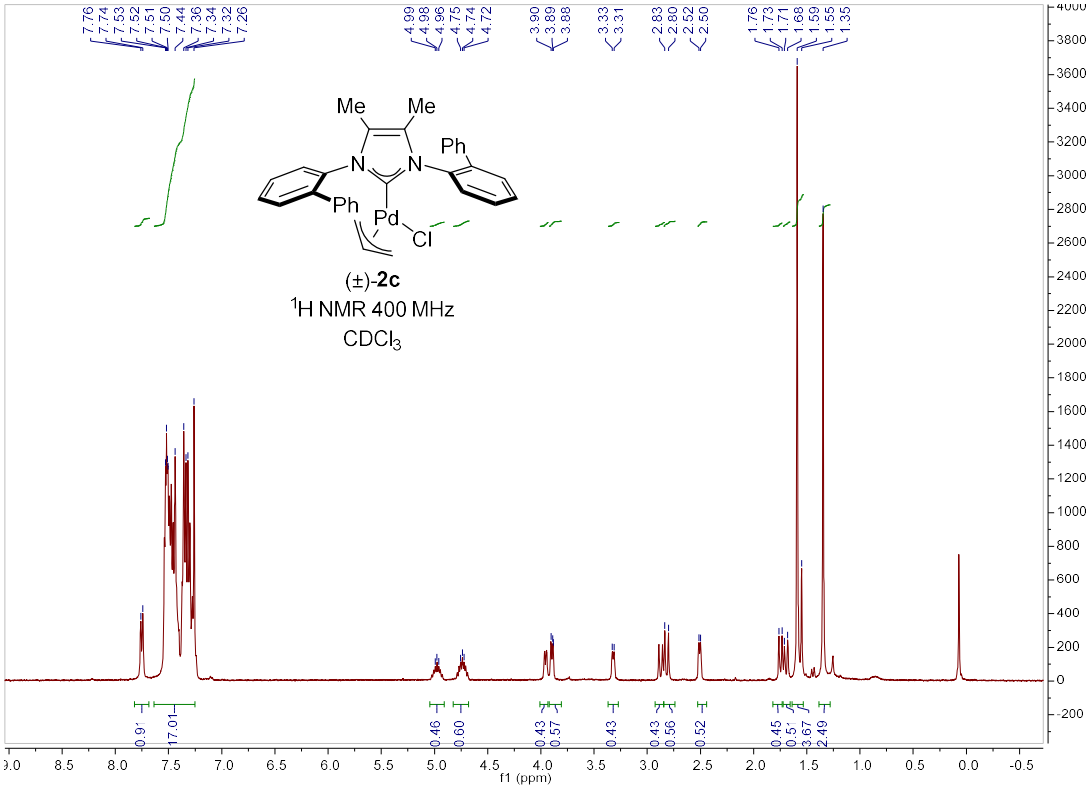

Figure S80. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**2c**

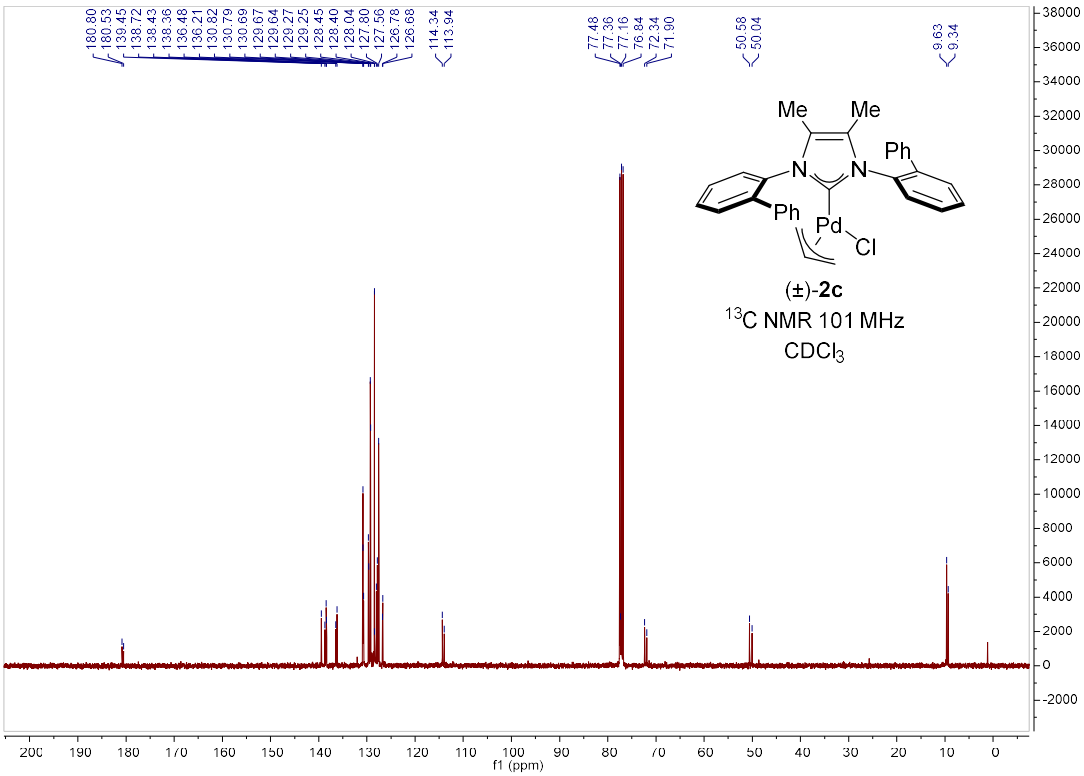

Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**2c**

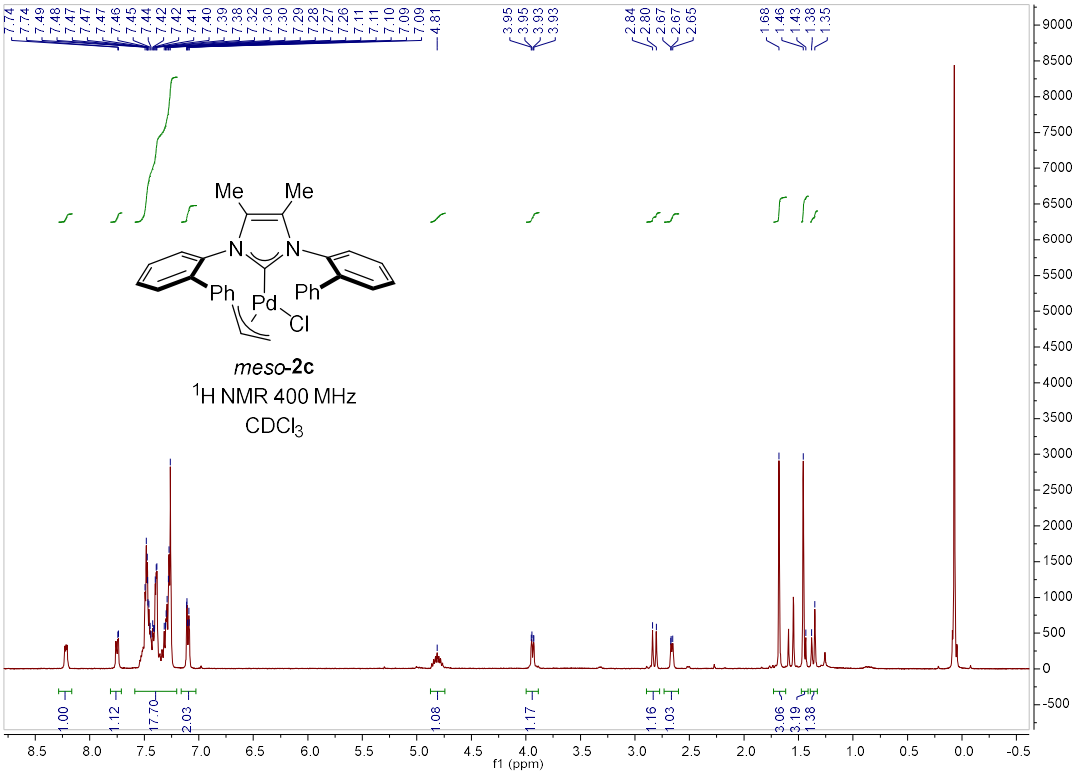

Figure S82. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex *meso*-**2c**

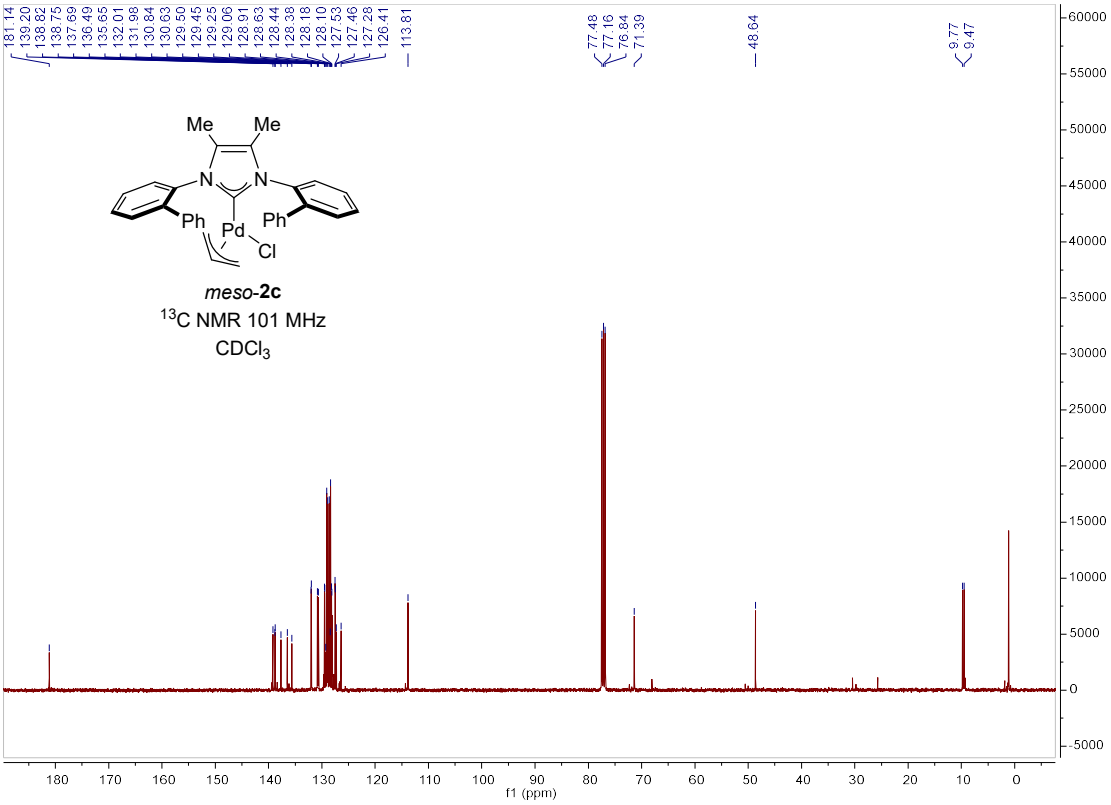

Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex *meso*-**2c**

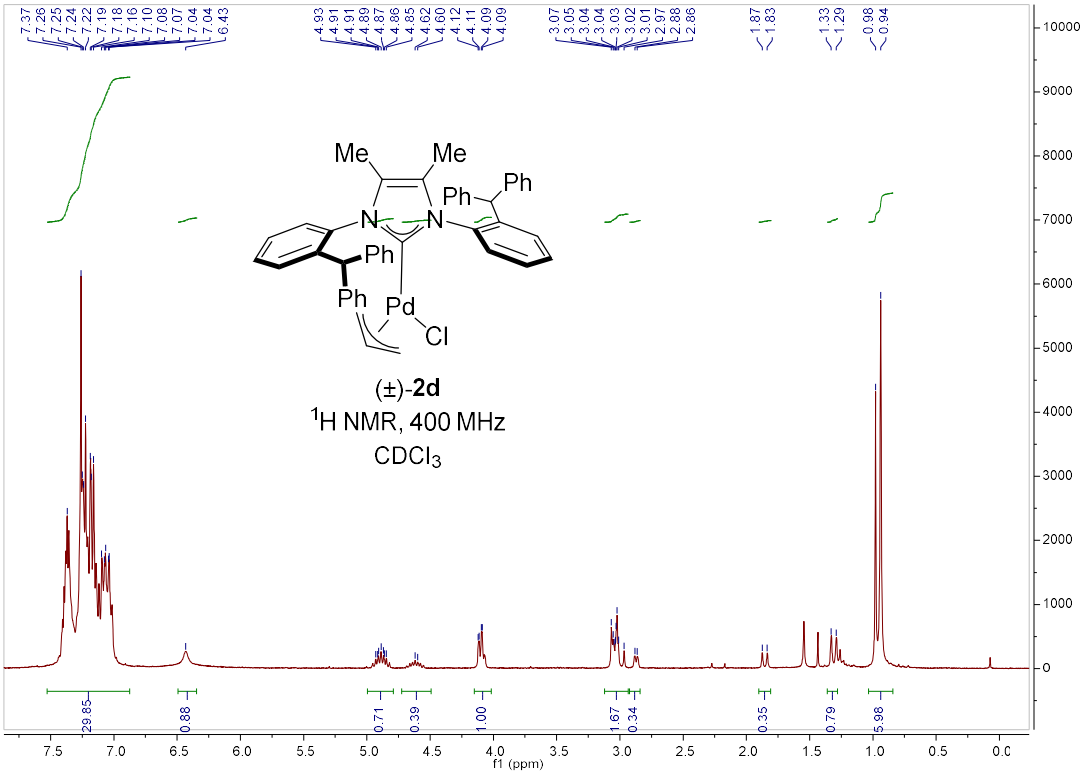

Figure S84. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**2d**

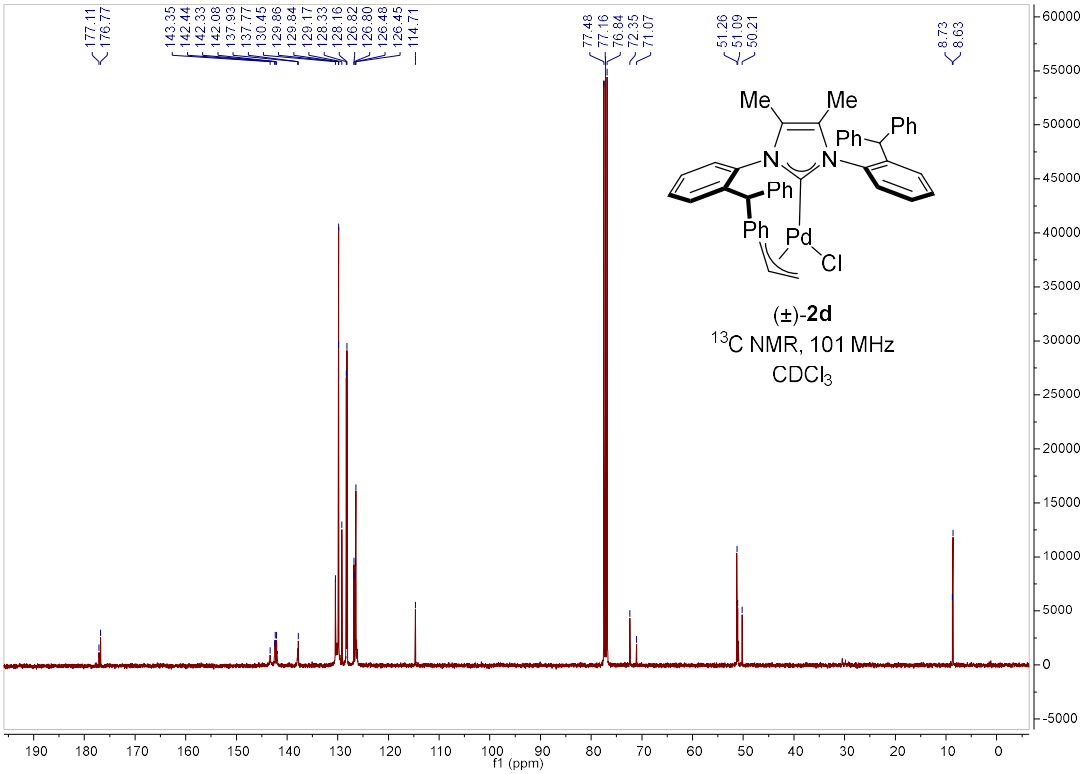

Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**2d**

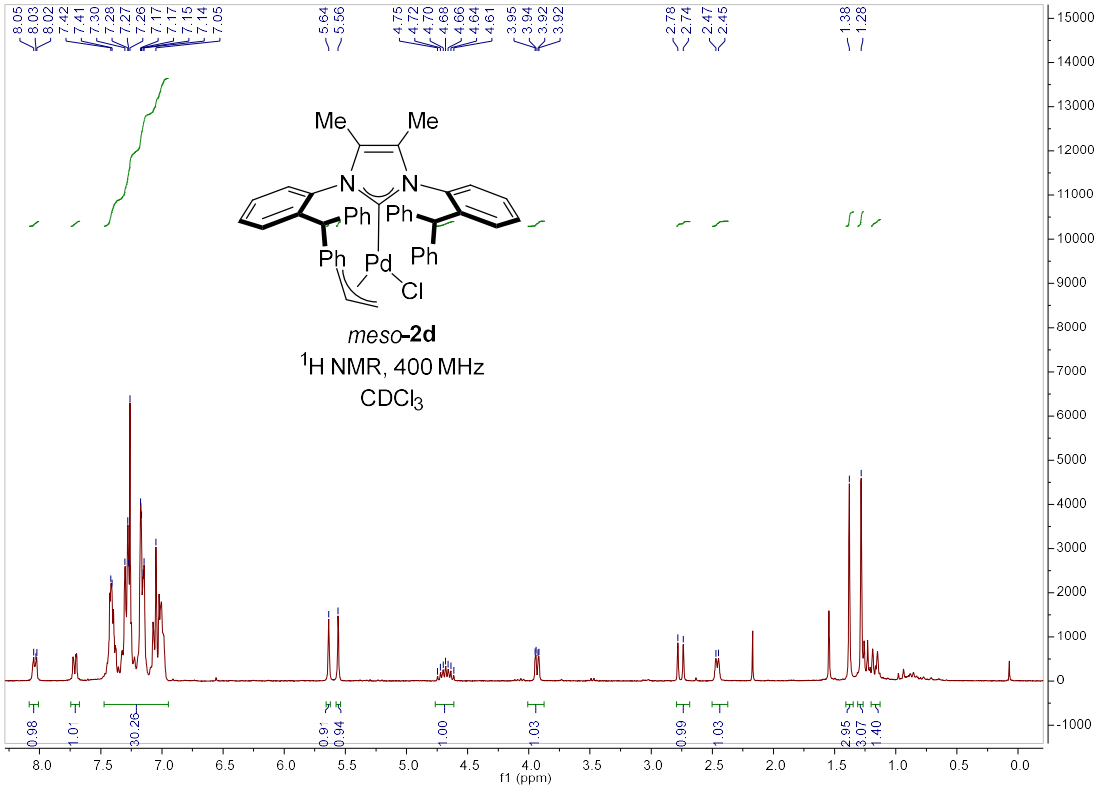

Figure S86. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (*meso*)-**2d**

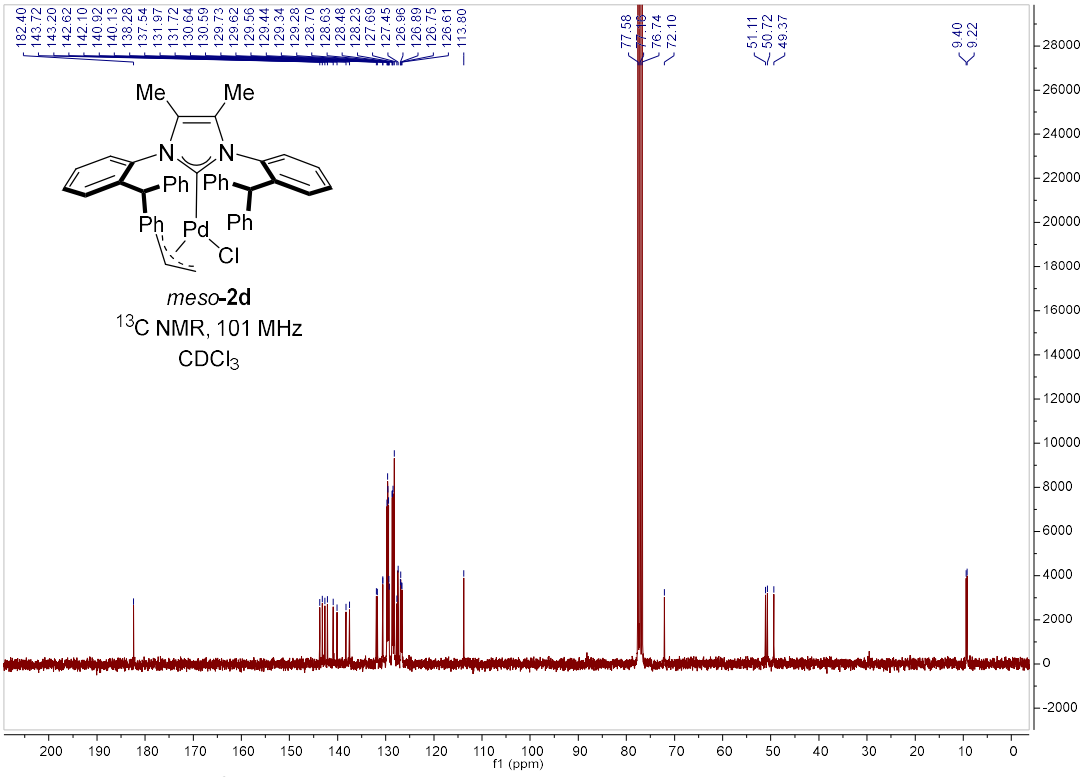

Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (*meso*)-**2d**

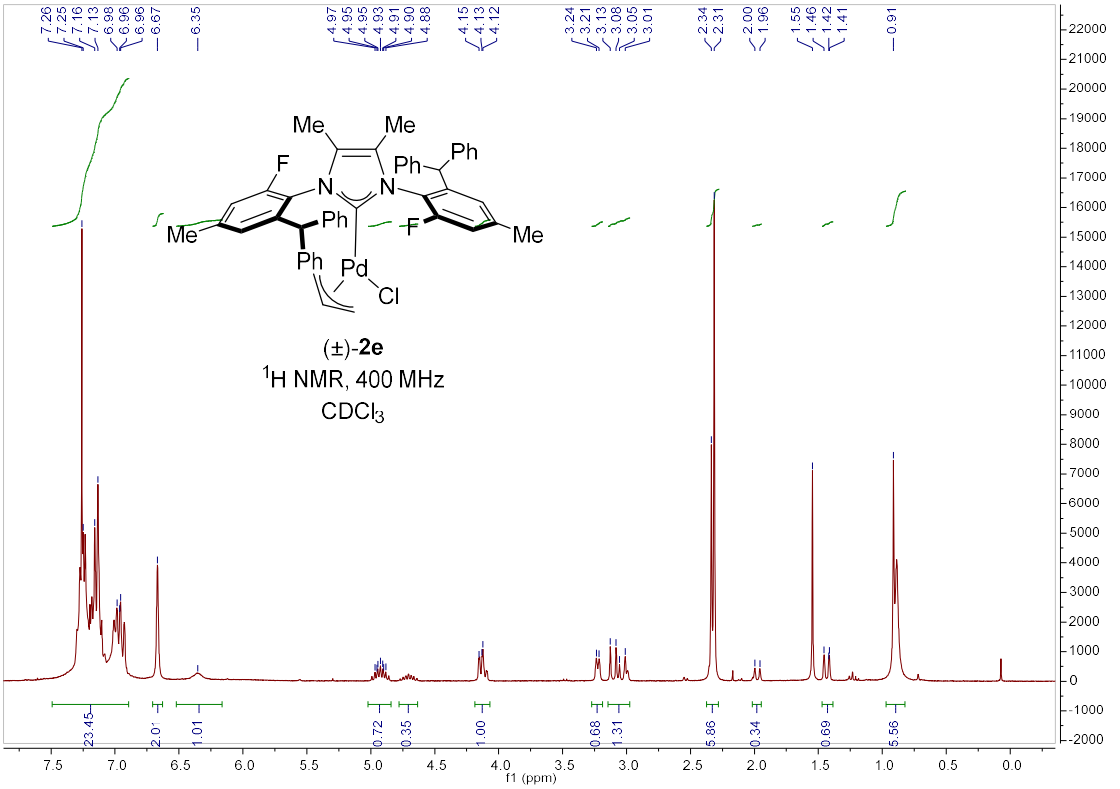

Figure S88. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**2e**

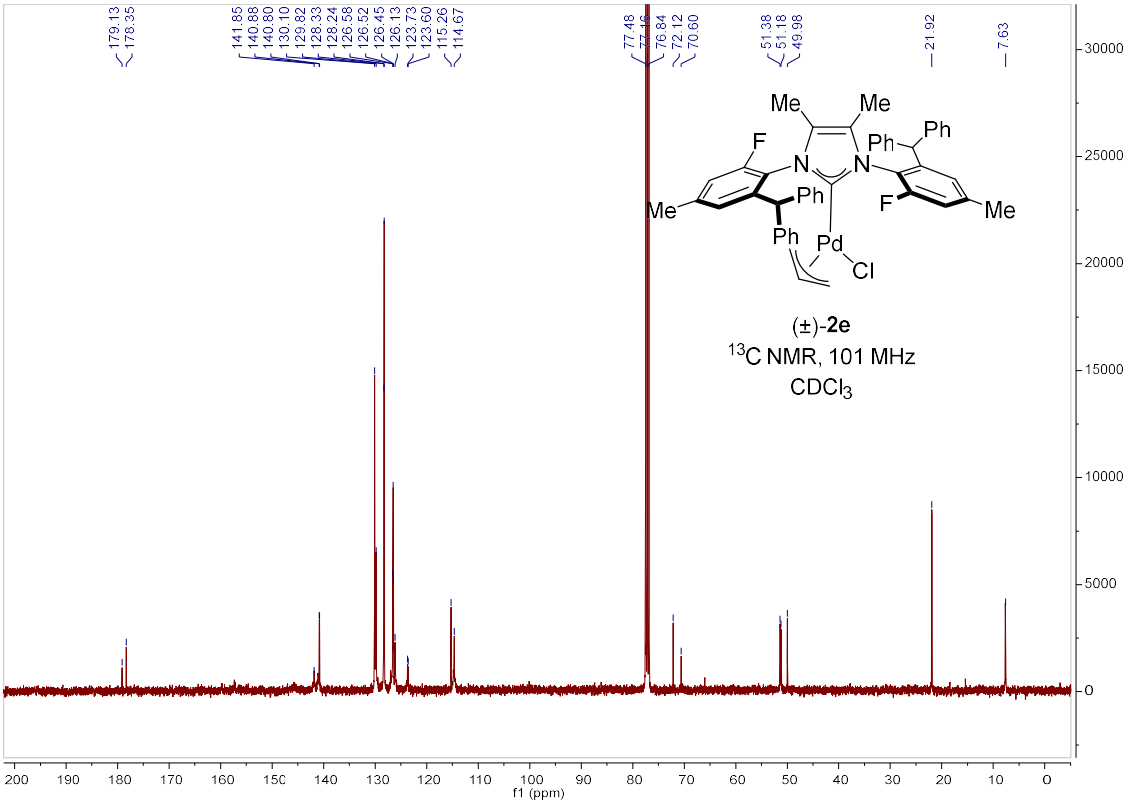

Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**2e**

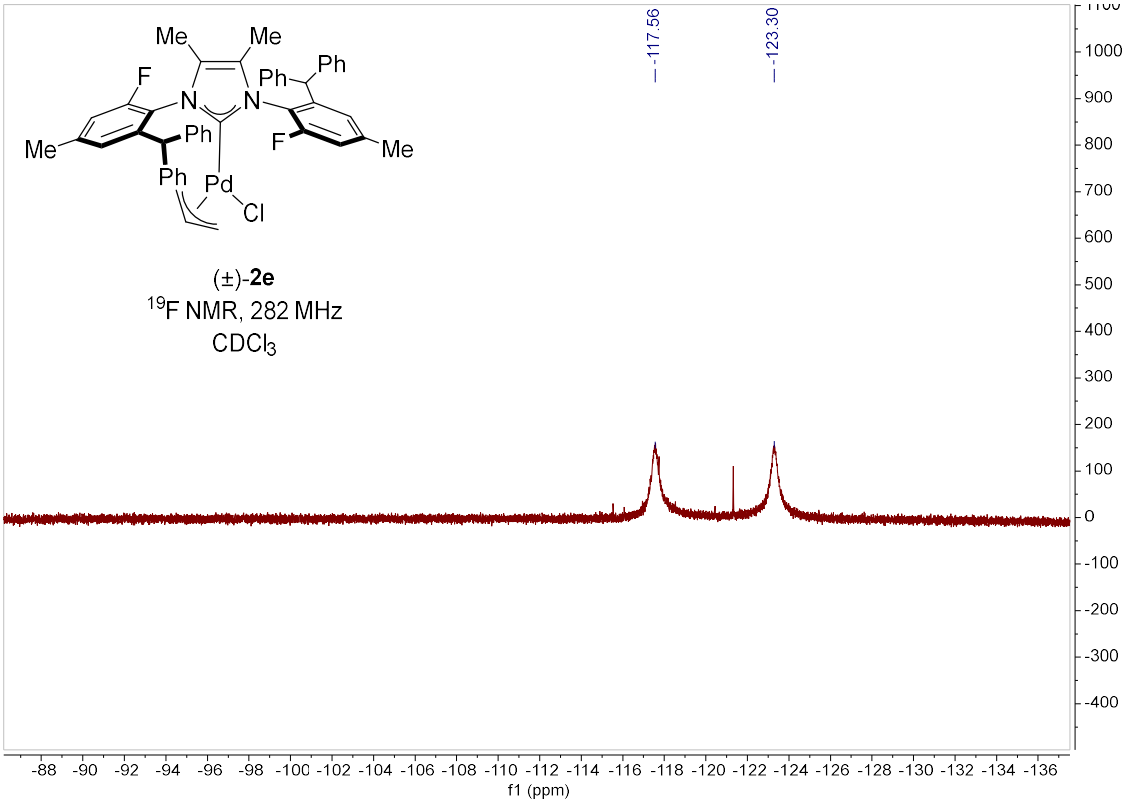

Figure S90. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of palladium complex (±)-**2e**

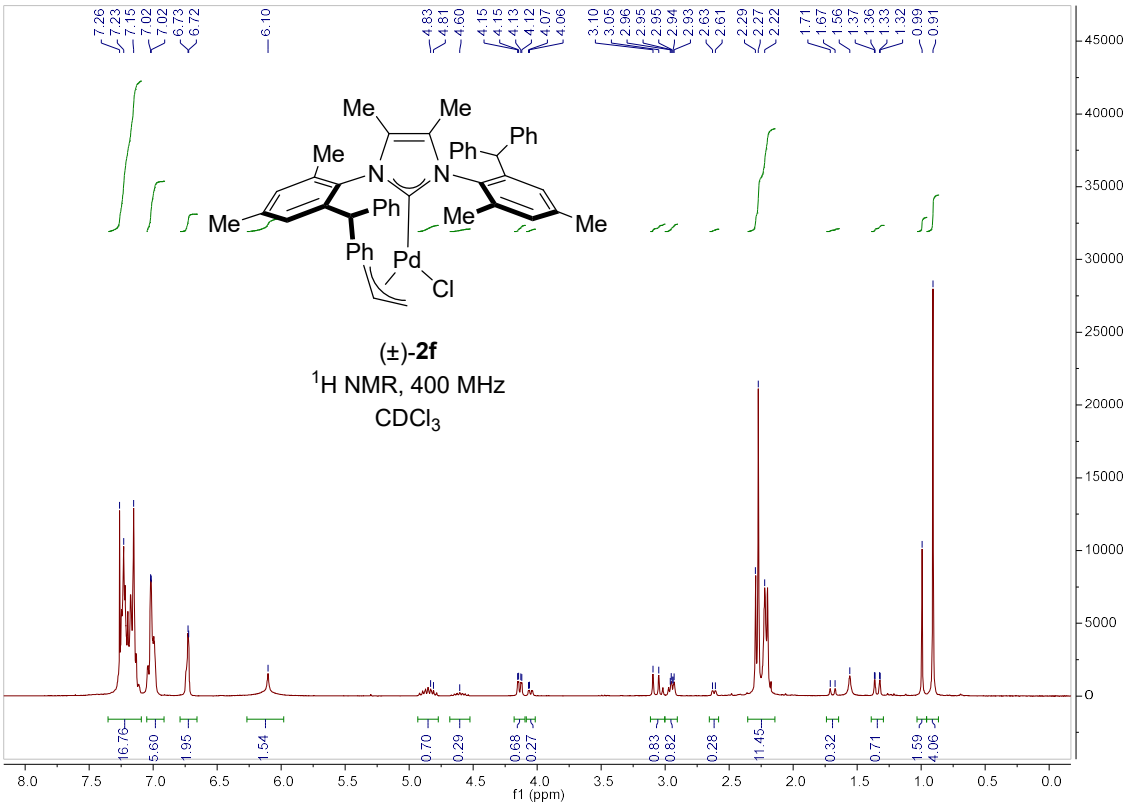

Figure S91. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**2f**

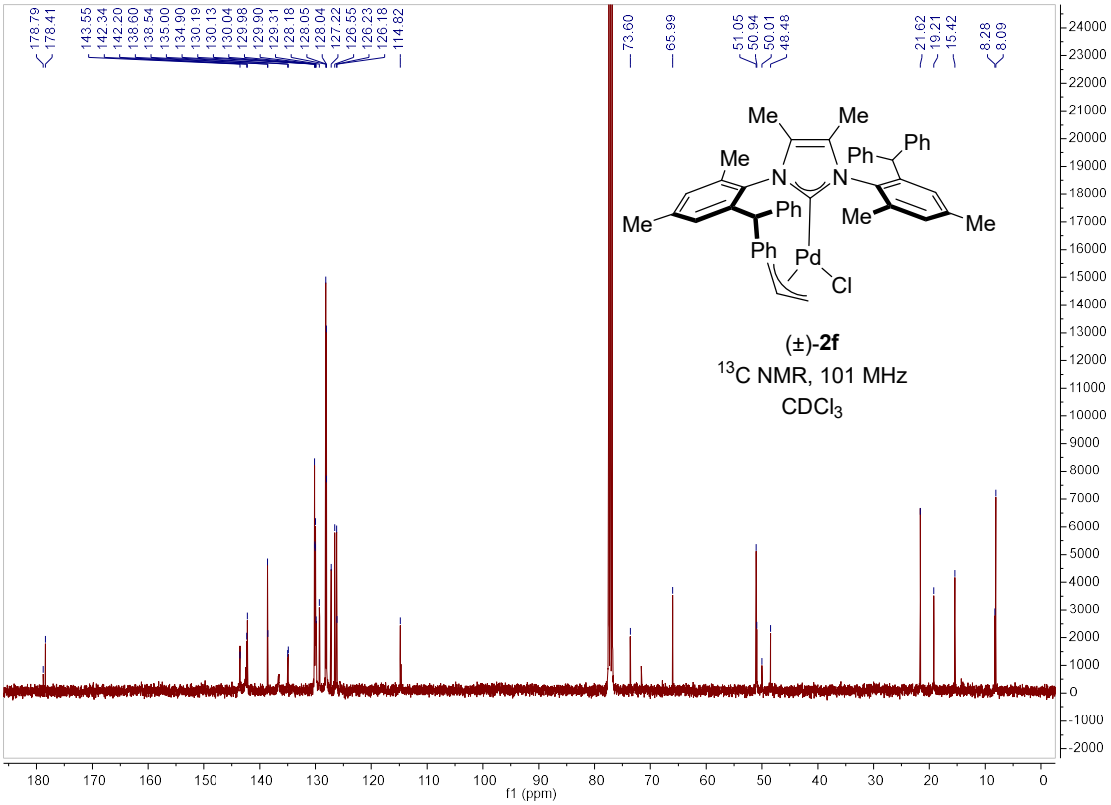

Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**2f**

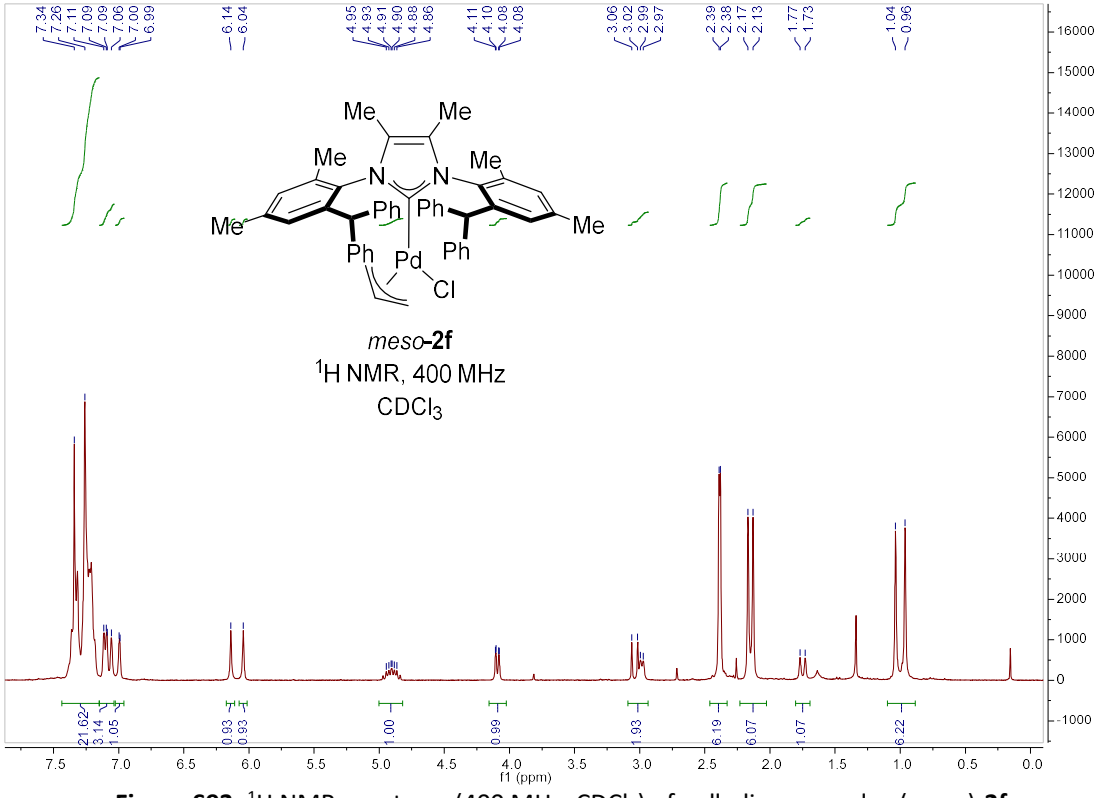

Figure S93. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (*meso*)-**2f**

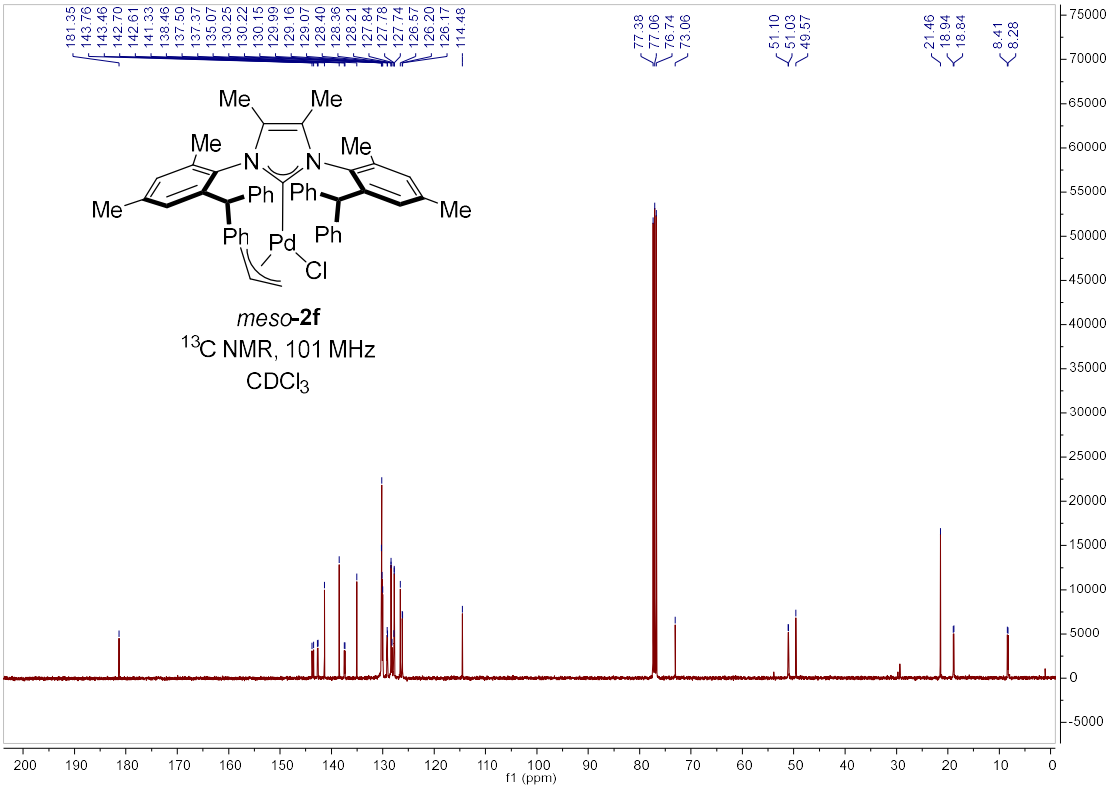

Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (*meso*)-**2f**

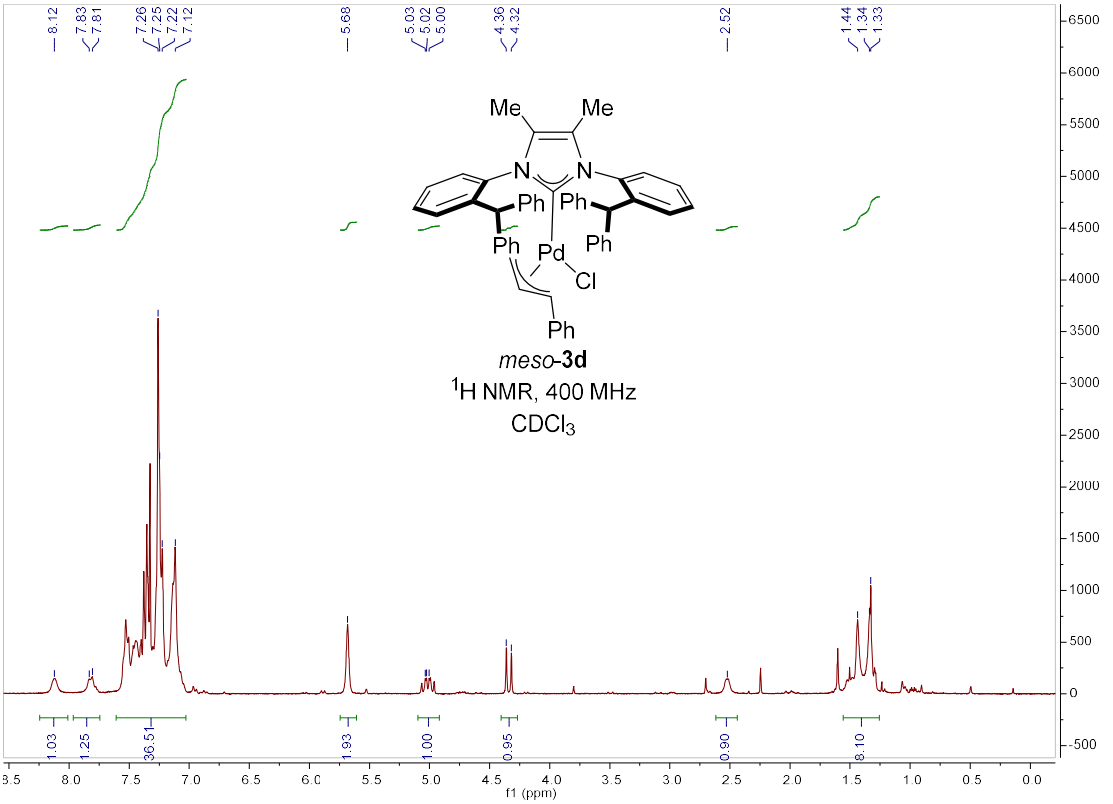

Figure S95. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (*meso*)-**3d**

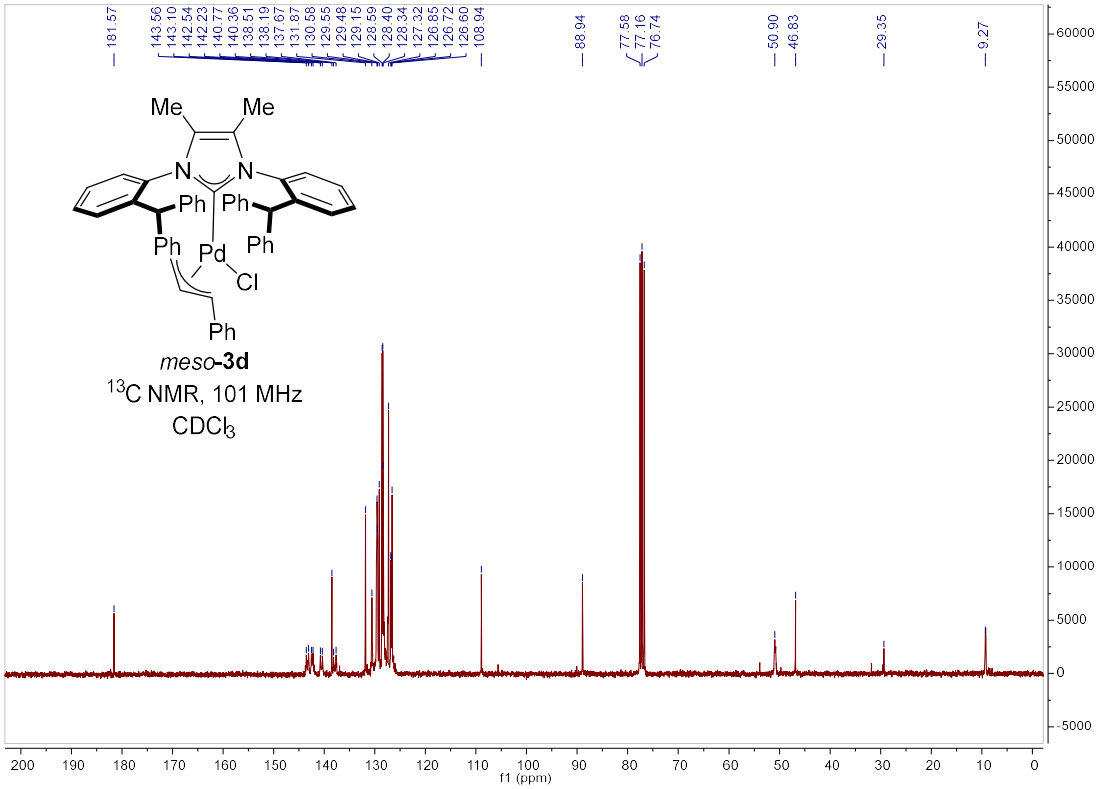

Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (*meso*)-**3d**

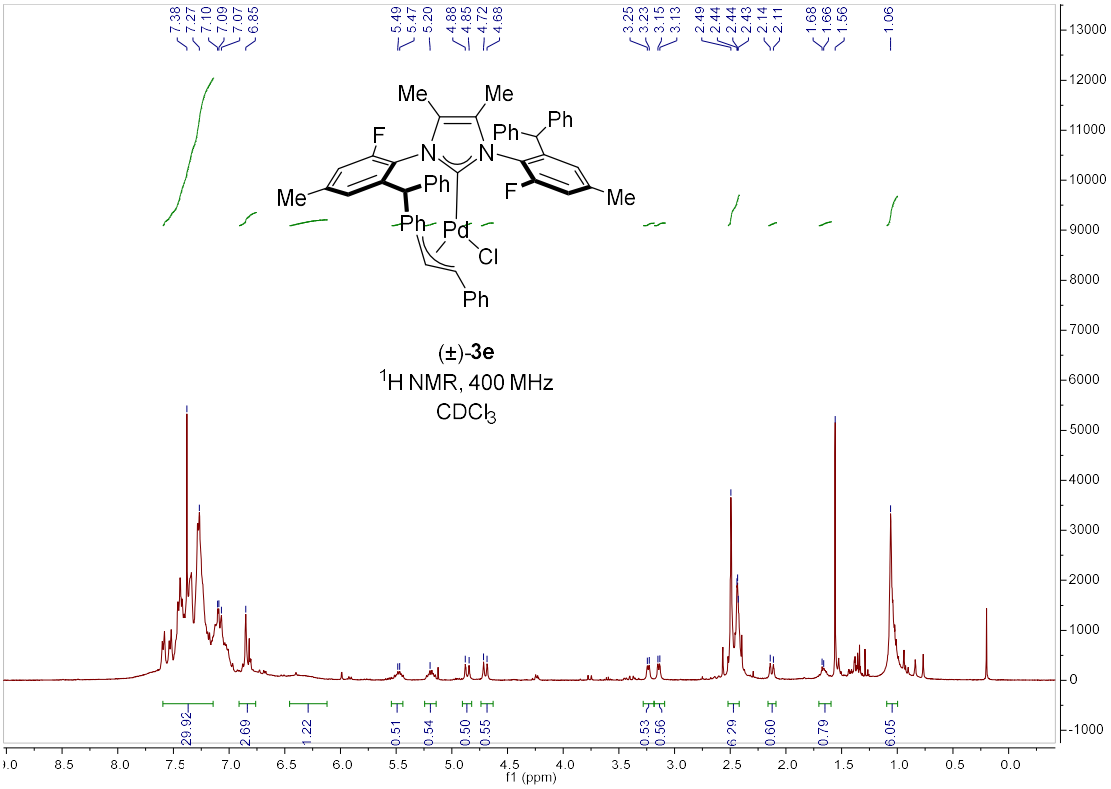

Figure S97. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**3e**

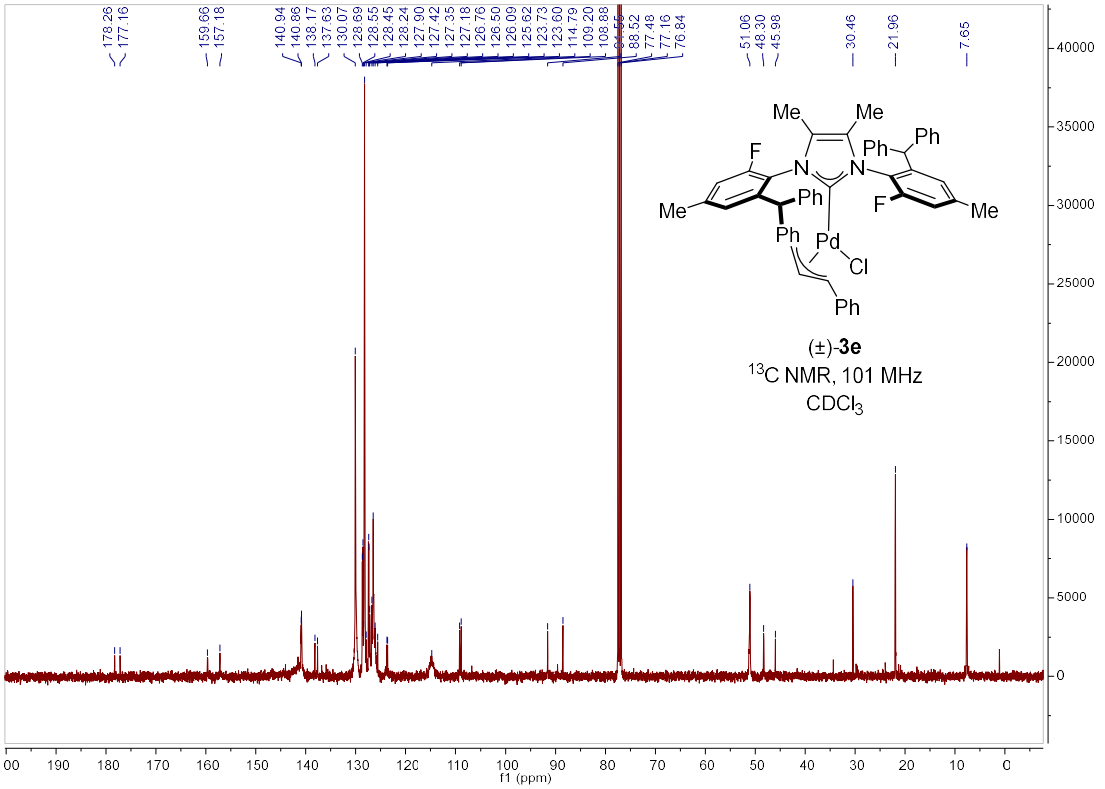

Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**3e**

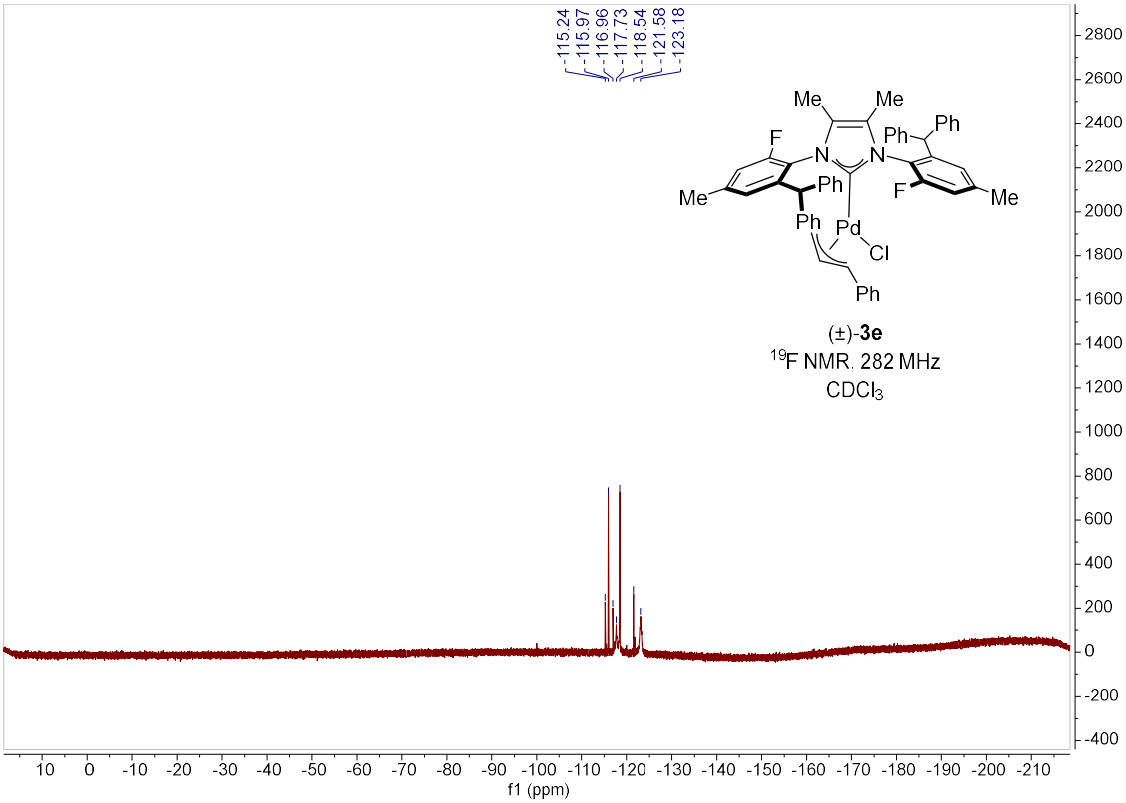

Figure S99. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of palladium complex (±)-**3e**

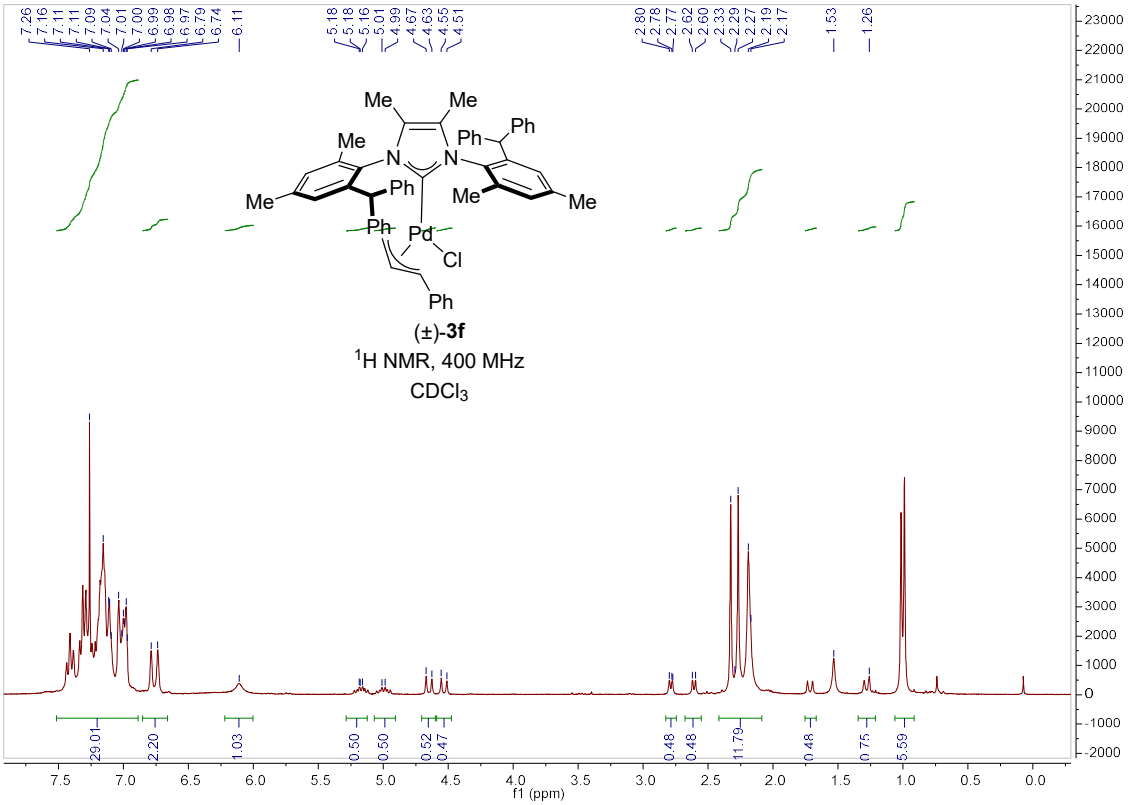

Figure S100. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**3f**

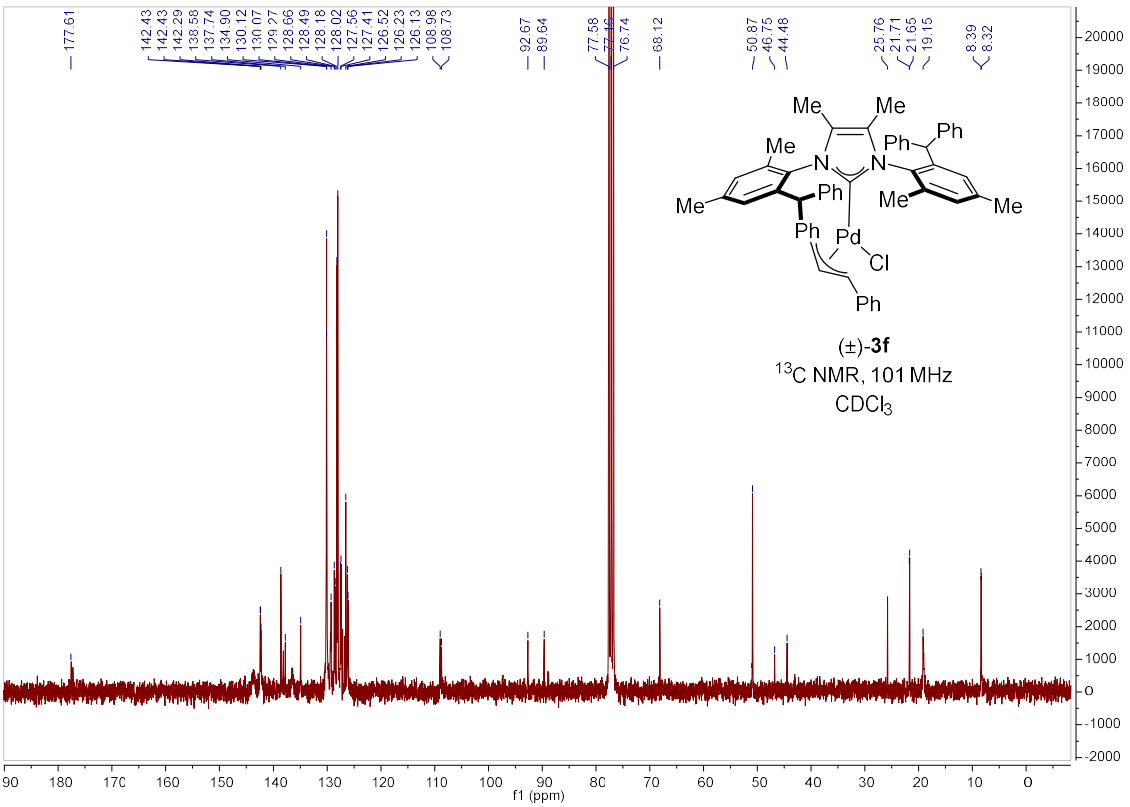

Figure S101. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**3f**

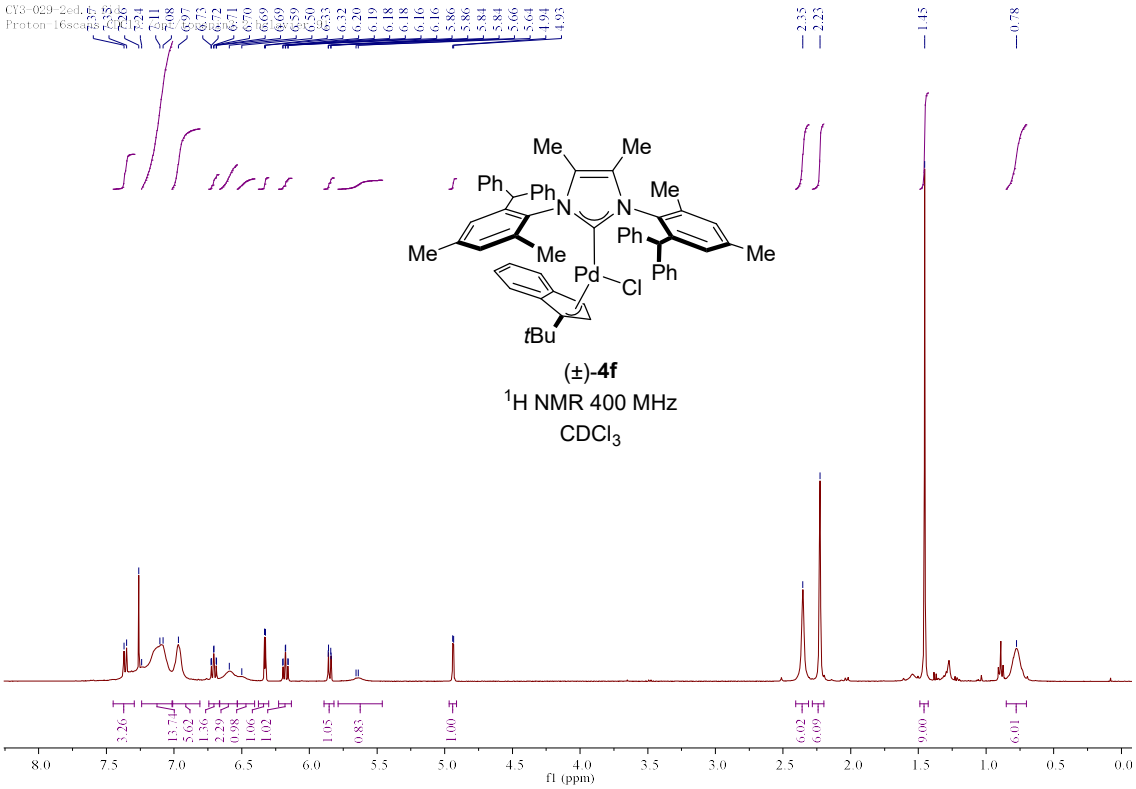

Figure S102. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of palladium complex (±)-**4f**

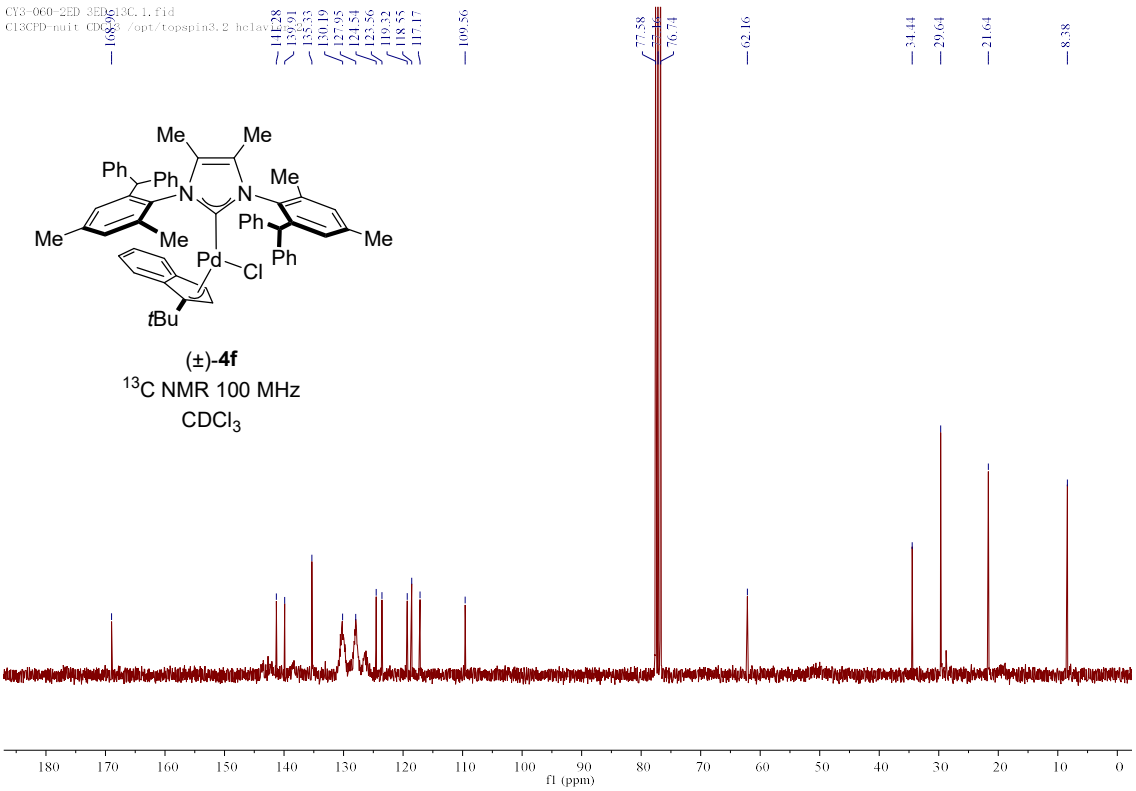

Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of palladium complex (±)-**4f**

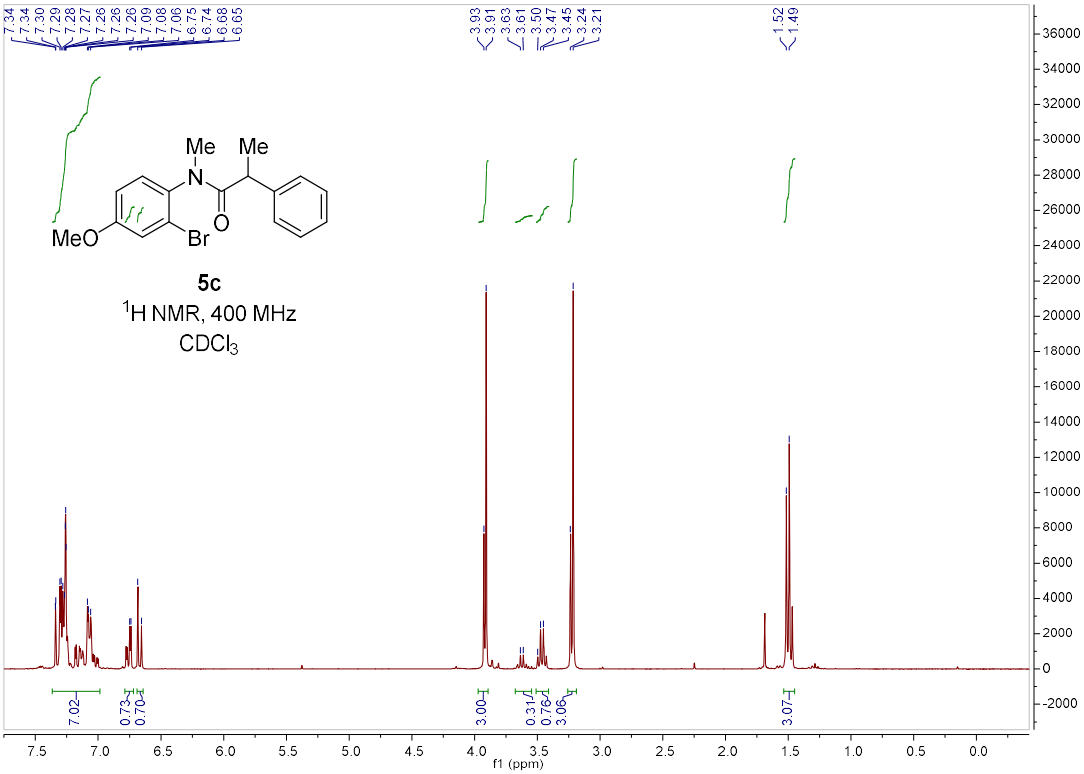

Figure S104. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of substrate **5c**

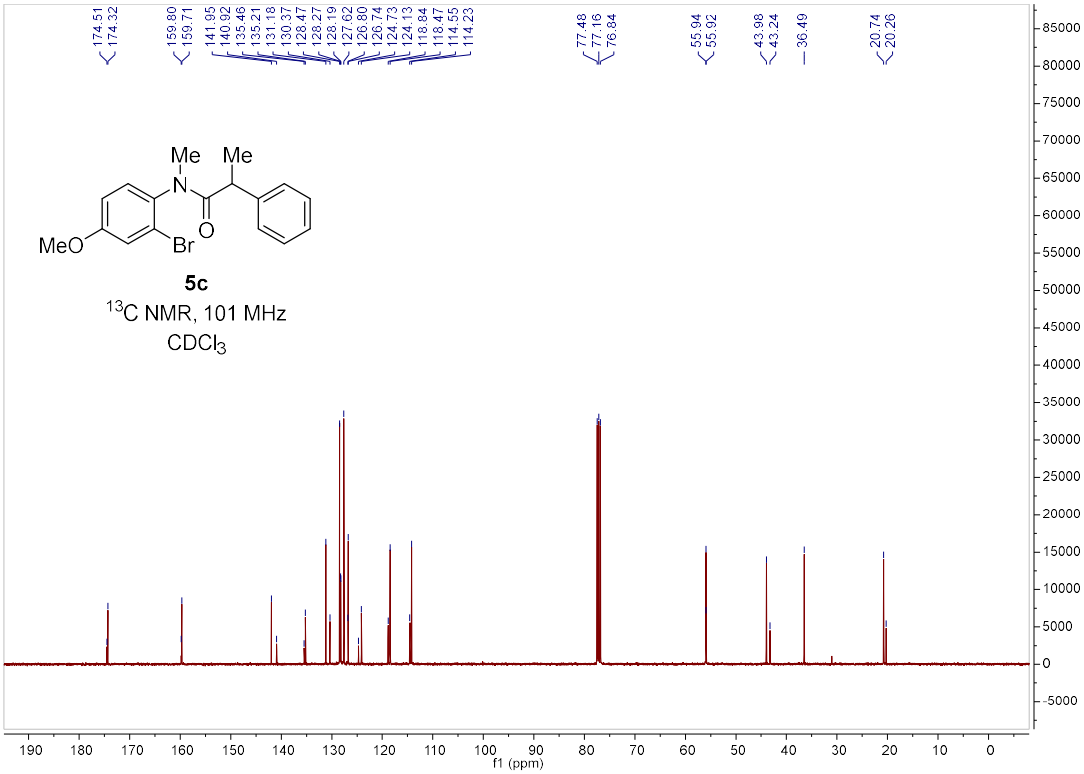

Figure S105. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of substrate **5c**

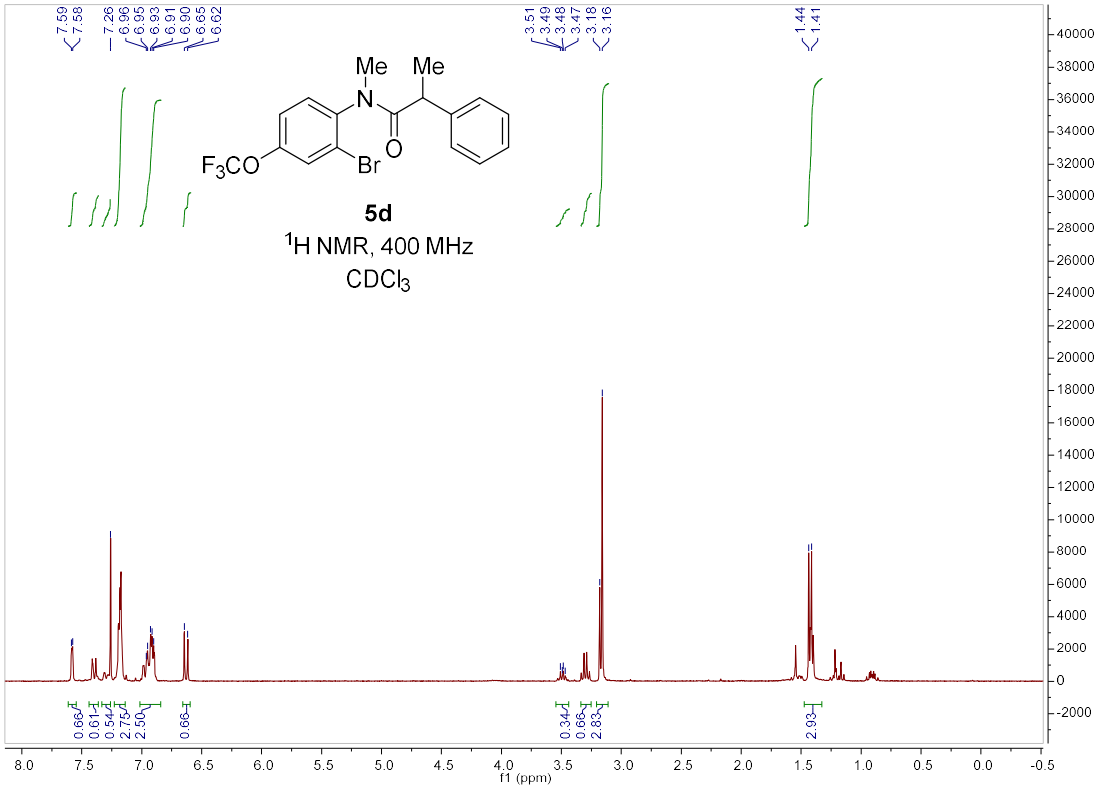

Figure S106. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of substrate **5d**

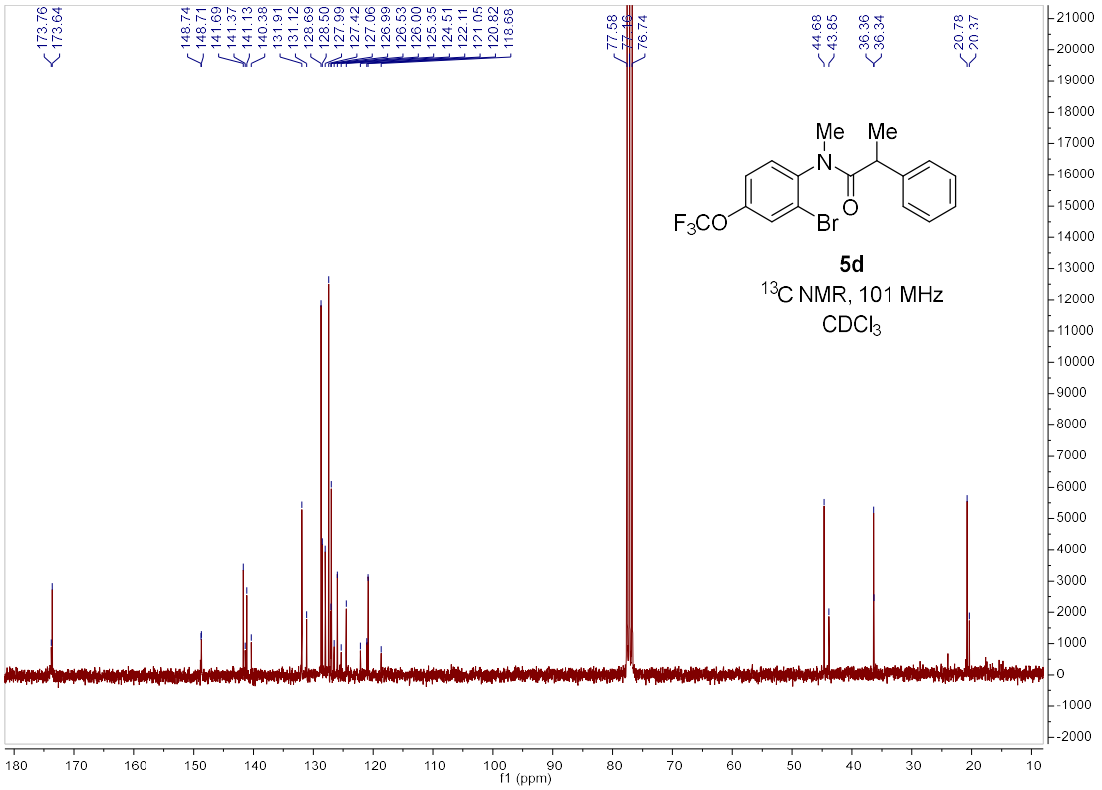

Figure S107. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of substrate **5d**

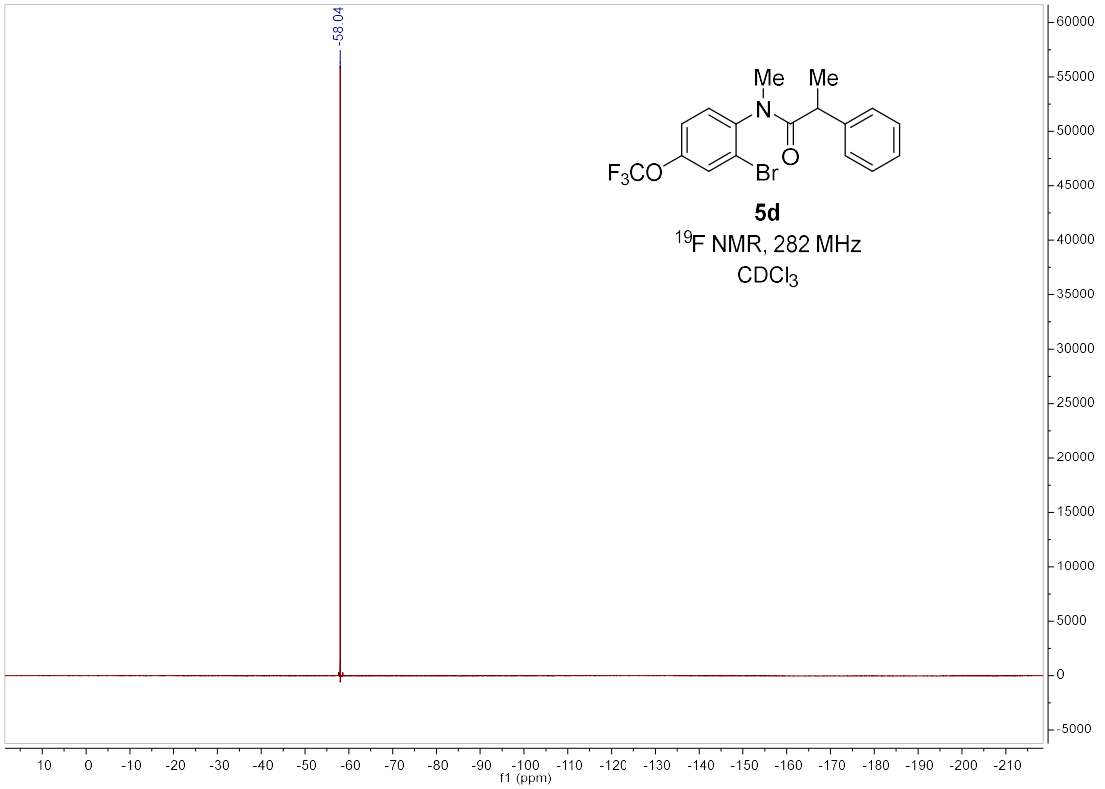

Figure S108. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of substrate **5d**

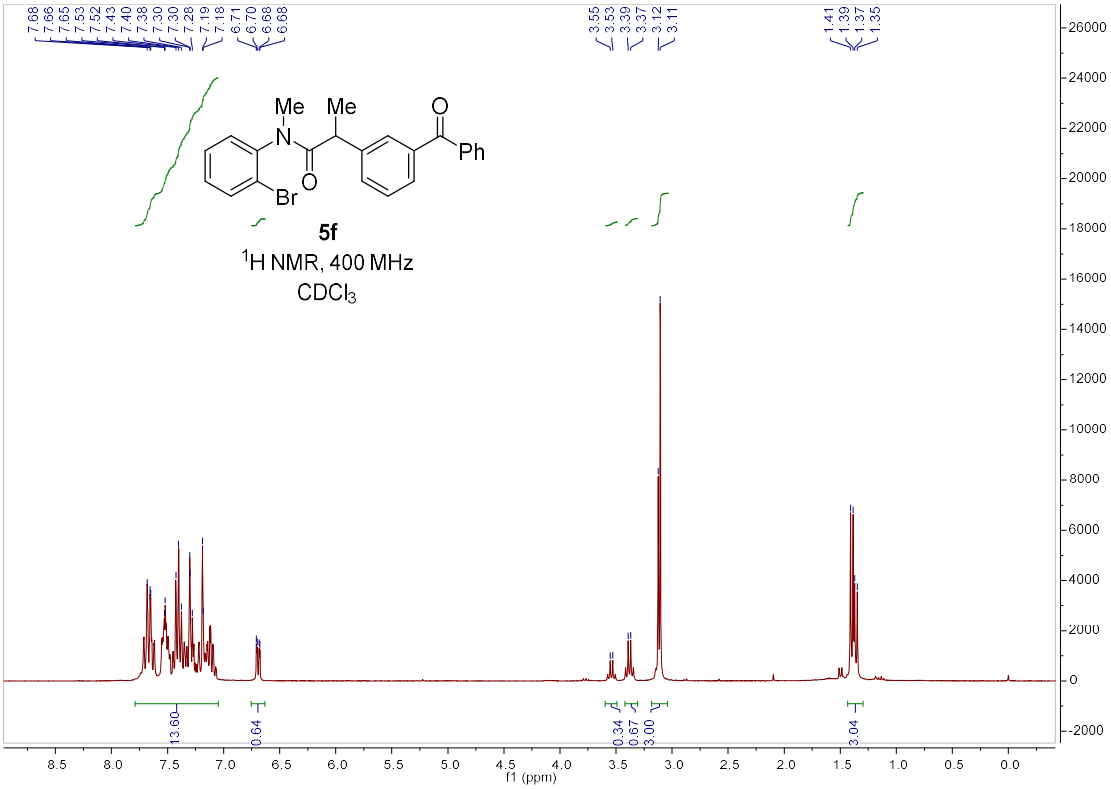

Figure S109. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of substrate **5f**

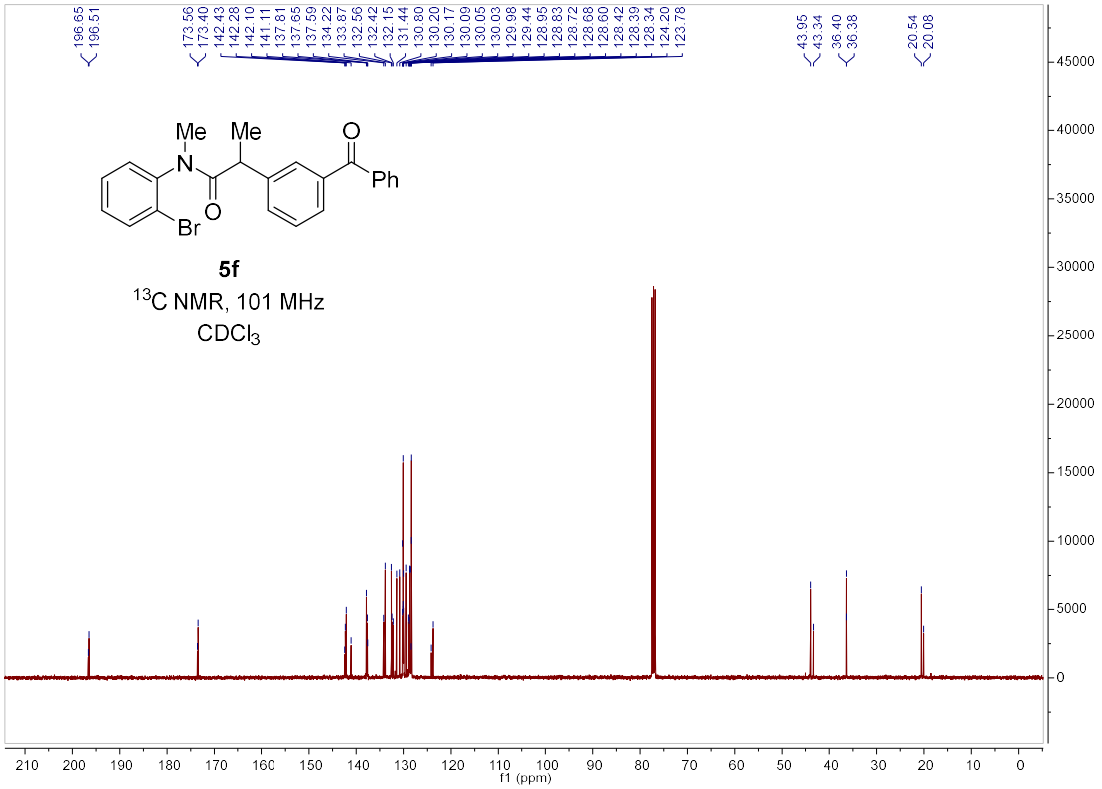

Figure S110. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of substrate **5f**

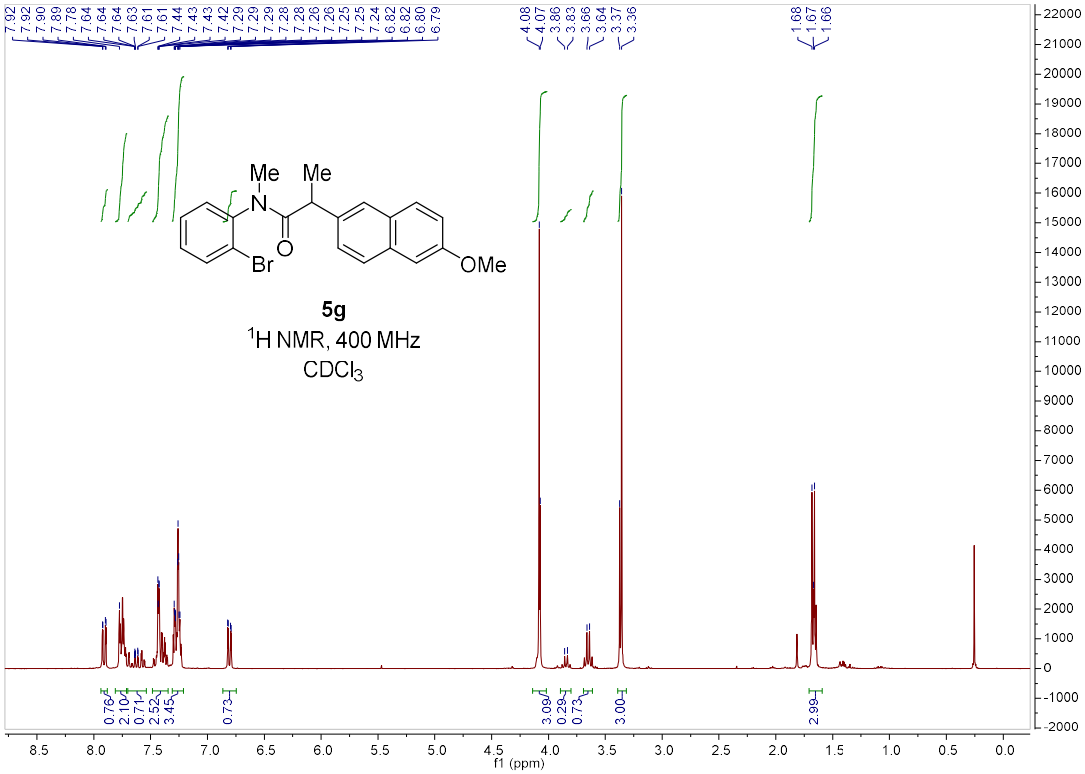

Figure S111. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of substrate **5g**

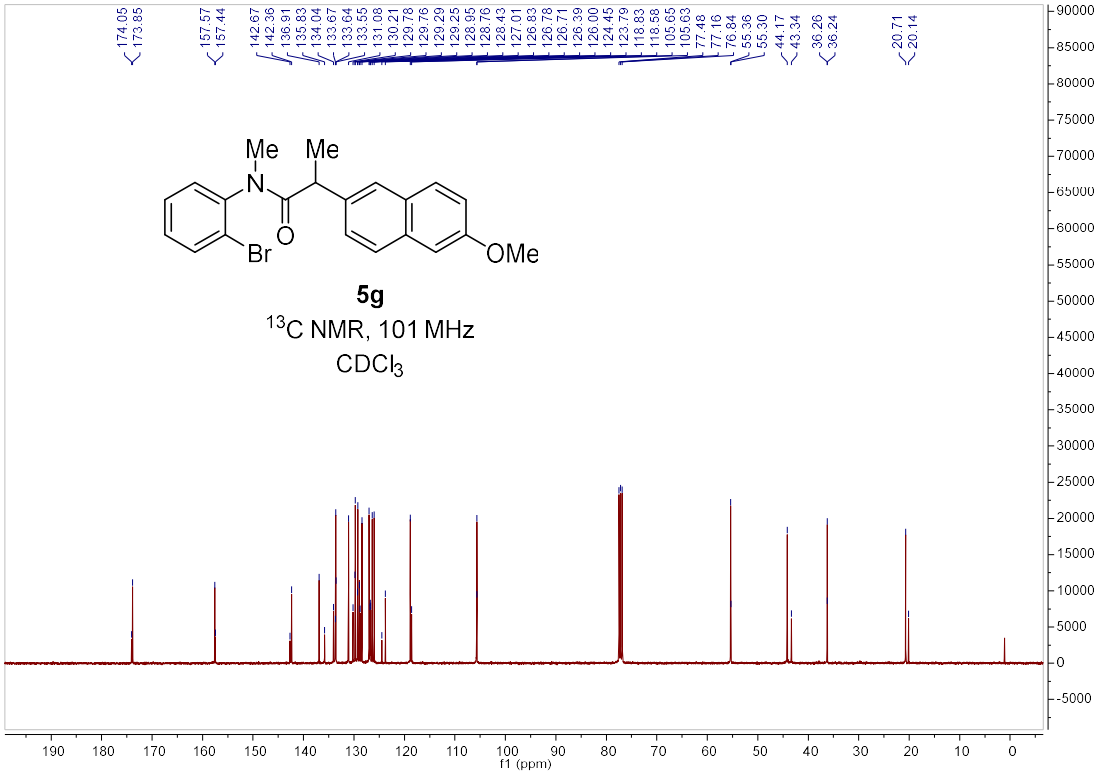

Figure S112. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of substrate **5g**

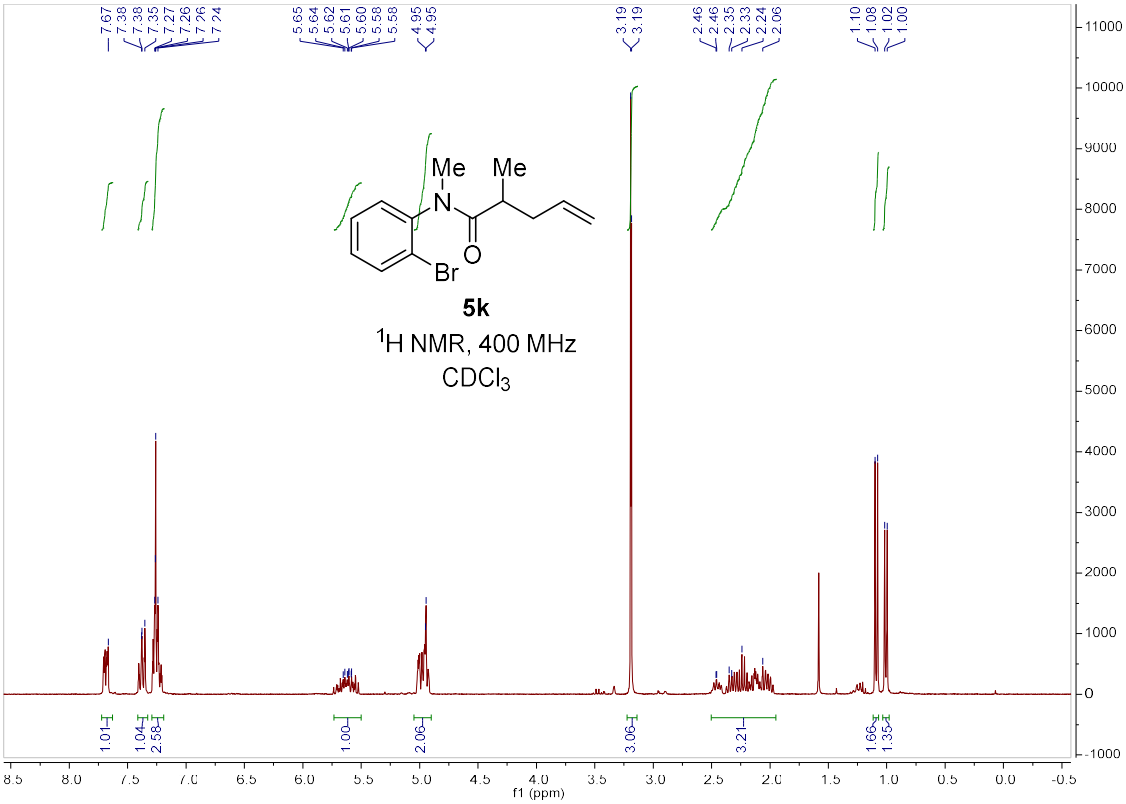

Figure S113. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of substrate **5k**

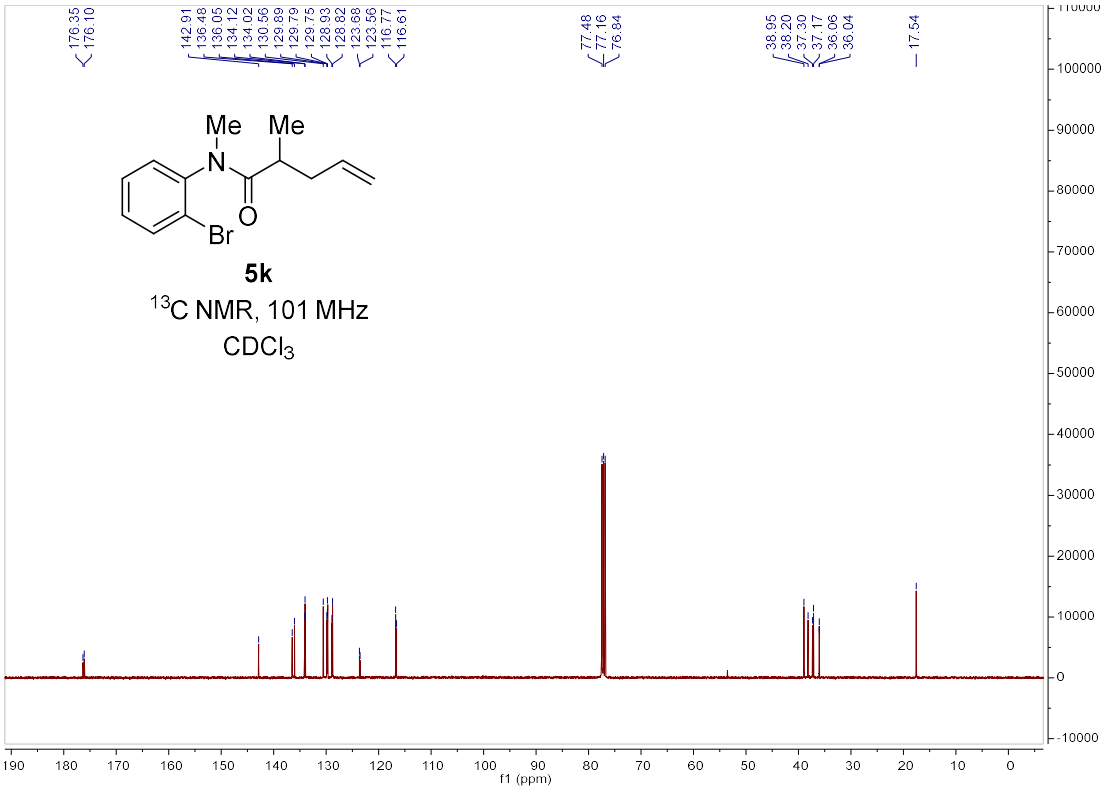

Figure S114. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of substrate **5k**

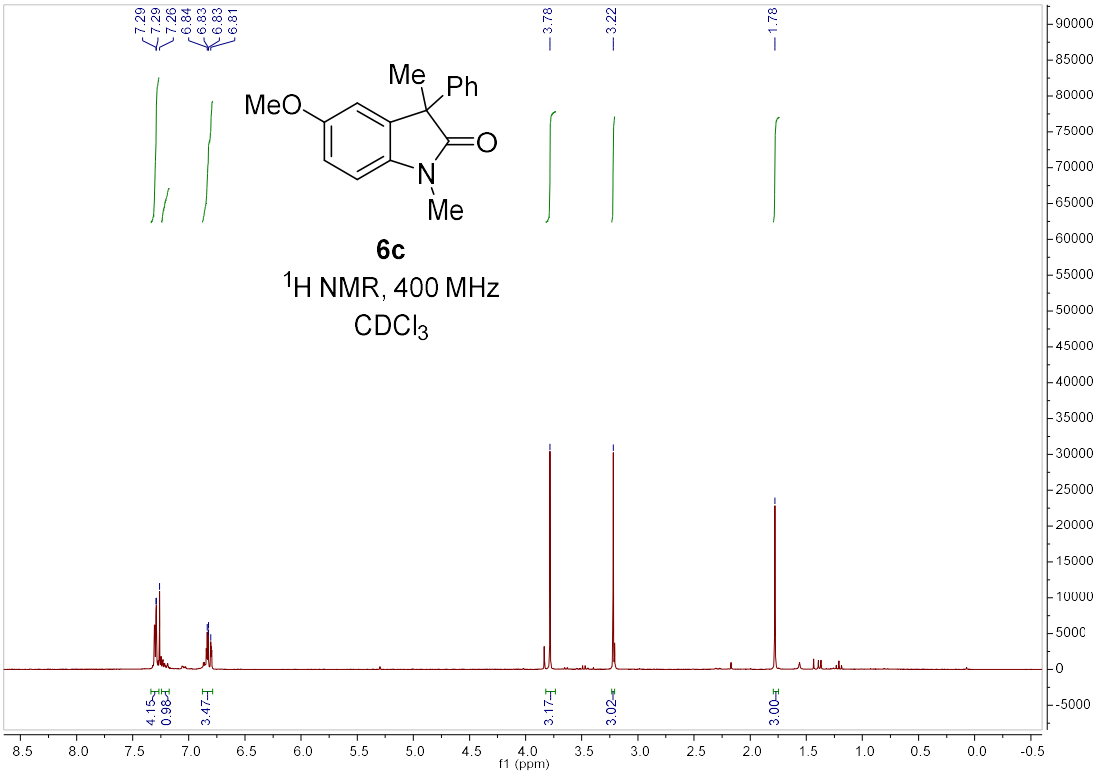

Figure S115. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product **6c**

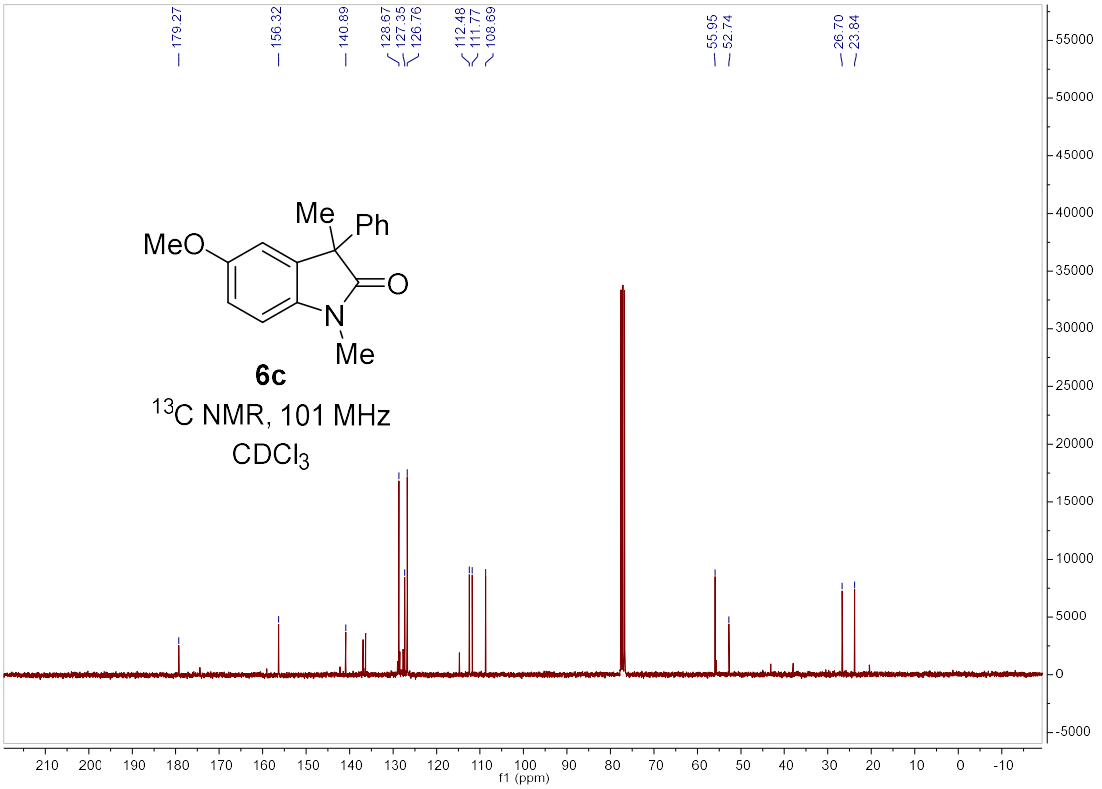

Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of product **6c**

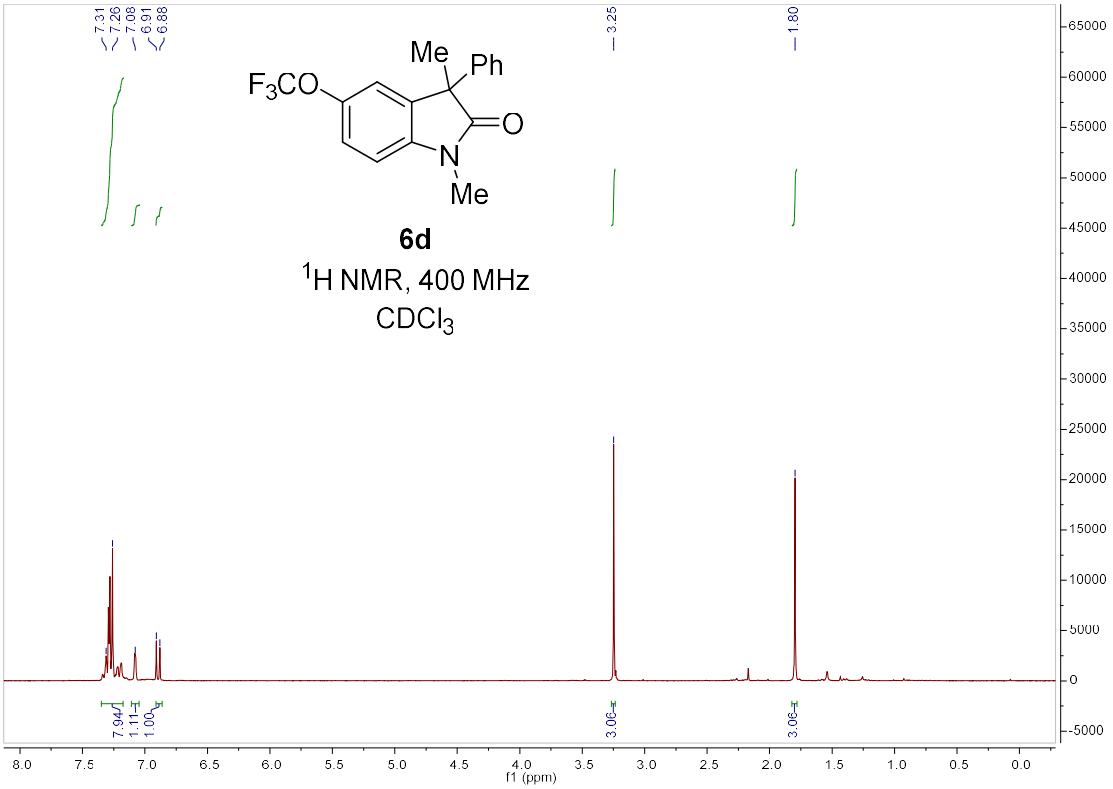

Figure S117. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product **6d**

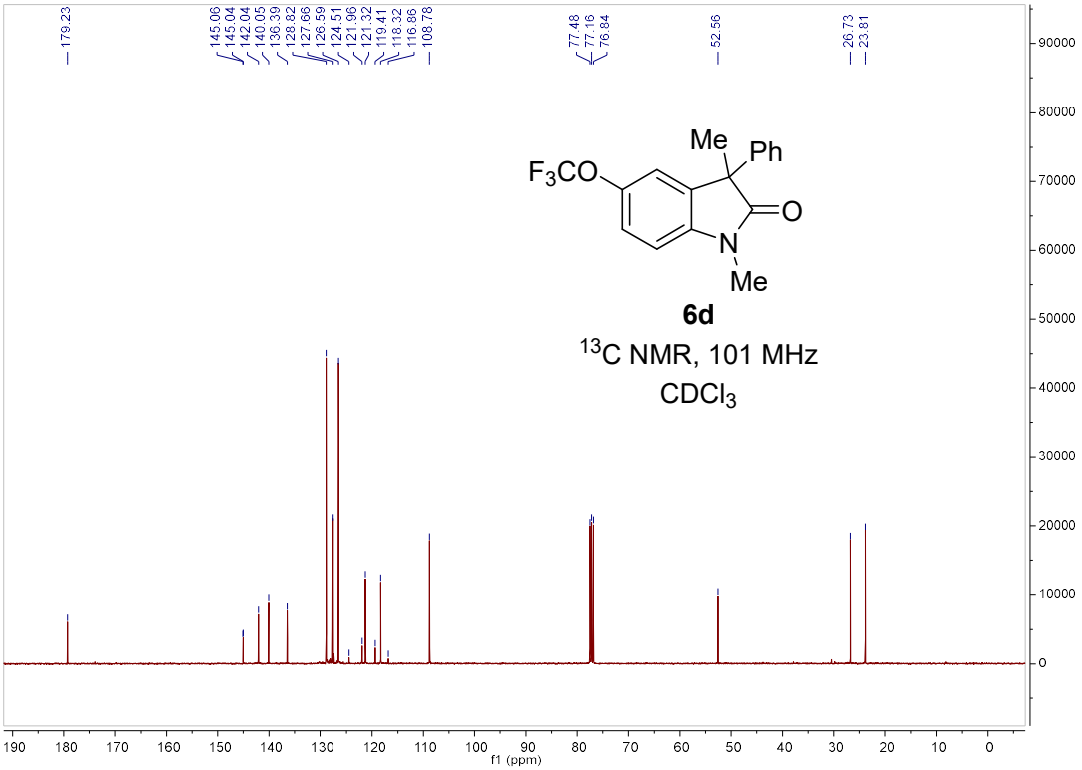

Figure S118. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of product **6d**

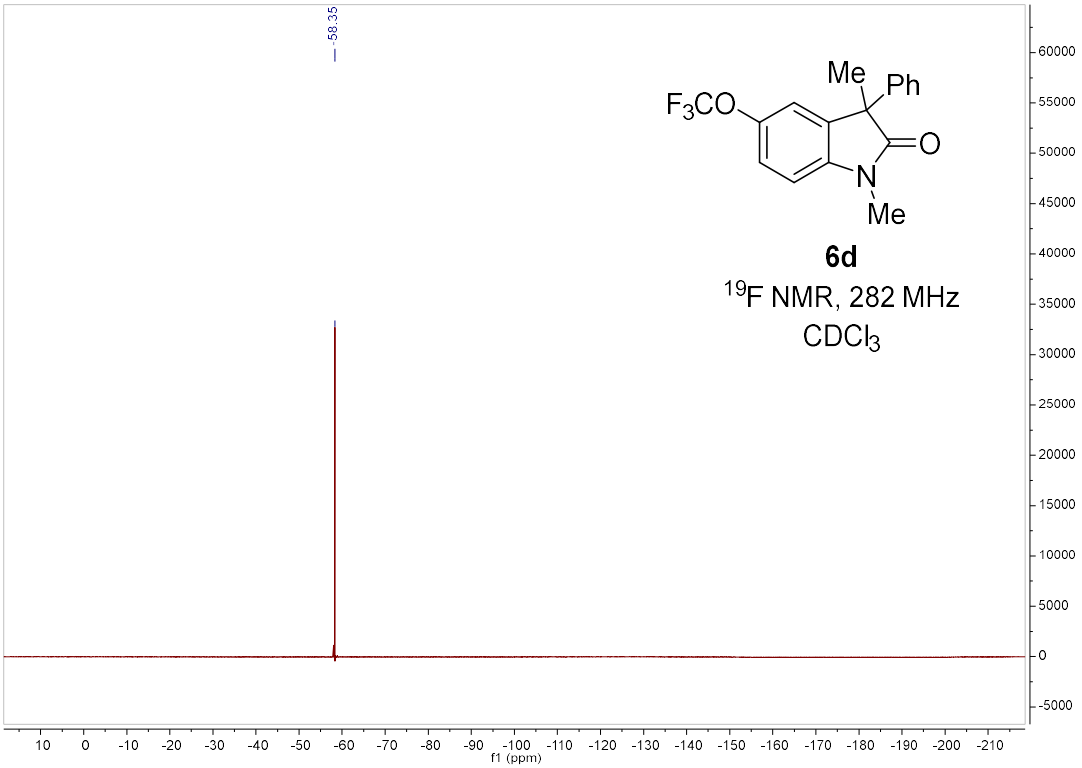

Figure S119. $^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, $CDCl_3$) of product **6d**

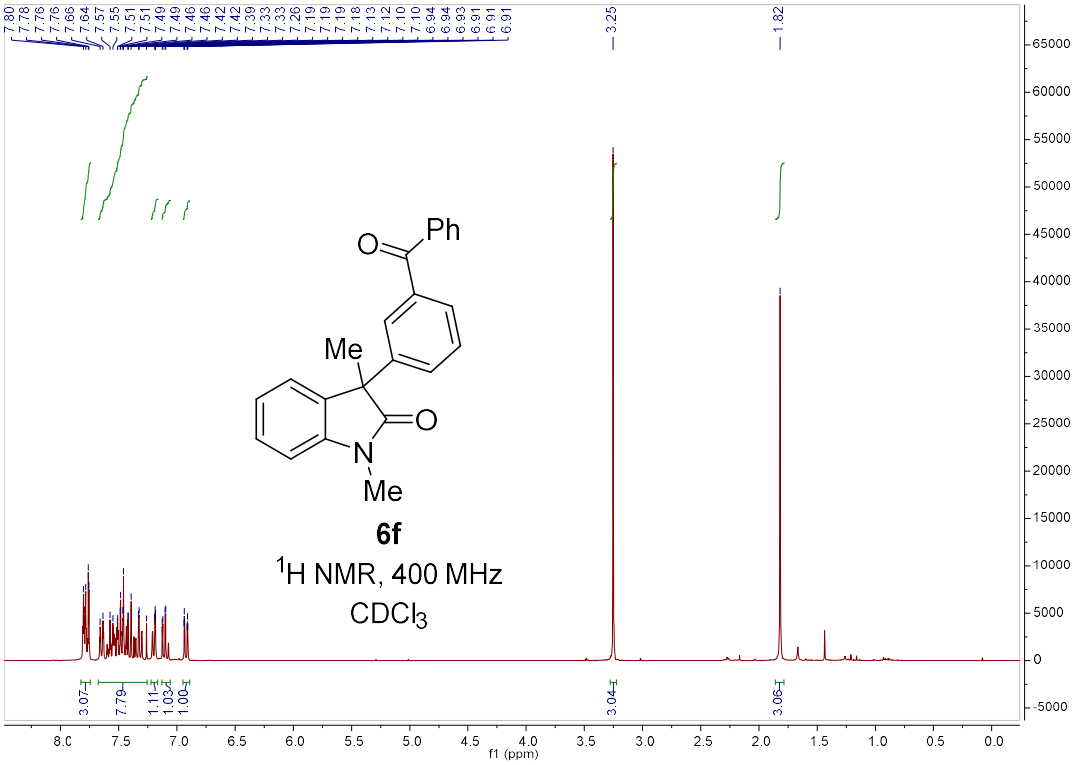

Figure S120. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product **6f**

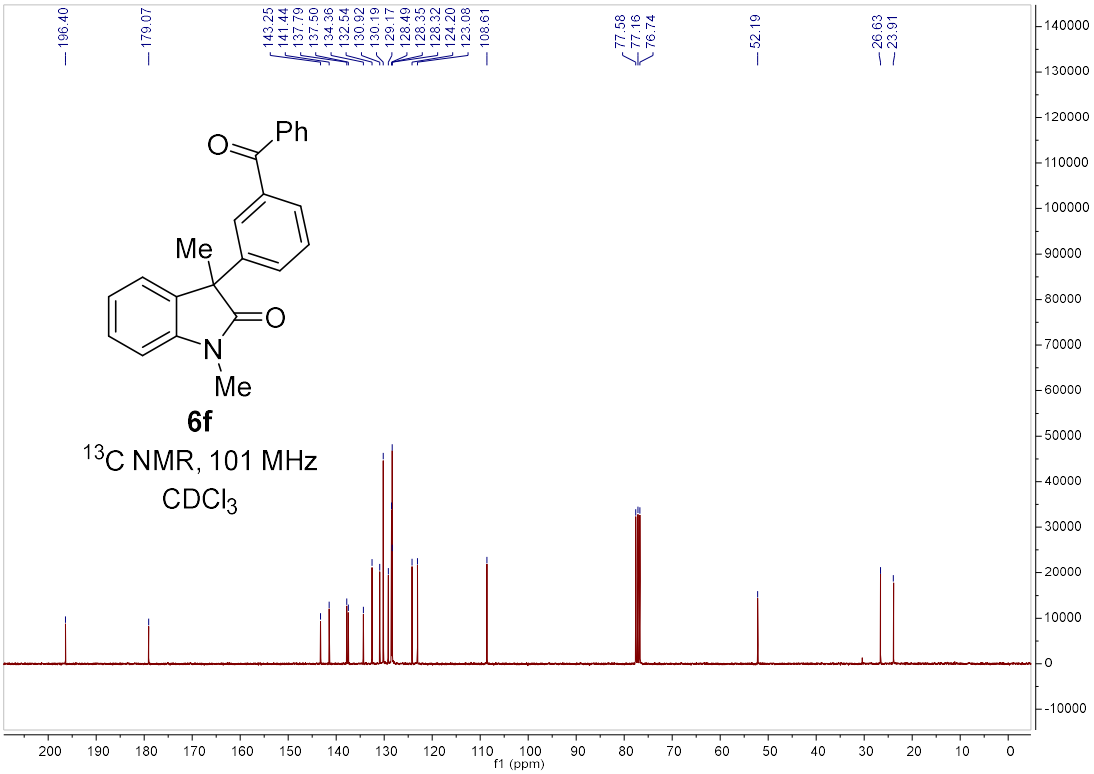

Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of product **6f**

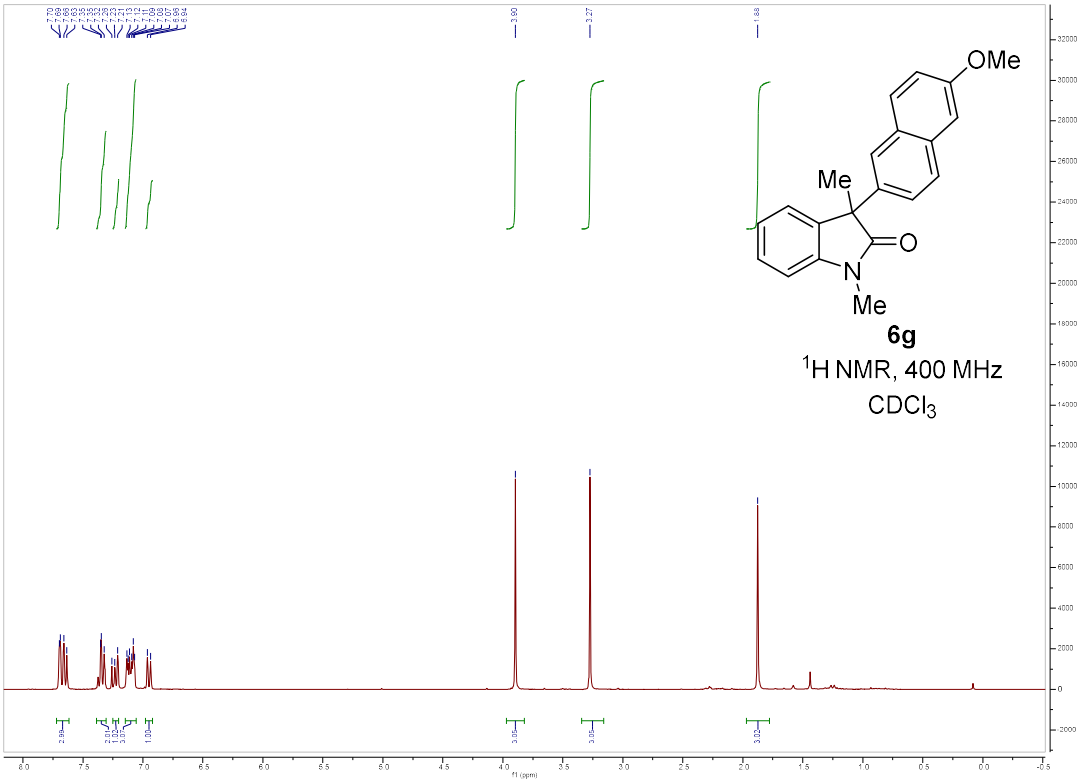

Figure S122. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product **6g**

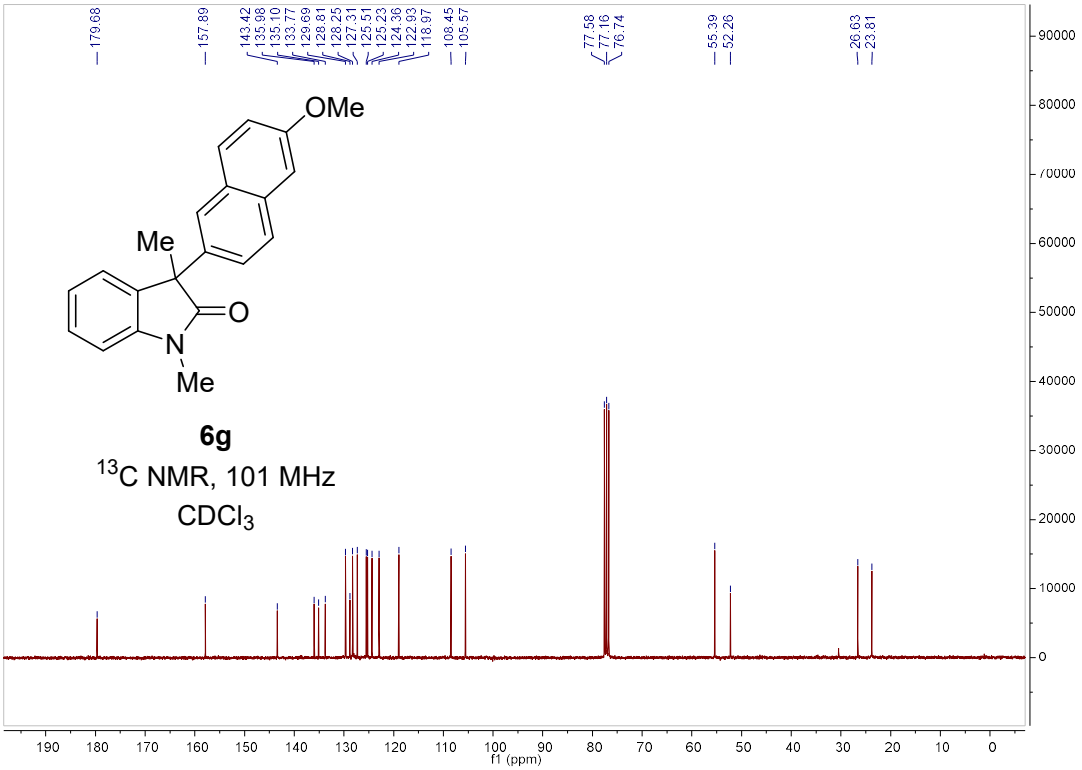

Figure S123. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of product **6g**

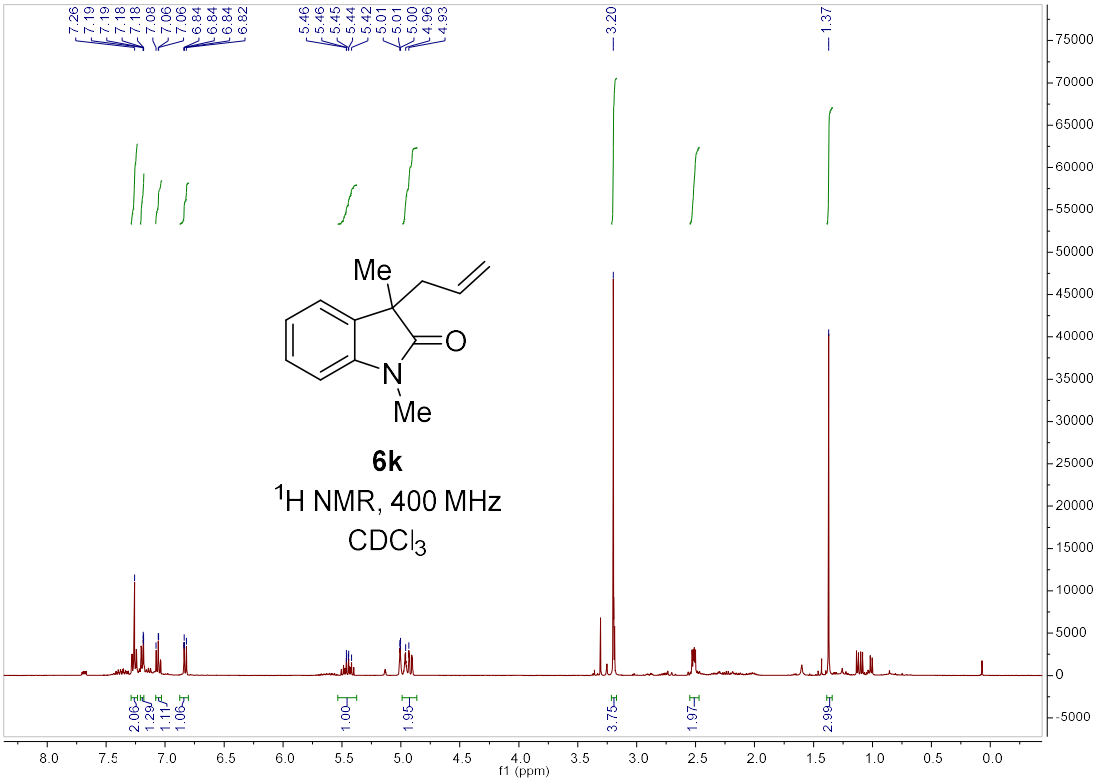

Figure S124. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product **6k**

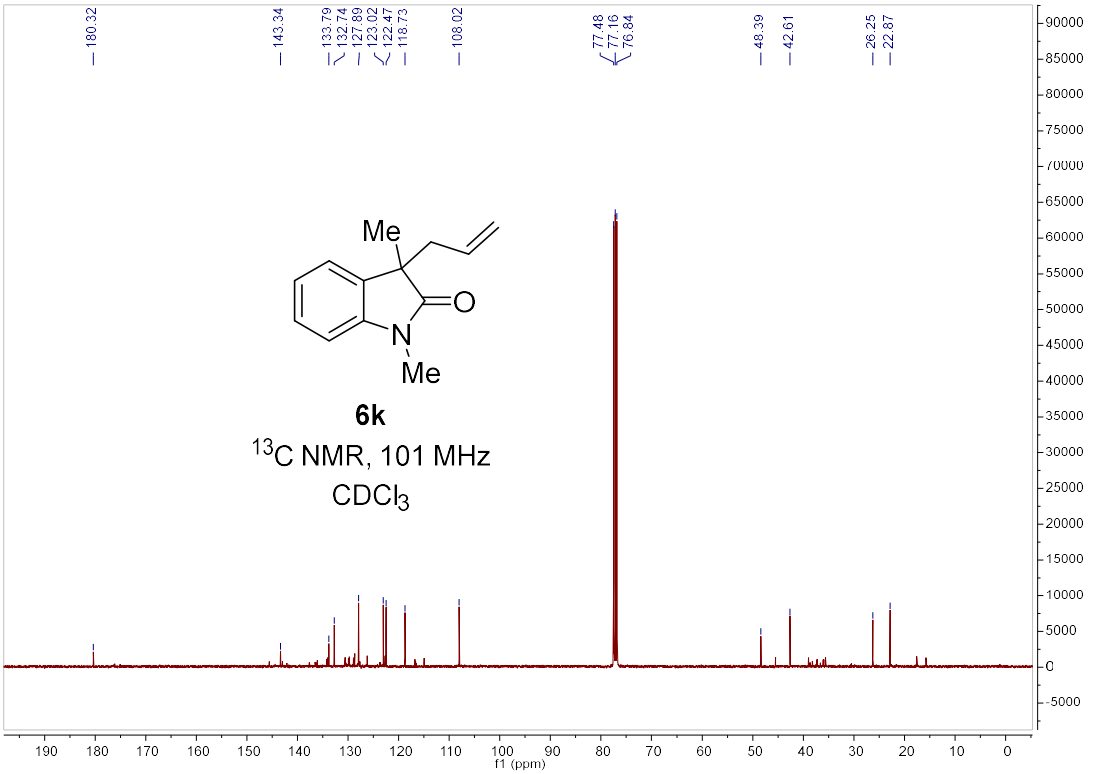

Figure S125. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of product **6k**