Scope and Mechanism of Asymmetric C(sp^3)-H/C(Ar)-X Coupling Reactions: Computational and Experimental Study

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Supporting Information

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1. General Information

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. ^{t}BuONa was sublimed and weighted in the glove box. Solvents were purified by filtration on drying columns using a Solvtec© system. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under nitrogen and glassware was further dried by heating under vacuum as necessary. F.c. (FC): silica gel 60 (40μm). Analysis with HPLC was performed using an Agilent 1100 series chromatograph with a JASCO PU–980 pump and Agilent 1100 Series detection system.

^{1}H, ^{13}C-NMR spectra were recorded on Bruker AMX-500, AMX-400 or AMX-300 MHz; δ-in ppm, pattern abbreviation: broad (*brd*), quartet (*q*), quintet (*quint*), multiplet (*m*). Fourier transform (FT) spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer Spectrum One photometer. HRMS analyses were measured on a VG analytical 7070E instrument.

Starting Materials:

Mesitylene was distilled over CaH_2 under nitrogen. Dry xylenes, benzene, trifluoroacetic acid, sodium triacetoxyborohydride, cesium carbonate, cesium pivalate, pivalic acid, molecular sieves 4Å, methyl chloroformate, ethyl chloroformate, benzyl chloroformate, isobutyryl chloride, pivaloyl chloride, 2-amino-3-bromopyridine, 3-amino-2-bromopyridine and 2-bromoaniline were purchased from Sigma-Aldrich, Fluka or Acros. 2-Bromo-3-methylaniline was prepared by general procedure.[i]

2. Experimental Details and Procedures

2.1 General procedures

General procedure for the synthesis of *N*-cycloalkyl-2-(pseudo)haloanilines (GP1):[ii]

2-(pseudo)haloaniline (3.4 g, 20 mmol), molecular sieves 4Å (6 g) and the corresponding cyclic ketone (2-5 equivs.) was dissolved in benzene (50 mL). The reaction mixture was refluxed with Dean-Stark apparatus for 3-4 days. The reaction mixture was cooled down and filtered through celite. The filtrate was evaporated by rotary evaporator and dried in vacuo. The crude imine was dissolved in dry methanol and $NaBH_4$ (3 equivs.) was added slowly under nitrogen. The reaction mixture as stirred for 2 hours. 1N-KOH aq. was added and the extracted with dichloromethane. The organic phase was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography (silica gel; diethyl ether/pentane as eluent) affording *N*-cycloalkyl-2-(pseudo)haloaniline.

General procedure for the synthesis of substrates 1a-r and 3a,b (GP2).

N-(cyclo)alkyl-*o*-(pseudo)haloaniline was dissolved in methyl chloroformate (15 equivs.) or the corresponding acyl chloride (for synthesis of **1h**, **1i** and **3b**). The reaction mixture was refluxed for 24 hours and then poured into water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and evaporated after filtration. The filtrate was evaporated by rotary evaporator and purified by f.c. (silica gel; ethyl acetate/pentane as eluent) affording the product**.**

General procedure for the racemic C(sp^3)-H activation using $PCy_3 \cdot HBF_4$ as a ligand (GP3).

Substrate (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), pivalic acid (6.1 mg, 0.06 mmol), cesium carbonate (97.5 mg, 0.3 mmol), and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol) were placed into a Schlenk tube. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) were added under nitrogen and the resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; ethyl acetate : pentane mixtures as eluent) to afford the racemic product.

General procedure for the racemic C(sp^3)-H activation using 6 as a ligand (GP4).

Substrate (0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), $[Pd(\pi\text{-cinnamyl})Cl]_2$ (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and **6** HCl (8.5 mg, 0.02 mmol) were placed in a Schlenk tube. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) were added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and

the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; ethyl acetate : pentane mixtures as eluent) to afford the racemic product.

General procedure for the asymmetric NHC-palladium catalyzed C-H activation (GP5).

Substrate (0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2.6 mg, 0.005 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and NHC-HI (0.01 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2mL) were added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 16 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; ethyl acetate : pentane mixtures as eluent) to afford product.

General procedure for the asymmetric NHC-palladium catalyzed C-H activation with cesium acetate as additive (GP6)

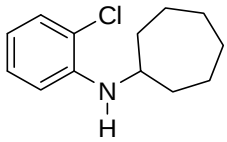
Substrate (0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2.6 mg, 0.005 mmol), cesium acetate (38.4 mg, 0.2 mmol) and NHC-HI (0.01 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2mL) were added under nitrogen. The resulting reaction mixture was stirred at 120 °C in the Schlenk tube behind a protective shield for 21 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; ethyl acetate : pentane mixtures as eluent) to afford product.

2.1. Characterization data

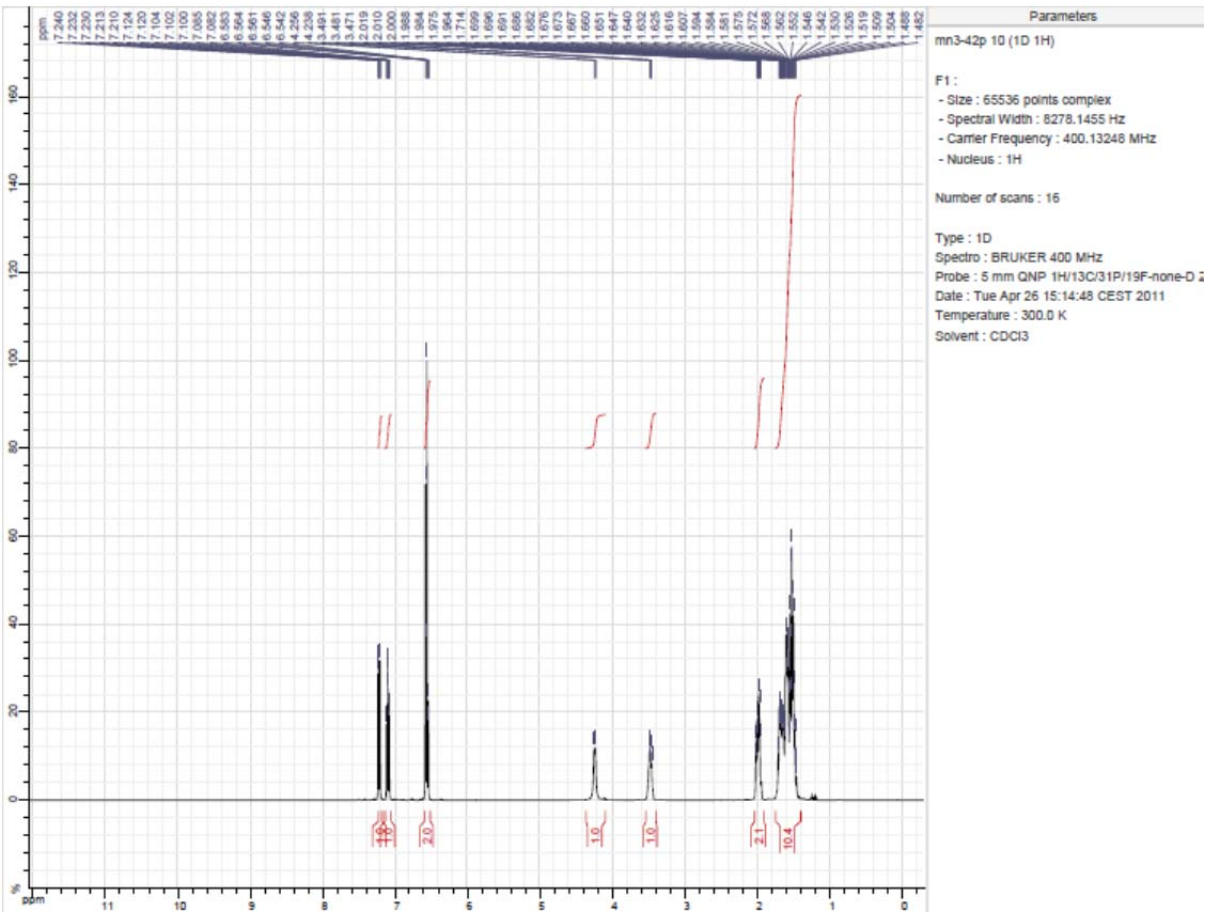
2.1.1 *N*-cycloalkyl-2-(pseudo)haloanilines

Table 1:

N-(2-Chlorophenyl)cycloheptanamine:



Prepared according to **GP1**. Colorless oil, 72% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.41-1.76 (m, 10H), 1.92-2.05 (m, 2H), 3.41-3.55 (m, 1H), 4.25 (d, J = 7.2 Hz, 1H), 6.55 (td, J = 7.6, 1.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 7.10 (dd, J = 8, 1.6 Hz, 1H), 7.22 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.5, 28.5, 34.9, 53.6, 111.9, 116.6, 119.2, 127.9, 129.4, 143.3. IR (neat): υ = 735, 831, 1032, 1079, 1132, 1177, 1236, 1288, 1322, 1431, 1458, 1508, 1596, 2853, 2924, 3418 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{19}ClN$ 224.1200, found 224.1200.



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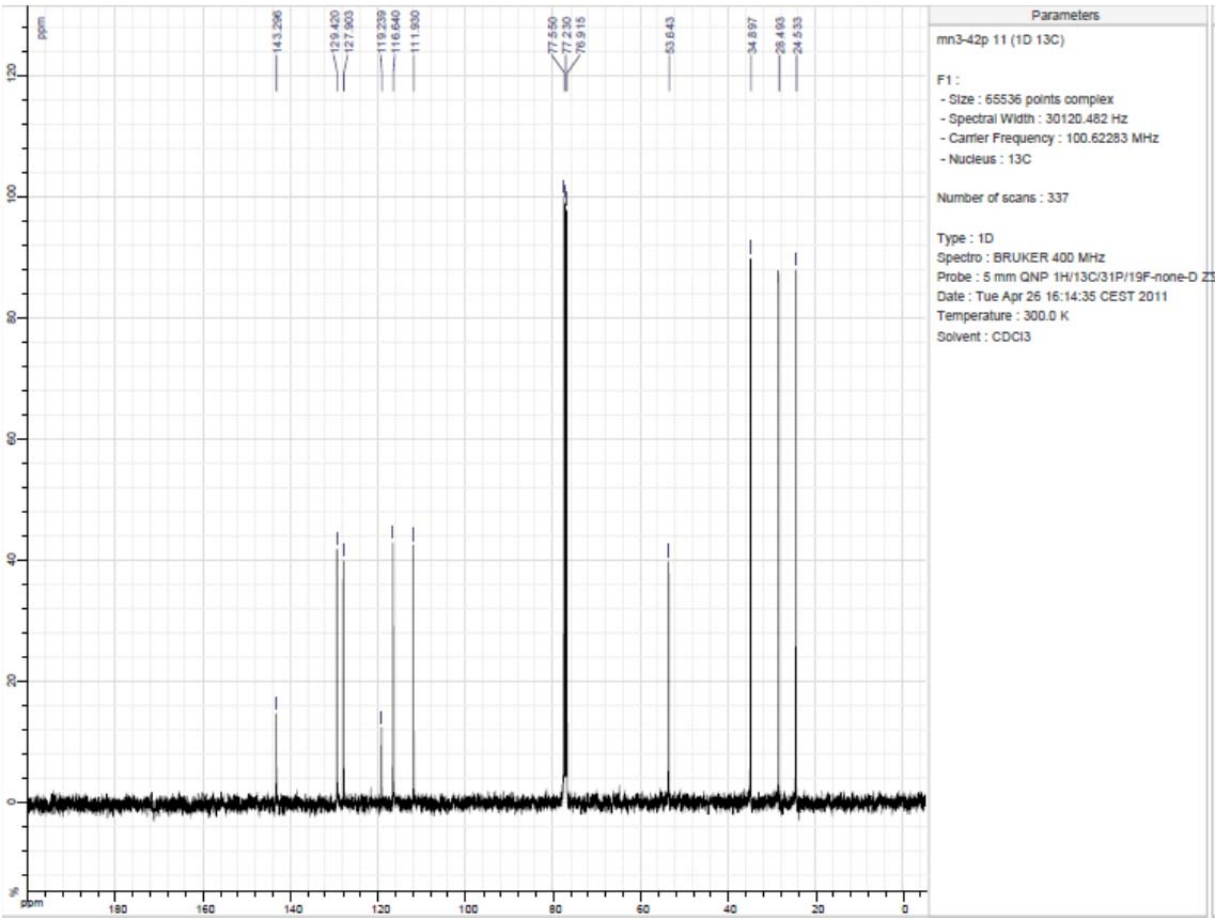
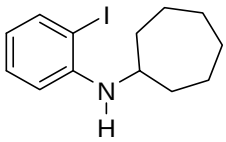


N-(2-Iodophenyl)cycloheptanamine:



Prepared according to **GP1**. White solid, 97% yield, M. p. 36 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.44-1.77 (m, 10H), 1.90-2.05 (m, 2H), 3.42-3.56 (m, 1H), 4.13 (d, J = 7.2 Hz, 1H), 6.38 (td, J = 7.6, 1.6 Hz, 1H), 6.48 (dd, J = 7.2, 1.2 Hz, 1H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.63 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.5, 28.5, 34.8, 54.1, 86.1, 111.4, 118.1, 129.5, 139.4, 146.5. IR (neat): υ = 736, 828, 923, 948, 1001, 1060, 1129, 1177, 1281, 1315, 1364, 1425, 1451, 1502, 1586, 2852, 2921, 3066, 3391 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}IN$ 374.0611, found 374.017.

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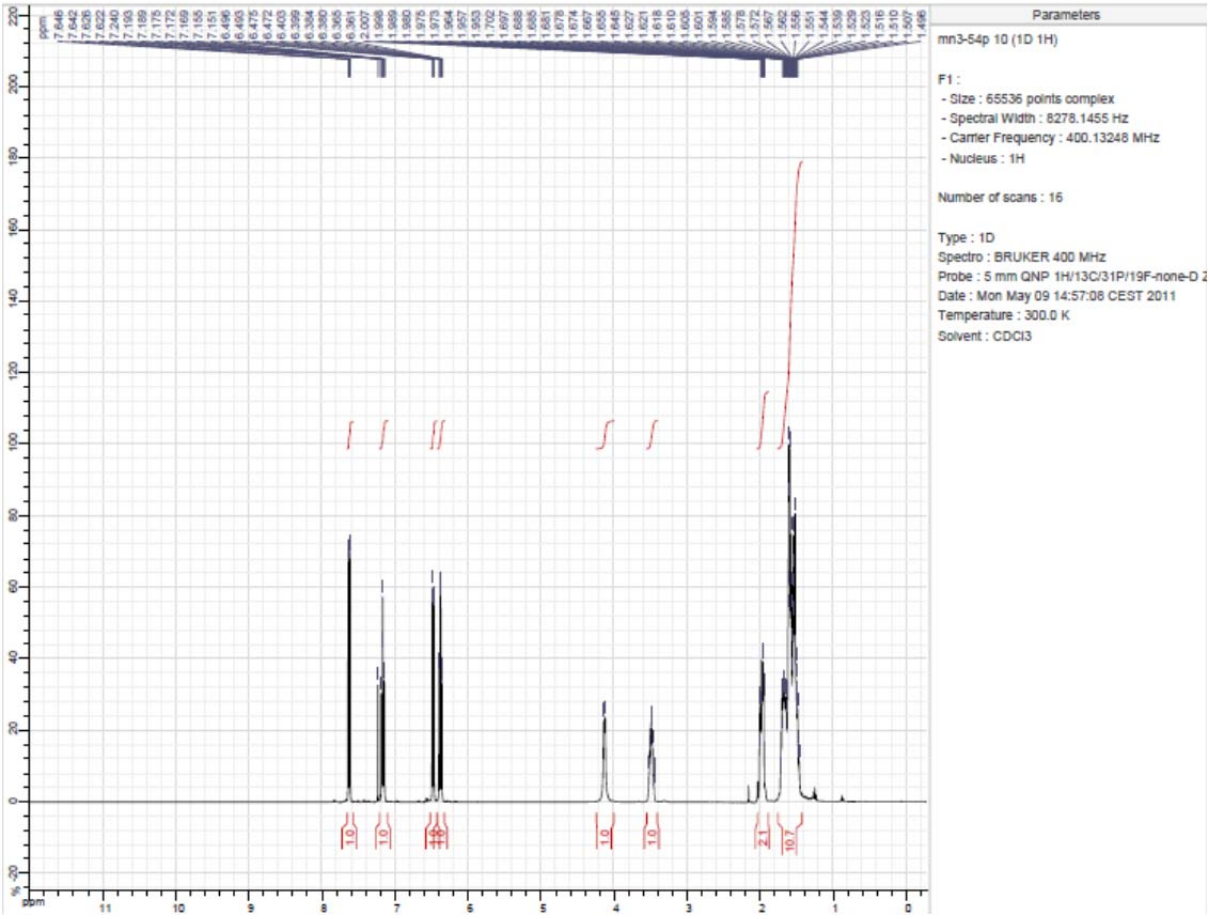
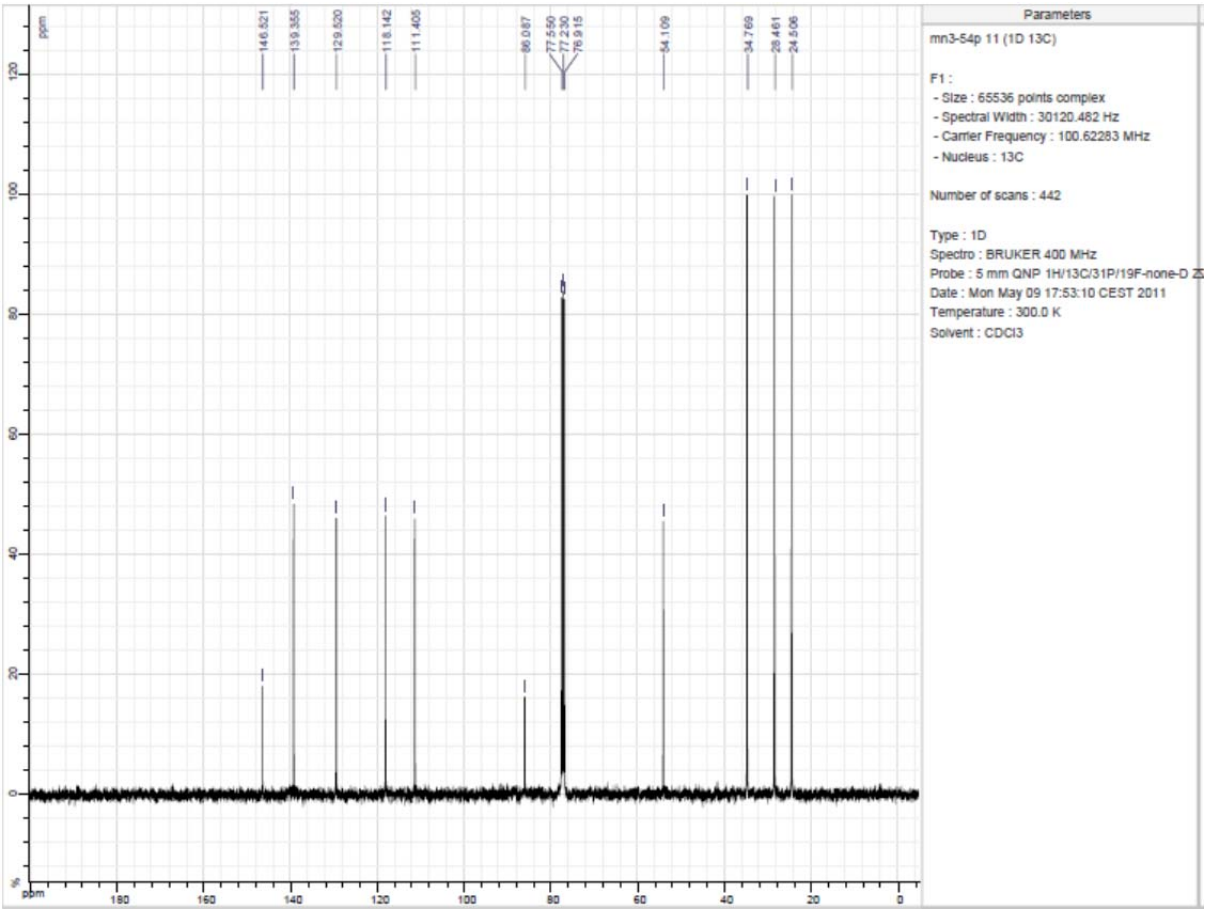
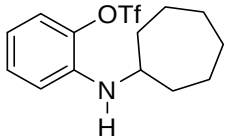
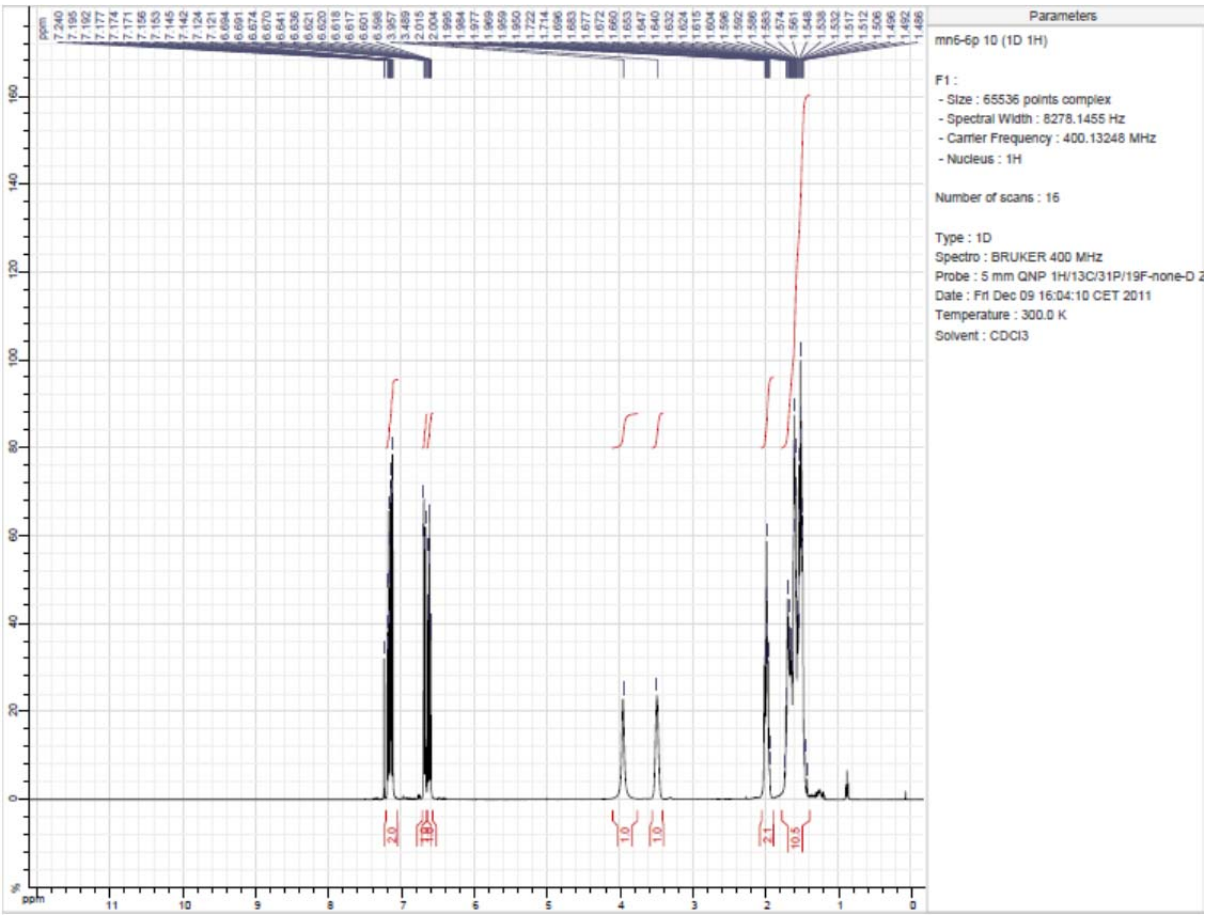




Methyl (2-trifluoromethanesulfonylphenyl)(cycloheptyl)amine:



Prepared according to **GP1**. Colorless oil, 58% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.40-1.76 (m, 10H), 1.90-2.06 (m, 2H), 3.42-3.56 (m, 1H), 3.96 (s, 1H), 6.62 (td, J = 7.6, 2.0 Hz, 1H), 6.68 (dd, J = 7.4, 1.2 Hz, 1H), 7.13 (dd, J = 8.4, 1.2 Hz, 1H), 7.17 (td, J = 7.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.4, 28.4, 34.7, 53.4, 113.4, 116.1, 118.8 (q, $^{1}J_{CF}$ = 318 Hz), 121.8, 129.3, 137.2, 139.6. IR (neat): υ = 749, 825, 880, 1043, 1087, 1137, 1205, 1241, 1298, 1327, 1416, 1460, 1513, 1615, 2858, 2929, 3434 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{19}NO_3F_3S$ 338.1032, found 338.1027.



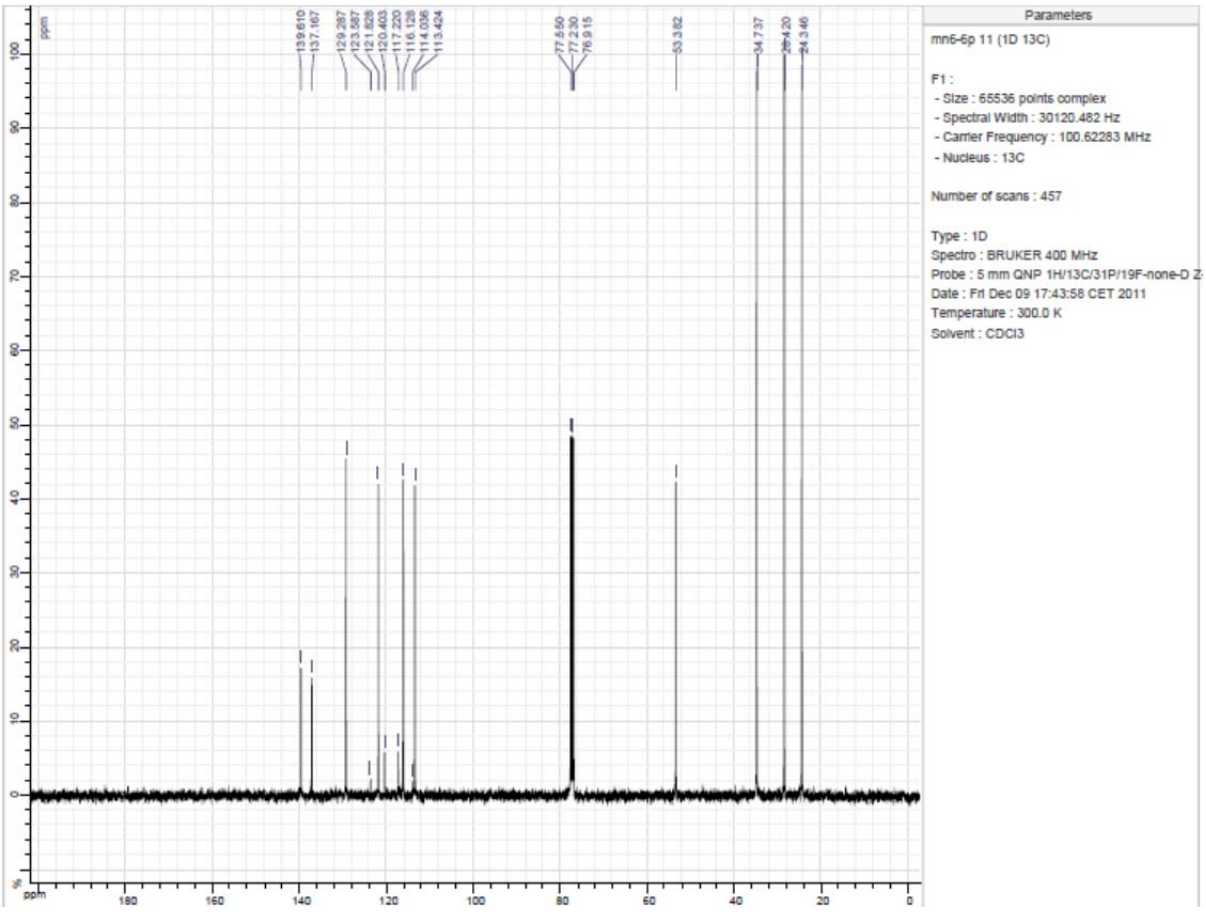
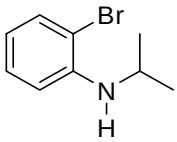


Table 2:

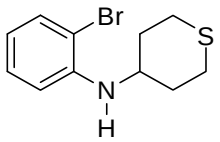
2-Bromo-*N*-isopropylaniline**:**



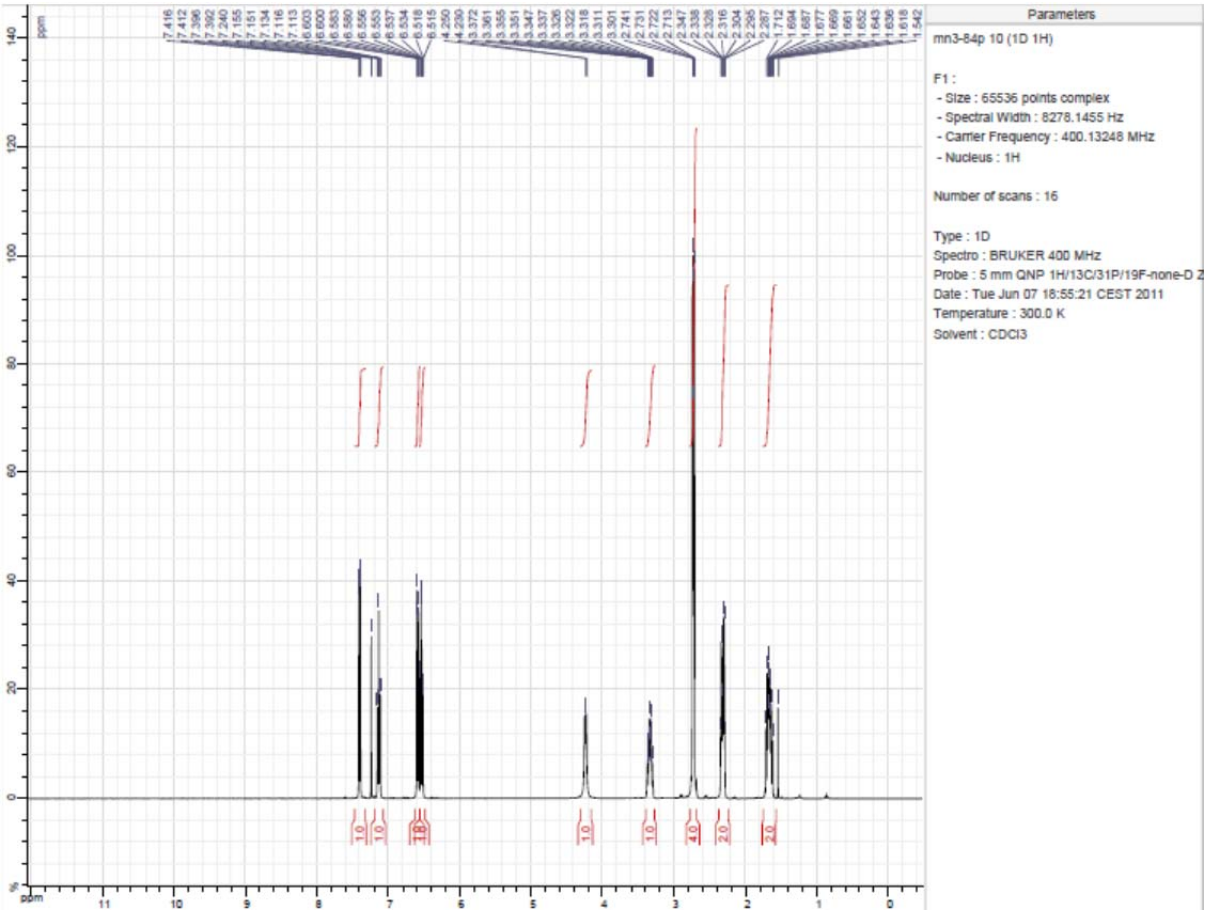
Colorless oil, 93% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.26 (d, J = 6.4 Hz, 6H), 3.67 (m, 1H), 4.15 (d, J = 6.8 Hz, 1H), 6.51 (td, J = 7.6, 1.6 Hz, 1H), 6.63 (dd, J = 7.6, 1.6Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 23.1, 44.5, 110.0, 112.0, 117.4, 128.6, 132.7, 144.4.

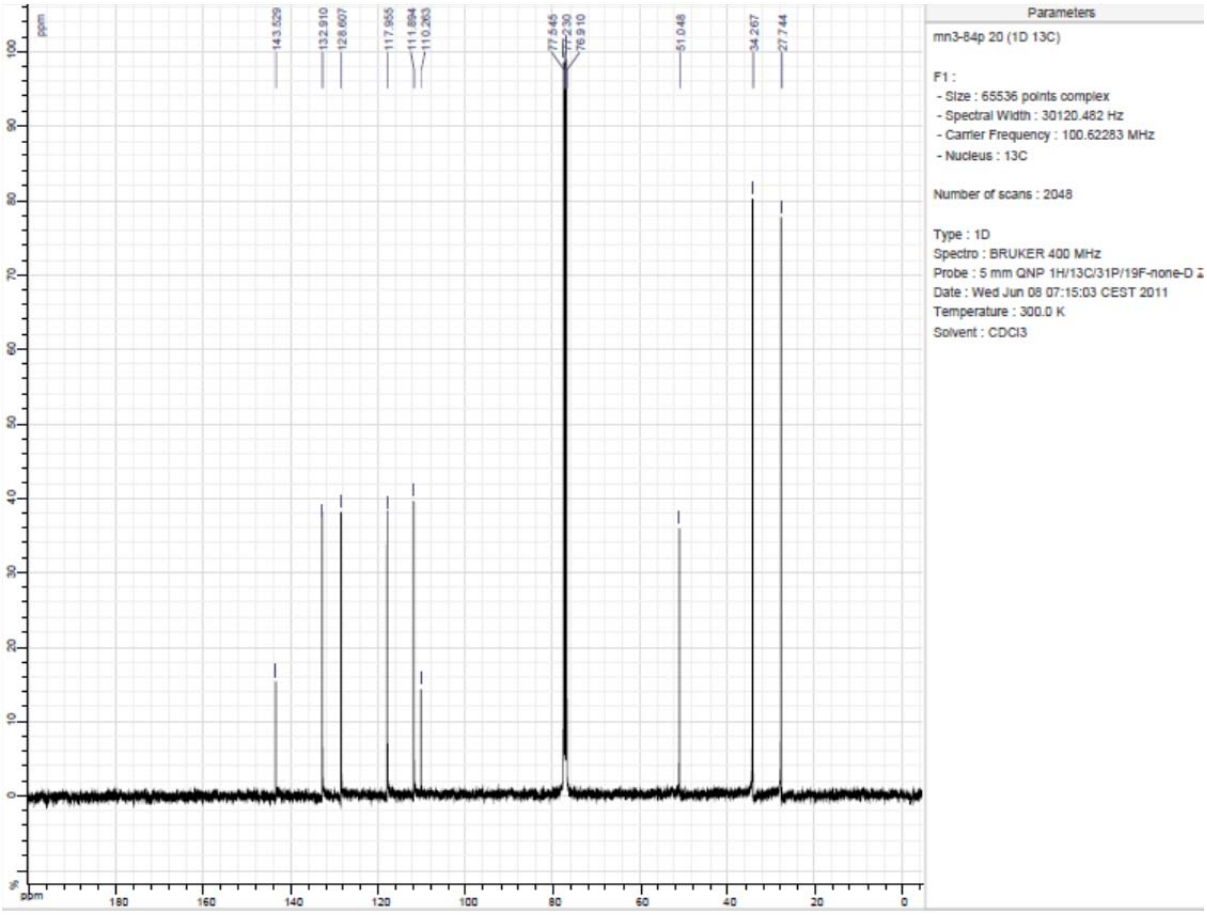
Table 3:

N-(2-bromophenyl)tetrahydro-2*H*-thiopyran-4-amine:

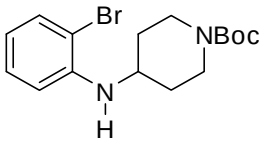


Prepared according to **GP1**. Colorless oil, 15% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.58-1.76 (m, 2H), 2.25-2.38 (m, 2H), 2.69-2.78 (m, 4H), 3.28-3.40 (m, 1H), 4.24 (d, J = 8 Hz, 1H), 6.54 (td, J = 7.6, 1.2 Hz, 1H), 6.59 (dd, J = 8, 1.2 Hz, 1H), 7.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 27.7, 34.3, 51.0, 110.3, 111.9, 118.0, 128.6, 132.9, 143.5. IR (neat): υ = 808, 885, 1033, 1099, 1157, 1186, 1237, 1272, 1257, 1337, 1412, 1450, 1515, 1598, 2216, 2854, 2930, 3401 cm^{-1}; ESI-HRMS calcd. for $C_{11}H_{15}NSBr$ 272.0103, found 272.0092.





tert-butyl 4-((2-bromophenyl)amino)piperidine-1-carboxylate:



Prepared according to **GP1**. Colorless oil, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.34-1.48 (m, 2H), 1.45 (s, 9H), 1.92-2.12 (m, 2H), 2.97 (t, J = 11.6 Hz, 1H), 3.35-3.55 (m, 1H), 4.00 (d, J = 9.2 Hz, 1H), 4.21 (d, J = 7.2 Hz, 1H), 6.54 (td, J = 8, 1.6 Hz, 1H), 6.64 (d, J = 8 Hz, 1H), 7.14 (dd, J = 7.8, 1.2 Hz, 1H), 7.40 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 28.7, 32.3, 42.5, 50.1, 79.9, 110.3, 112.0, 118.0, 128.7, 132.9, 143.8, 154.9. IR (neat): υ = 697, 761, 818, 888, 901, 974, 1032, 1109, 1152, 1187, 1224, 1247, 1258, 1277, 1334, 1409, 1448, 1521, 1596, 1707, 2853, 2930, 3402 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{18}BrNO_2$ 312.0593, found 312.0594.

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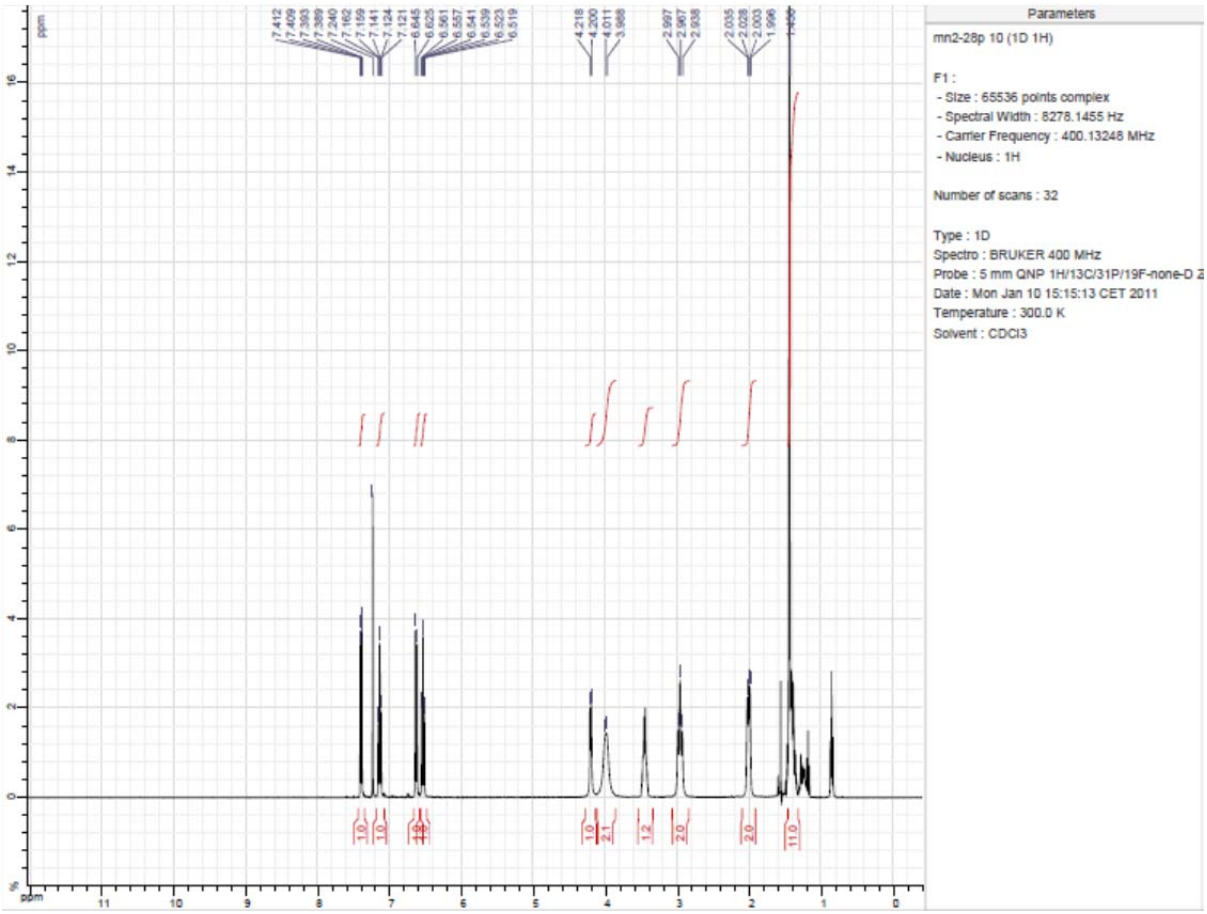
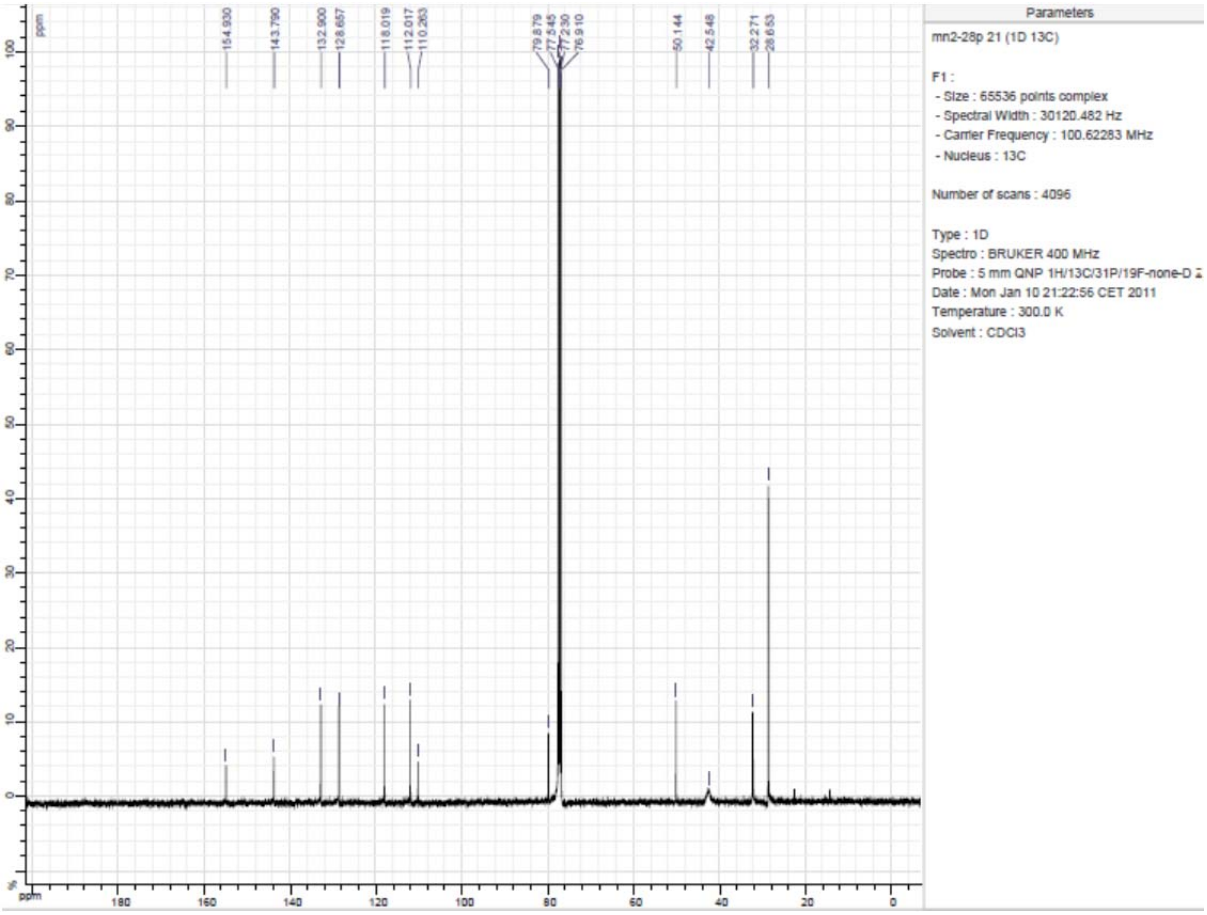
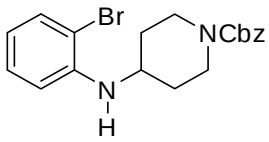
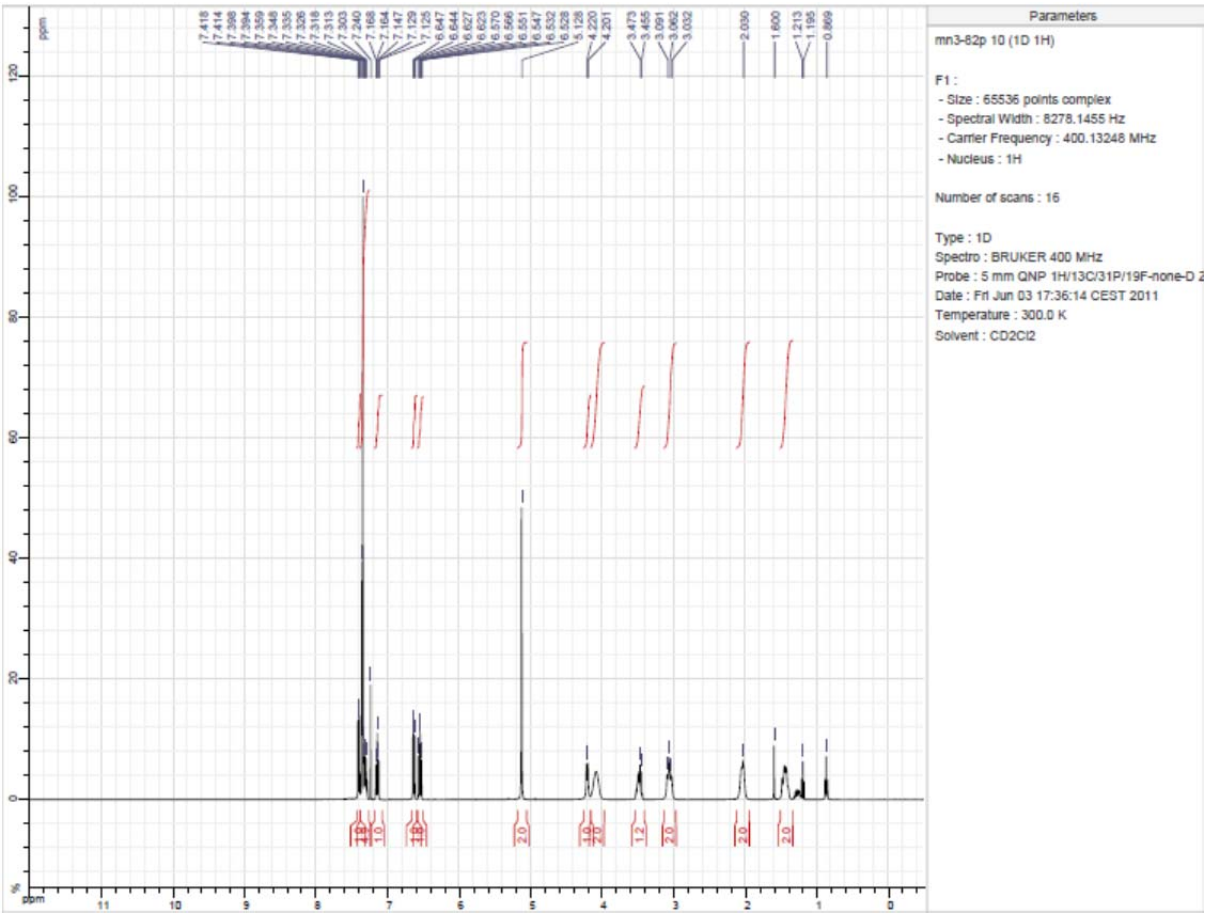


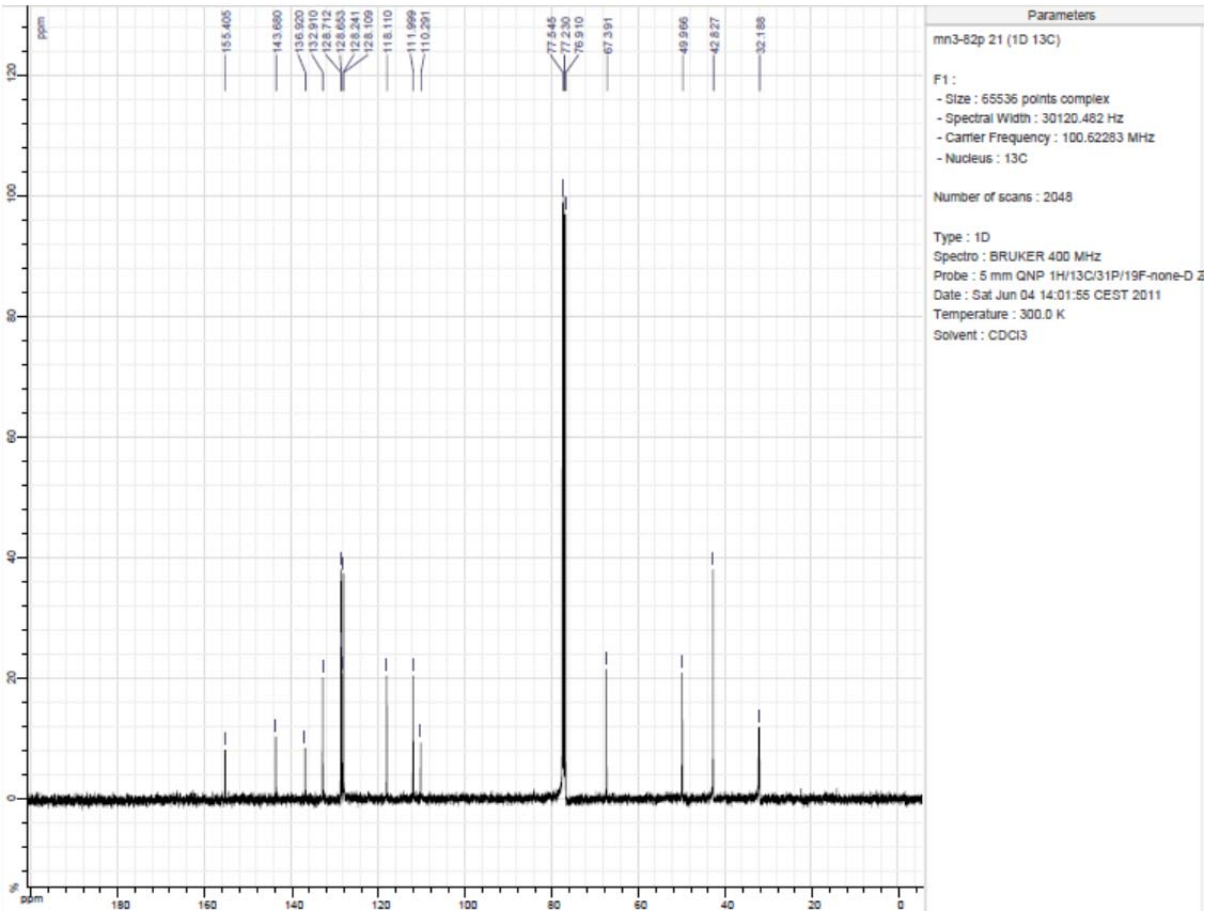


Benzyl 4-((2-bromophenyl)amino)piperidine-1-carboxylate:

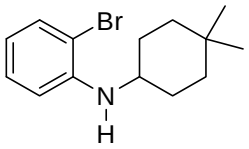


Prepared according to **GP1**. Colorless oil, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.35-1.52 (m, 2H), 1.95-2.13 (m, 2H), 3.06 (t, J = 11.6 Hz, 2H), 3.42-3.55 (m, 1H), 3.98-4.17 (brd, 2H), 4.21 (d, J = 7.6 Hz, 1H), 5.13 (s, 4H), 6.55 (td, J = 7.6, 1.6 Hz, 1H), 6.64 (dd, J = 8, 1.2 Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.27-7.39 (m, 5H), 7.41 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 32.2, 42.8, 50.0, 67.4, 110.3, 112.0, 118.1, 128.1, 128.2, 128.7, 132.9, 136.9, 143.7, 155.4. IR (neat): υ = 697, 761, 818, 888, 901, 974, 1032, 1109, 1152, 1187, 1224, 1247, 1258, 1277, 1334, 1409, 1448, 1521, 1596, 1707, 2853, 2930, 3402 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{18}BrNO_2$ 312.0593, found 312.0594.





2-Bromo-*N*-(4,4-dimethylcyclohexyl)aniline:



Prepared according to **GP1**. Colorless oil, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.94 (s, 3H), 0.95 (s, 3H), 1.23-1.49 (m, 6H), 1.82-1.95 (m, 2H), 3.15-3.35 (m, 1H), 4.23 (d, J = 7.2 Hz, 1H), 6.50 (td, J = 7.6, 1.6 Hz, 1H), 6.62 (dd, J = 8.4, 1.6 Hz, 1H), 7.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.8, 29.0, 30.1, 31.5, 37.8, 51.9, 110.0, 111.9, 117.3, 128.6, 132.7, 144.4. IR (neat): υ = 723, 798, 835, 865, 1029, 1104, 1153, 1229, 1265, 1317, 1393, 1448, 1464, 1497, 1591, 2853, 2927, 3403 cm^{-1}; ESI-HRMS calcd. for $C_{12}H_{16}BrClN$ 288.0149, found 288.0140.

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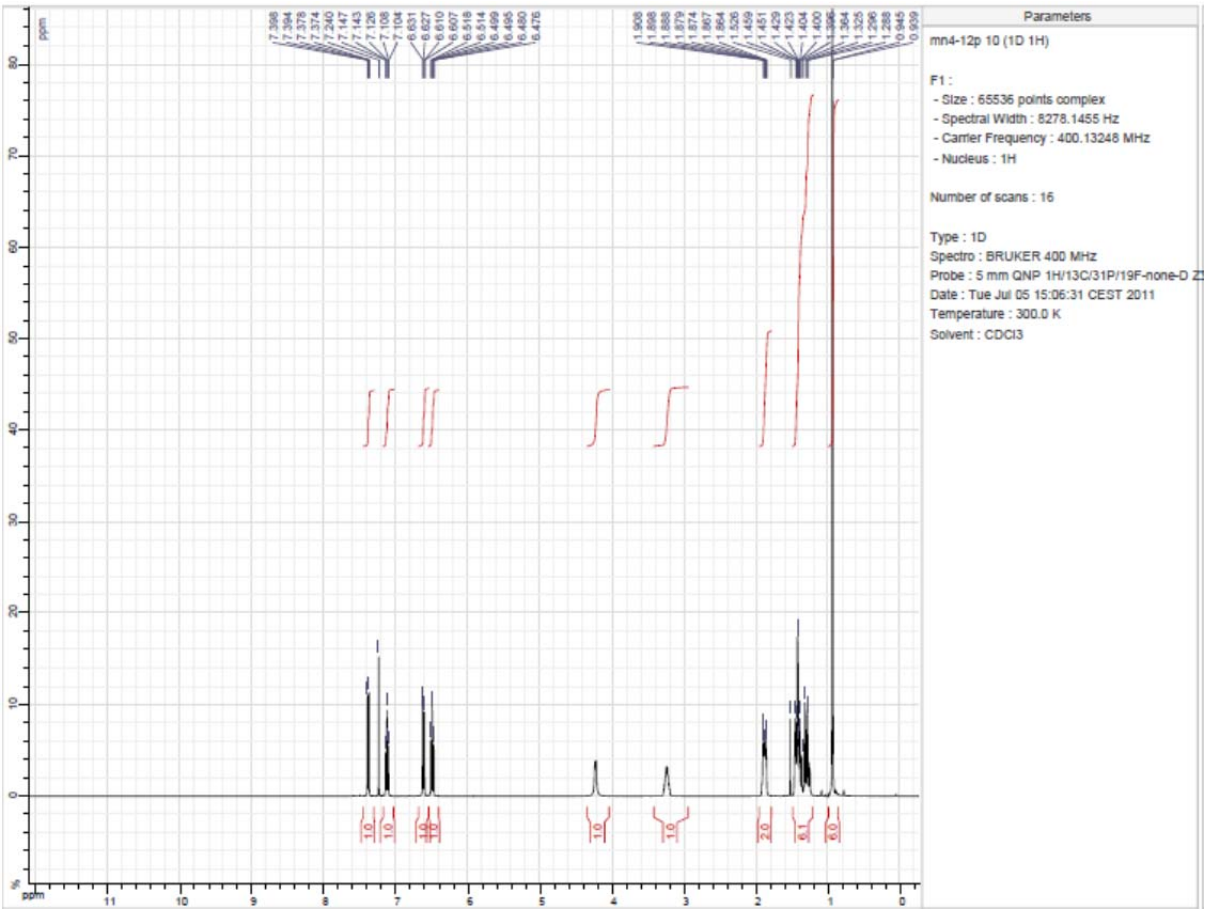
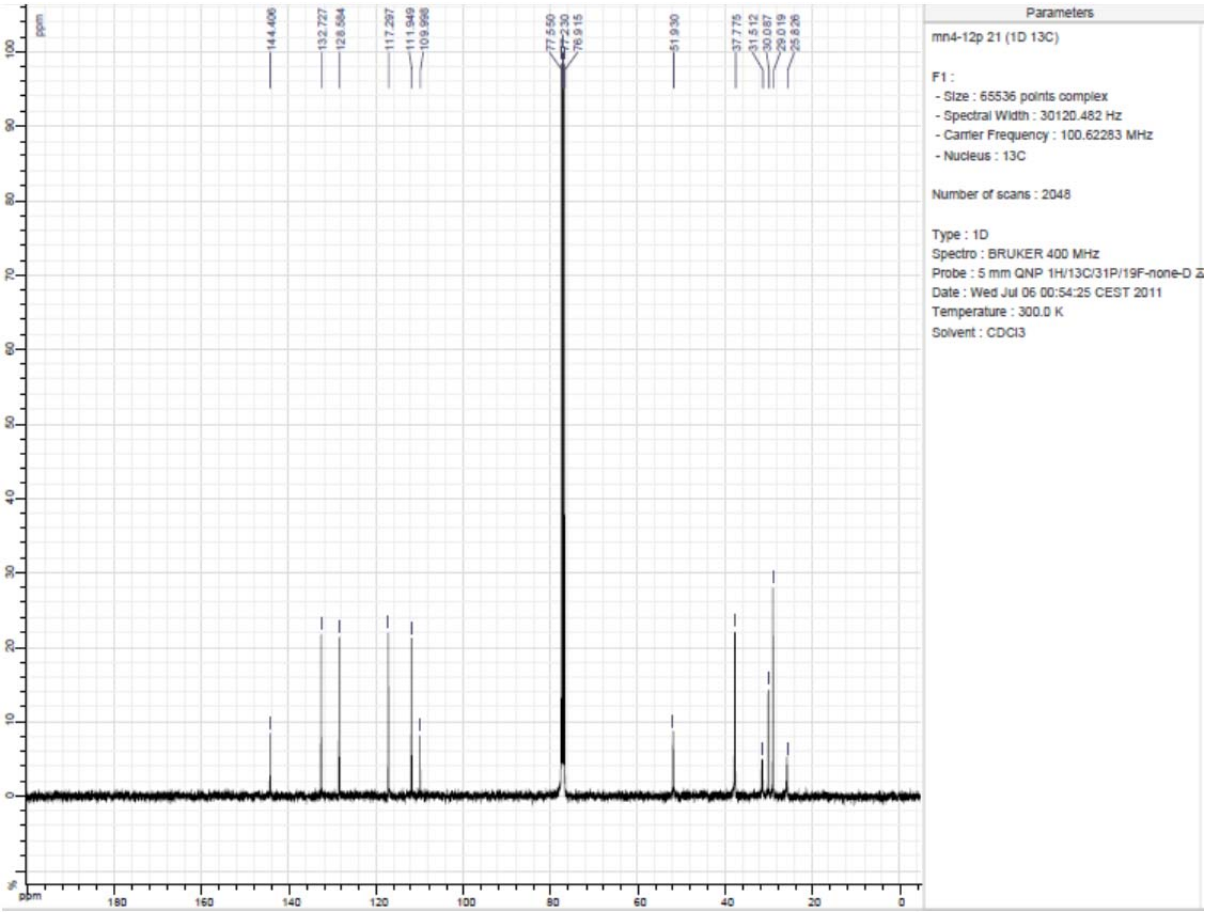
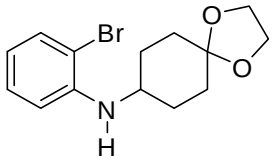
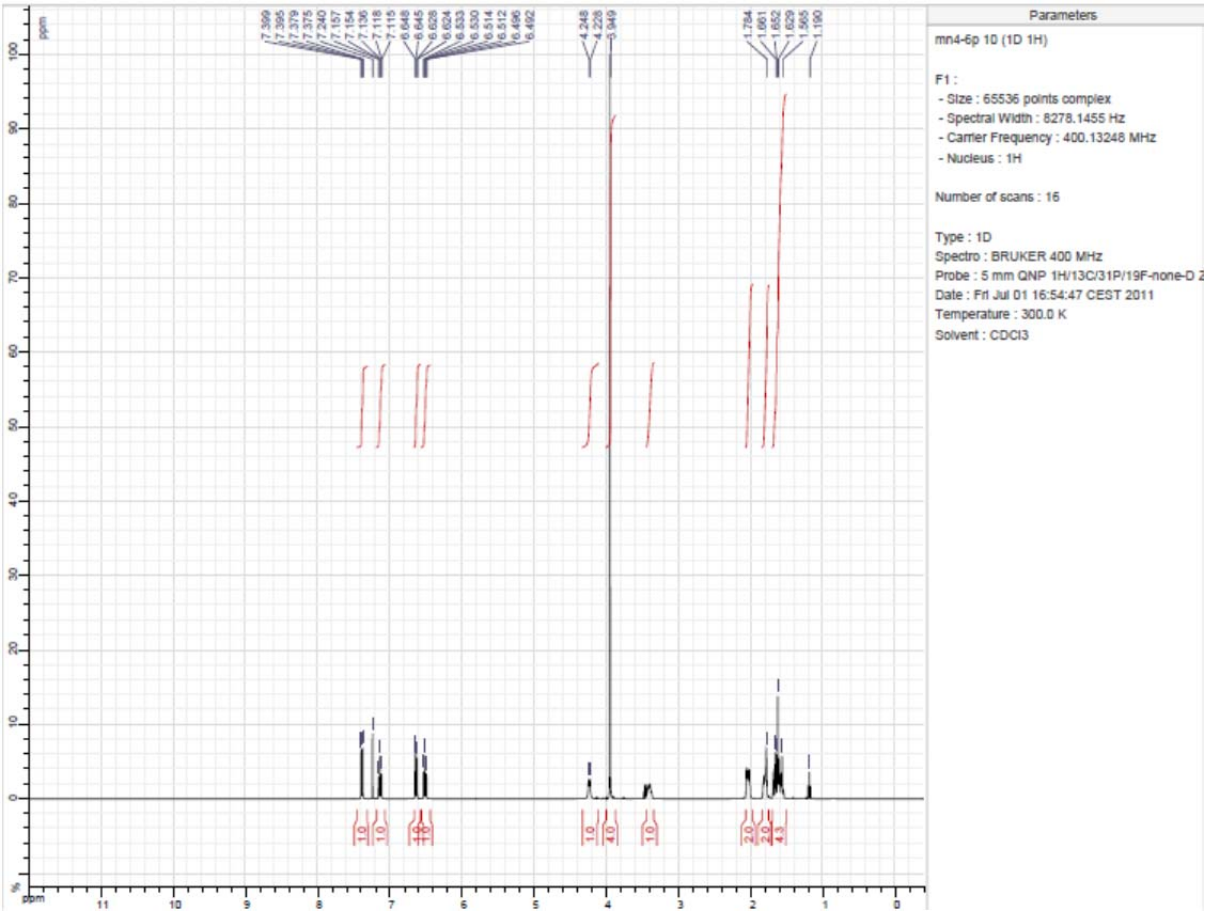


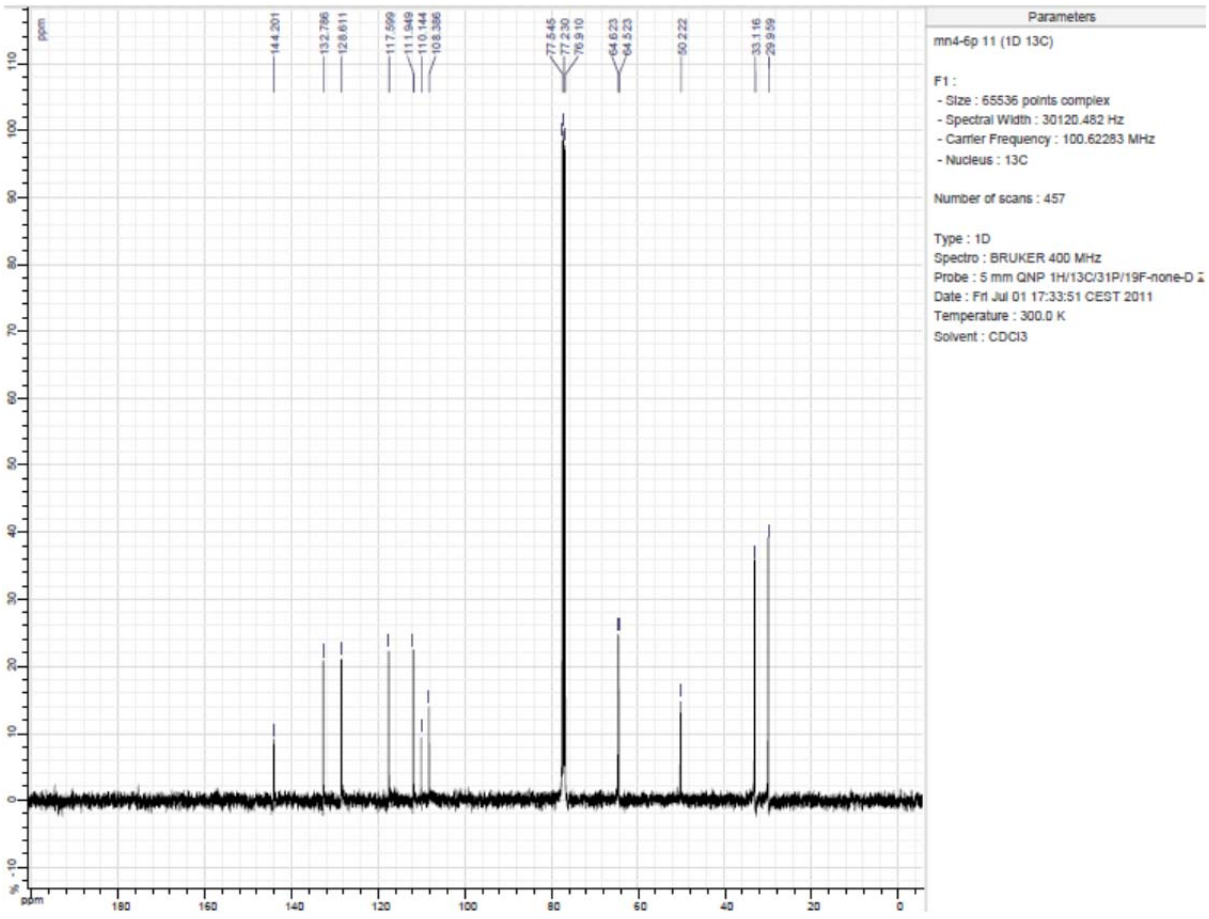


N-(2-Bromophenyl)-1,4-dioxaspiro[4.5]decan-8-amine:[iii]

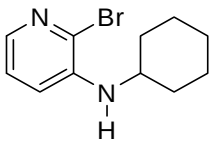


Prepared according to **GP1**. Colorless oil, 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.52-1.71 (m, 4H), 1.76-1.85 (m, 2H), 1.98-2.08 (m, 2H), 3.35-3.45 (m, 1H), 3.95 (s, 4H), 4.24 (d, J = 8 Hz, 1H), 6.51 (td, J = 7.6, 1.2 Hz, 1H), 6.64 (td, J = 8, 1.2 Hz, 1H), 7.14 (dd, J = 7.8, 1.2 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 29.6, 33.1, 50.2, 64.5, 64.6, 108.4, 110.1, 111.9, 117.6, 128.6, 132.8, 144.2. IR (neat): υ = 791, 854, 883, 1028, 1100, 1148, 1190, 1236, 1265, 1315, 1399, 1453, 1506, 1587, 1609, 2853, 2928, 3407 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{19}NO_2Br$ 312.0593, found 312.0599.





2-Bromo-*N*-cyclohexylpyridin-3-amine:[iv]



2-Bromoaniline (1.0 g, 5.78 mmol) and the cyclohexanone (627 mg, 6.4 mmol) were dissolved in *i*PrOAc (12 mL). After trifluoroacetic acid (1.32 g, 20 mmol) and $NaHB(OAc)_3$ (1.47 g, 11.6 mmol.) were added into the reaction mixture over the1 min, the reaction mixture was stirred at room temperature for 10 min. The reaction mixture was added into 1N-KOH aq. and extracted with dichloromethane. The organic phase was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by flash column chromatography (silica gel; ethyl acetate/pentane = 1 : 10 as eluent) affording 2-bromo-*N*-cyclohexylpyridin-3-amine as white solid, 54% yield, M. p. 50 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.17-1.44 (m, 5H), 1.59-1.88 (m, 3H), 1.94-2.06 (m, 2H), 3.16-3.30 (m, 1H), 4.30 (d, J = 7.6 Hz, 1H), 7.04 (dd, J = 8.4, 1.6 Hz, 1H), 6.80 (dd, J = 8.4, 4.4 Hz, 1H), 7.62 (dd, J = 4.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.9, 25.9, 33.0, 51.5, 117.6, 123.8, 130.6, 136.7, 141.6. IR (neat): υ = 785, 888, 1038, 1097, 1148, 1244, 1266, 1325, 1383, 1450, 1487, 1578, 1710, 2853, 2928, 3059, 3401 cm^{-1}; ESI-HRMS calcd. for $C_{11}H_{16}N_2Br$ 255.0491, found 255.0490.

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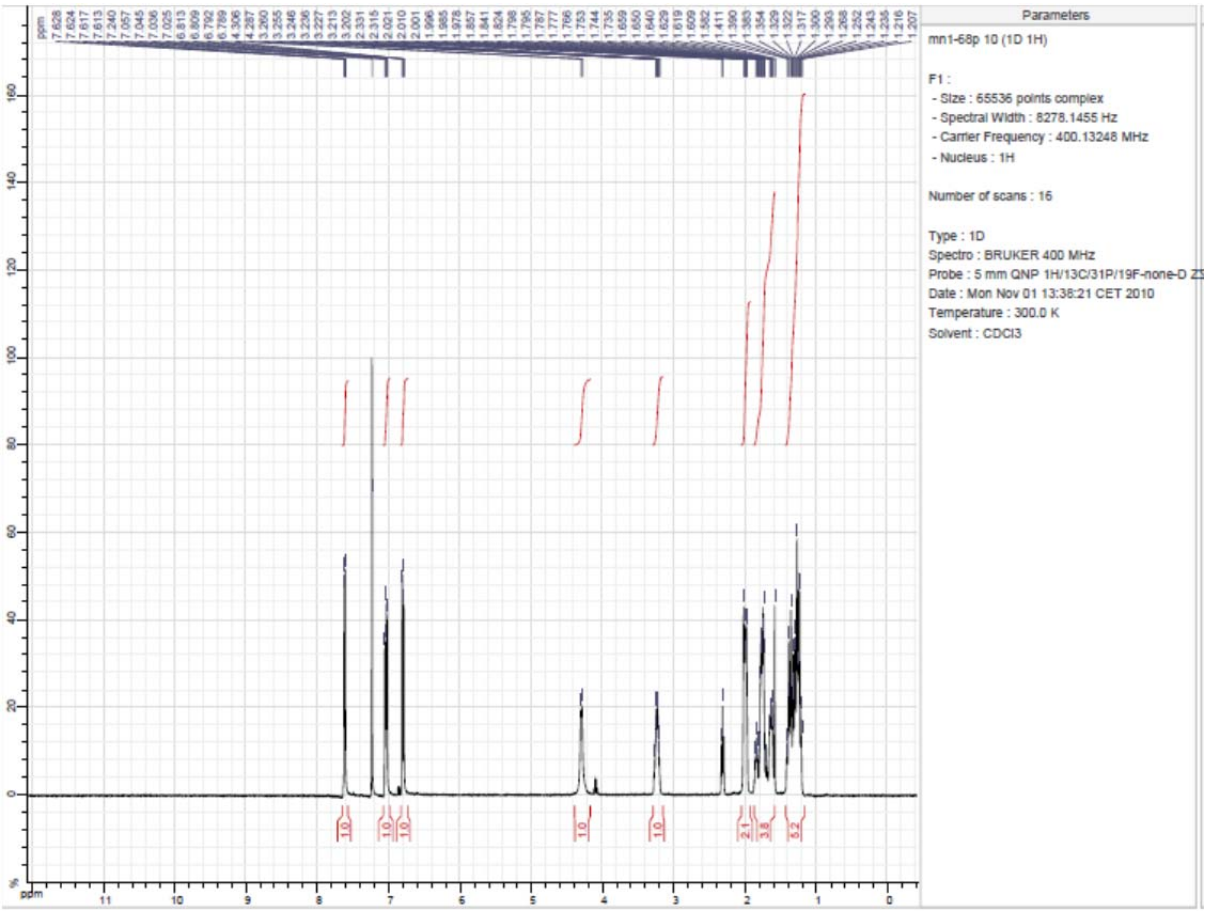
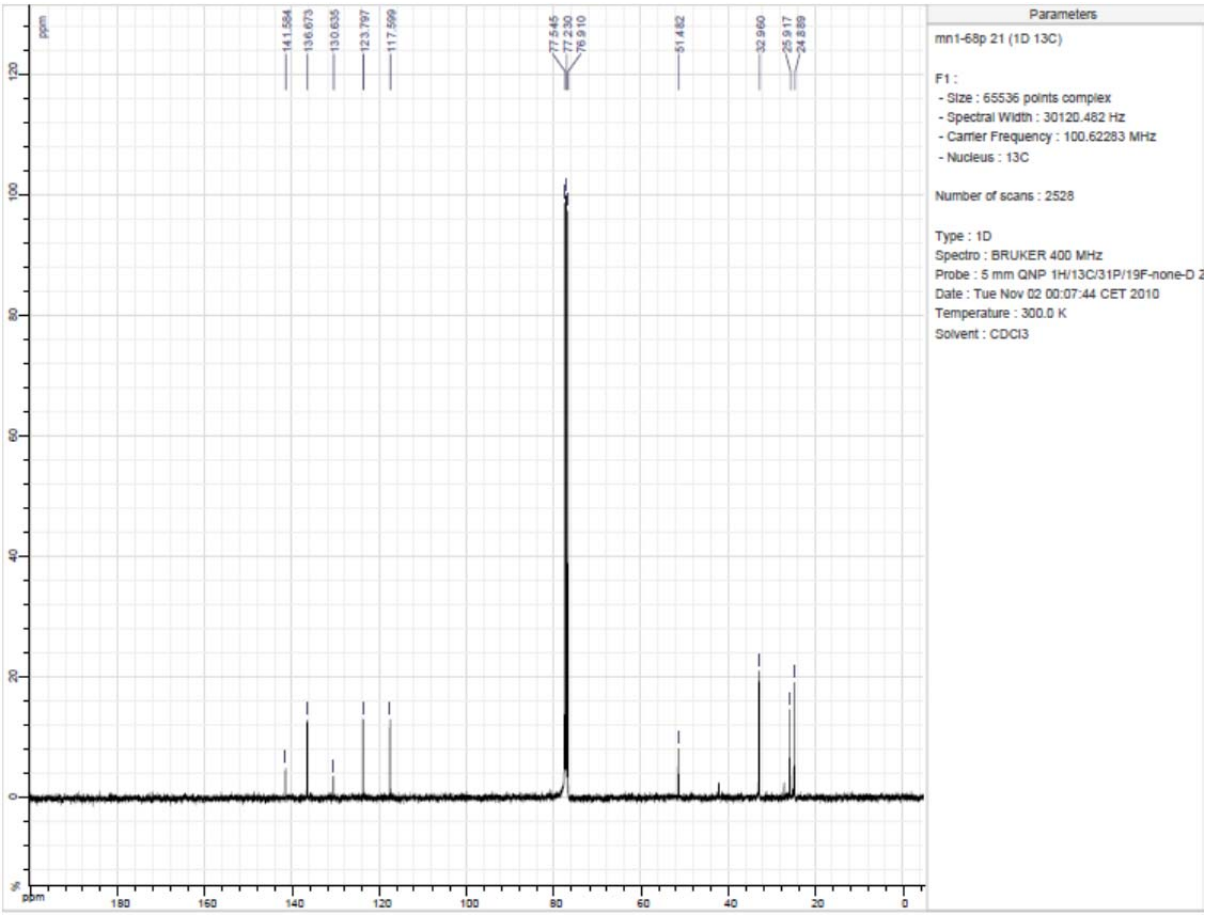
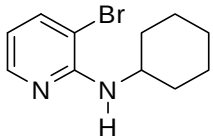
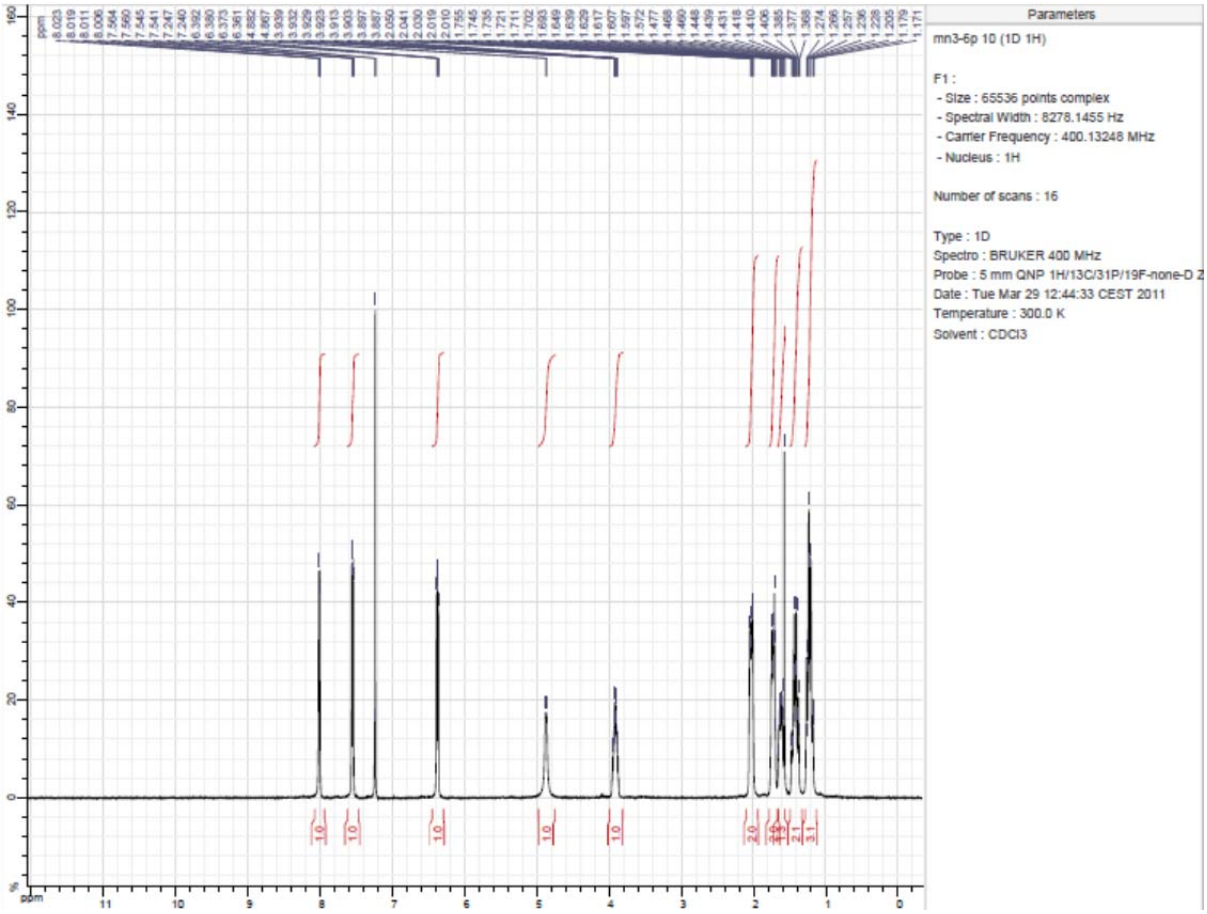


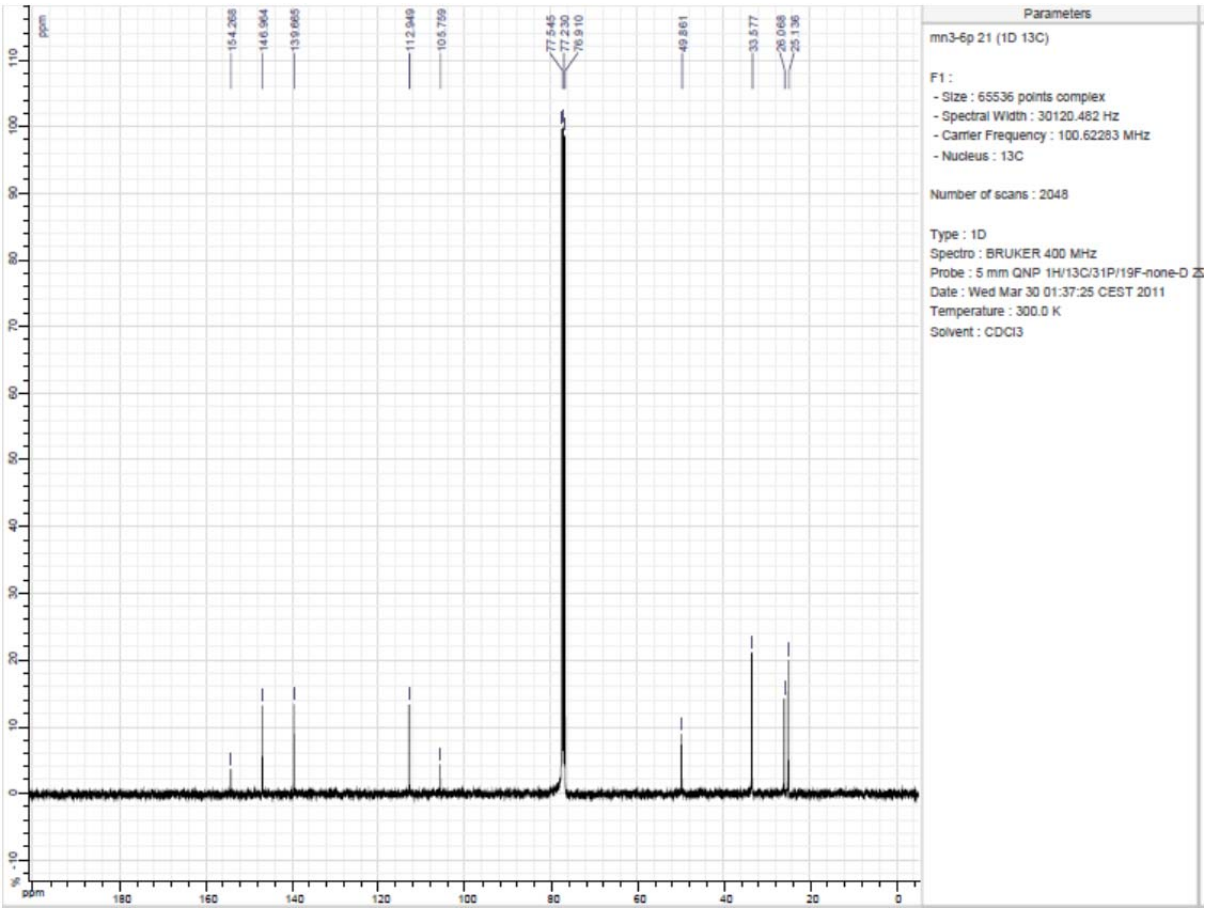


3-Bromo-*N*-cyclohexylpyridin-2-amine:

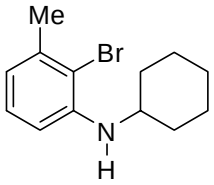


Prepared according to **GP1**. White solid, 39% yield, M. p. 64 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.14-1.30 (m, 3H), 1.34-1.50 (m, 2H), 1.57-1.67 (m, 1H), 1.67-1.79 (m, 2H), 1.95-2.11 (m, 2H), 3.82-4.00 (m, 1H), 4.87 (d, J = 6 Hz, 1H), 6.31 (dd, J = 7.6, 4.8 Hz, 1H), 7.55 (dd, J = 7.6, 1.6 Hz, 1H), 8.01 (dd, J = 4.8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.1, 26.1, 33.6, 49.9, 105.8, 112.9, 139.7, 147.0, 154.3. IR (neat): υ = 622, 687, 747, 777, 867, 891, 929, 1007, 1098, 1121, 1148, 1214, 1252, 1330, 1362, 1403, 1447, 1492, 1583, 2851, 2916, 3387 cm^{-1}; ESI-HRMS calcd. for $C_{11}H_{16}BrN_2$ 255.0491, found 255.0496.





2-Bromo-*N*-cyclohexyl-3-methylaniline:



Prepared according to **GP1**. White solid, 94% yield, M. p. 66 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.18-1.46 (m, 5H), 1.58-1.70 (m, 1H), 1.70-1.81 (m, 2H), 1.96-2.12 (m, 1H), 2.36 (s, 3H), 3.23-3.36 (m, 1H), 4.40 (brd, 1H), 6.50 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.1, 25.0, 26.1, 33.3, 52.0, 109.4, 112.7, 118.5, 127.7, 138.7, 144.4. IR (neat): υ = 765, 886, 1012, 1122, 1146, 1229, 1257, 1277, 1322, 1347, 1380, 1448, 1468, 1496, 1567, 1590, 2849, 2927, 3384 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{19}BrN$ 268.0695, found 268.0703.

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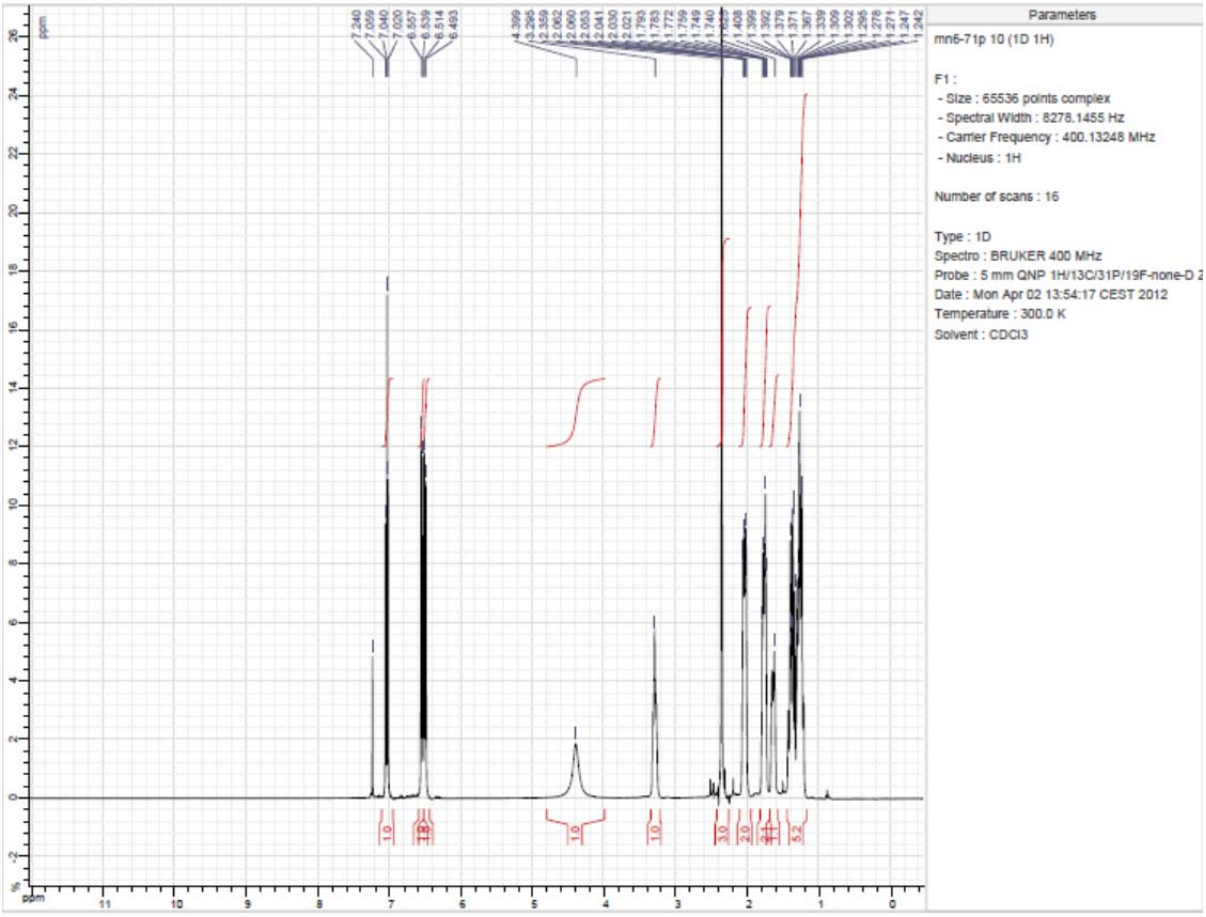
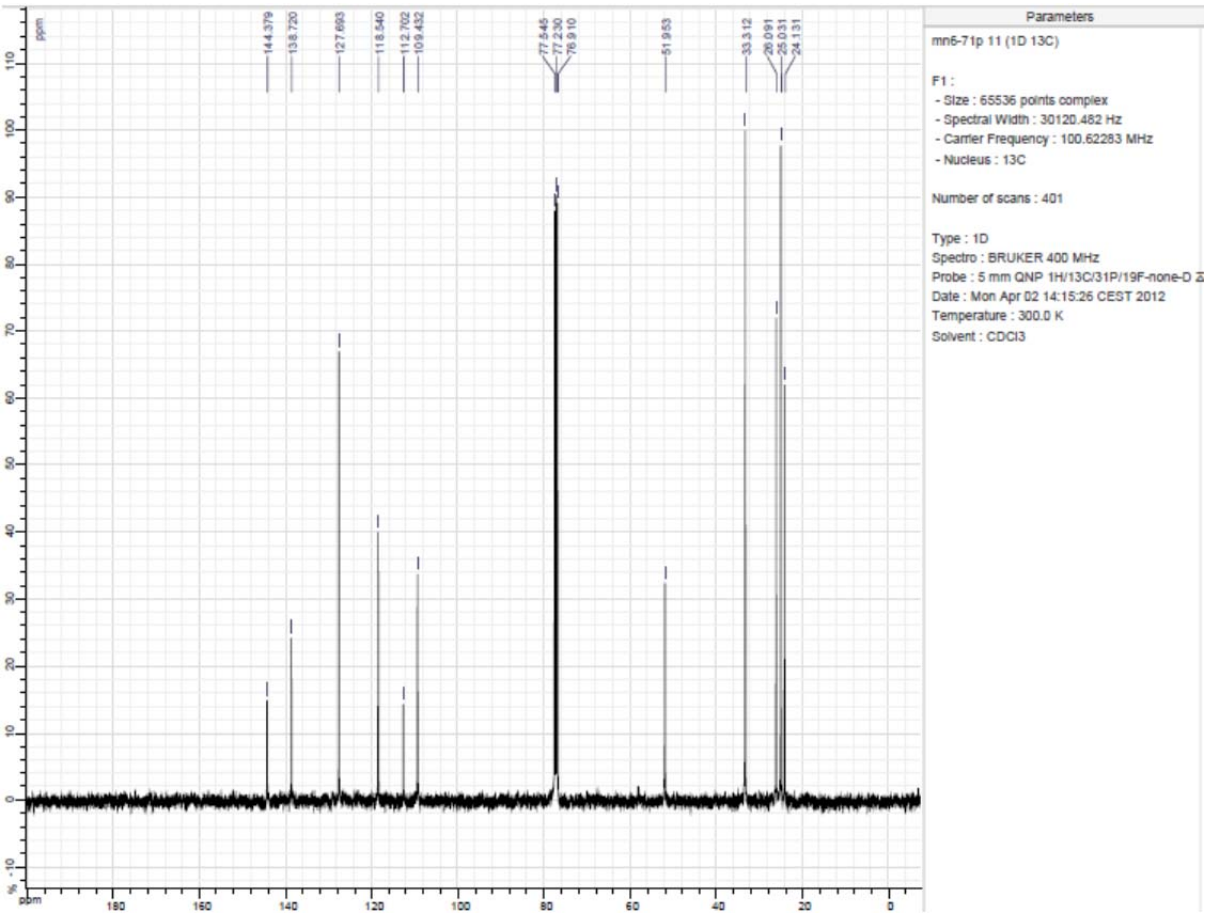
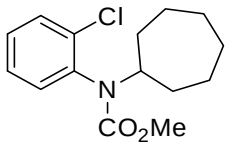




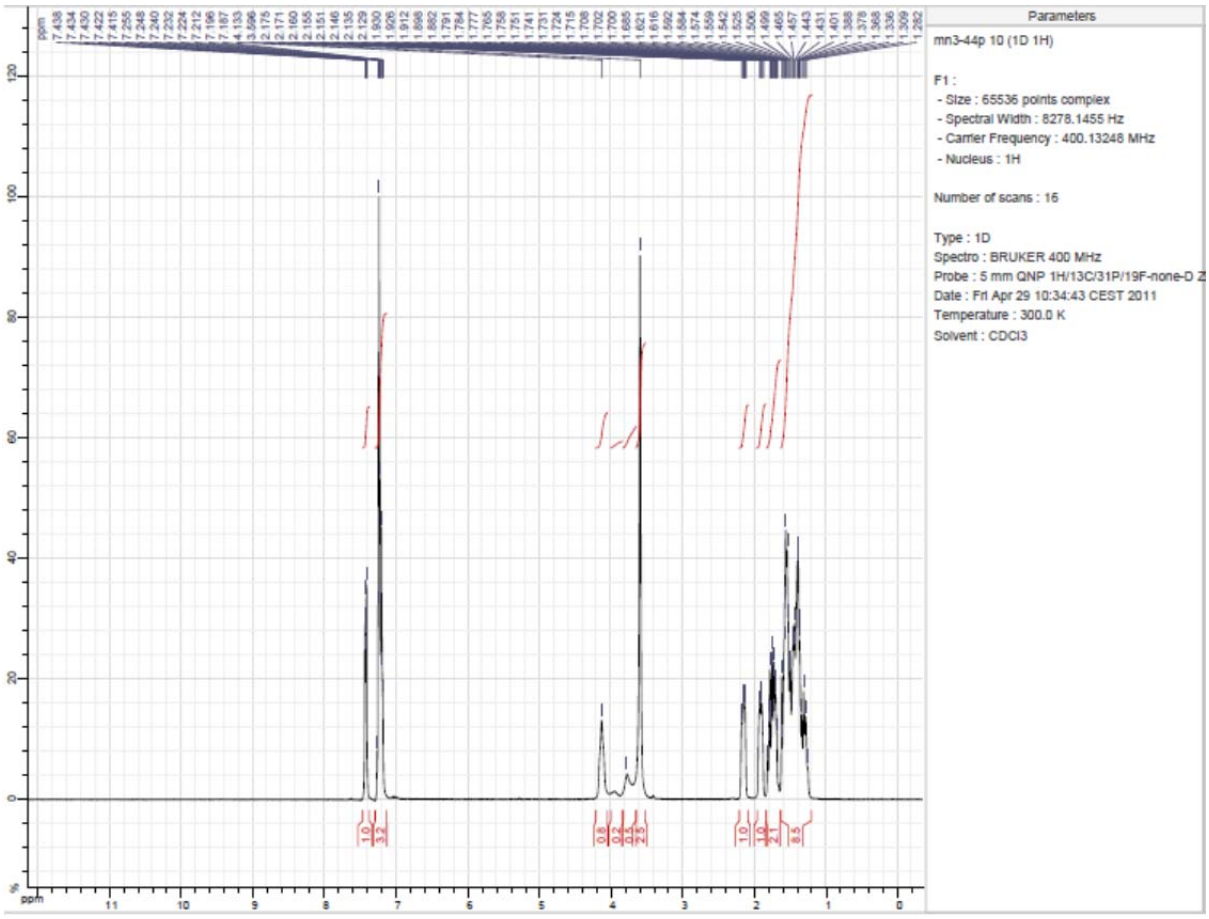
2.2.2 Substrates 1a-r and 3a,b.

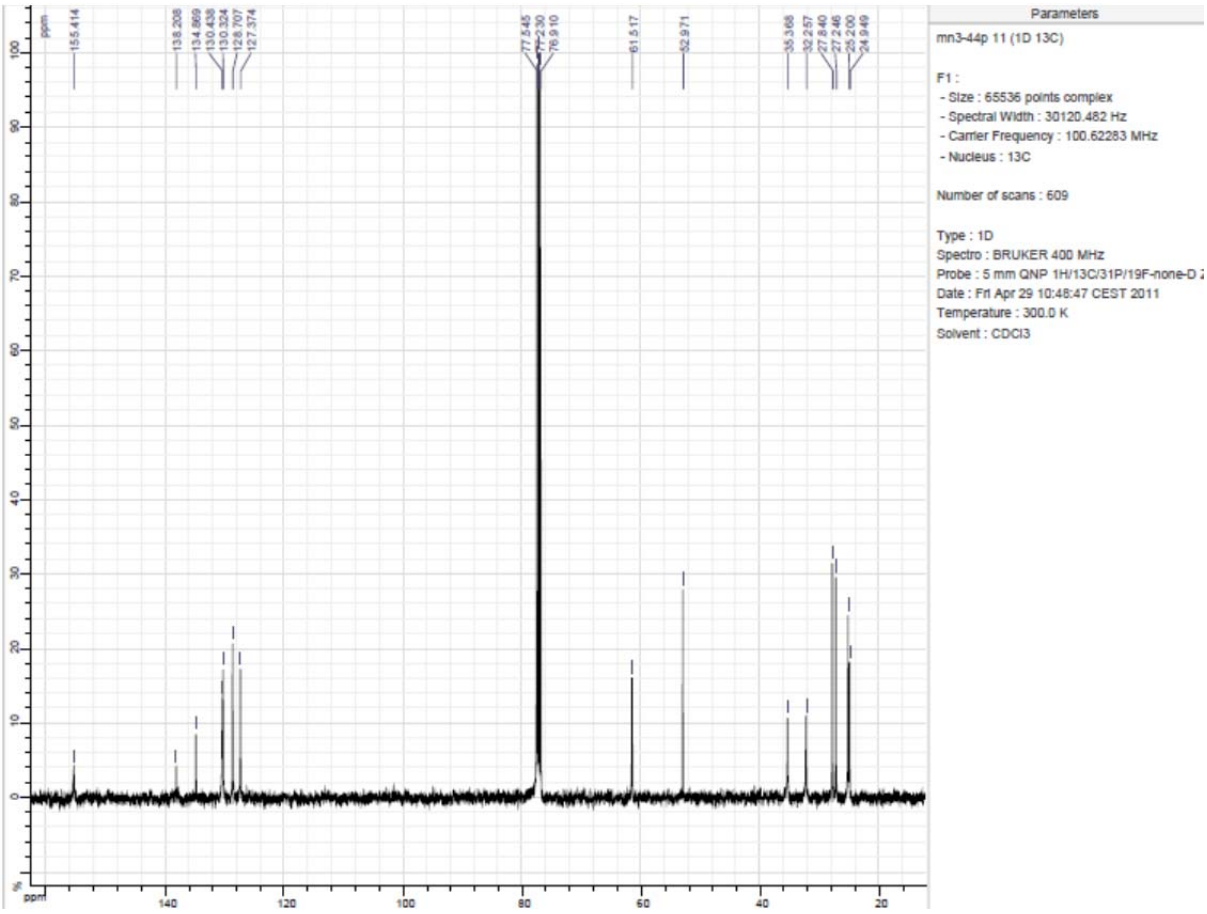
Table 1:

Methyl (2-chlorophenyl)(cycloheptyl)carbamate **1b**:

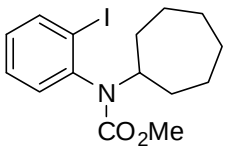


Prepared according to **GP2**. White solid, 94% yield, M. p. 52 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.15-1.30 (m, 3H), 1.30-1.43 (m, 3H), 1.57-1.67 (m, 1H), 1.69-1.80 (m, 2H), 1.97-2.08 (m, 2H), 3.18-3.30 (m, 1H), 3.75 (s, 3H), 4.19 (d, J = 7.2 Hz, 1H), 6.57 (dd, J = 8.4, 2.4 Hz, 1H), 6.19 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.0, 26.0, 33.2, 51.8, 55.6, 98.8, 101.4, 101.9, 132.8, 145.1, 160.4. IR (neat): υ = 768, 815, 826, 888, 1012, 1056, 1098, 114, 1170, 1211, 1311, 1342, 1367, 1426, 1449, 1507 1575, 1596, 2852, 2928, 3405 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}ClNO_2$ 282.1255, found 282.1255.





Methyl (2-iodophenyl)(cycloheptyl)carbamate **1c**:



Prepared according to **GP2.** White solid, 83% yield, M. p. 99 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.19-1.33 (m, 3H), 1.33-1.47 (m, 2H), 1.59-1.69 (m, 1H), 1.71-1.82 (m, 2H), 1.96-2.08 (m, 2H), 3.25-3.40 (m, 1H), 4.41 (d, J = 7.6 Hz, 1H), 6.72 (dd, J = 8, 2 Hz, 1H),6.76 (d, J = 2 Hz, 1H), 7.47 (d, J = 8 Hz, 1H). ^{13}C NMR (125 MHz): δ = 25.2, 25.4, 27.2, 27.9, 32.4, 35.7, 53.0, 61.6, 128.9, 129.1, 129.4, 139.9, 143.4, 155.0. IR (neat): υ = 799, 852, 934, 1018, 1075, 1119, 1164, 1293, 1281, 1335, 1370, 1437, 1517, 1584, 1600, 2856, 2931, 3410 cm^{-1}; EI-HRMS calcd. for $C_{15}H_{21}NO_2I$ 374.0611, found 374.0617.

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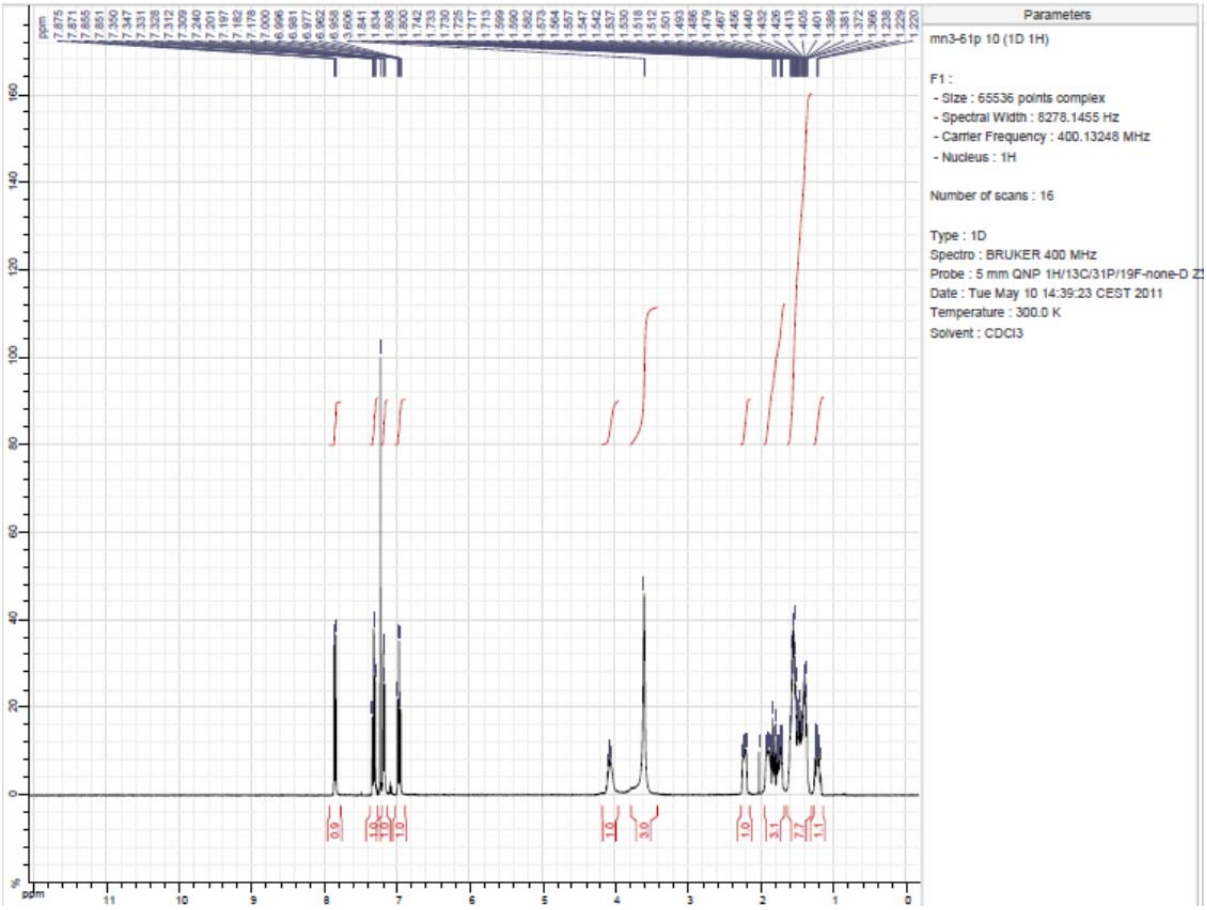
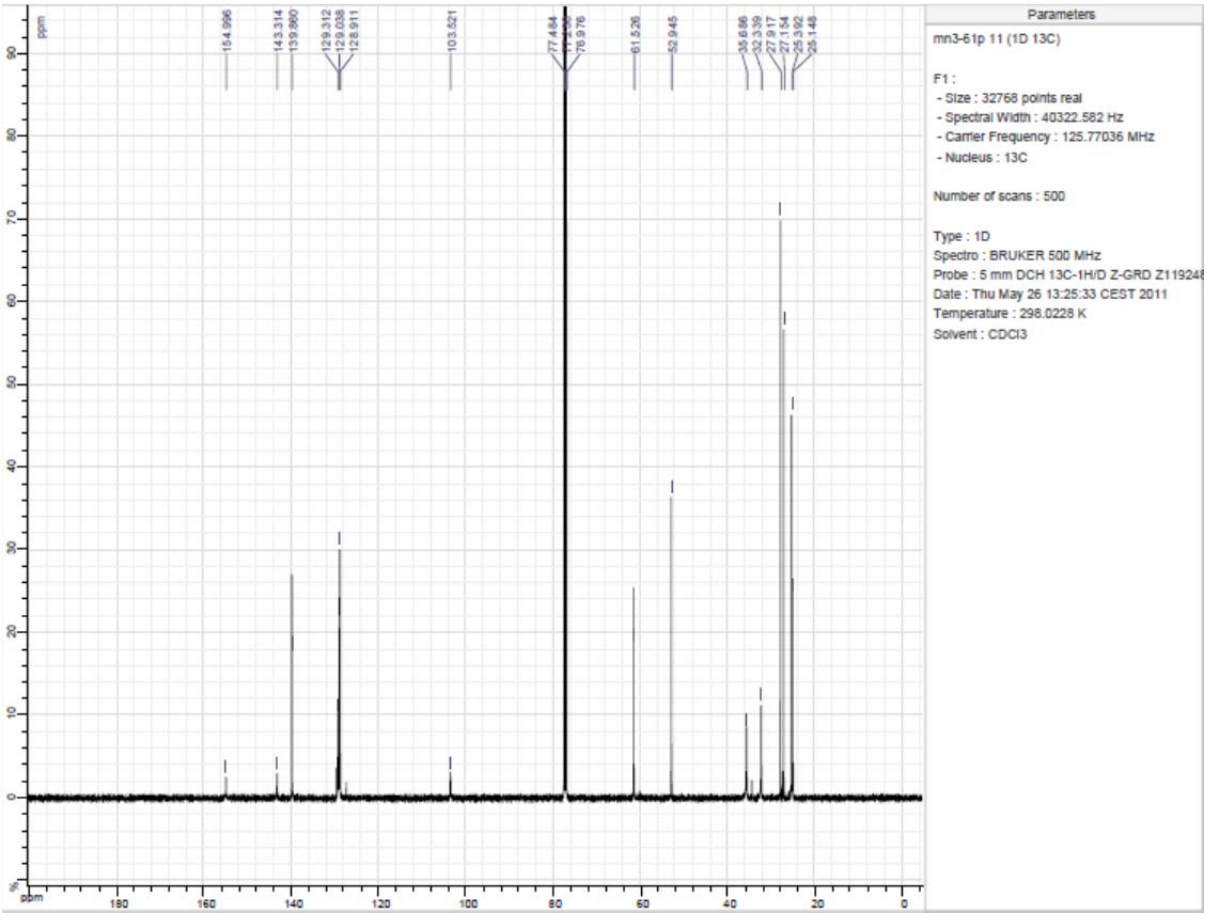
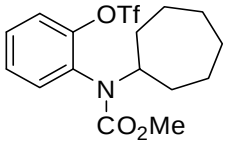
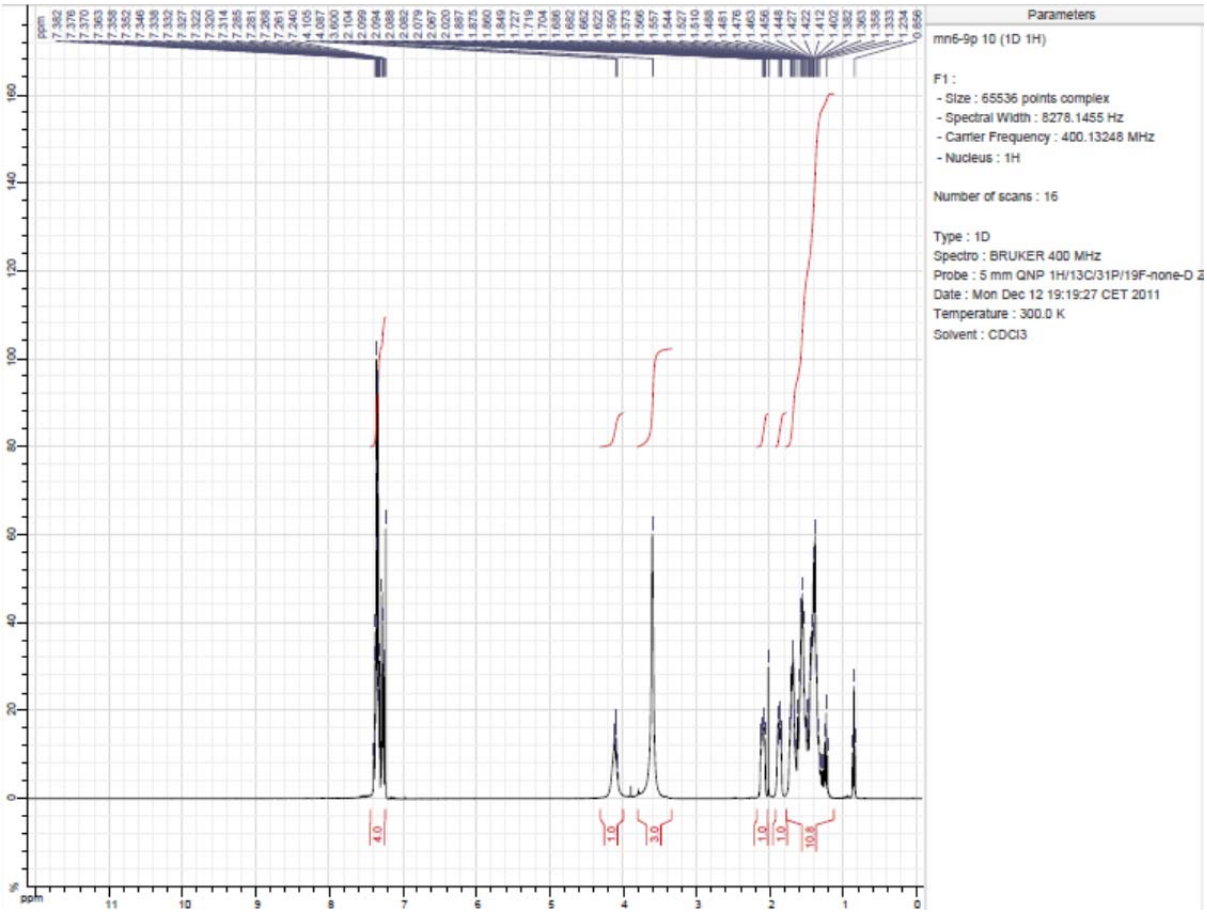




Methyl (2-trifluoromethanesulfonylphenyl)(cycloheptyl)carbamate **1d**:



Prepared according to **GP2.** Colorless oil, 67% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.35-1.58 (m, 9H), 3.17-3.27 (m, 1H), 3.35-3.46 (m, 1H), 3.61 (s, 3H), 3.75-4.00 (m, 1H), 4.60-4.85 (brd, 1H), 7.09-7.21 (m, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.62 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (125 MHz): δ = 24.9, 25.1, 27.2, 27.7, 32.9, 35.0, 53.0, 61.6, 118.5 (q, $^{1}J_{CF}$ = 318 Hz), 122.0, 128.5, 129.2, 131.4, 133.3, 146.8, 155.1. IR (neat): υ = 767, 788, 886, 1019, 1042, 1099, 1140, 1209, 1247, 1311, 1357, 1420, 1442, 1495, 1606, 1714, 2861, 2930 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{21}F_3NO_2S$ 396.1087, found 396.1097.



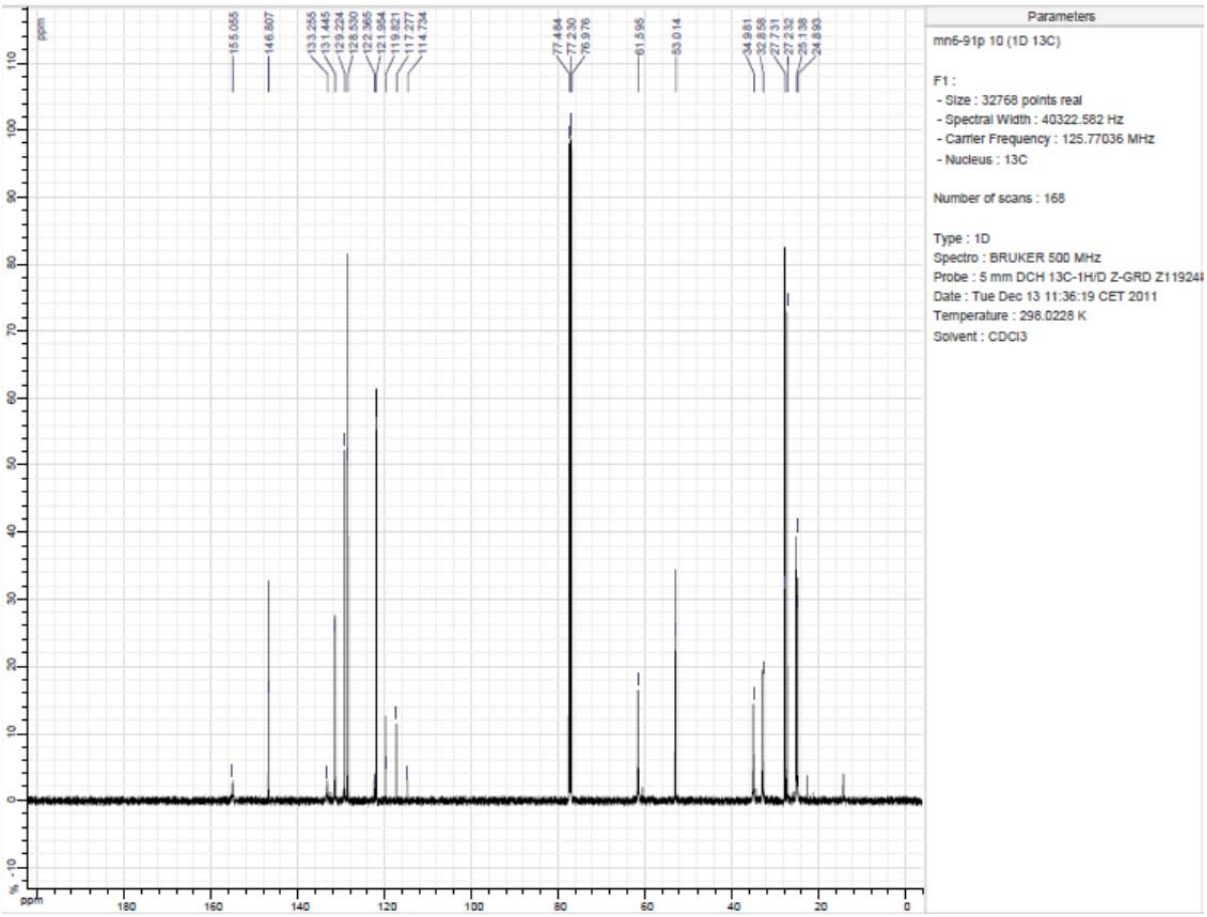
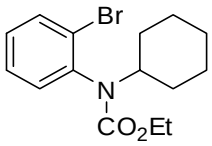


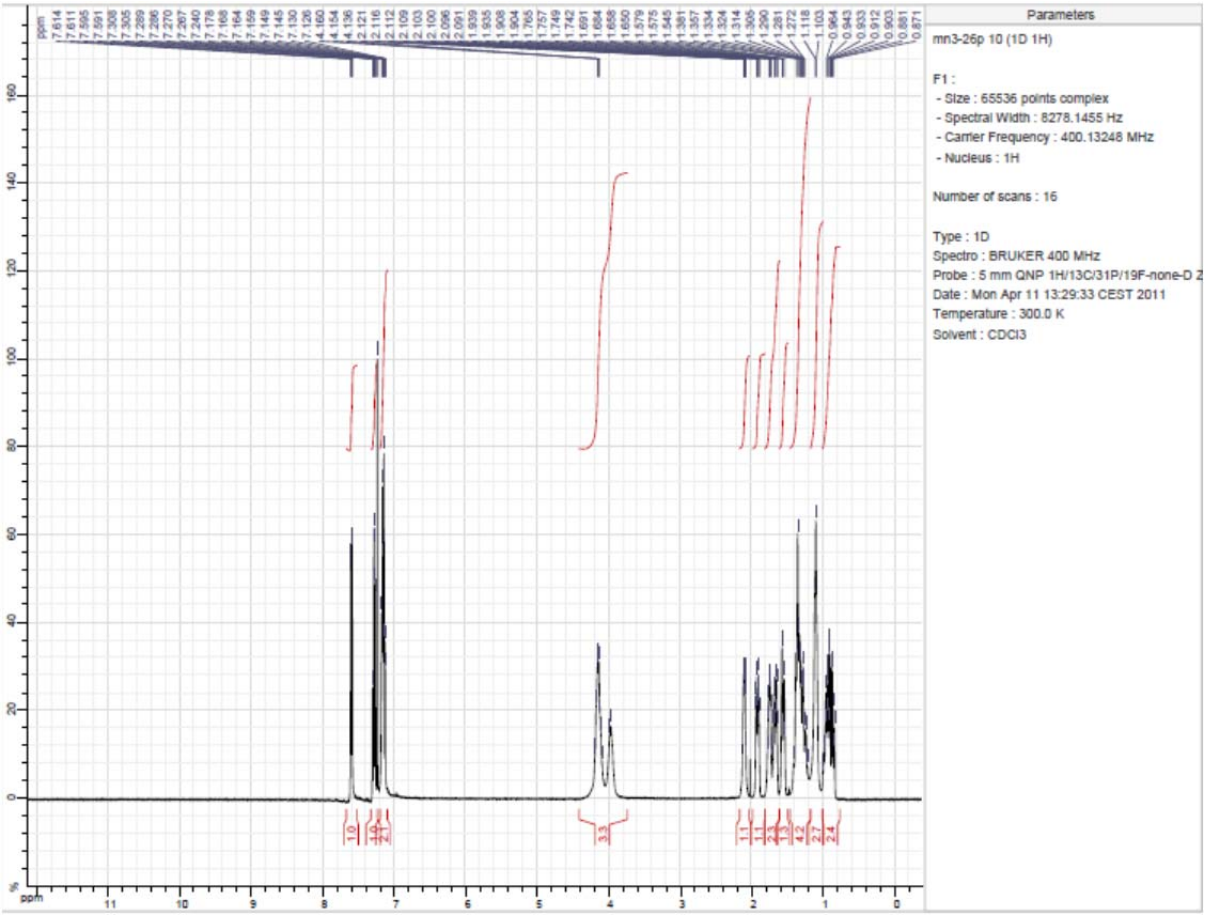
Table 2:

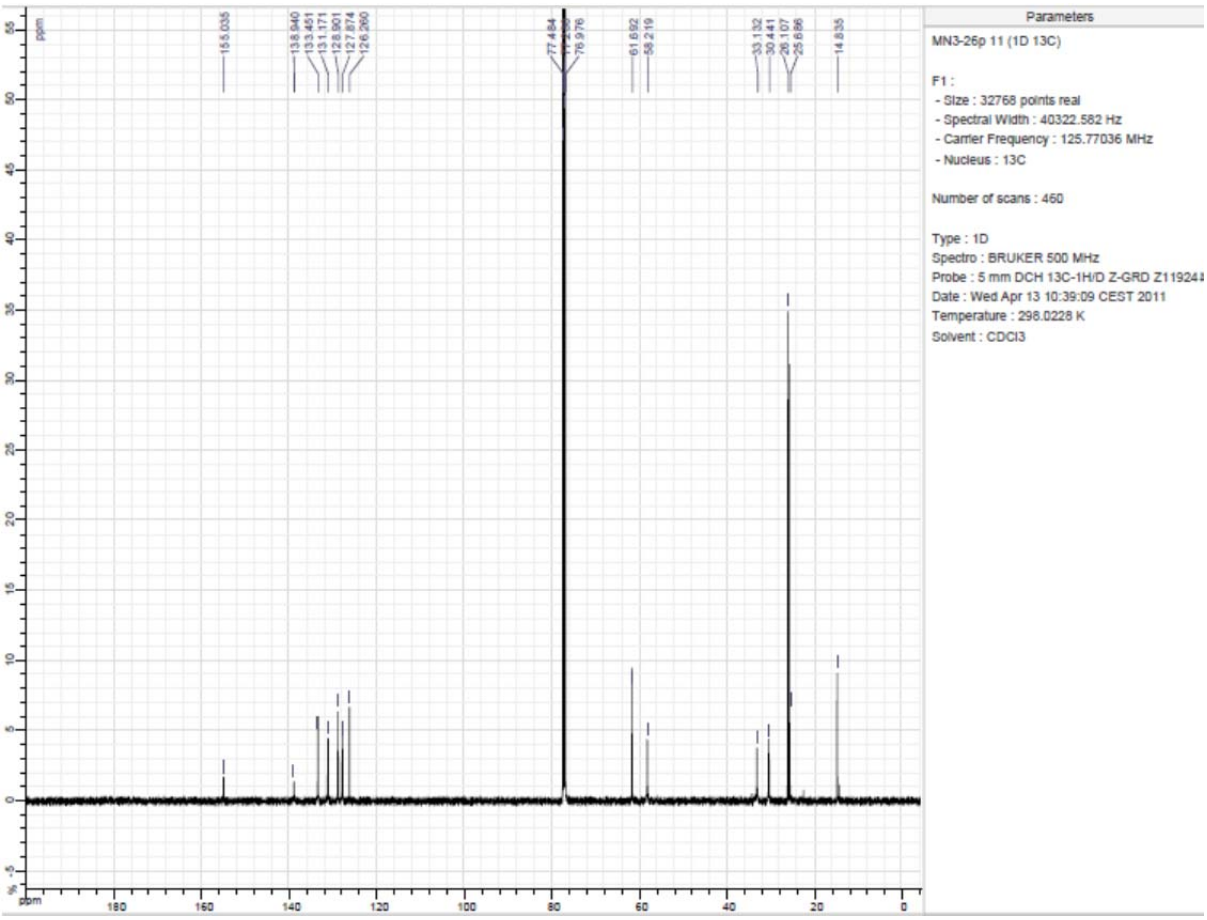
Ethyl (2-bromophenyl)(cyclohexyl)carbamate **1f**:



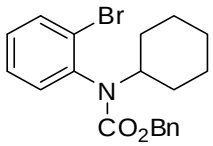
Prepared according to **GP2** from 2-bromo-*N*-cyclohexylaniline and ethyl chloroformate. White solid, 97% yield, M. p. 86 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.83-1.02 (m, 2H), 1.20-1.44 (m, 3H), 1.51-1.62 (m, 1H), 1.62-1.81 (m, 2H), 1.87-1.96 (m, 1H), 2.03-2.12 (m, 1H), 2.33 (s, 3H), 3.60 (s, 3H), 3.89-4.30 (m, 1H), 7.00-7.12 (m, 2H), 7.43 (s, 1H). ^{13}C NMR (125 MHz): δ = 21.0, 25.7, 26.1, 30.4, 33.1, 53.0, 58.3, 125.8, 128.7, 130.6, 134.0, 136.0, 139.3, 155.7. IR (neat): υ = 737, 768, 827, 857, 893, 960, 1030, 1065, 1127, 1154, 1190, 1239, 1258, 1276, 1310, 1353, 1383, 1440, 1492, 1704, 2856, 2929 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}BrNO_2$ 326.0750, found 326.0750.

Supporting Information for Chem. Sci.

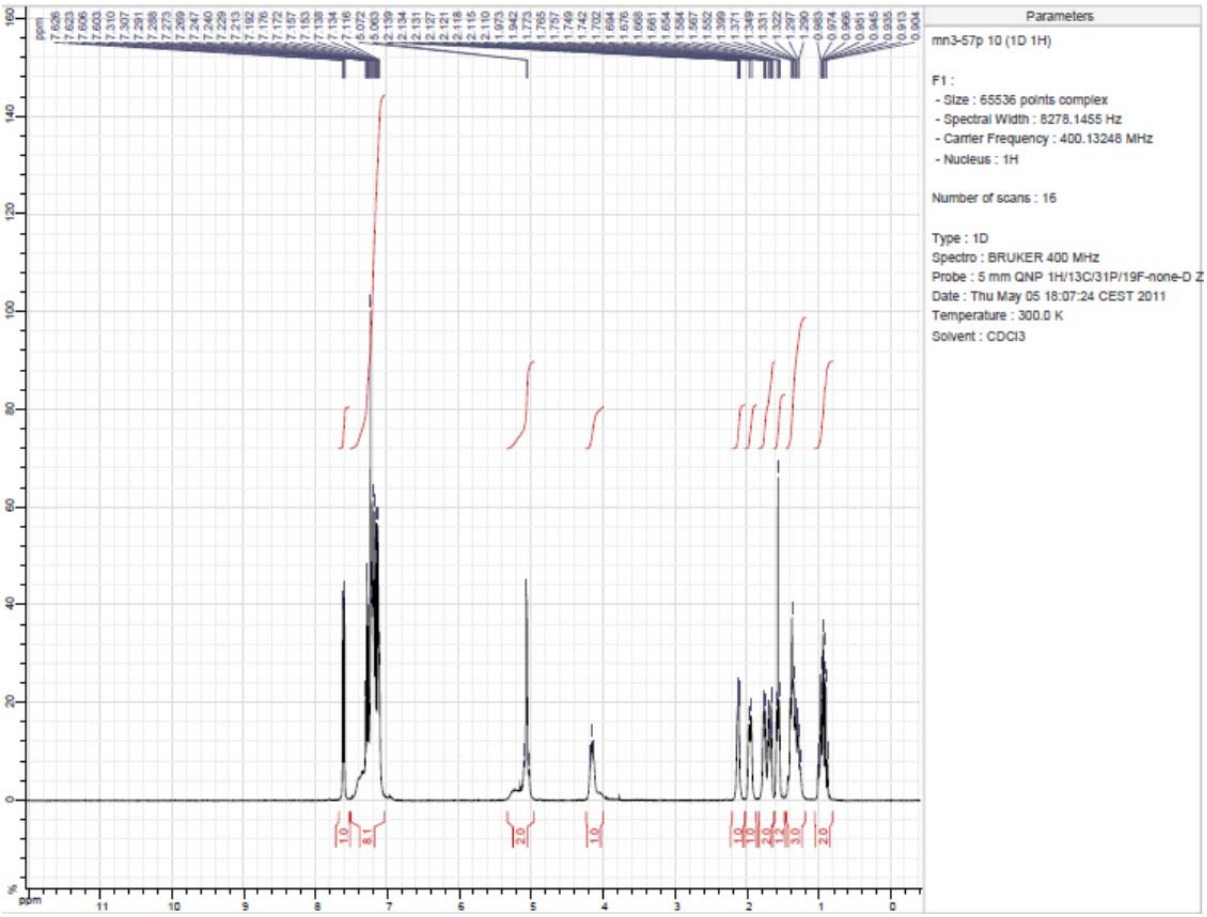


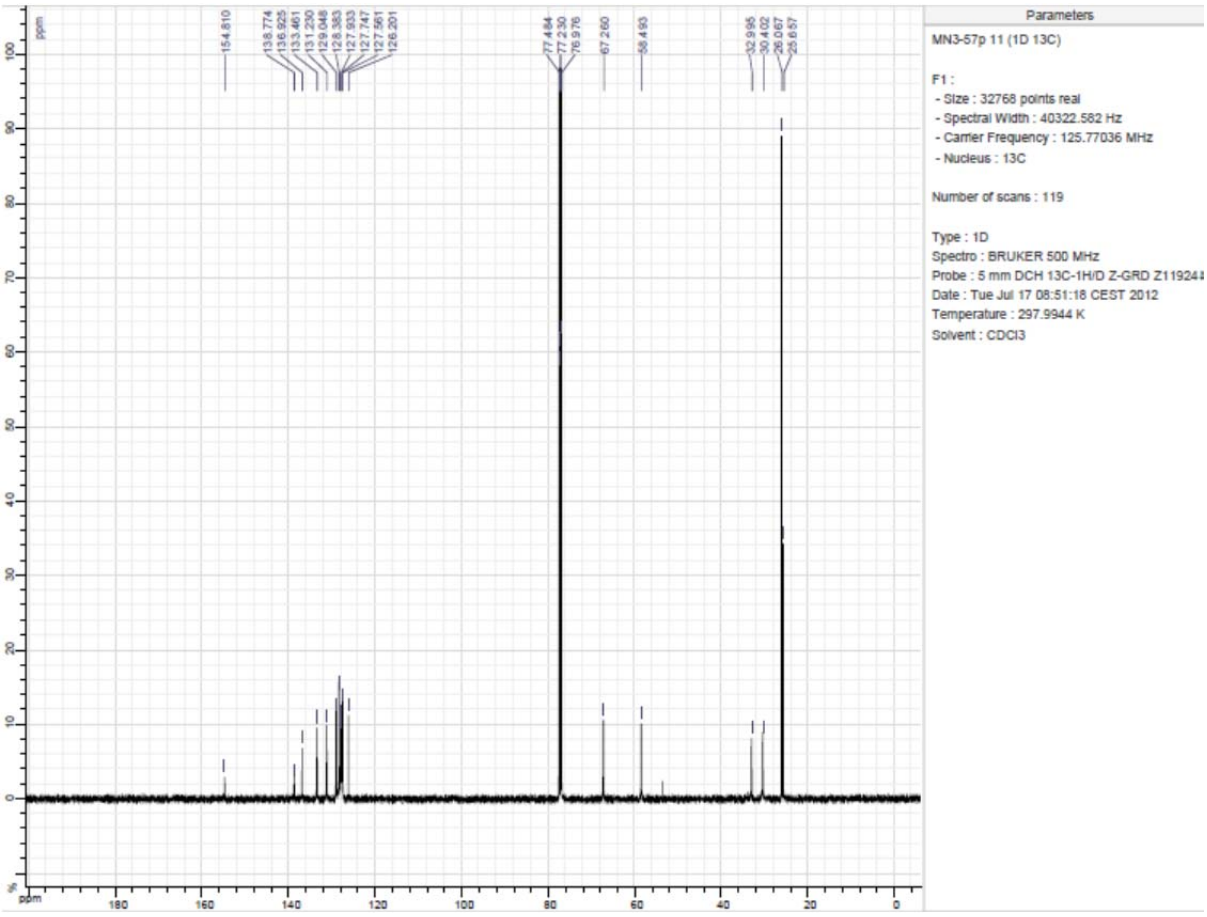


Benzyl (2-bromophenyl)(cyclohexyl)carbamate **1g**:

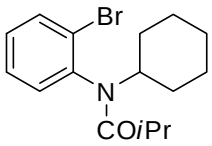


Prepared according to **GP2** from 2-bromo-*N*-cyclohexylaniline and benzyl chloroformate. White solid, 92% yield, M. p. 79-81 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.82-1.07 (m, 2H), 1.20-1.45 (m, 3H), 1.57 (d, J = 12.8 Hz, 1H), 1.63-1.84 (m, 2H), 1.96 (d, J = 12.4 Hz, 1H), 4.01-4.25 (m, 1H), 4.97-5.35 (m, 1H), 7.05-7.52 (m, 8H), 7.61 (dd, J = 8, 1.2 Hz, 1H). ^{13}C NMR (125 MHz): δ = 25.7, 26.1, 30.4, 33.0, 58.5, 67.3, 126.2, 127.6, 127.7, 127.9, 128.4, 129.0, 131.2, 133.5, 136.9, 138.8, 154.8. IR (neat): υ = 734, 744, 764, 860, 895, 915, 967, 1022, 1064, 1110, 1153, 1192, 1217, 1264, 1304, 1348, 1401, 1460, 1477, 1585, 1689, 2855, 2931, 3062 cm^{-1}; ESI-HRMS calcd. for $C_{20}H_{23}BrNO_2$ 388.0906, found 388.0897.



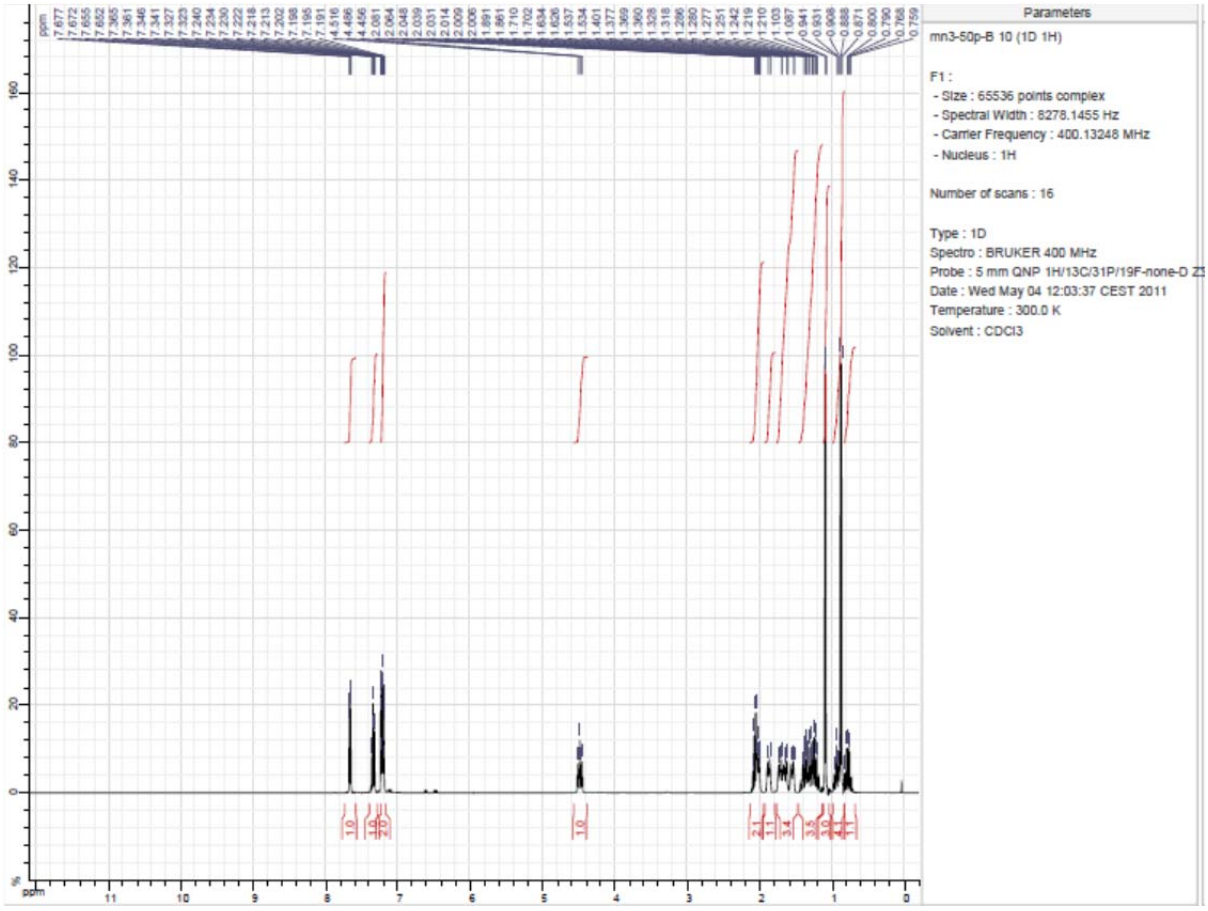


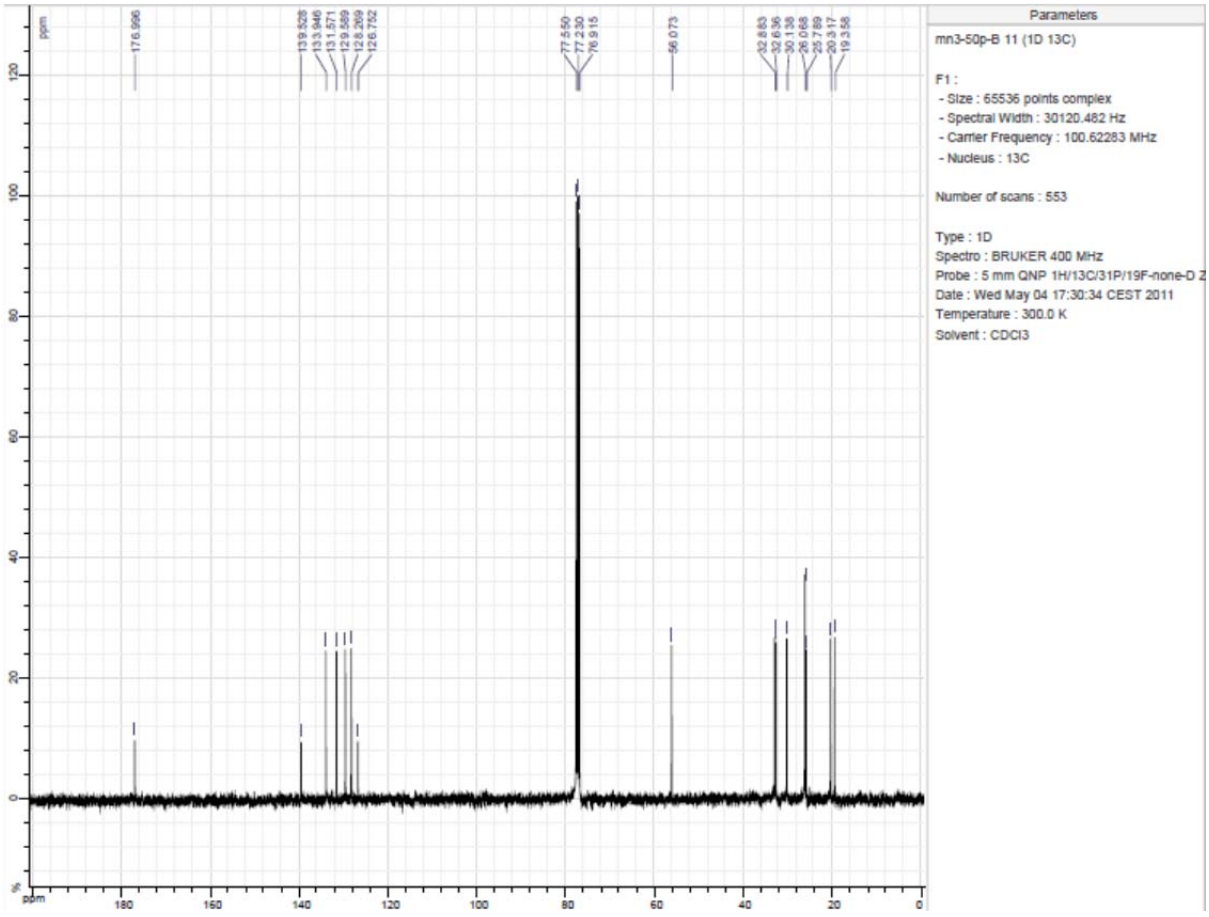
N-(2-bromophenyl)-*N*-cyclohexylisobutyramide **1h**:



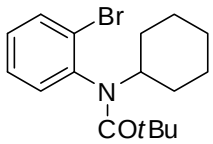
Prepared according to **GP2** from 2-bromo-*N*-cyclohexylaniline and isobutyril chloride. White solid, 95% yield, M. p. 66 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.78 (qd, J = 12.4, 4 Hz, 1H), 0.88 (d, J = 6.8 Hz, 3H), 0.94 (tt, J = 12.4, 3.6 Hz, 1H), 1.10 (d, J = 6.4 Hz, 3H), 1.15-1.47 (m, 3H), 1.49-1.77 (m, 3H), 1.80-1.93 (m, 1H), 1.96-2.15 (m, 2H), 4.49 (tt, J = 12, 3.6, Hz, 1H), 7.18-7.23 (m, 2H), 7.30-7.39 (m, 1H), 7.62-7.70 (m, 1H). ^{13}C NMR (100 MHz): δ = 19.4, 20.3, 25.8, 26.1, 30.1, 32.6, 32.9, 56.1, 126.8, 128.3, 129.6, 131.6, 133.9, 139.5, 177.0. IR (neat): υ = 736, 763, 783, 837, 868, 945, 1012, 1060, 1115, 1182, 1241, 1310, 1359, 1391, 1435, 1475, 1583, 1697, 2858, 2924 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}NOBr$ 326.0750, found 326.0753.

Supporting Information for Chem. Sci.

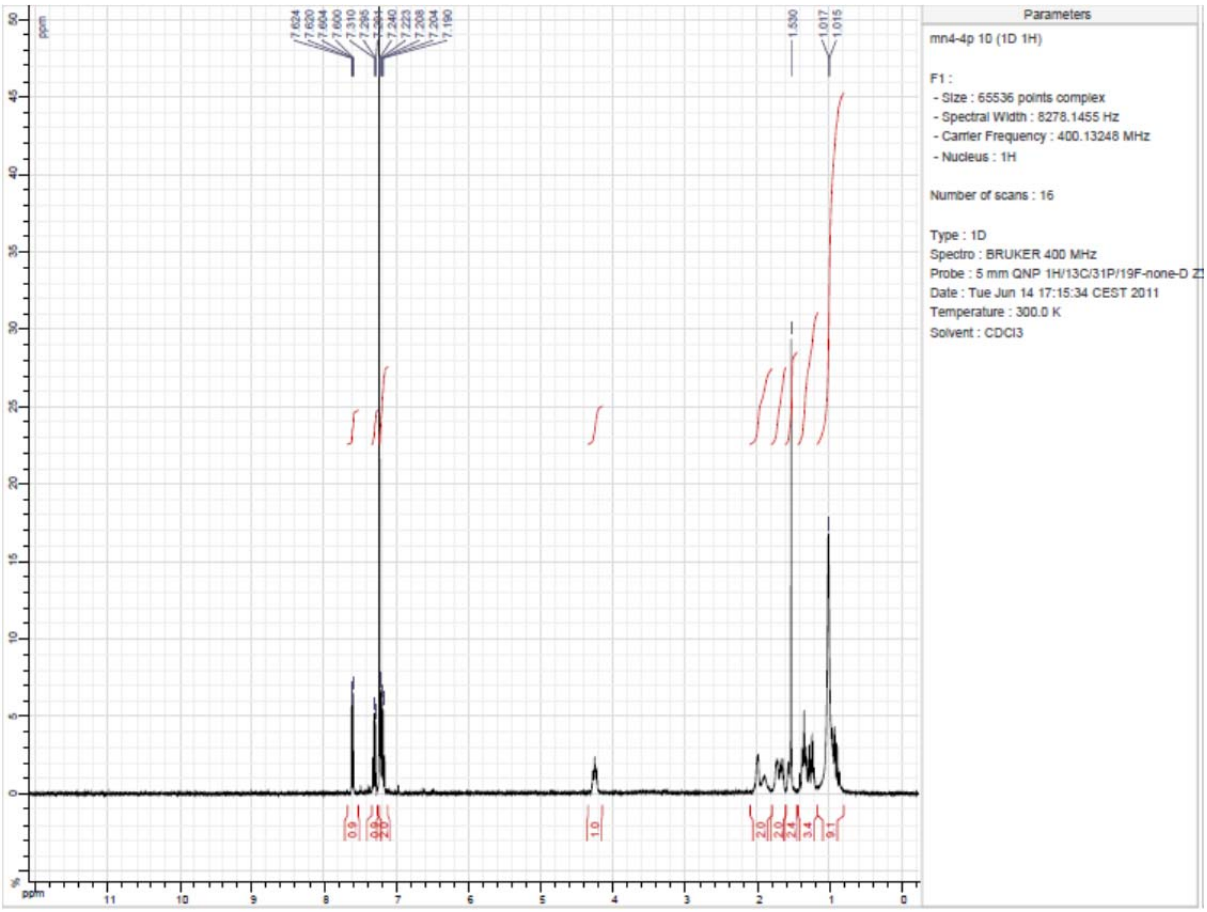


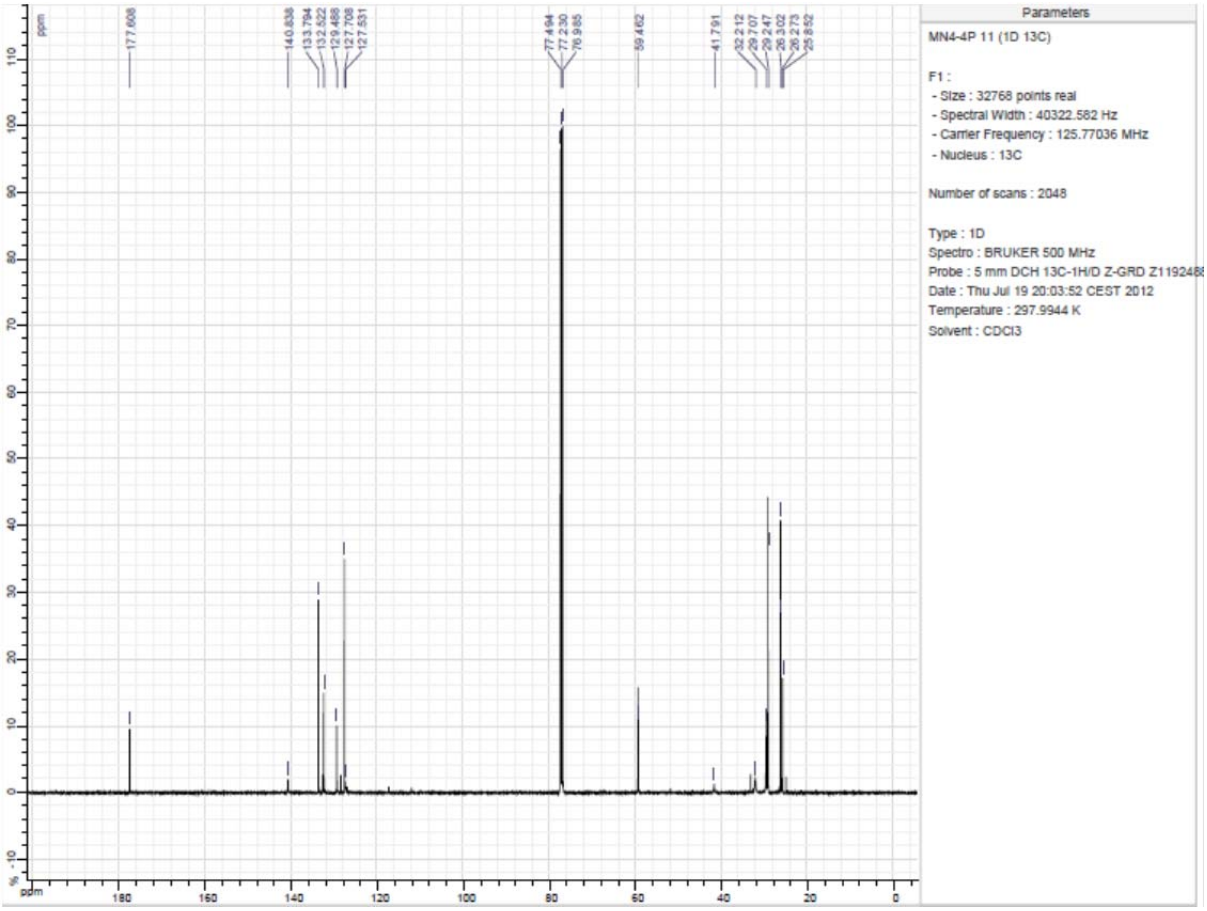


N-(2-Bromophenyl)-*N*-cyclohexylpivalamide **1i**:

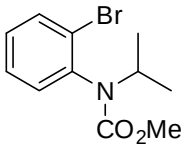


Prepared according to **GP2** from 2-bromo-*N*-cyclohexylaniline and pyvalyl chloride. White solid, 96% yield, M. p. 97 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.78-1.05 (m, 2H), 1.20-1.44 (m, 3H), 1.50-1.60 (m, 1H), 1.63-1.71 (m, 1H), 1.71-1.82 (m, 1H), 1.85-1.98 (m, 1H), 2.02-2.17 (m, 1H), 3.60 (s, 3H), 3.96-4.28 (m, 1H), 7.11-7.21 (m, 2H), 7.25-7.33 (m, 1H), 7.54-7.68 (m, 1H). ^{13}C NMR (125 MHz): δ = 25.8, 26.3, 29.2, 29.7, 32.2, 41.8, 59.5, 127.5, 127.7, 129.5, 132.5, 133.8, 140.8, 177.6. IR (neat): υ = 744, 762, 782, 896, 961, 1023, 1063, 1154, 1186, 1251, 1265, 1312, 1354, 1391, 1438, 1474, 1711, 2857, 2933 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{19}NO_2Br$ 312.0593, found 312.0600.



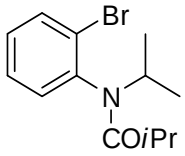


Methyl (2-bromophenyl)(isopropyl)carbamate **3a**:

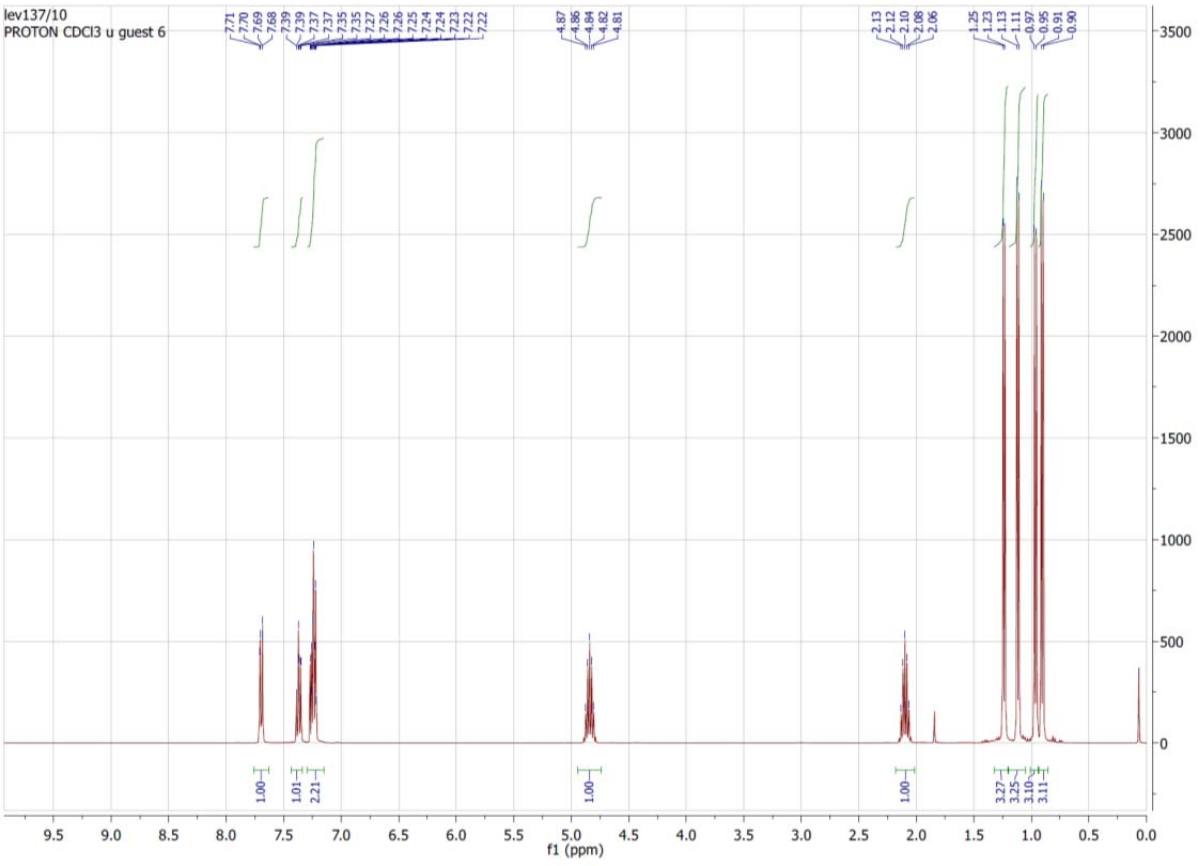


Prepared according to **GP2**. Pale yellow oil, 1.25 g, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.03 (d, J = 7.2 Hz, 3H), 1.32 (d, J = 6.4 Hz, 3H), 3.61 (s, 3H), 4.36-4.42 (m, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.62 (d, J = 7.6, 1.2 Hz, 1H).

N-(2-bromophenyl)-N-isopropylisobutyramide **3b**:



Prepared according to **GP2** from 2-bromo-*N*-isopropylaniline and isobutyril chloride. White solid (900 mg, 82%), m.p. 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.19 (m, 2H), 4.84 (hept, *J* = 6.8 Hz, 1H), 2.10 (hept, *J* = 6.7 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 139.3, 134.0, 131.4, 129.7, 128.3, 126.7, 48.1, 33.0, 22.4, 20.2, 19.5, 19.3. HRMS calcd. for $C_{13}H_{19}N_1O_1Br$ 284.0644, found 284.0644 (accuracy 0.2 ppm). IR (neat): υ = 2973 (m), 2933 (w), 1645 (vs), 1471 (s), 1433 (m), 1394 (s), 1366 (m), 1256 (s), 1243 (s), 1112 (m), 1027 (m), 773 (s) cm^{-1}.



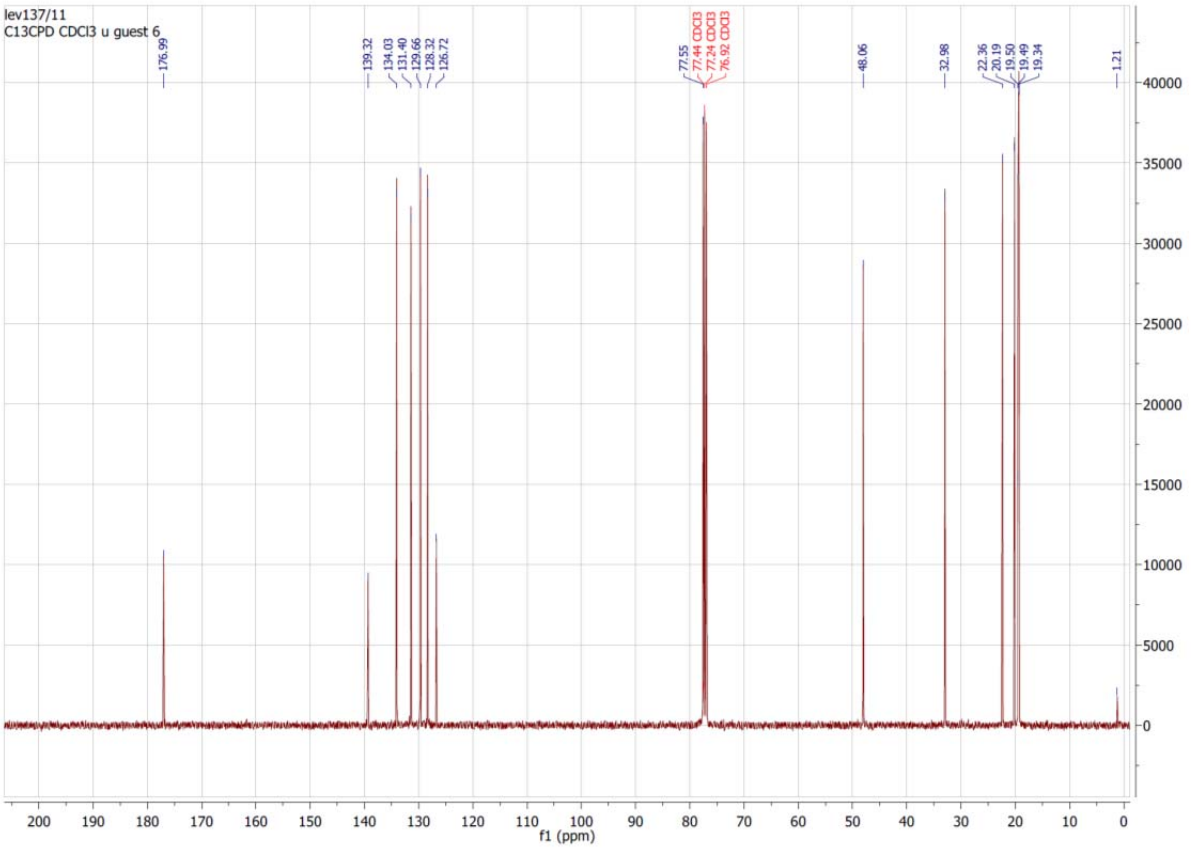
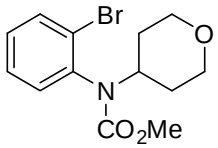


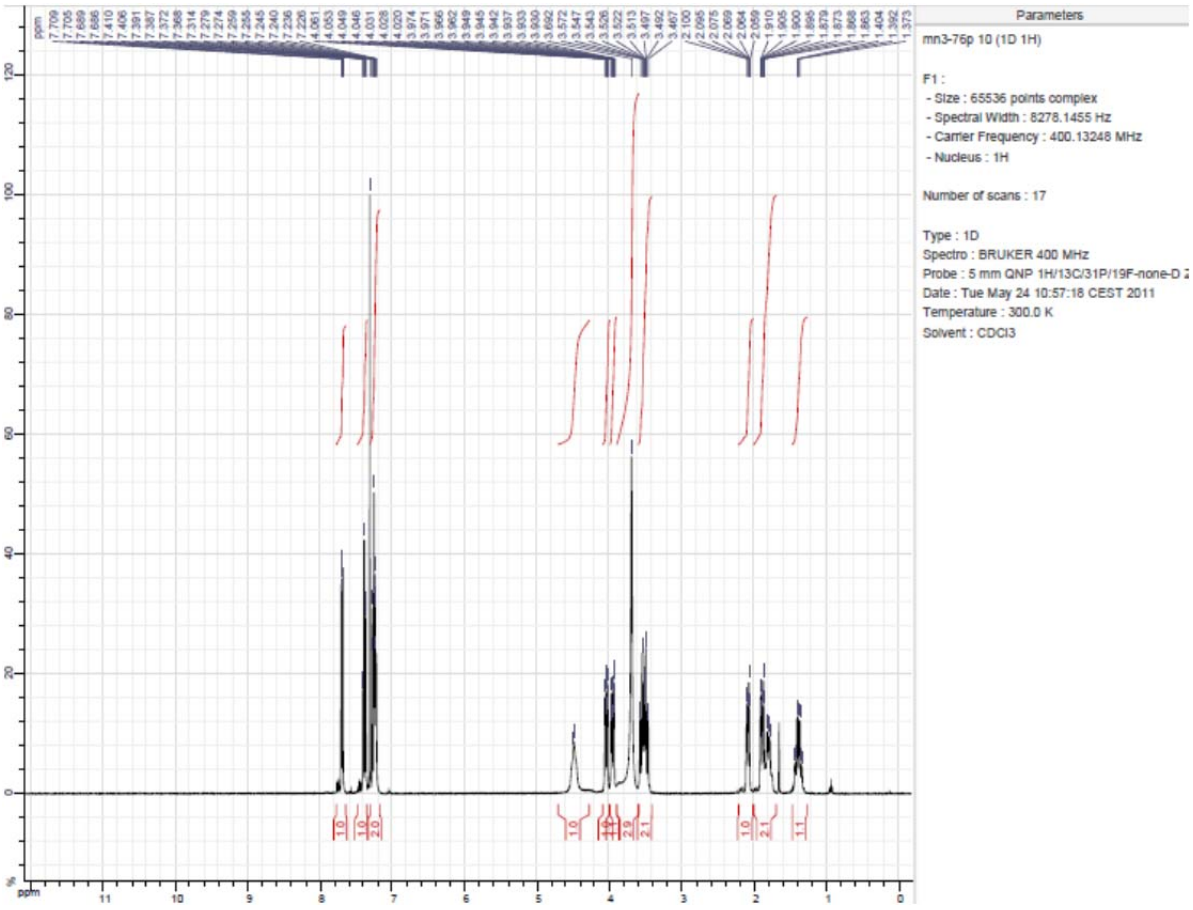
Table 3:

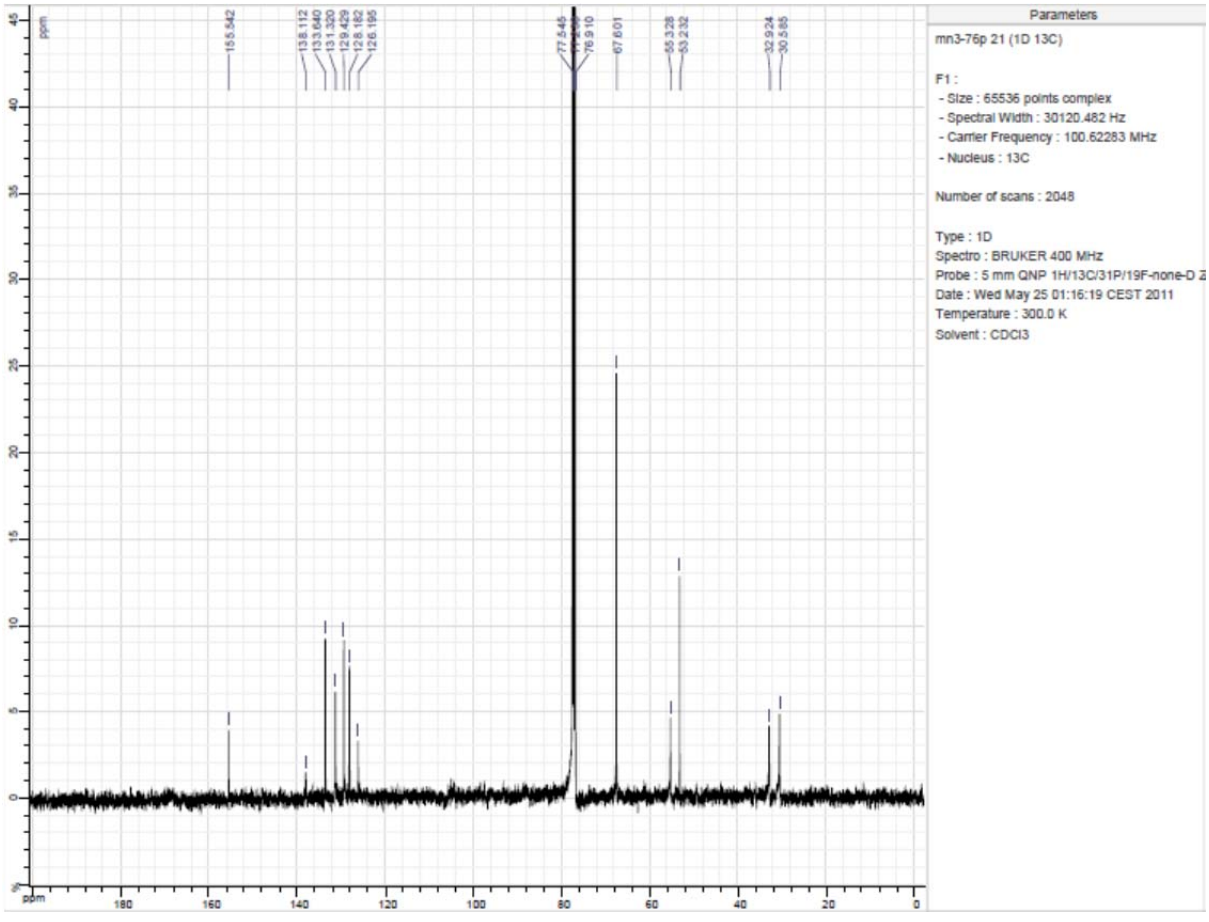
Methyl (2-bromophenyl)(tetrahydro-2*H*-pyran-4-yl)carbamate **1j**:



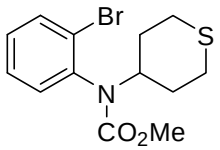
Prepared according to **GP2.** White solid, 92% yield, M. p. 82 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.38 (qd, J = 12.4, 4.8 Hz, 1H), 1.70-2.01 (m, 2H), 2.02-2.22 (m, 1H), 3.42-3.60 (m, 2H), 3.69 (s, 3H), 3.95 (ddt, J = 11.6, 4.8, 1.6 Hz, 1H), 4.04 (ddt, J = 12, 4.8, 1.2 Hz, 1H), 4.37-4.60 (m, 1H), 7.18-7.31 (m, 2H), 7.36-7.49 (m, 1H), 7.65-7.78 (m, 1H). ^{13}C NMR (100 MHz): δ = 30.6, 32.9, 53.2, 55.3, 67.6, 126.2, 128.2, 129.4, 131.3, 133.6, 138.1, 155.5. IR (neat): υ = 746, 766, 784, 825, 871, 959, 994, 1010, 1036, 1061, 1086, 1130, 1170, 1192, 1237, 1292, 1320, 1352, 1378, 1442, 1474, 1583, 1704, 2852, 2949 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{17}BrNO_3$ 314.0386, found 314.0380.

Supporting Information for Chem. Sci.

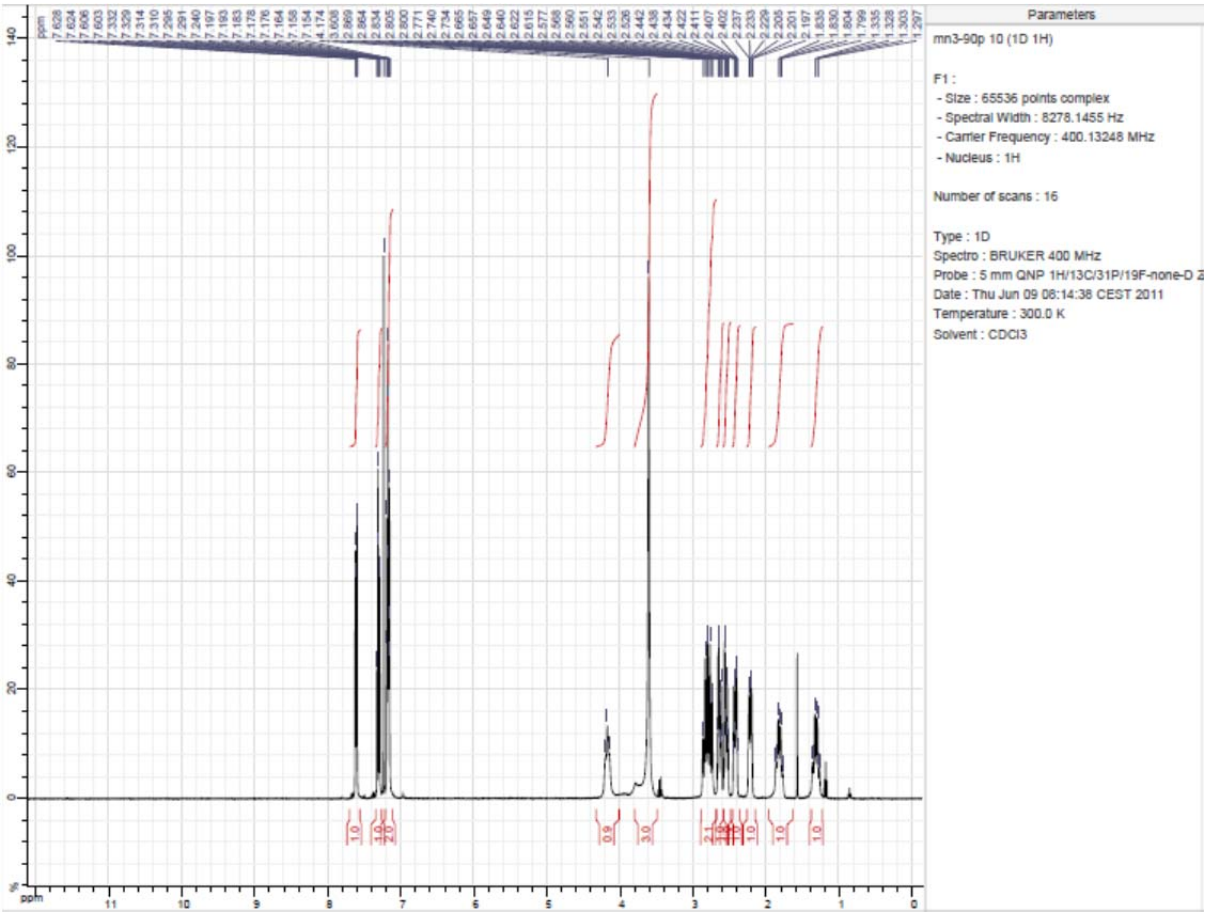


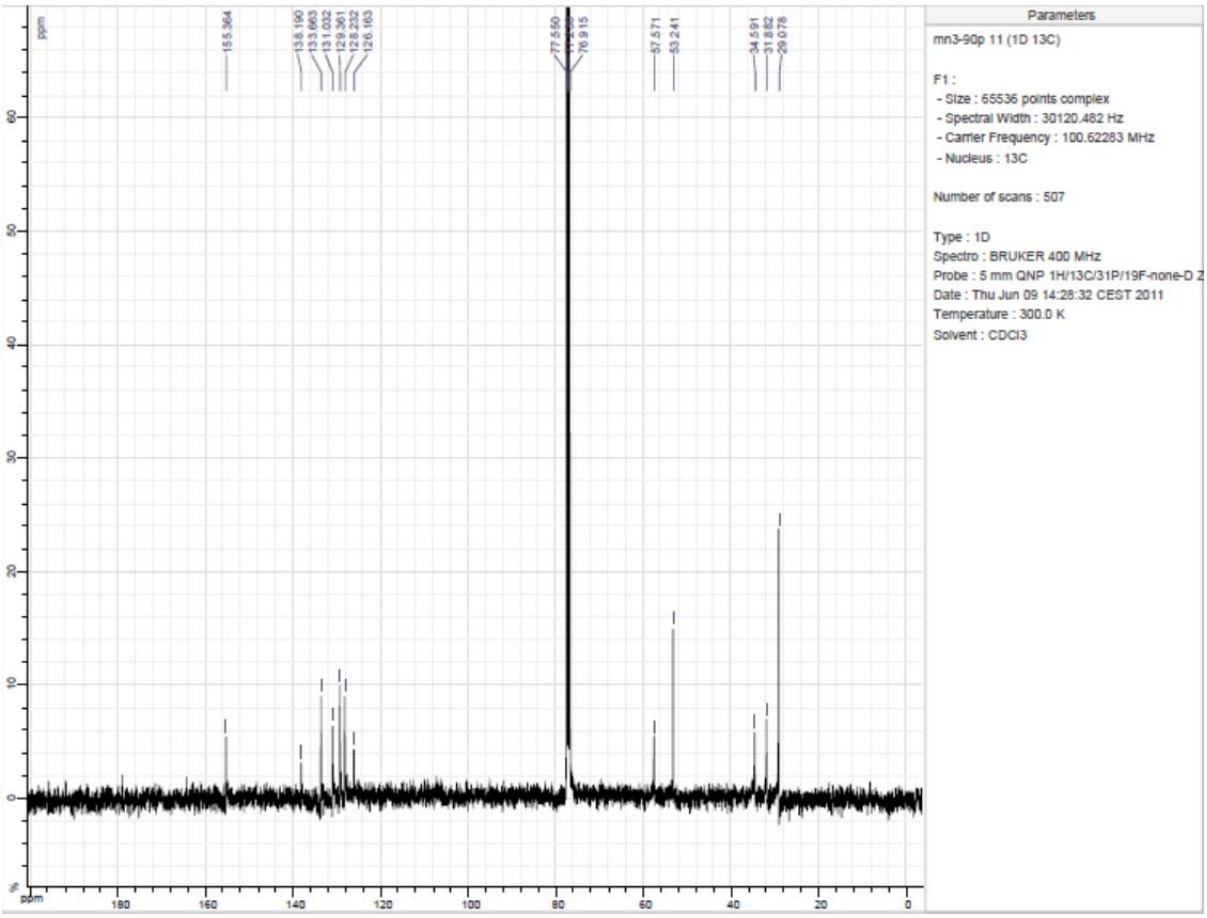


Methyl (2-bromophenyl)(tetrahydro-2*H*-thiopyran-4-yl)carbamate **1k**:

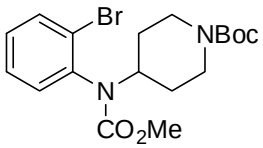


Prepared according to **GP2.** White solid, 62% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.16-1.46 (m, 5H), 1.60-1.67 (m, 2H), 1.72-1.82 (m, 2H), 1.96-2.06 (m, 2H), 3.27-3.40 (m, 1H), 4.77 (d, J = 7.2 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 8.4, 2 Hz, 1H), 7.64 (d, J = 2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.8, 25.8, 32.9, 51.6, 98.9, 108.7, 110.7, 119.4, 133.1, 136.2, 147.4. IR (neat): υ = 808, 885, 1033, 1099, 1157, 1186, 1237, 1272, 1257, 1337, 1412, 1450, 1515, 1598, 2216, 2854, 2930, 3401 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{17}BrSNO_2$ 330.0157, found 330.0154.

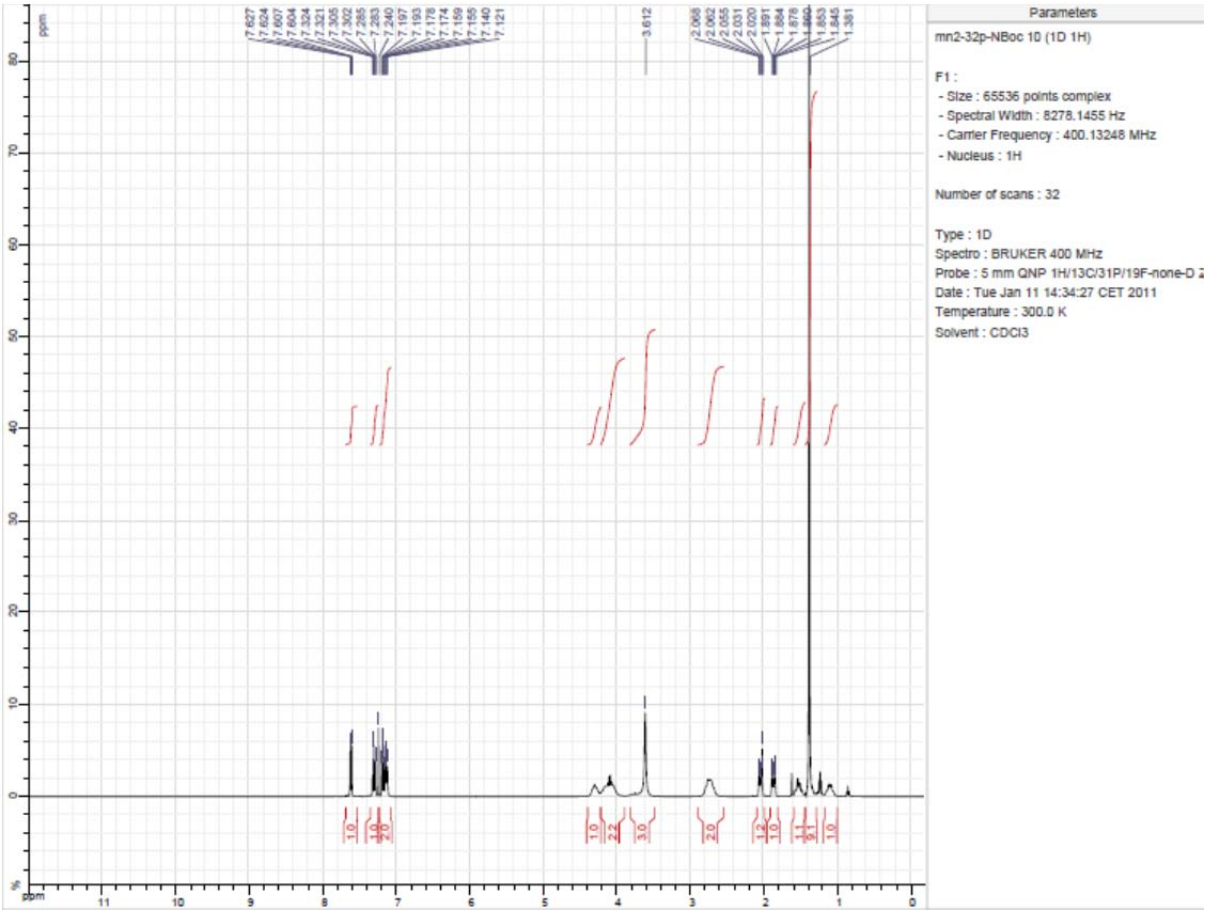


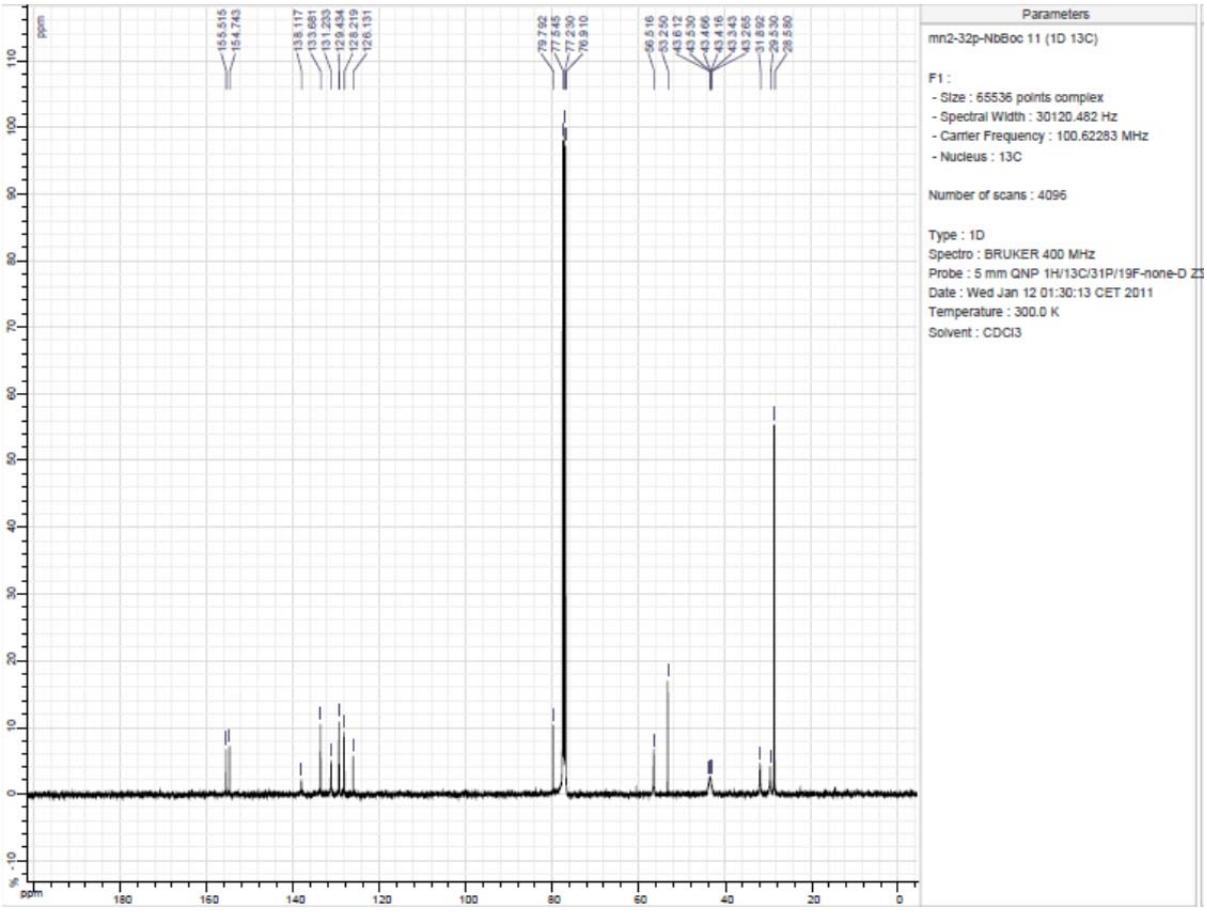


tert-Butyl 4-((2-bromophenyl)(methoxycarbonyl)amino)piperidine-1-carboxylate **1l**:

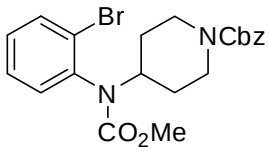


Prepared according to **GP2.** White solid, 79% yield, M. p. 137 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.01-1.18 (m, 1H), 1.38 (s, 9H), 1.45-1.60 (m, 1H), 1.82-1.92 (m, 1H), 2.00-2.10 (m, 1H), 2.56-2.90 (m, 2H), 3.61 (s, 3H), 3.90-4.22 (m, 2H), 4.22-4.40 (m, 1H 7.14 (t, J = 7.6 Hz, 1H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.62 (dd, J = 8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 28.6, 29.5, 31.9, 43.4, 53.3, 56.5, 79.8, 126.1, 128.2, 129.4, 131.2, 133.7, 138.1, 154.7, 155.5. IR (neat): υ = 746.8, 765, 820, 868, 957, 1030, 1060, 1085, 1136, 1167, 1233, 1248, 1281, 1314, 1364, 1395, 1427, 1470, 1682, 2856, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{18}H_{26}BrN_2O_4$ 413.1070, found 413.1082.

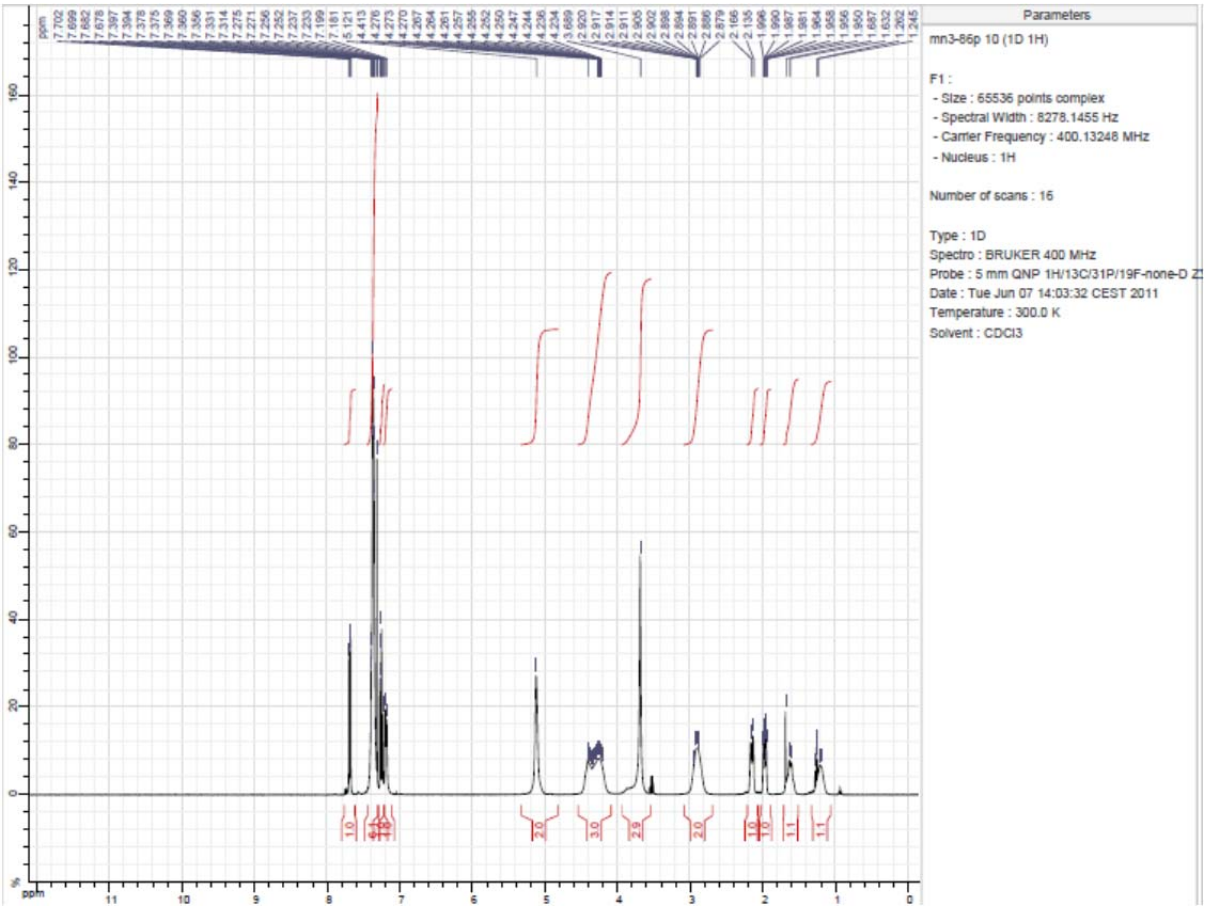

Parameters
mn2-32p-NBoc 10 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 8278.1455 Hz
- Carrier Frequency : 400.13248 MHz
- Nucleus : 1H
Number of scans : 32
Type : 1D
Spectro : BRUKER 400 MHz
Date : Tue Jan 11 14:34:27 CET 2011
Temperature : 300.0 K
Solvent : CDCl3

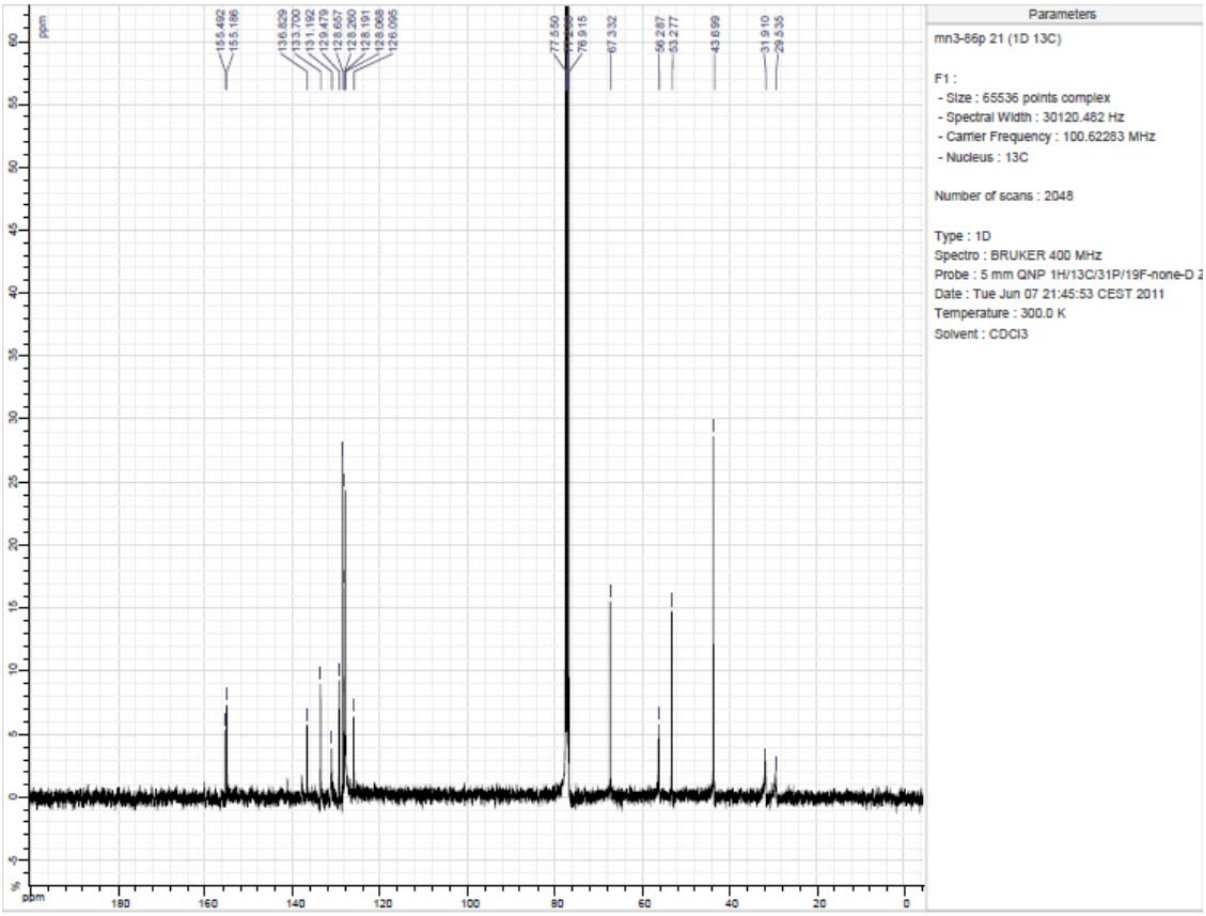

Parameters
mn2-32p-NbBoc 11 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 4096
Type : 1D
Spectro : BRUKER 400 MHz
Date : Wed Jan 12 01:30:13 CET 2011
Temperature : 300.0 K
Solvent : CDCl3

Benzyl 4-((2-bromophenyl)(methoxycarbonyl)amino)piperidine-1-carboxylate **1m**:

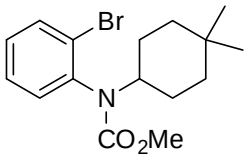


Prepared according to **GP2.** Colorless oil, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.18-1.32 (m, 3H), 1.32-1.45 (m, 2H), 1.59-1.69 (m, 1H), 1.71-1.82 (m, 2H), 1.96-2.08 (m, 2H), 3.29-3.42 (m, 1H), 3.83 (s, 3H), 4.70 (d, J = 7.6 Hz, 1H), 6.57 (d, J = 8.8 Hz, 1H), 7.80 (dd, J = 8.8, 2 Hz, 1H), 8.08 (d, J = 2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.9, 25.9, 33.0, 51.6, 51.9, 108.7, 110.1, 118.5, 130.8, 134.5, 147.7, 166.5. IR (neat): υ = 697, 761, 818, 888, 901, 974, 1032, 1109, 1152, 1187, 1224, 1247, 1258, 1277, 1334, 1409, 1448, 1521, 1596, 1707, 2853, 2930, 3402 cm^{-1}; ESI-HRMS calcd. for $C_{21}H_{24}BrN_2O_4$ 447.0913, found 447.0930.



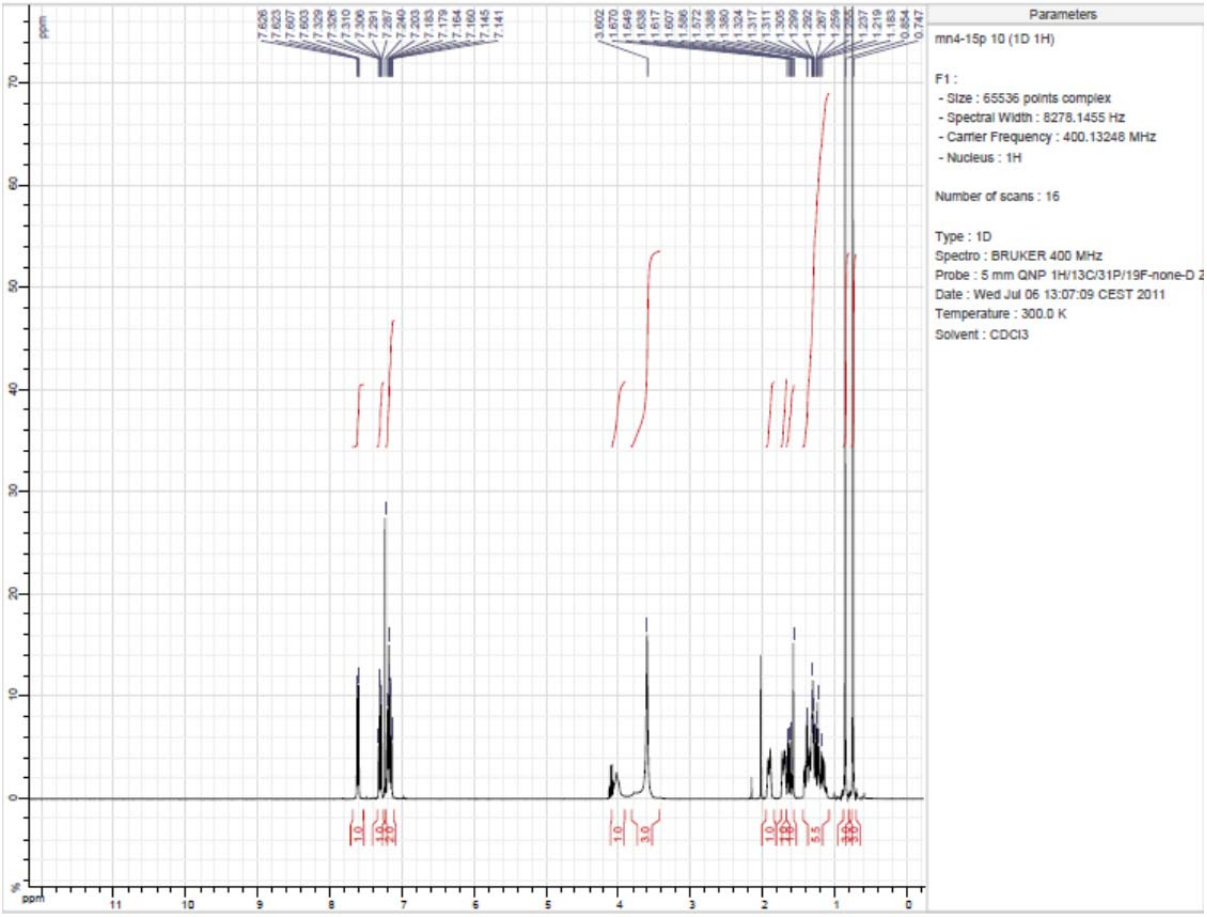


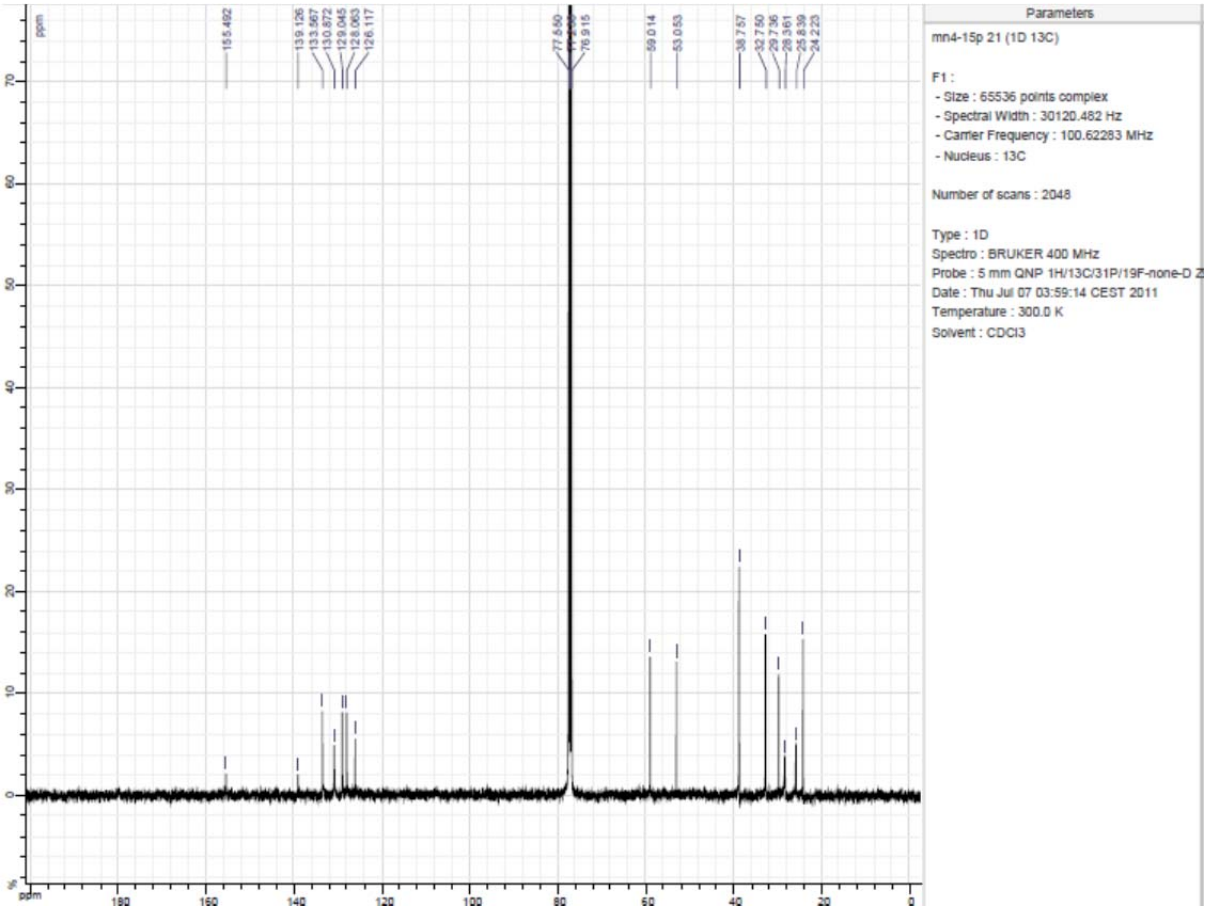
Methyl (2-bromophenyl)(4,4-dimethylcyclohexyl)carbamate **1n**:



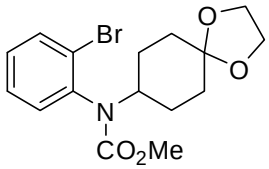
Prepared according to **GP2.** Colorless oil, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.74 (s, 3H), 0.85 (s, 3H), 1.09-1.45 (m, 5H), 1.57-1.67 (m, 1H), 1.67-1.75 (m, 1H), 1.85-1.96 (m, 1H), 3.60 (s, 3H), 3.92-4.10 (m, 1H), 7.12-7.23 (m, 2H), 7.31 (td, J = 7.6, 1.2 Hz, 1H), 7.61 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 24.2, 25.8, 28.4, 29.7, 32.8, 38.3, 53.1, 59.0, 126.1, 128.1, 129.0, 130.9, 133.6, 139.1, 155.5. IR (neat): υ = 723, 798, 835, 865, 1029, 1104, 1153, 1229, 1265, 1317, 1393, 1448, 1464, 1497, 1591, 2853, 2927, 3403 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{23}BrNO_2$ 340.0906, found 340.0898.

Supporting Information for Chem. Sci.

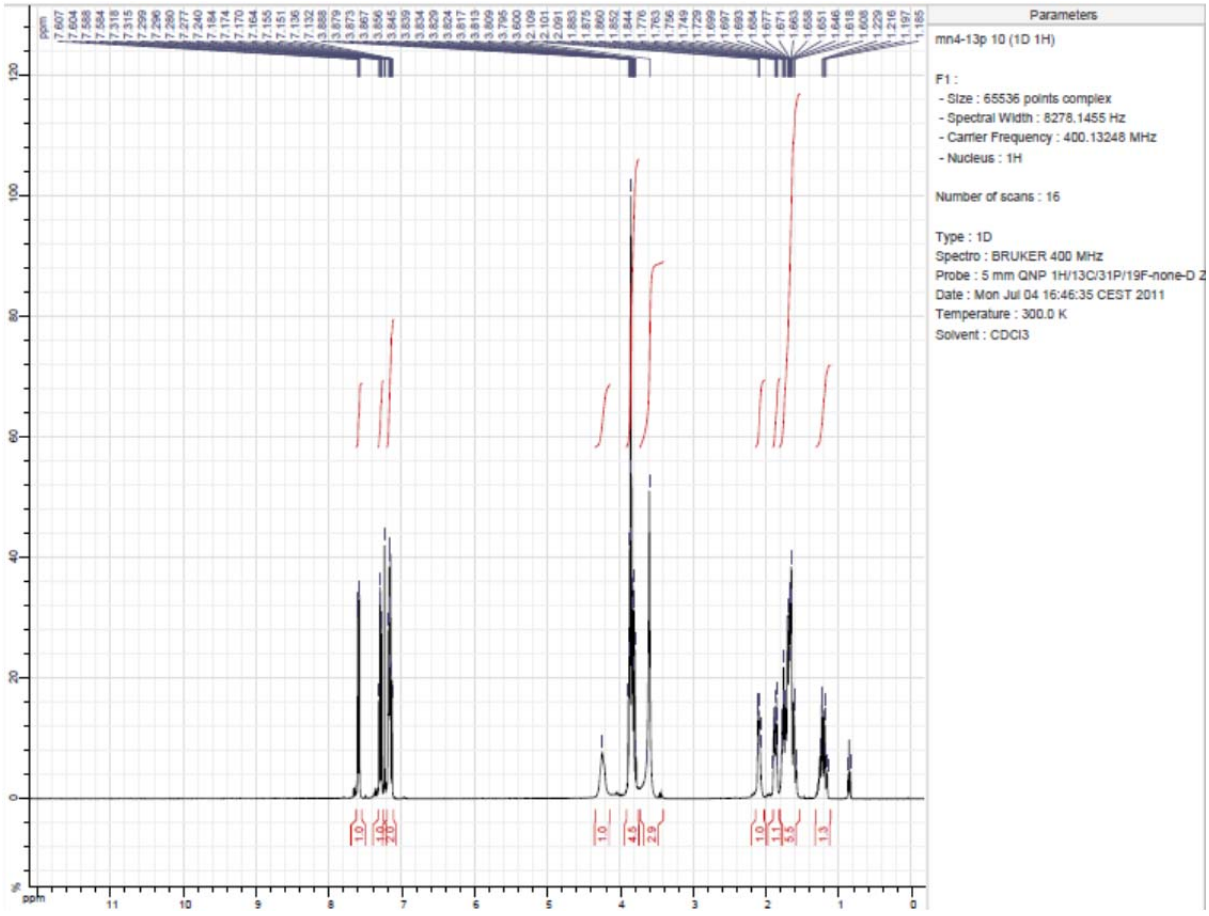


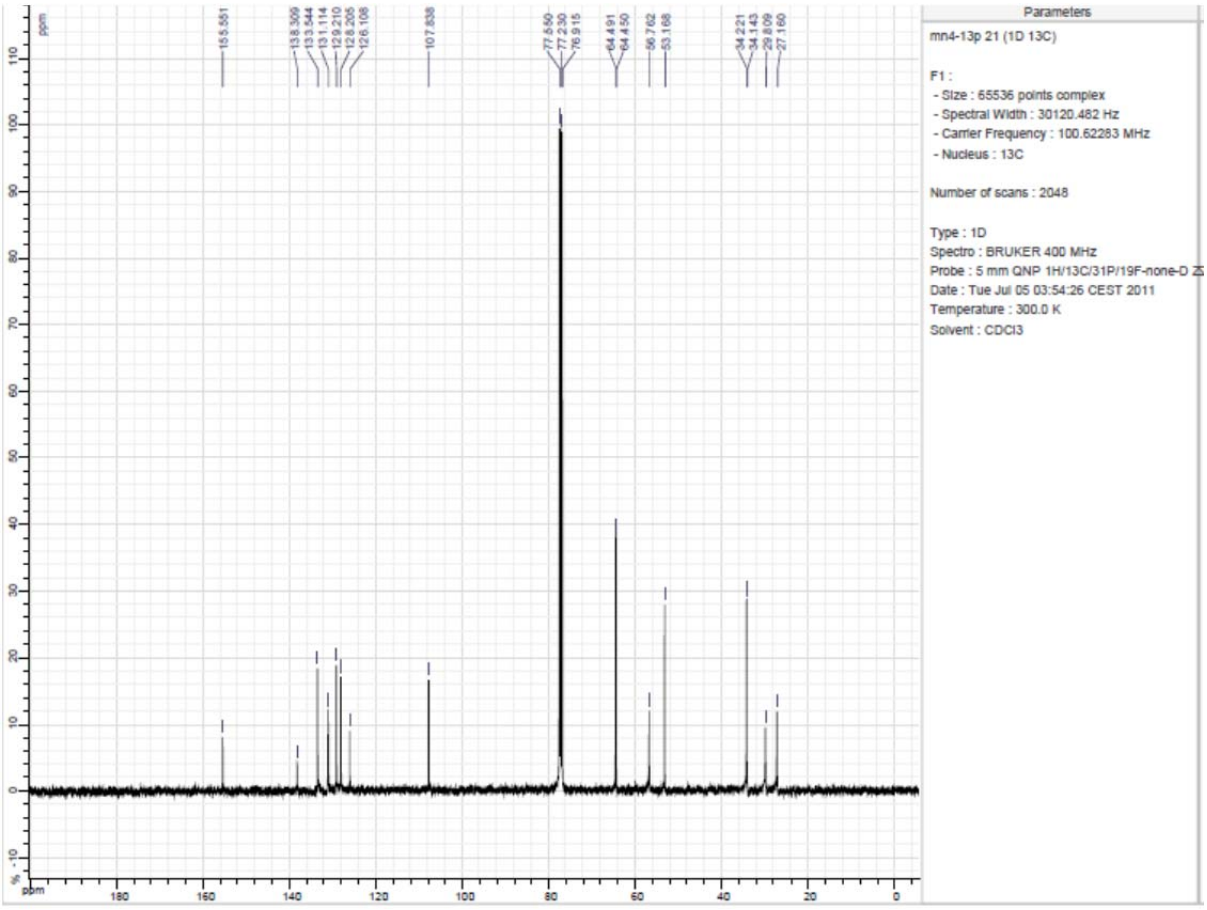


Methyl (2-bromophenyl)(1,4-dioxaspiro[4.5]decan-8-yl)carbamate **1o**:

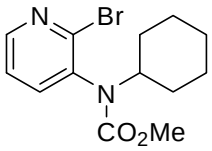


Prepared according to **GP2.** Colorless oil, 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.12-1.32 (m, 1H), 1.54-1.82 (m, 6H), 1.82-1.91 (m, 1H), 3.60 (s, 3H), 3.76-3.92 (m, 4H), 4.15-4.35 (m, 1H), 7.12-7.21 (m, 2H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.60 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 27.2, 29.8, 34.1, 34.2, 53.2, 56.8, 64.5, 64.5, 107.8, 126.1, 128.2, 129.2, 131.1, 133.5, 138.3, 155.6. IR (neat): υ = 791, 854, 883, 1028, 1100, 1148, 1190, 1236, 1265, 1315, 1399, 1453, 1506, 1587, 1609, 2853, 2928, 3407 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{21}NO_4Br$ 370.0648, found 370.0655.



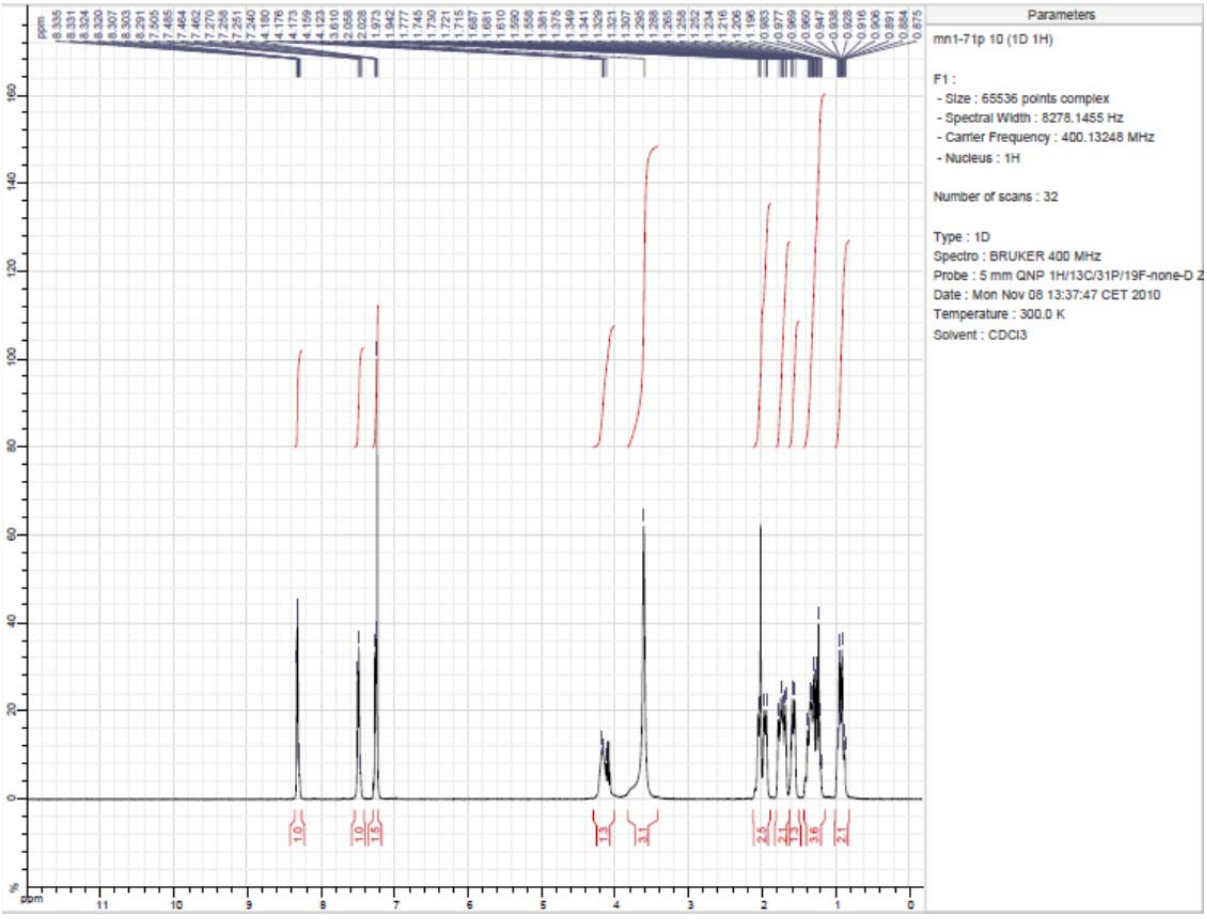


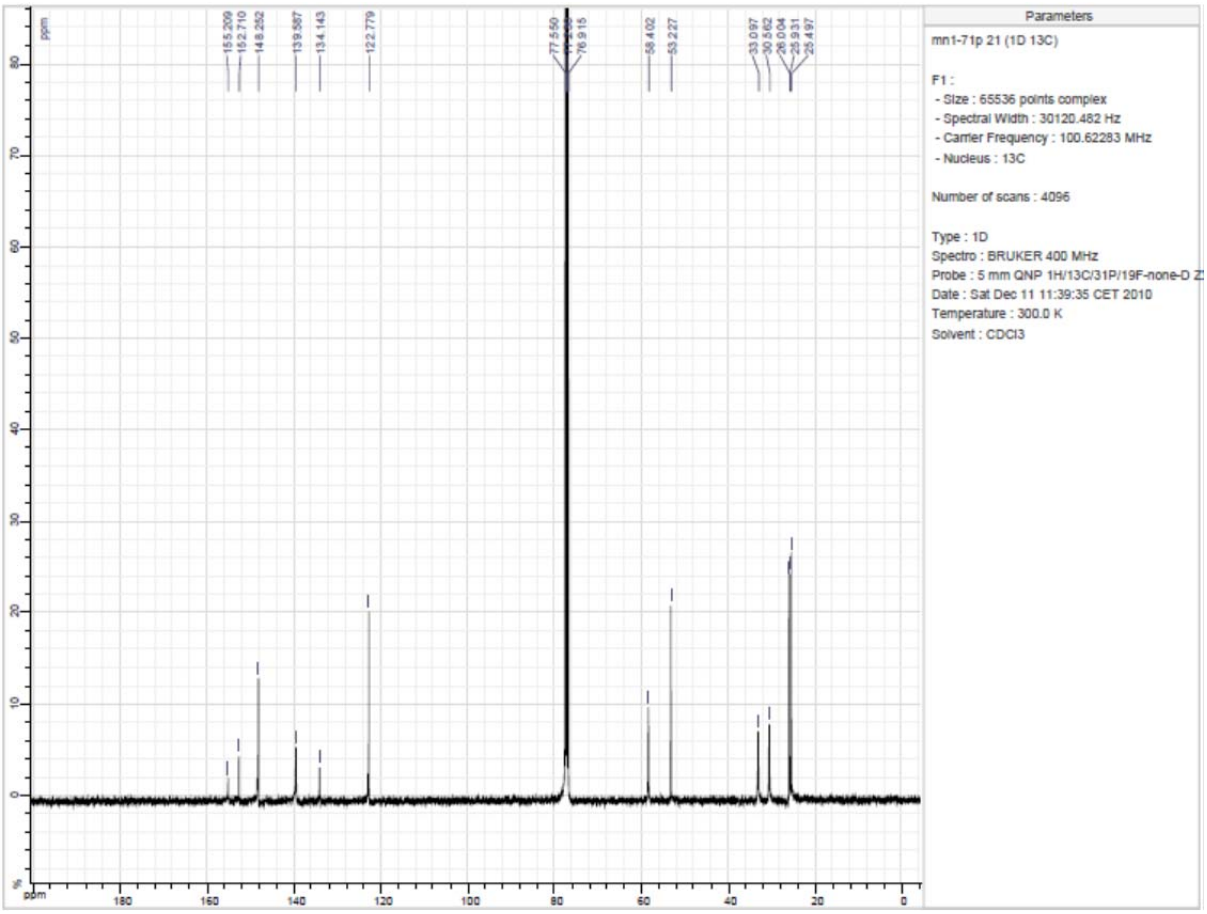
Methyl (2-bromopyridin-3-yl)(cyclohexyl)carbamate **1p**:



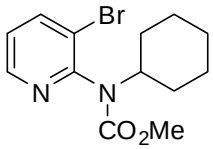
Prepared according to **GP2.** White solid, 53% yield, M. p. 69 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.83-1.02 (m, 2H), 1.16-1.44 (m, 3H), 1.51-1.64 (m, 1H), 1.64-1.82 (m, 2H), 1.90-2.13 (m, 1H), 3.61 (s, 3H), 4.01-4.25 (m, 1H), 7.23-7.30 (m, 1H), 7.42-7.55 (m, 1H), 8.27-8.36 (m, 1H). ^{13}C NMR (100 MHz): δ = 25.5, 25.9, 26.0, 53.2, 58.4, 122.8, 134.1, 139.6, 148.3, 152.7, 155.2. IR (neat): υ = 761, 813, 823, 890, 960, 1027, 1061, 1094, 1136, 1155, 1191, 1242, 1254, 1282, 1310, 1354, 1386, 1404, 1440, 1561, 1697, 1716, 2856, 2930 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{17}BrN_2NaO_2$ 335.0366, found 335.0366.

Supporting Information for Chem. Sci.

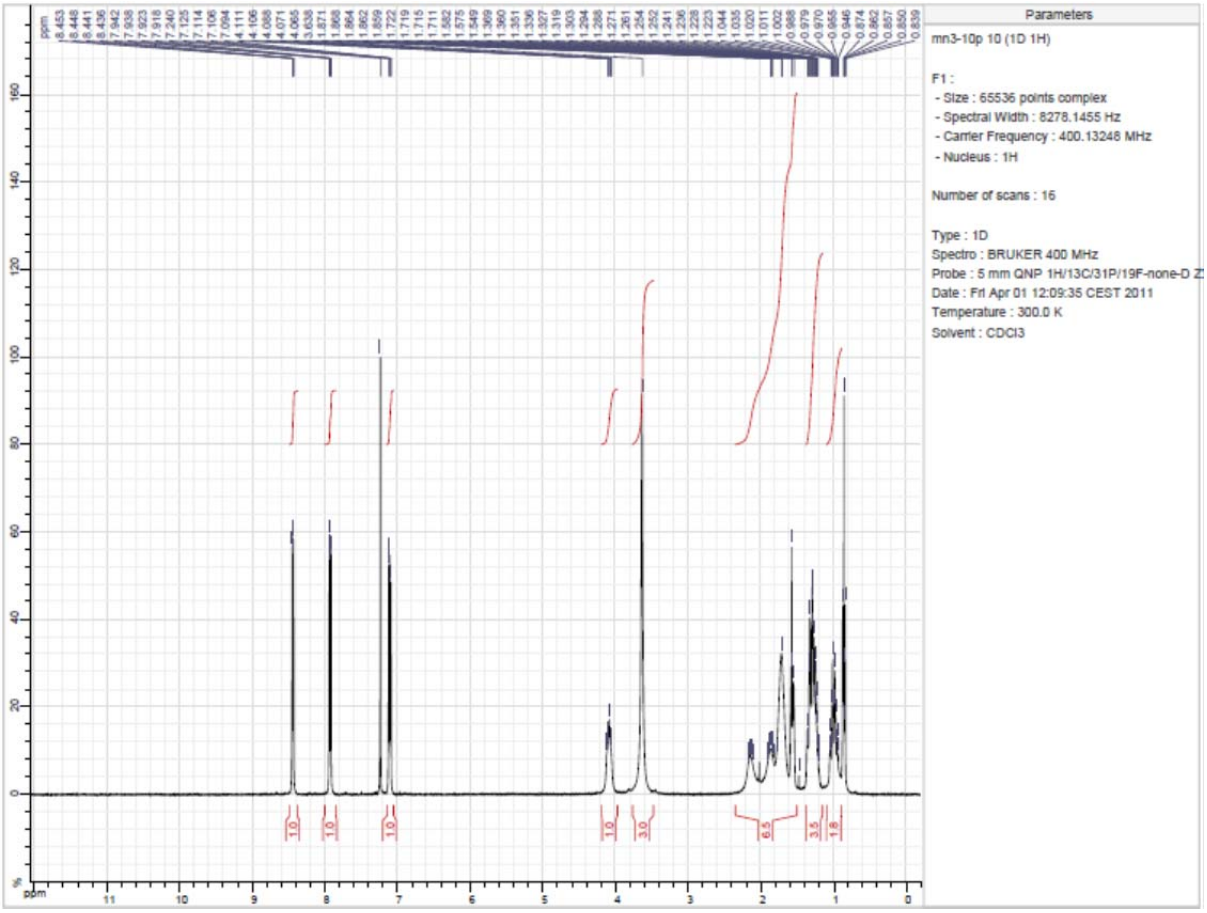


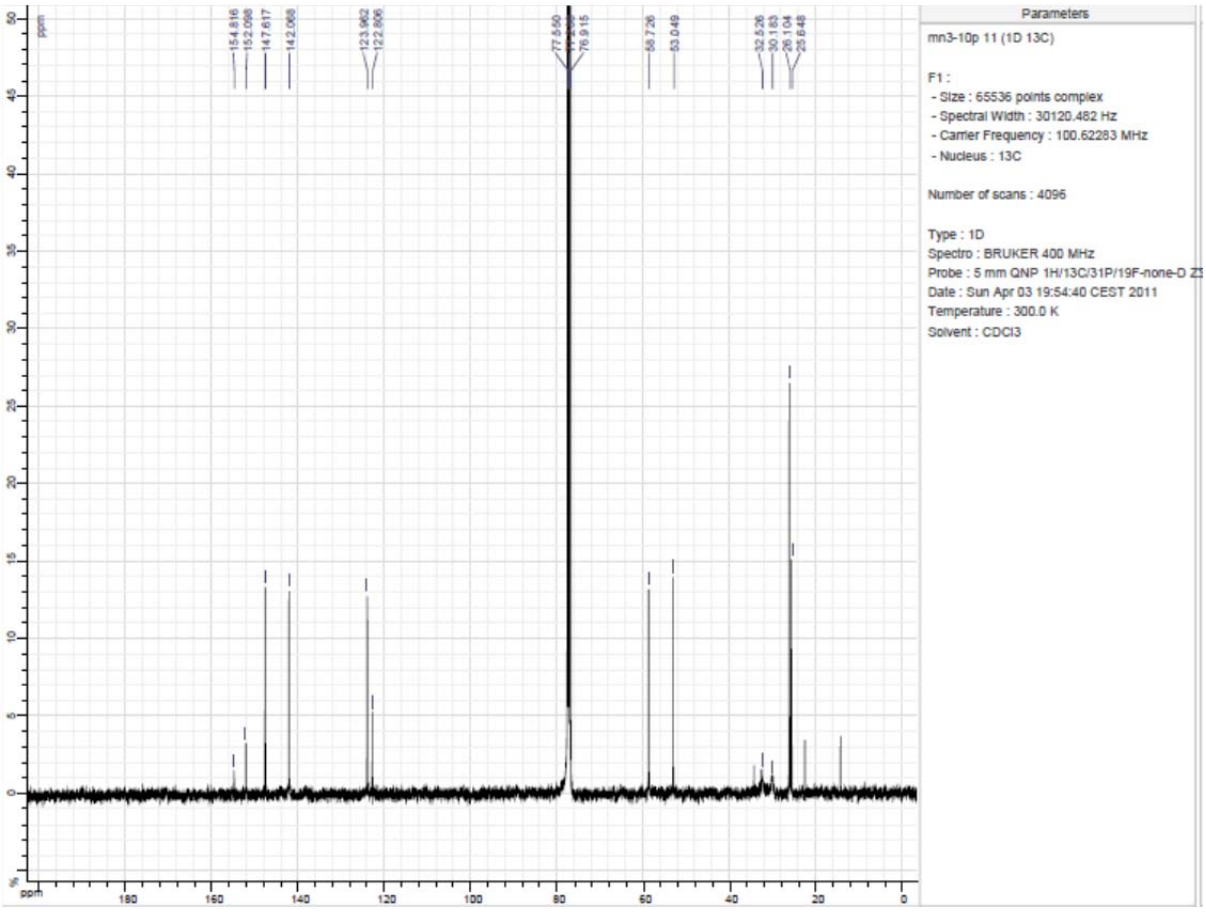


Methyl (3-bromopyridin-2-yl)(cyclohexyl)carbamate **1q**:

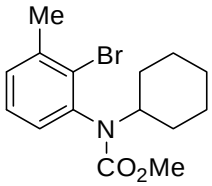


Prepared according to **GP2.** White solid, 82% yield, M. p. 63 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.88-1.10 (m, 2H), 1.17-1.40 (m, 2H), 1.50-2.36 (m, 6H), 3.64 (s, 3H), 3.98-4.20 (m, 1H), 7.11 (dd, J = 7.6, 4.8 Hz, 1H), 7.93 (dd, J = 7.6, 1.6 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.6, 26.1, 30.2, 32.6, 53.0, 58.7, 122.8, 124.0, 142.2, 147.6, 152.1, 154.8. IR (neat): υ = 630, 671, 713, 765, 811, 892, 963, 983, 1025, 1048, 1084, 1123, 1159, 1201, 1240, 1281, 1319, 1353, 1387, 1427, 1446, 1572, 1696, 2856, 2938 cm^{-1}; EI-HRMS calcd. for $C_{13}H_{17}N_2O_2Br$ 312.0473, found 312.0471.



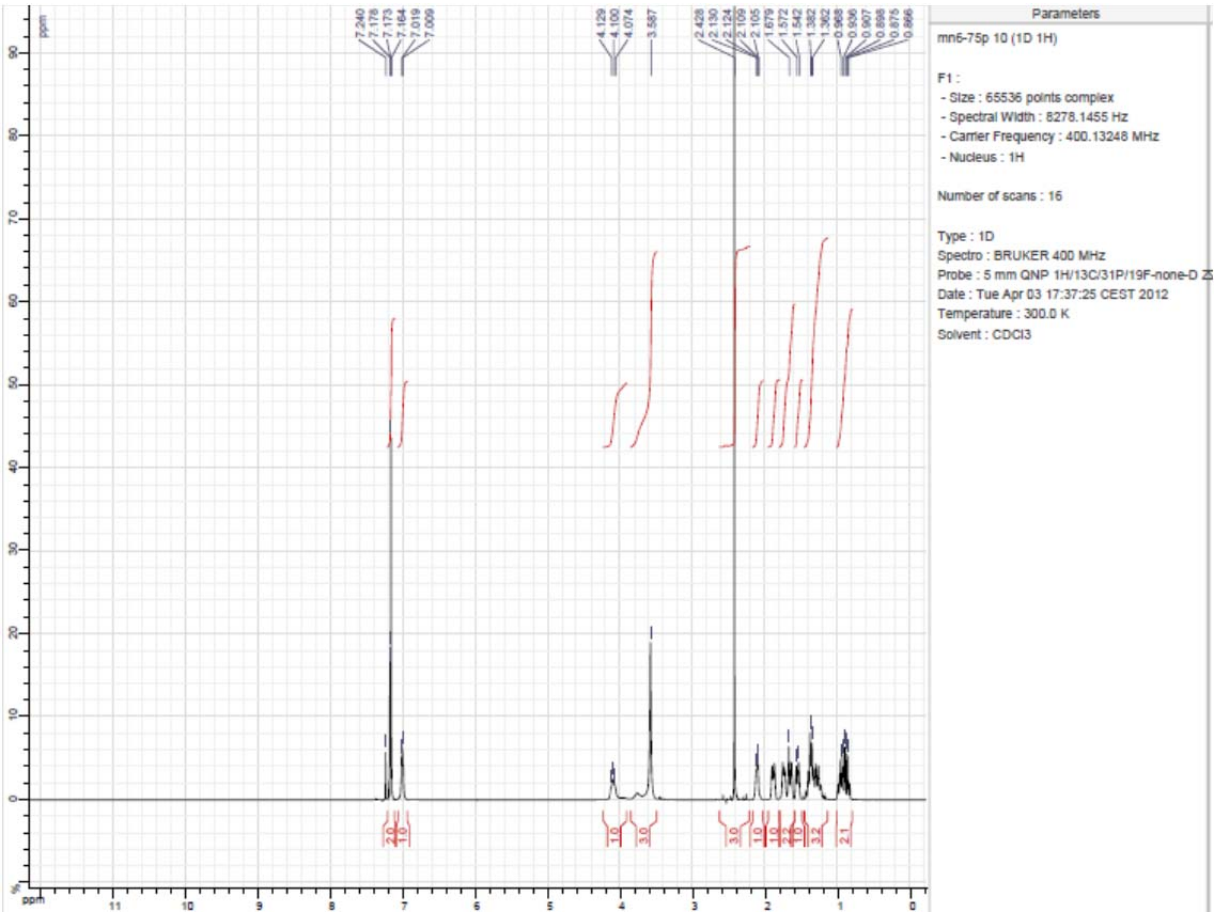


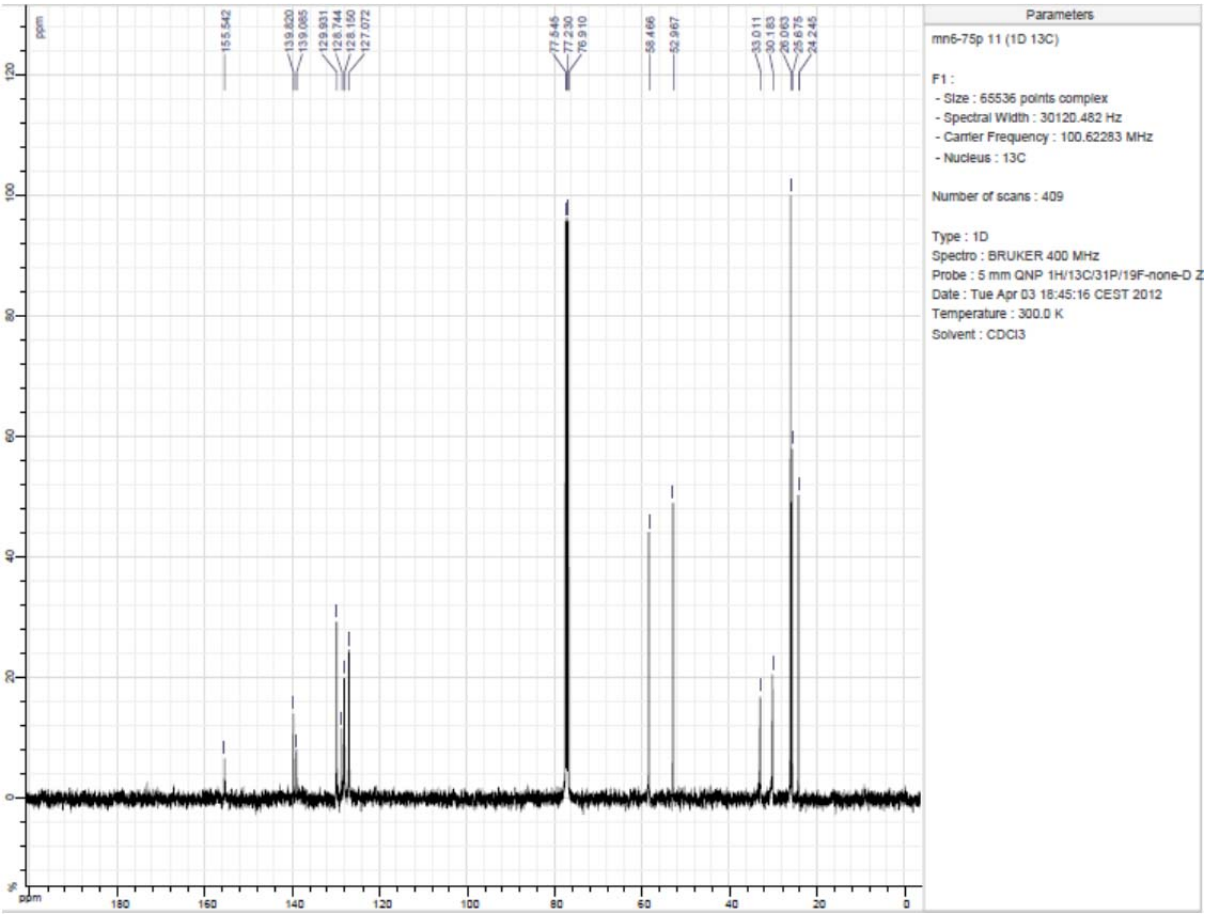
Methyl (2-bromo-3-methylphenyl)(cyclohexyl)carbamate **1r**:



Prepared according to **GP2.** White solid, 88% yield, M. p. 115 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.81-1.03 (m, 2H), 1.15-1.42 (m, 3H), 1.49-1.60 (m, 1H), 1.61-1.81 (m, 2H), 2.04-2.18 (m, 1H), 2.42 (s, 3H), 3.58 (s, 3H), 3.92-4.24 (m, 1H), 6.94-7.07 (m, 1H), 7.12-7.22 (m, 1H). ^{13}C NMR (100 MHz): δ = 24.2, 25.7, 26.1, 30.2, 33.0, 53.0, 58.5, 127.1, 128.2, 128.7, 129.9, 139.1, 139.8, 155.5. IR (neat): υ = 742, 764, 797, 872, 887, 962, 1012, 1033, 1069, 1106, 1152, 1190, 1241, 1274, 1306, 1352, 1387, 1411, 1440, 1469, 1572, 1696, 2854, 2931 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}NO_2Br$ 326.0750, found 326.0742.

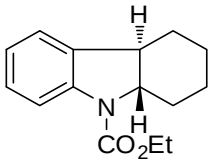
Supporting Information for Chem. Sci.



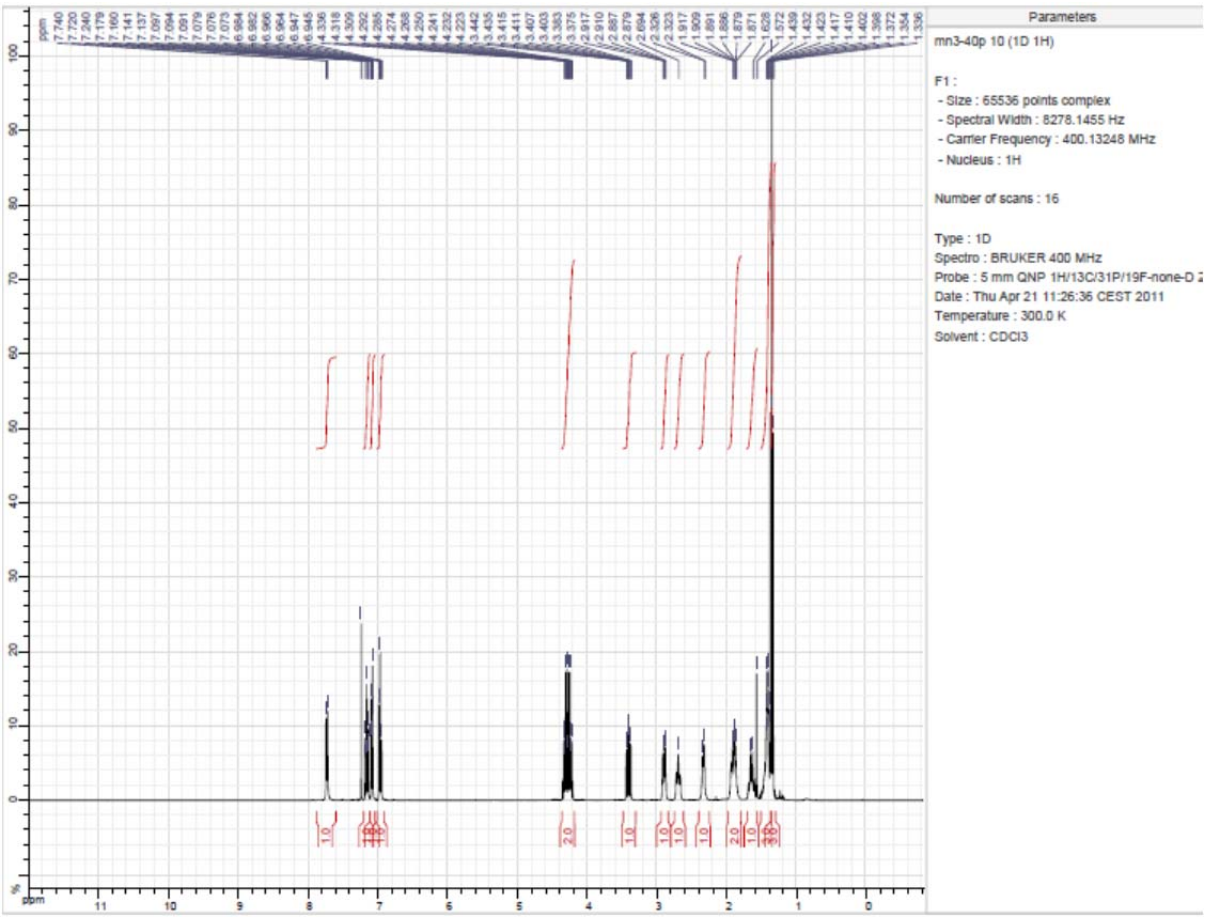


2.2.3 Characterization data and HPLC traces of C-H activation products

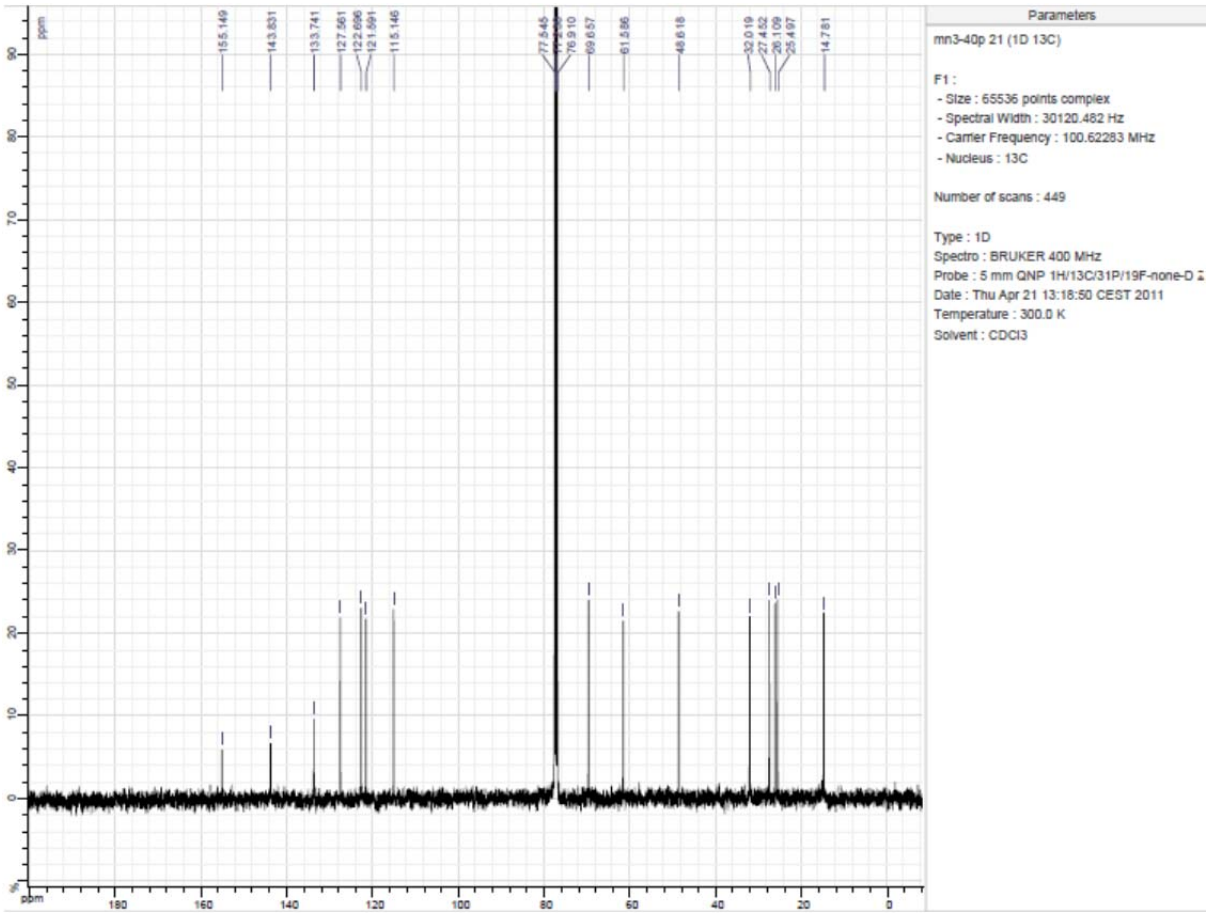
Ethyl 2,3,4,4a-tetrahydro-1*H*-carbazole-9(9a*H*)-carboxylate **2f**:

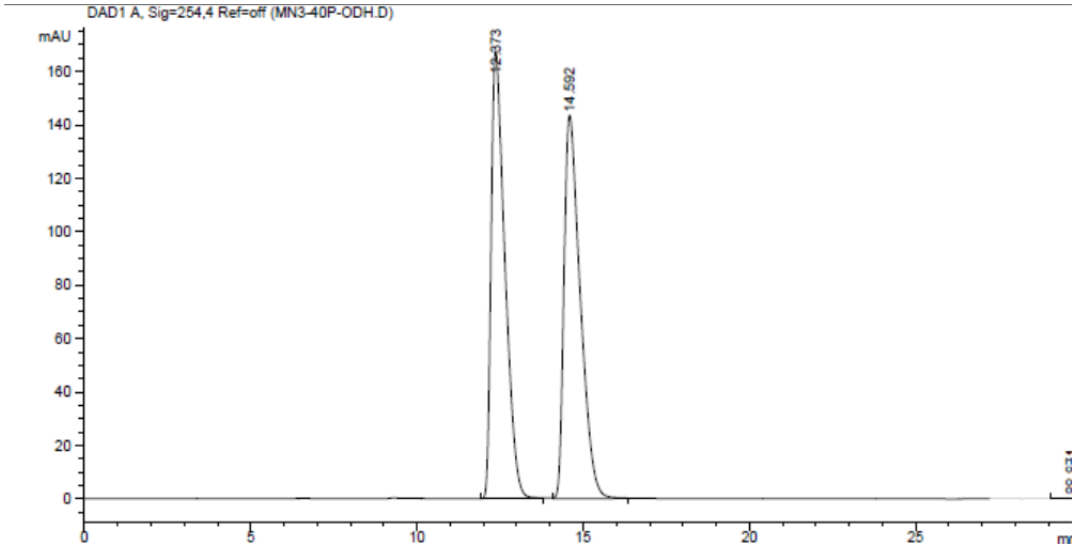


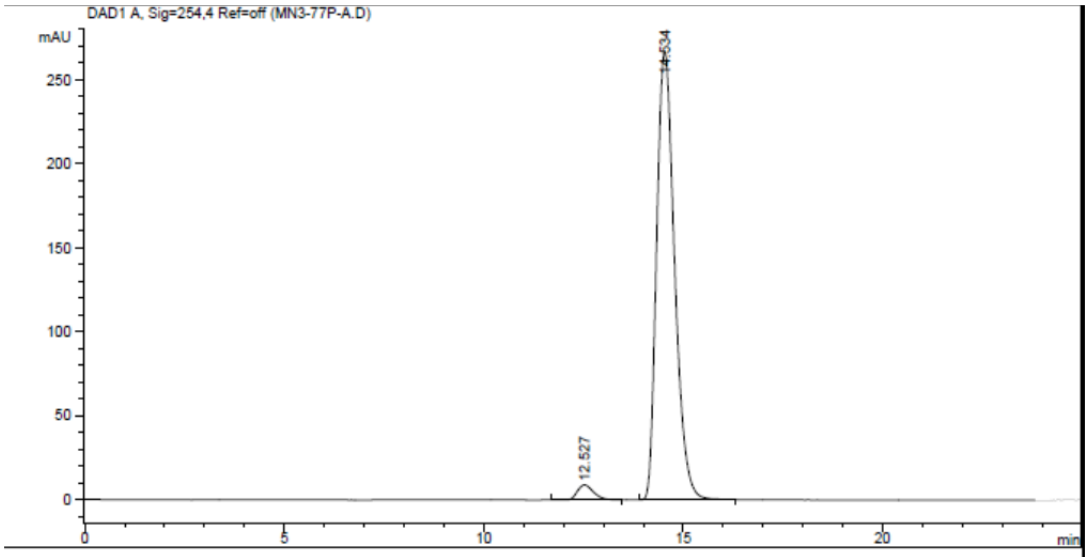
White solid, 92% yield, M. p. 57 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.35 (t, J = 7.2 Hz, 3H), 1.37-1.52 (m, 3H), 1.58-1.72 (m, 1H), 1.82-1.98 (m, 2H), 2.26-2.42 (m, 1H), 2.66-2.77 (m, 1H), 2.85-2.95 (m, 1H), 3.41 (dd, J = 10.8, 2.8 Hz, 1H), 4.19-4.37 (m, 2H), 6.96 (td, J = 7.2, 0.8 Hz, 1H), 7.09 (dt, J = 7.2, 1.2 Hz, 1H), 7.16 (tt, J = 7.6, 1.2 Hz, 1H), 7.73 (d, J = 8 Hz, 1H) ^{13}C NMR (100 MHz): δ = 14.8, 25.5, 26.1, 27.5, 32.0, 48.6, 61.6, 69.7, 115.1, 121.6, 122.7, 127.6, 133.7, 143.8, 155.1. IR (neat): υ = 637, 652, 727, 749, 819, 837, 859, 894, 825, 969, 1035, 1043, 1025, 1043, 1055, 1114, 1128, 1152, 1194, 1225, 1245, 1261, 1308, 1329, 1354, 1369, 1381, 1408, 1459, 1475, 1606, 1703, 2857, 2930, 2982 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{20}NO_2$ 246.1488, found 246.1486.



Supporting Information for Chem. Sci.





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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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   2  14.534 BB    0.4884 8333.43066  266.81314  97.0692
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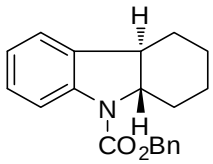
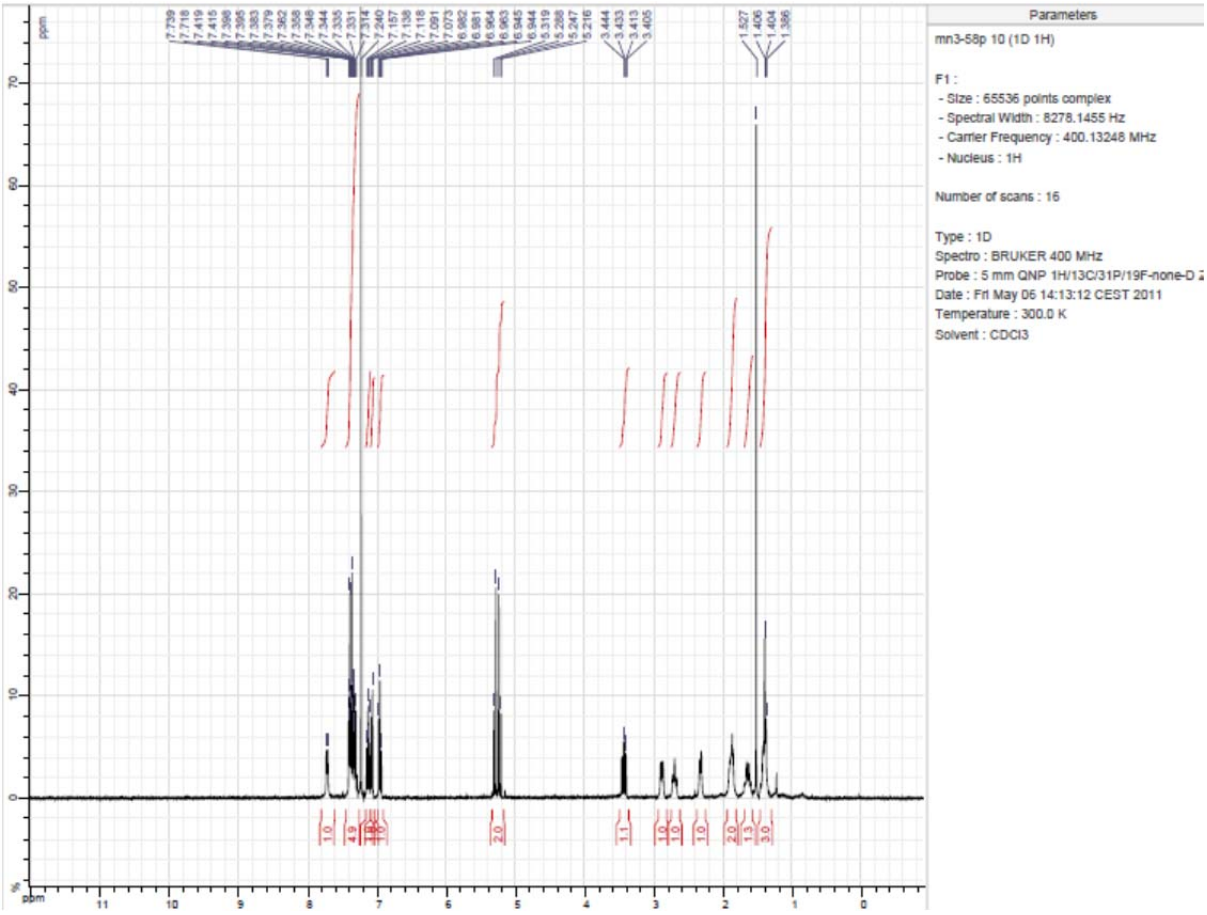
The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 12.5 min [minor] and 14.5 min [major]. $[\alpha]_D^{20}$ = +66 (*c* = 1.0 in CH_2Cl_2).

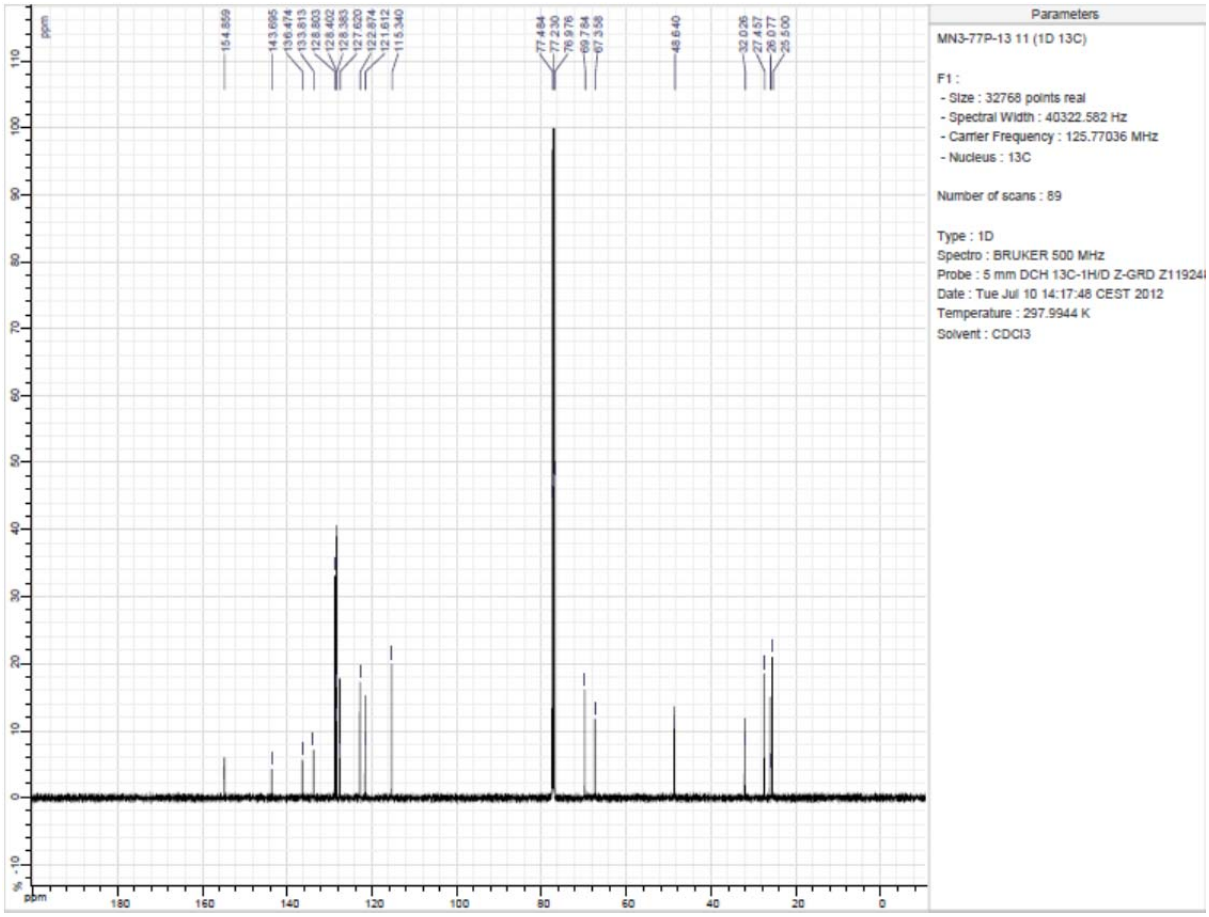
(4a*R*,9a*S*)-Benzyl 2,3,4,4a-tetrahydro-1*H*-carbazole-9(9a*H*)-carboxylate **2g**:

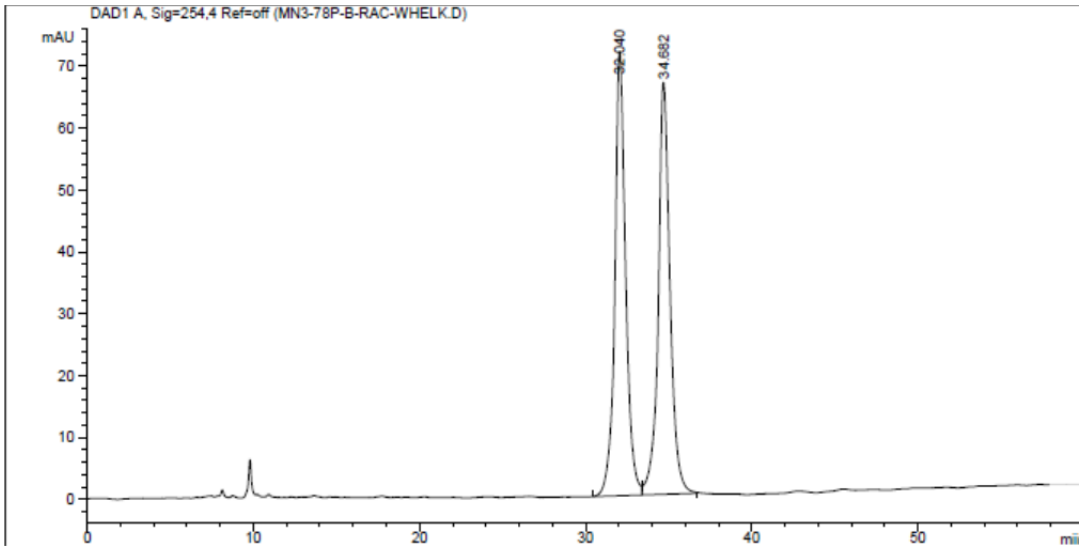


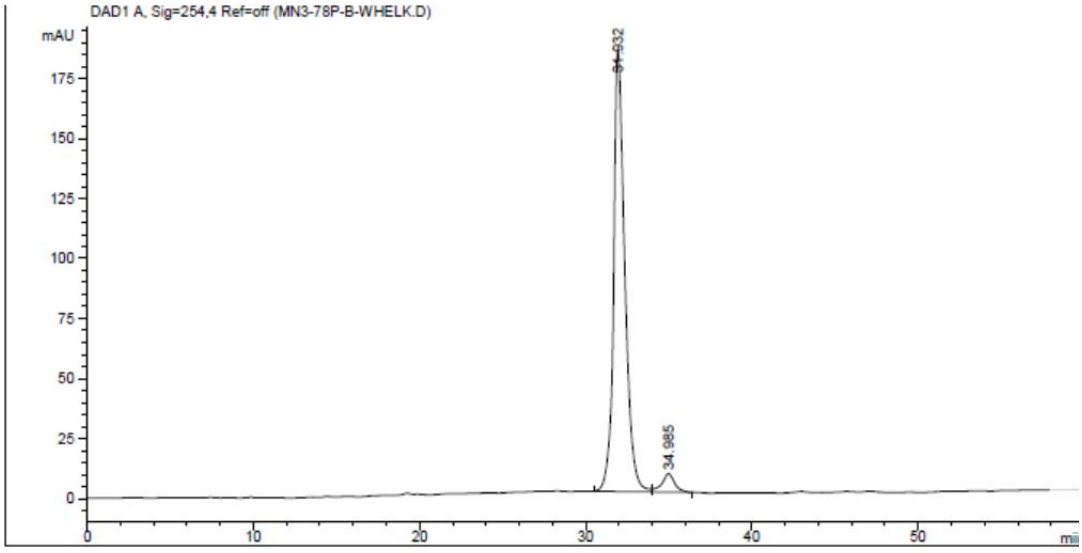
White solid, 52% yield, 91% ee, M. p. 78 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.34-1.48 (m, 3H), 1.59-1.71 (m, 1H), 1.81-1.95 (m, 2H), 2.27-2.39 (m, 1H), 2.64-2.77 (m, 1H), 2.83-2.95 (m, 1H), 5.23 (d, J = 12.4 Hz, 1H), 5.30 (d, J = 12.4 Hz, 1H), 6.96 (td, J = 7.2, 0.4 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz): δ = 25.5, 26.1, 27.5, 32.0, 48.6, 67.4, 69.8, 115.3, 121.6, 122.9, 127.6, 128.4, 128.8, 133.8, 136.5, 143.7, 154.9. IR (neat): υ = 654, 695, 748, 788, 835, 860, 900, 933, 1014, 1033, 1053, 1112, 1152, 1188, 1225, 1262, 1307, 1331, 1356, 1399, 1459, 1475, 1605, 1703, 2856, 2929, 3033 cm^{-1}; ESI-HRMS calcd. for $C_{20}H_{22}NO_2$ 308.1645, found 308.1644.



Supporting Information for Chem. Sci.





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Use Multiplier & Dilution Factor with ISTDs


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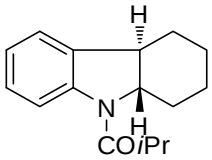
```

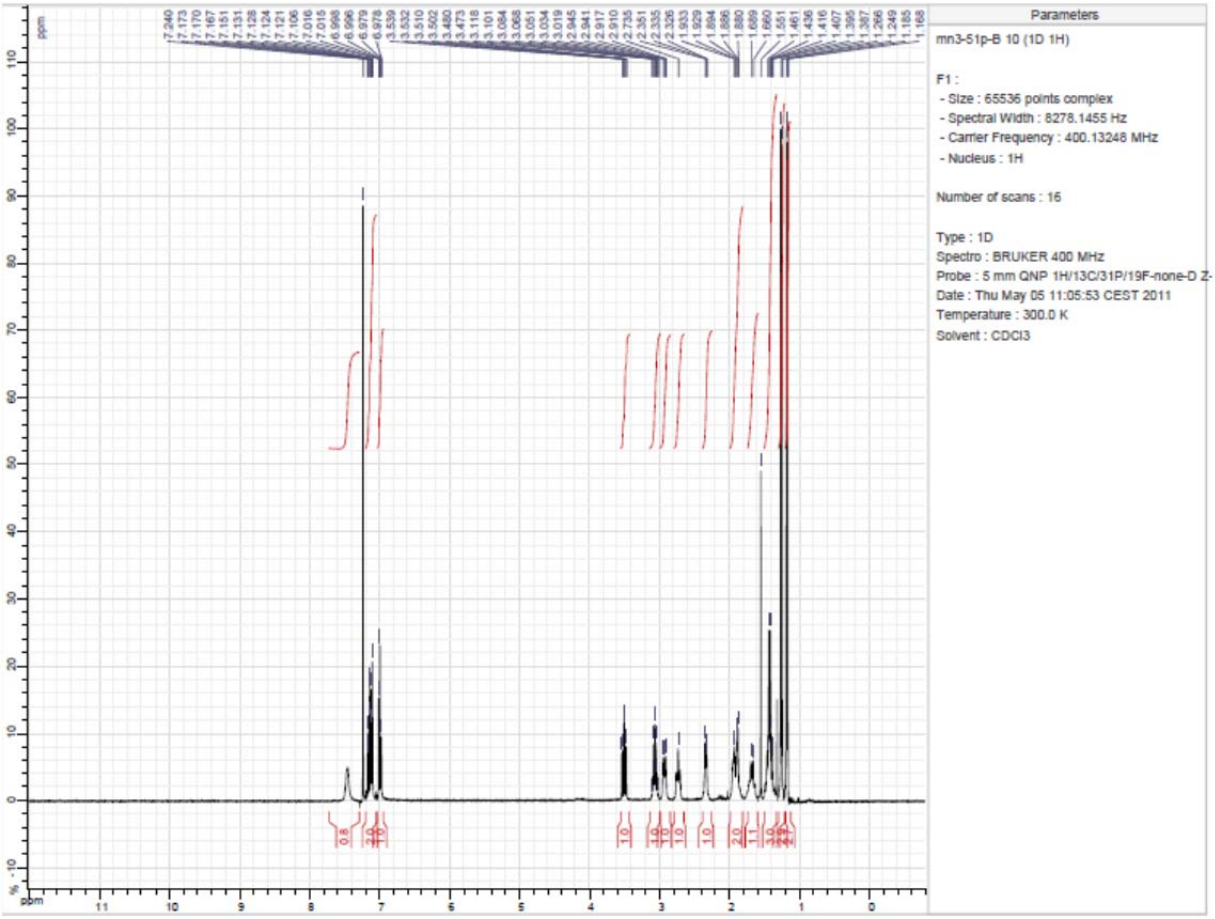
The enantiomer ratio was determined by HPLC: (chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 31.9 min [major] and 35.0 min [minor]. $[\alpha]_D^{20}$ = +0.4 (*c* = 1.0 in CH_2Cl_2).

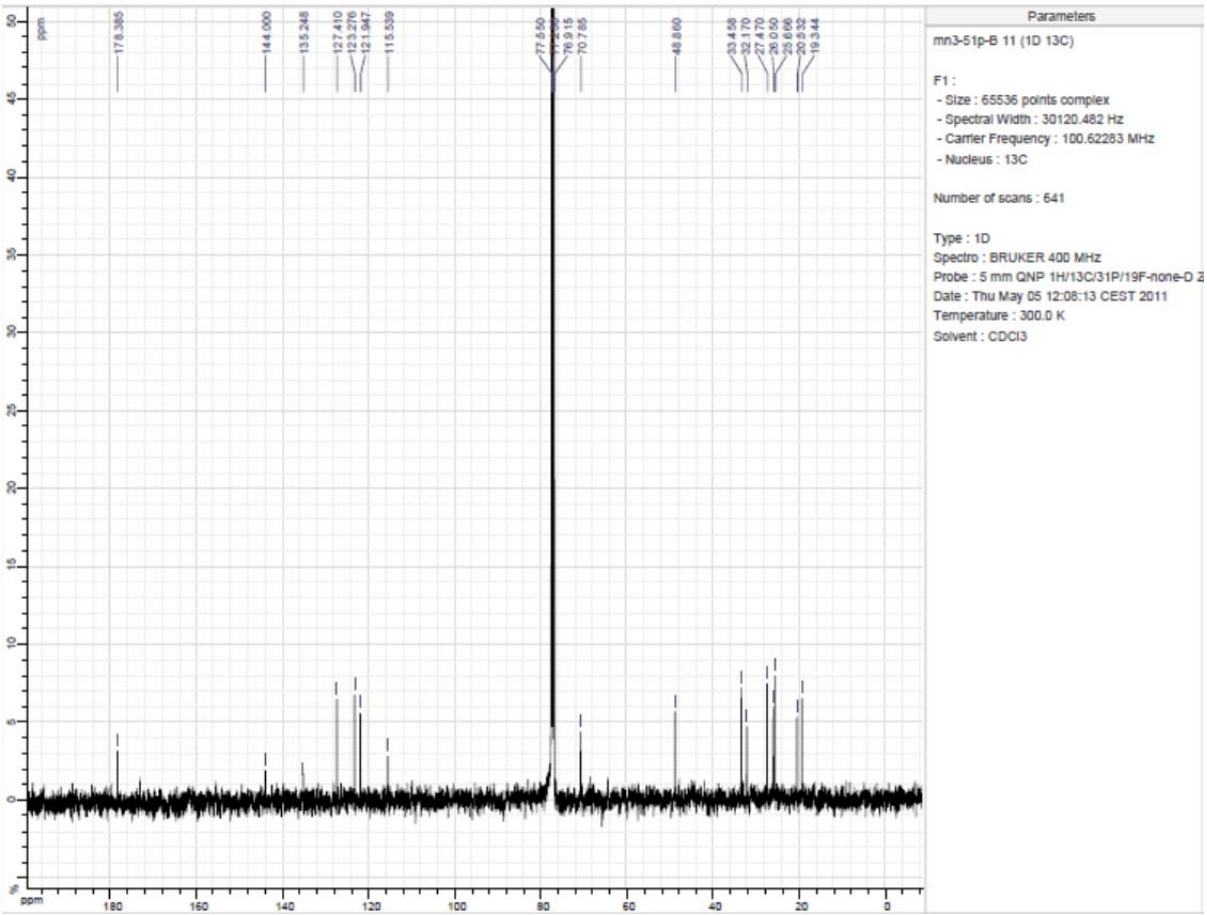
2-Methyl-1-(2,3,4,4a-tetrahydro-1*H*-carbazol-9(9a*H*)-yl)propan-1-one **2h**:

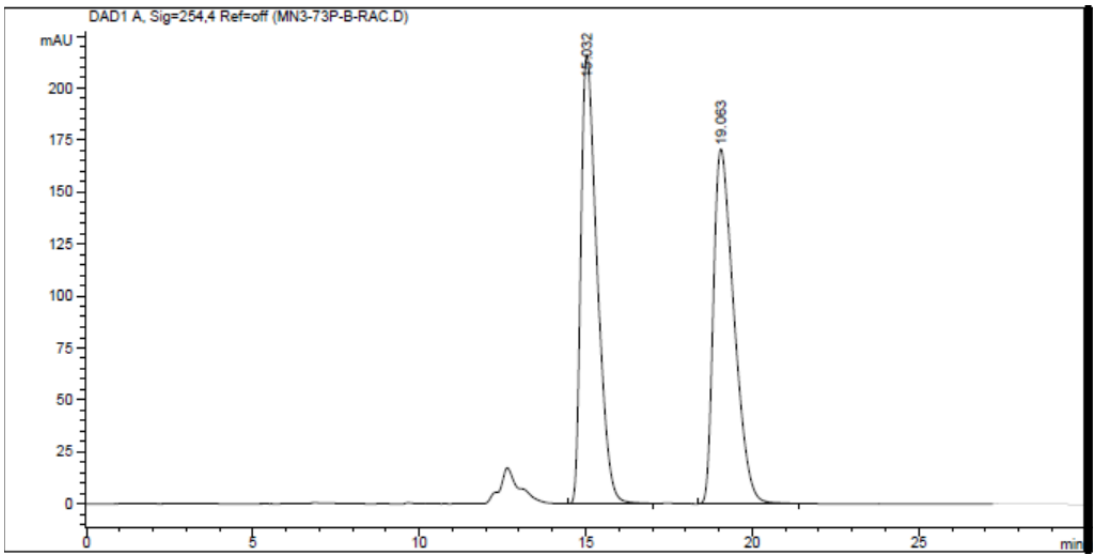


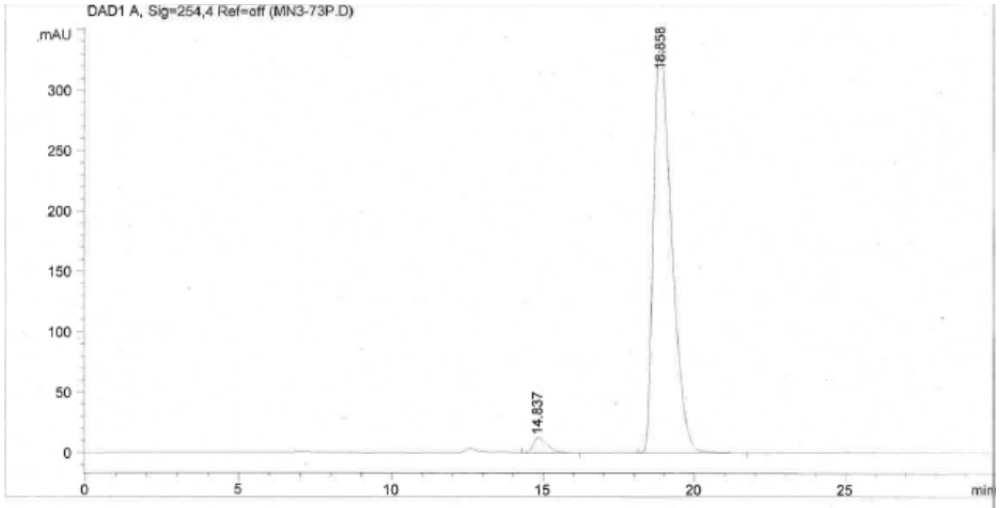
White solid, 68% yield, , 94% ee. M. p. 38 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.18 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.34-1.51 (m, 3H), 1.61-1.75 (m, 1H), 1.82-2.00 (m, 2H), 3.07 (sept, *J* = 6.8 Hz, 1H), 3.51 (td, *J* = 11.6, 2.8 Hz, 1H), 7.00 (td, *J* = 7.2, 0.4 Hz, 1H), 7.06-7.22 (m, 2H), 7.30-7.74 (brd, 1H). ^{13}C NMR (100 MHz): δ = 19.3, 20.5, 25.7, 26.1, 27.4, 32.2, 33.5, 48.9, 70.8, 115.5, 121.9, 123.3, 127.4, 135.2, 144.0, 178.4. IR (neat): υ = 751, 836, 933, 965, 1041, 1090, 1160, 1179, 1221, 1362, 1395, 1459, 1474, 1605, 1658, 2858, 2931 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{22}NO$ 244.1695, found 244.1685.

Supporting Information for Chem. Sci.









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Use Multiplier & Dilution Factor with ISTDs

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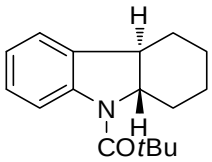
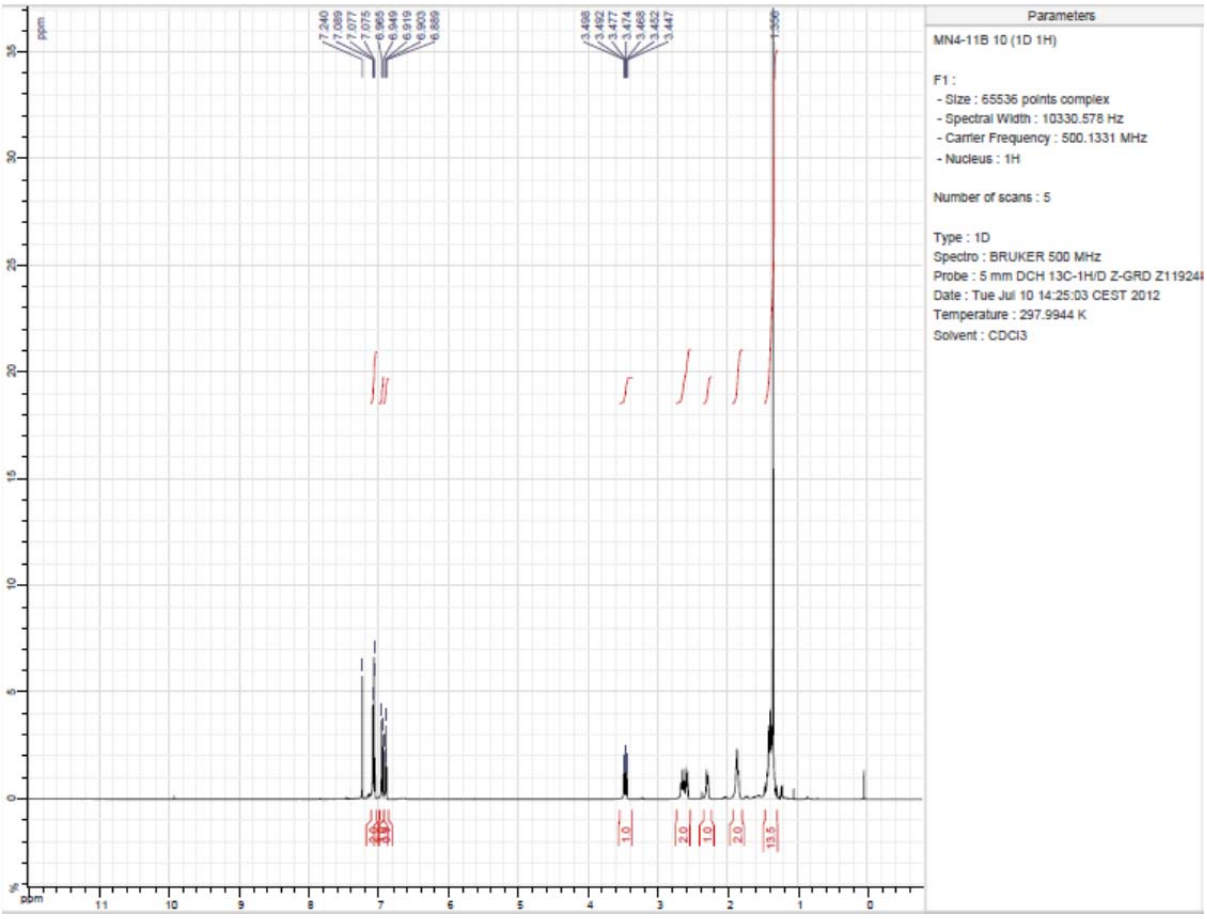
2	18.858	VB	0.6423	1.40986e4	335.44720	97.1580

The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 14.8 min [minor] and 18.9 min [major]. $[\alpha]_D^{20}$ = -64 (*c* = 1.0 in CH_2Cl_2).

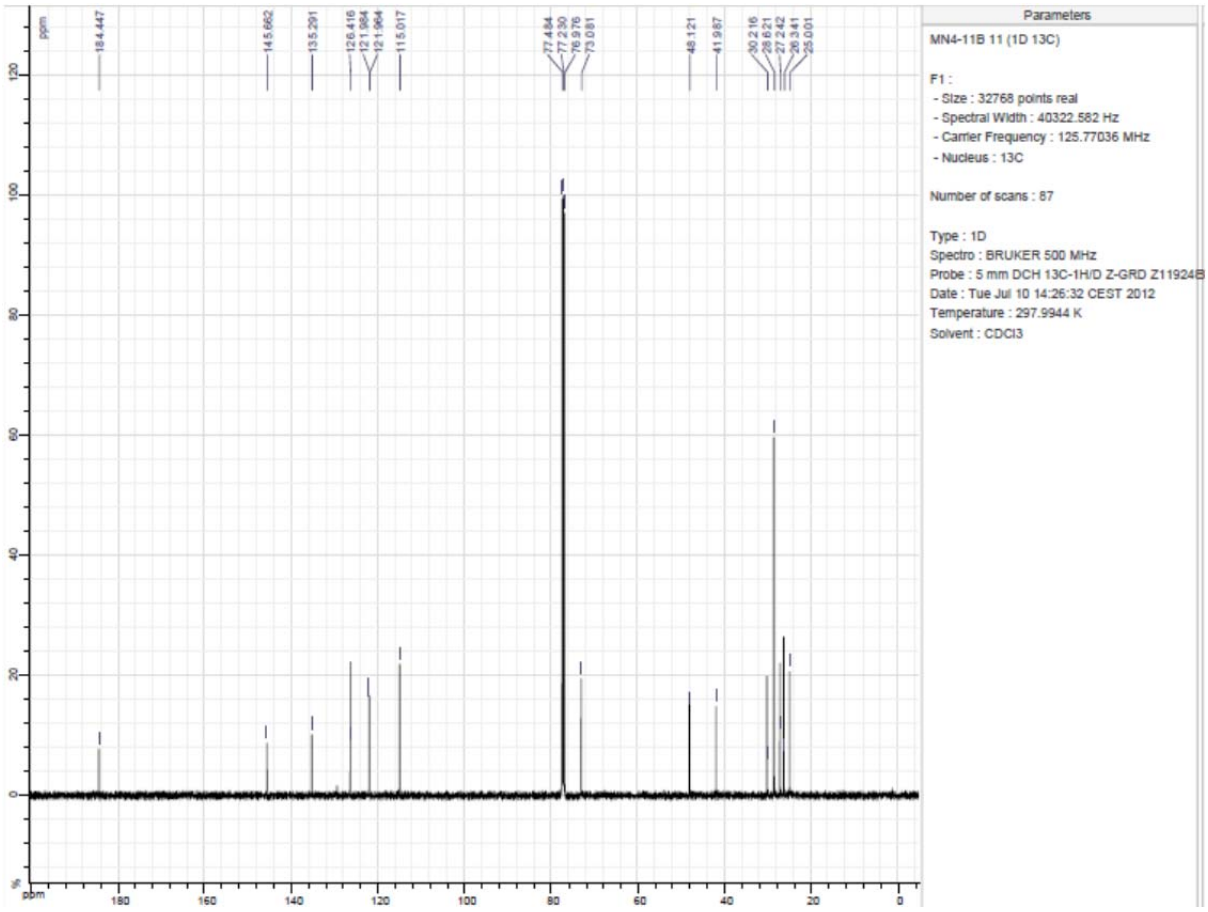
2,2-Dimethyl-1-(2,3,4,4a-tetrahydro-1*H*-carbazol-9(9a*H*)-yl)propan-1-one **2i**:

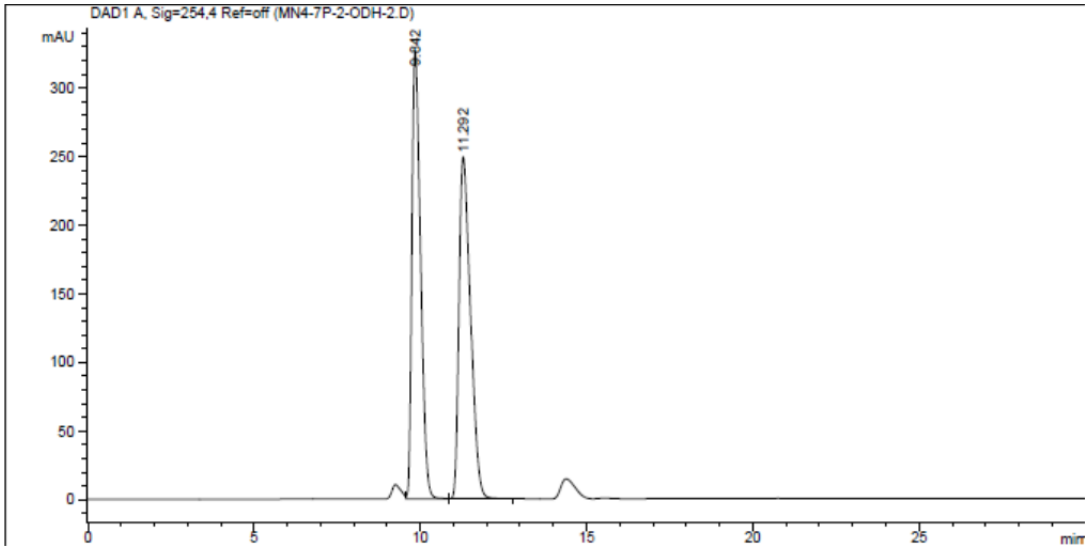


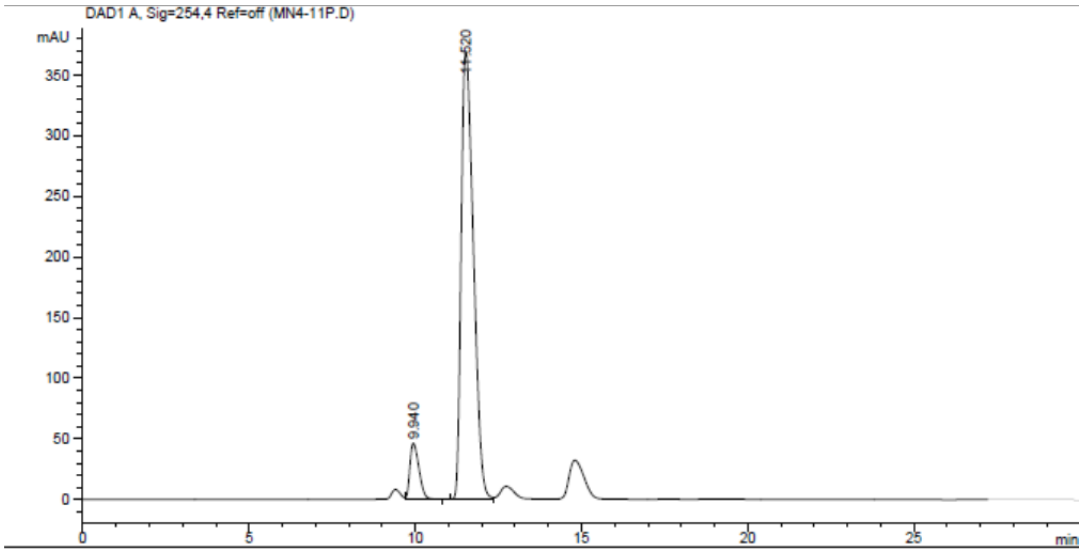
Colorless oil, 33% yield, 83% ee, ^{1}H NMR (500 MHz, $CDCl_3$): 1.36 (s, 9H), 1.36-1.50 (m, 4H), 1.82-1.95 (m, 2H), 2.25-2.36 (m, 1H), 2.55-2.75 (m, 2H), 3.47 (dd, J = 10.5, 3 Hz, 1H), 6.09 (t, J = 8 Hz, 1H), 6.96 (d, J = 8 Hz, 1H), 7.04-7.12 (m, 2H). ^{13}C NMR (125 MHz): δ = 25.0, 26.3, 27.2, 28.6, 30.2, 42.0, 48.1, 73.1, 115.0, 122.0, 122.2, 126.4, 135.3, 145.7, 184.4. IR (neat): υ = 639, 699, 731, 746, 835, 904, 925, 957, 1027, 1079, 1107, 1125, 1168, 1189, 1205, 1229, 1261, 1291, 1320, 1348, 1356, 1397, 1459, 1471, 1606, 1657, 2856, 2928 cm^{-1}; ESI-HRMS calcd. for $C_{17}H_{24}NO$ 258.1852, found 258.1857.



Supporting Information for Chem. Sci.





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   2  11.520 BV    0.4079 9356.96973  368.95554  91.3008
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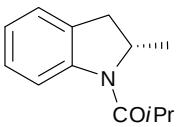
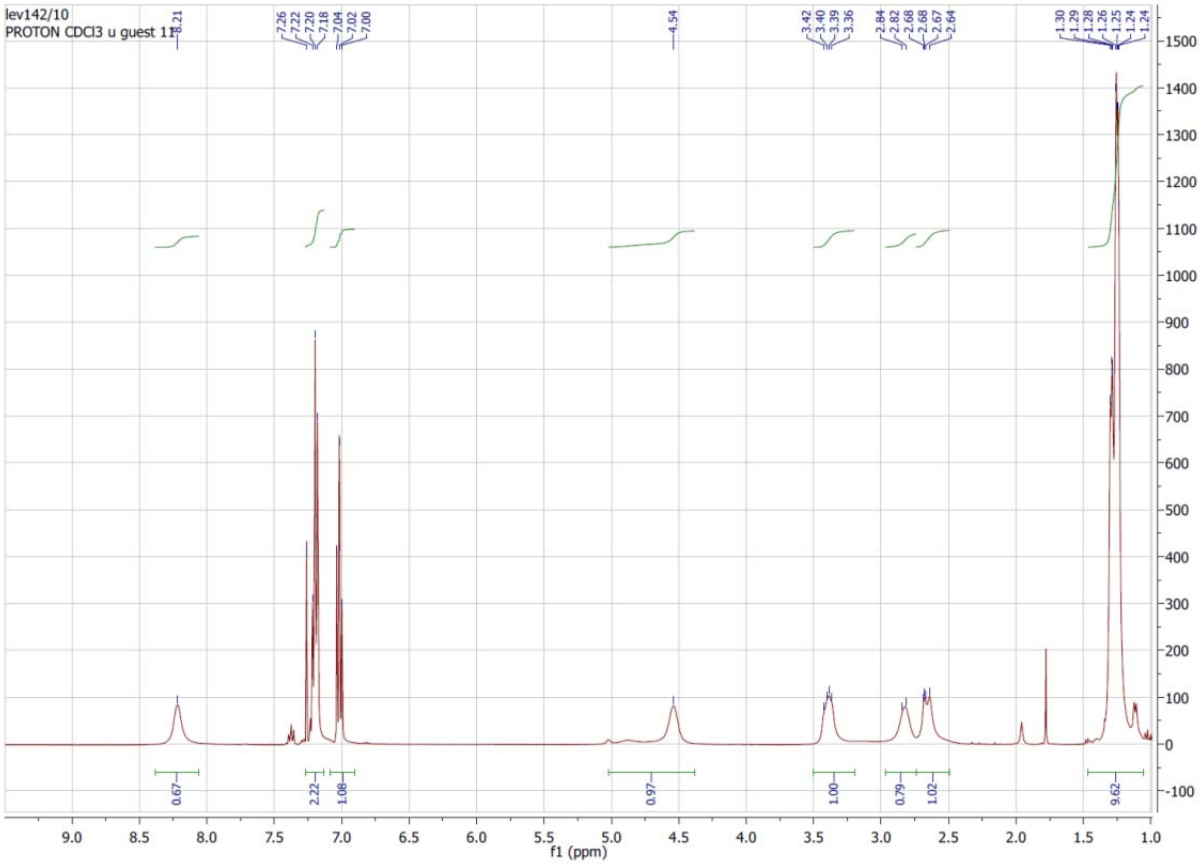
The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 9.9 min [minor] and 11.5 min [major]. $[\alpha]_D^{20}$ = -1.8 (*c* = 0.2 in CH_2Cl_2).

(*S*)-2-methyl-1-(2-methylindolin-1-yl)propan-1-one **7b:**



Asymmetric synthesis of indoline **7b** was carried out according to General procedure 3 with 0.30 mmol of compound **3b** using (*R*,*R*)-**4** as a ligand (10 mol%). Usual work up gives 60 mg (99 %) of (*S*)-**7b** as a colorless oil with ee 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br s, 1H), 7.23 – 7.14 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 4.54 (s, 1H), 3.53 – 3.34 (m, 1H), 2.90 – 2.74 (m, 1H), 2.66 (d, *J* = 13.9 Hz, 1H), 1.40 – 1.19 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 142.0, 130.6, 127.7, 125.1, 123.9, 118.3, 55.5, 36.6, 32.9, 22.6, 20.7, 19.6. HRMS calcd. for $C_{13}H_{18}NO$ 204.1382, found 204.1381 (accuracy 0.9 ppm).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7.26
7.22
7.20
7.18
7.04
7.02
7.00
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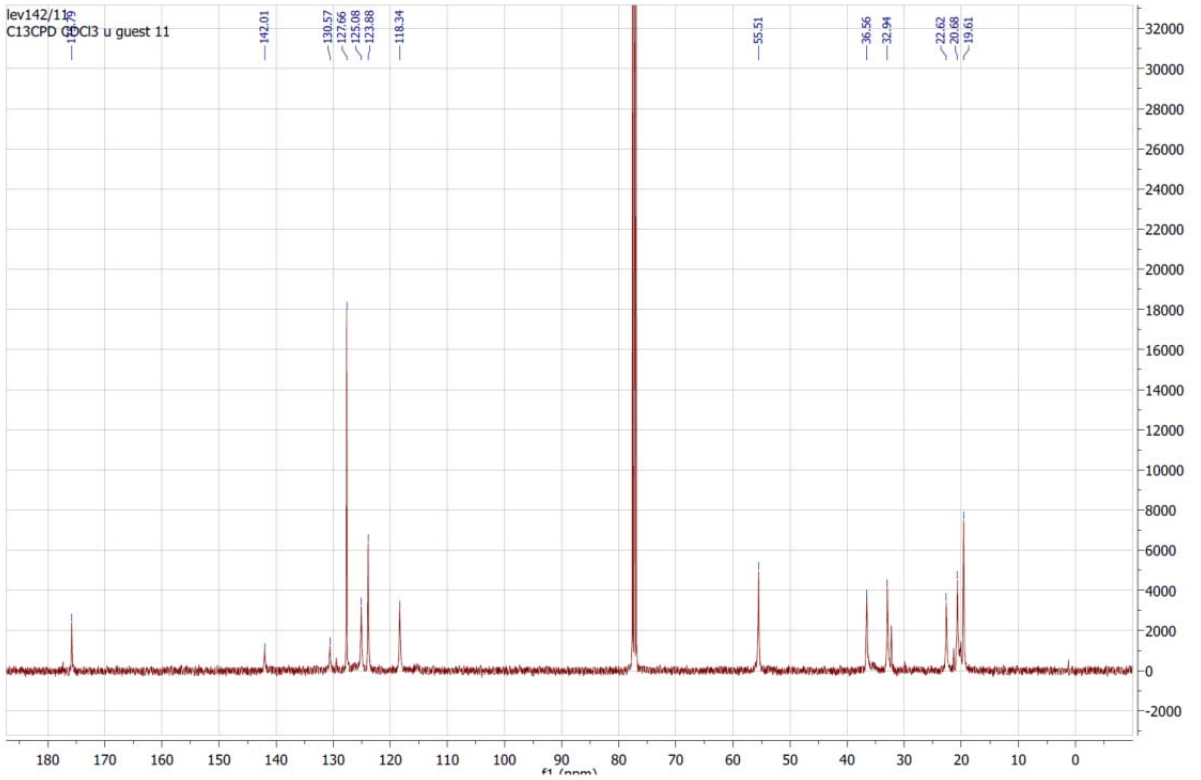
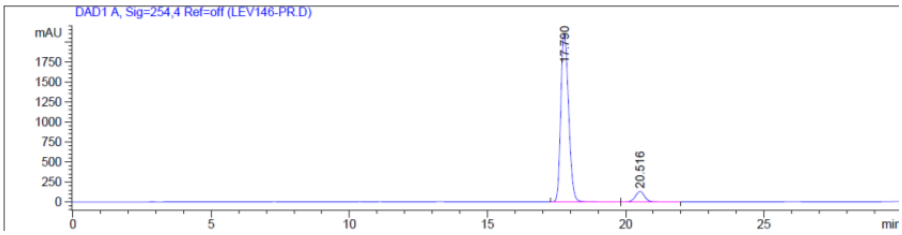
3.42
3.40
3.39
3.36
2.84
2.82
2.68
2.68
2.67
2.64
1.30
1.29
1.28
1.26
1.25
1.24
1.24
0.67
2.22
1.08
0.97
1.00
0.79
1.02
9.62
f1 (ppm)


lev142/11
C13CPD CDCl3 u guest 11
142.01
130.57
127.66
125.08
123.88
118.34
55.51
36.56
32.94
22.62
20.68
19.61
f1 (ppm)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.790 BV    0.3287 4.16850e4  2090.21777  92.9046
   2  20.516 VB    0.3822 3183.62671  129.79970   7.0954

Totals :                  4.48686e4  2220.01747
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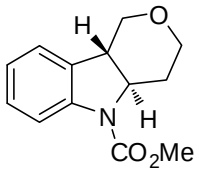
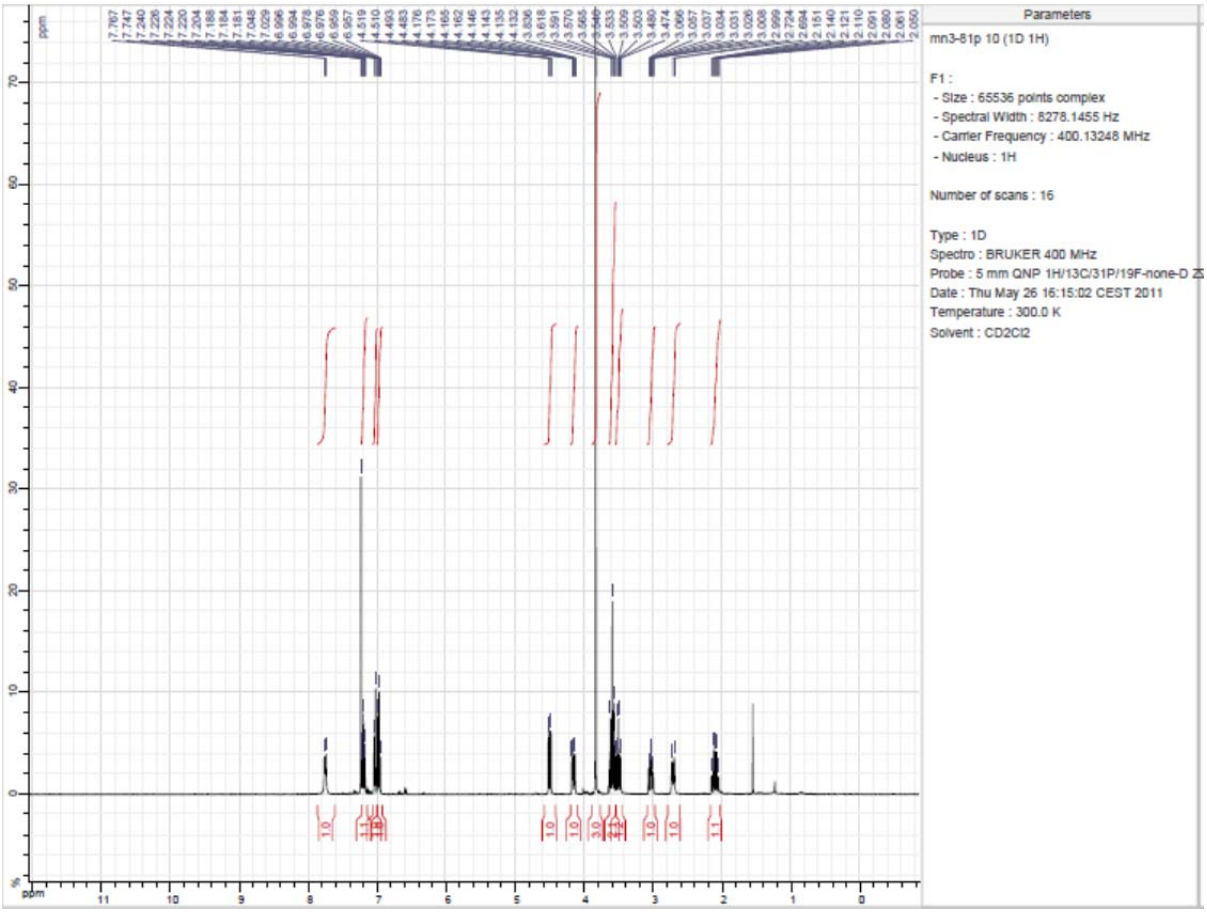
The enantiomeric ratio was determined by HPLC: (chiral column: AD-H, *n*-hexane/ *i*-propanol = 99 : 1, 1 mL/min, 254 nm); t_R = 17.8 min [major] and 20.5 min [minor]. $[\alpha]_D^{22}$ = +27.5 (*c* = 1.0 in CH_2Cl_2).

Table 3:

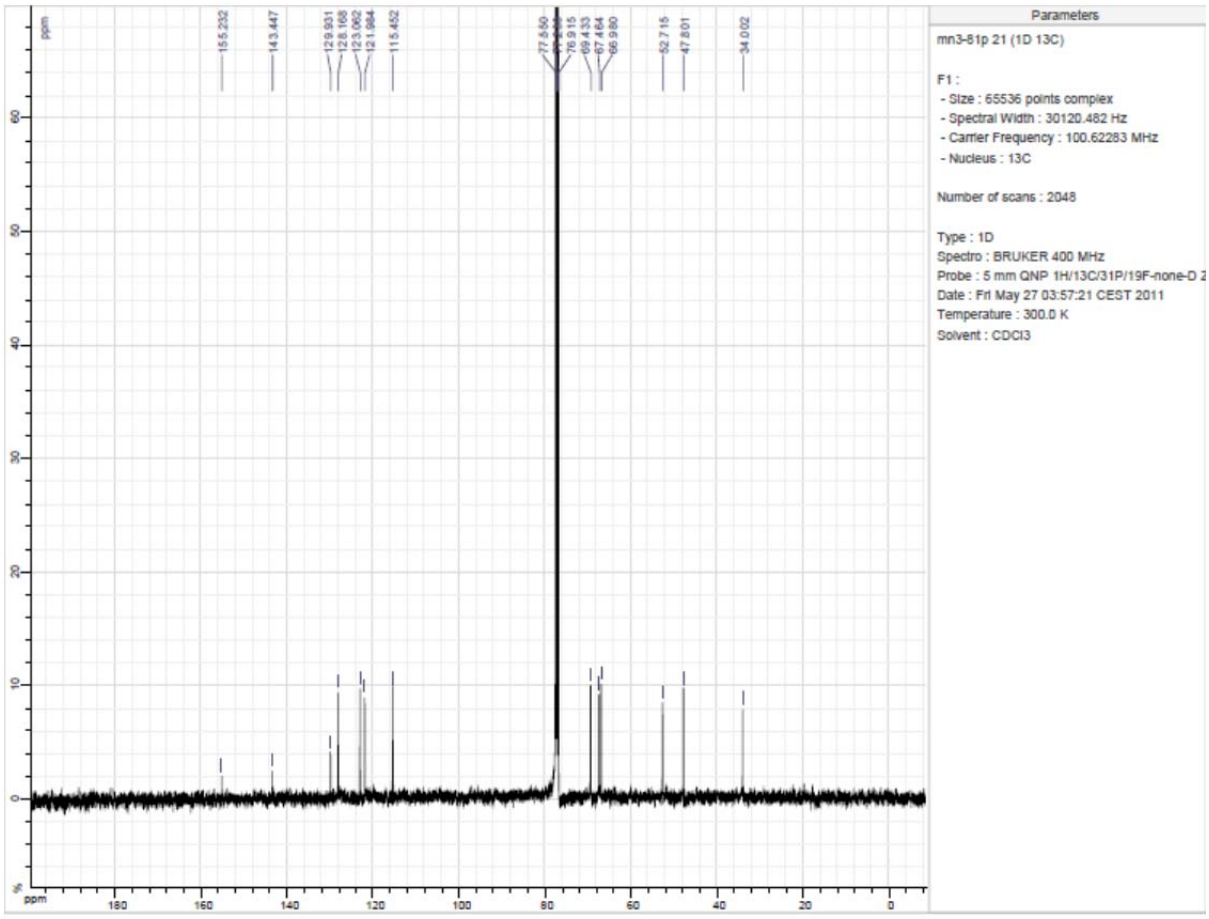
(4a*R*,9b*S*)-Methyl 1,4,4a,9b-tetrahydropyrano[4,3-b]indole-5(3*H*)-carboxylate **2j**:

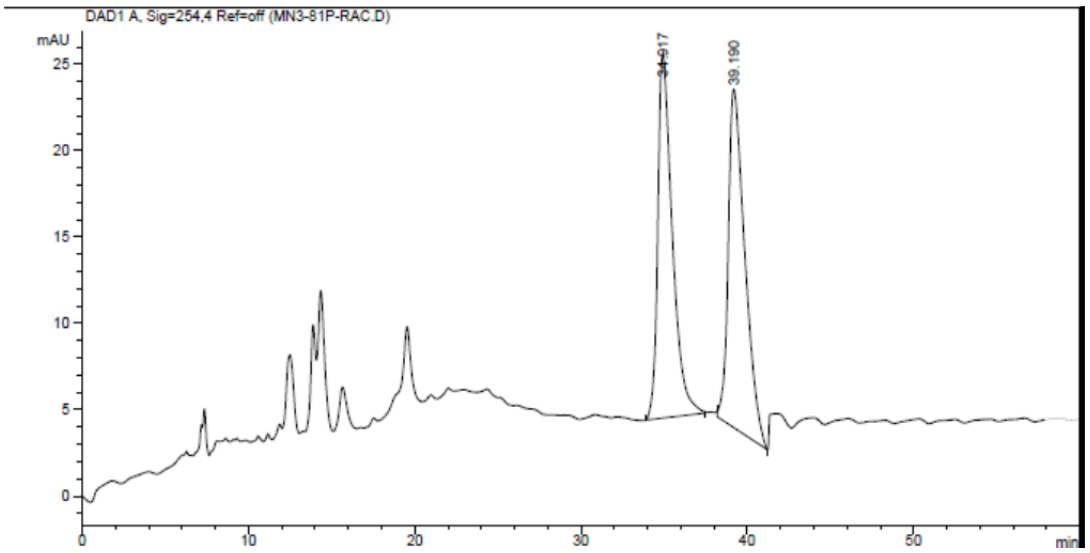


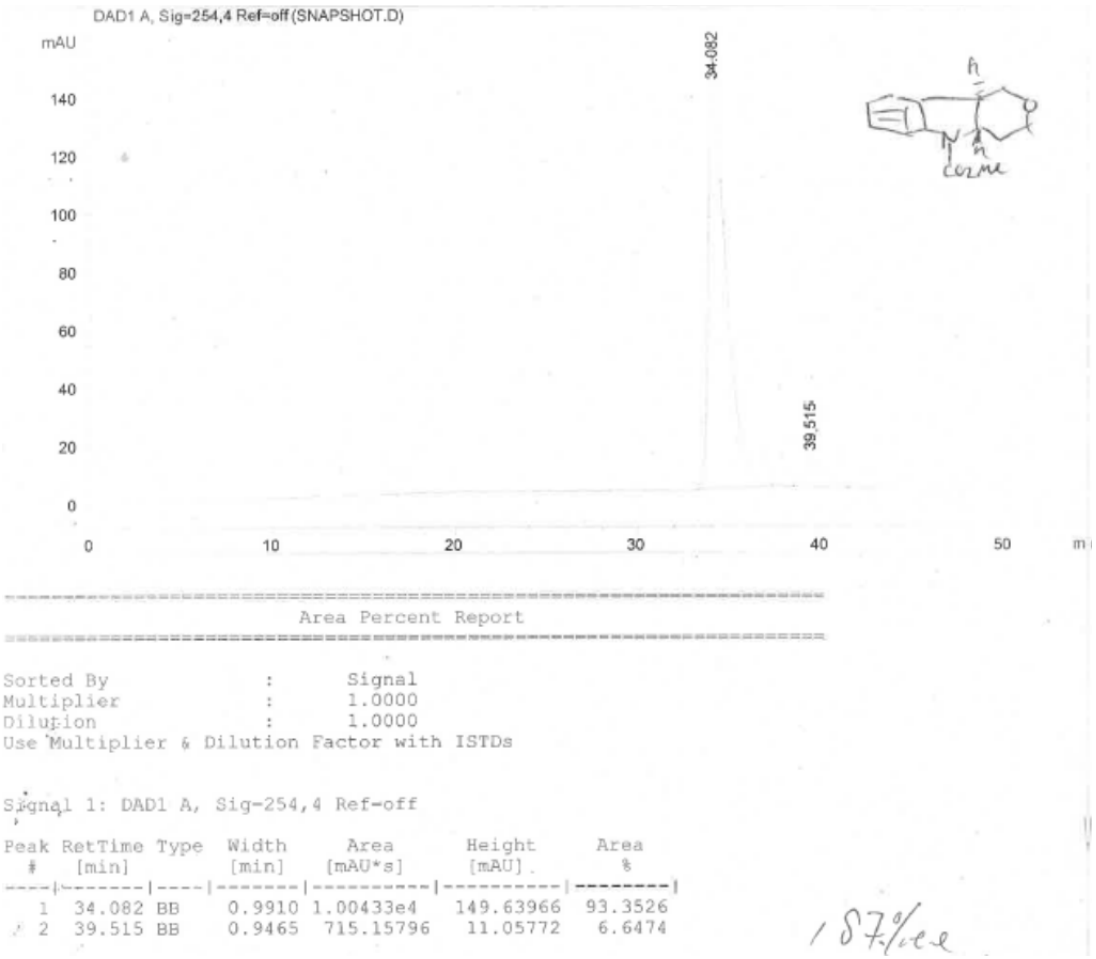
Colorless oil, 69% yield, 87% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 2.10 (qd, J = 12, 4.4 Hz, 1H), 2.71 (d, J = 12 Hz, 1H), 3.03 (qd, J = 12, 3.6 Hz, 1H), 3.51 (td, J = 12.4, 2.8 Hz, 1H), 3.55-3.65 (m, 2H), 3.84 (s, 3H), 4.15 (ddd, J = 12, 4.4, 1.2 Hz, 1H), 4.50 (dd, J = 10.4, 3.6 Hz, 1H), 6.98 (t, J = 7.2, 0.8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.20 (tt, J = 8, 0.8 Hz, 1H), 7.76 (t, J = 8 Hz, 1H). ^{13}C NMR (100 MHz): δ = 34.0, 47.8, 52.7, 67.0, 67.5, 69.4, 115.5, 122.0, 123.1, 128.2, 129.9, 143.4, 155.2. IR (neat): υ = 730, 751, 862, 915, 976, 1018, 1044, 1090, 1127, 1165, 1201, 1224, 1261, 1321, 1342, 1363, 1392, 1443, 1477, 1607, 1689, 2865, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{16}NO_3$ 234.1124, found 234.1120.



Supporting Information for Chem. Sci.

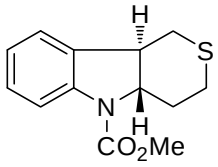






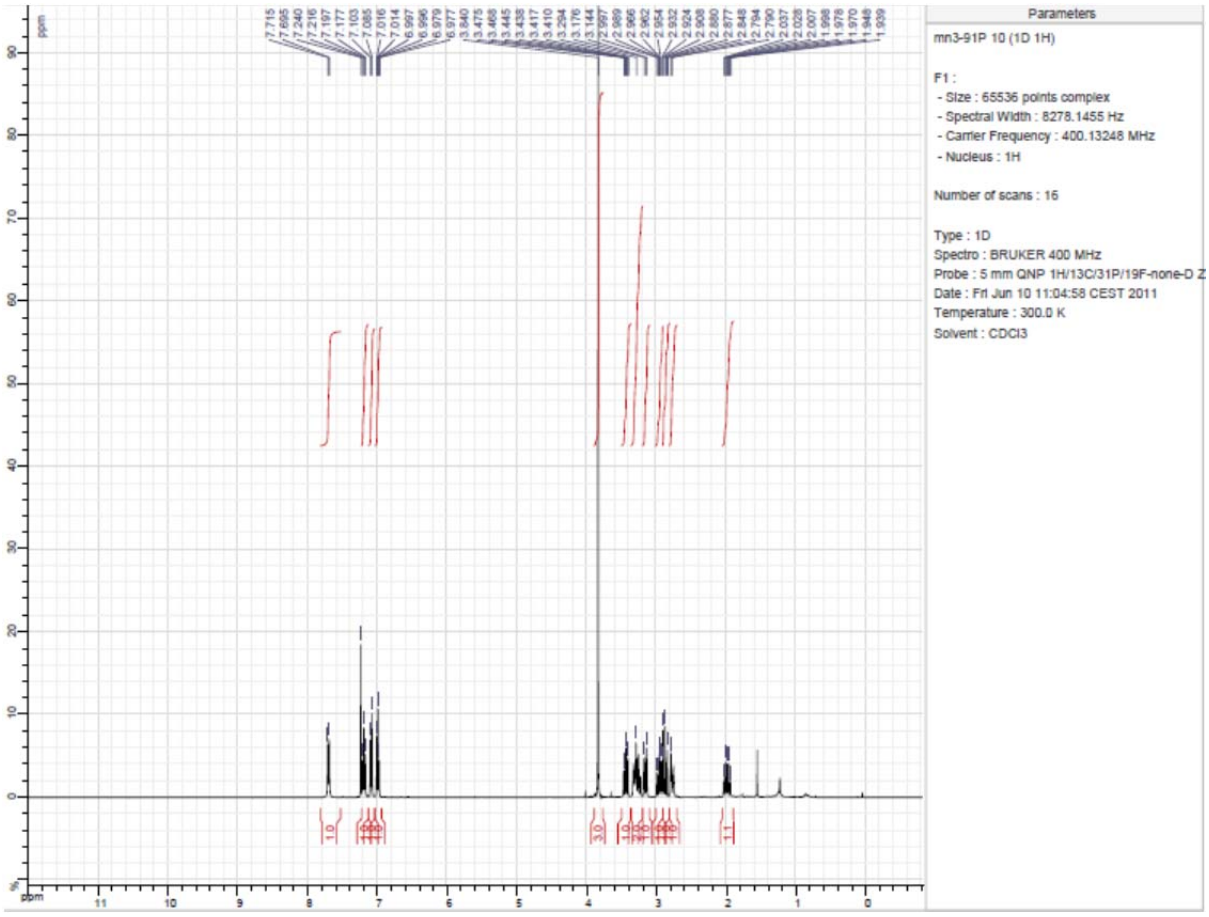
The enantiomer ratio was determined by HPLC: (chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/2-propanol = 98 : 2, 0.5 mL/min, 254 nm); ret. time = 34.1 min [major] and 39.5 min [minor]. $[\alpha]_D^{20}$ = +49 (*c* = 1.0 in CH_2Cl_2).

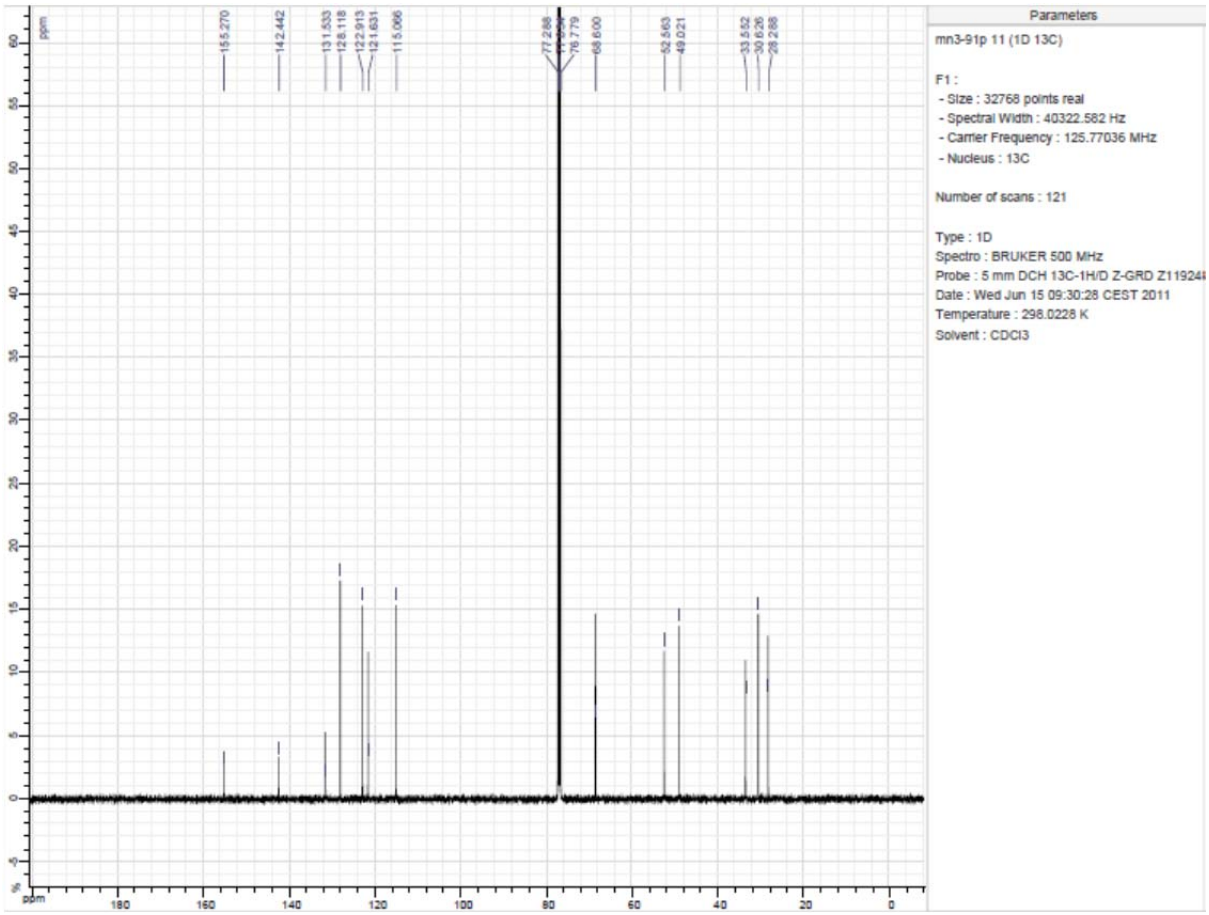
(4a*S*,9b*R*)-Methyl 1,4,4a,9b-tetrahydrothiopyrano[4,3-b]indole-5(3*H*)-carboxylate **2k**:

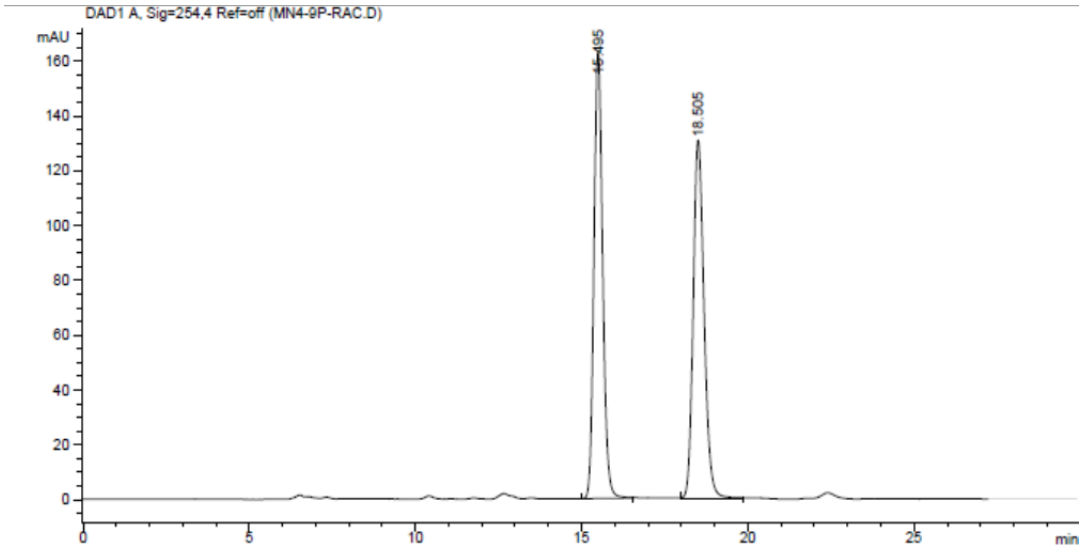


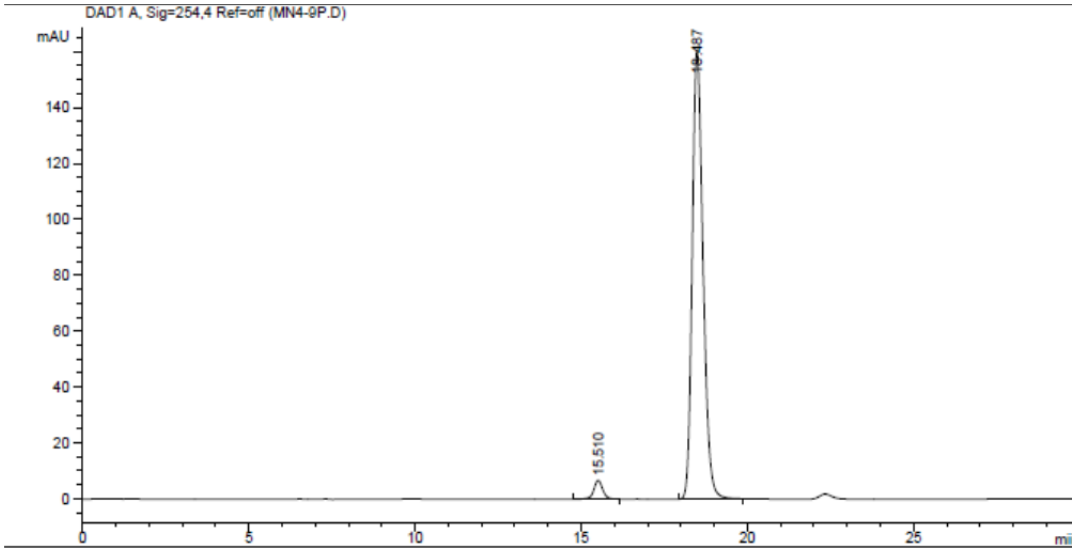
Colorless oil, 92% yield, 93% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 1.85 (qd, *J* = 12, 3.6 Hz, 1H), 2.72-2.82 (m, 4H), 2.88 (dd, *J* = 12.4, 11.2 Hz, 1H), 2.96 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.11-3.12 (m, 1H), 3.21-3.37 (m, 2H), 3.44 (td, *J* = 12, 2.8 Hz, 1H), 3.84 (s, 3H), 7.00 (td, *J* = 7.6, 0.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.6, Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H). ^{13}C NMR (100 MHz): δ = 28.3, 30.6, 33.6, 49.0, 52.7, 115.1, 121.6, 122.9, 128.1, 131.5, 142.4, 155.3. IR (neat): υ = 730, 751, 862, 915, 976, 1018, 1044, 1090, 1127, 1165, 1201, 1224, 1261, 1321, 1342, 1363, 1392, 1443, 1477, 1607, 1689, 2865, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{16}NO_2S$ 250.0896, found 249.0893.

Supporting Information for Chem. Sci.







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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
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   1  15.510 BB    0.2851  128.22096    6.76723   3.3990
   2  18.487 BB    0.3489 3644.12451  160.50089  96.6010
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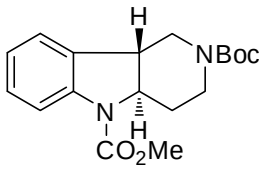
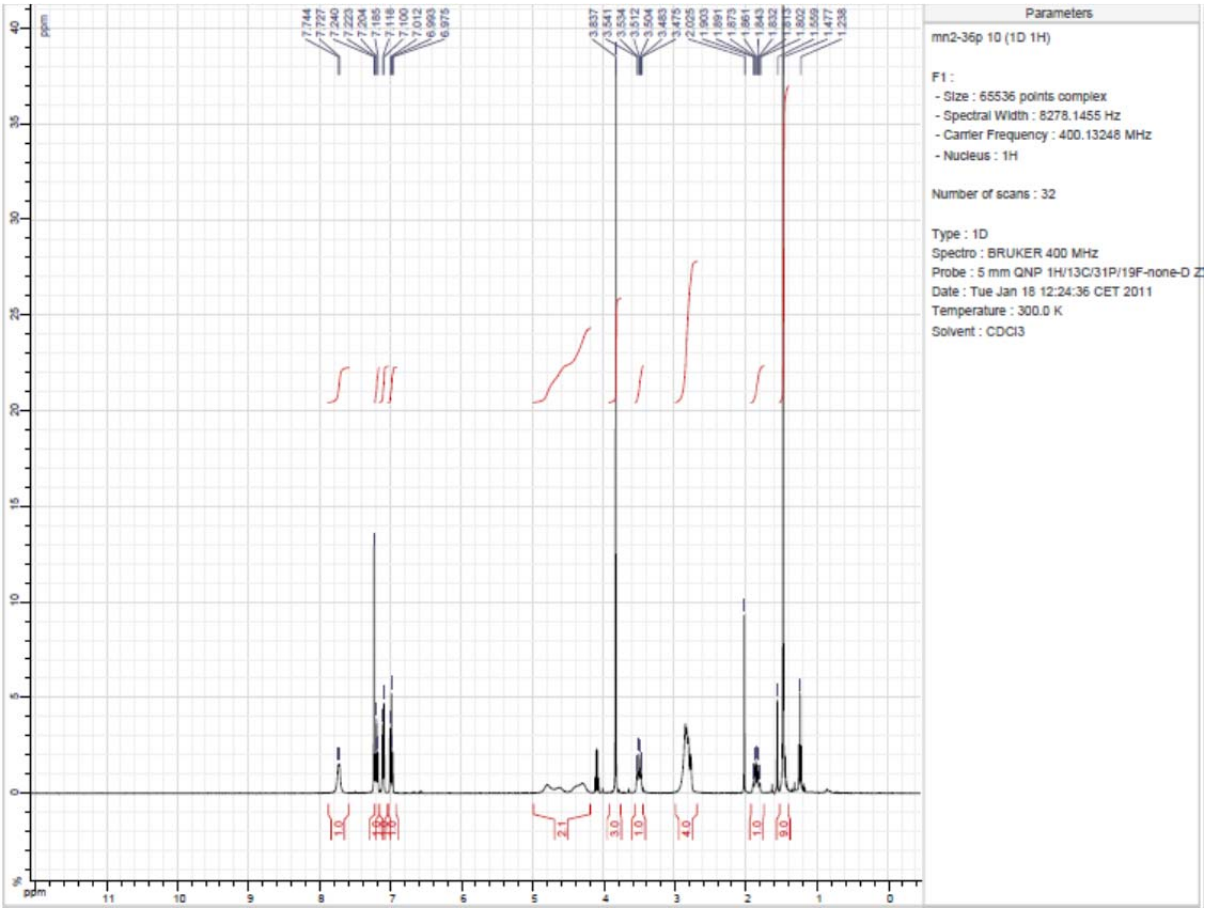
The enantiomer ratio was determined by HPLC: (chiral column: AS-H, *n*-hexane/2-propanol = 98 : 2, 0.5 mL/min, 254 nm); ret. time = 15.8 min [major] and 18.9 min [minor]. $[\alpha]_D^{20}$ = +0.9 (*c* = 1.0 in CH_2Cl_2).

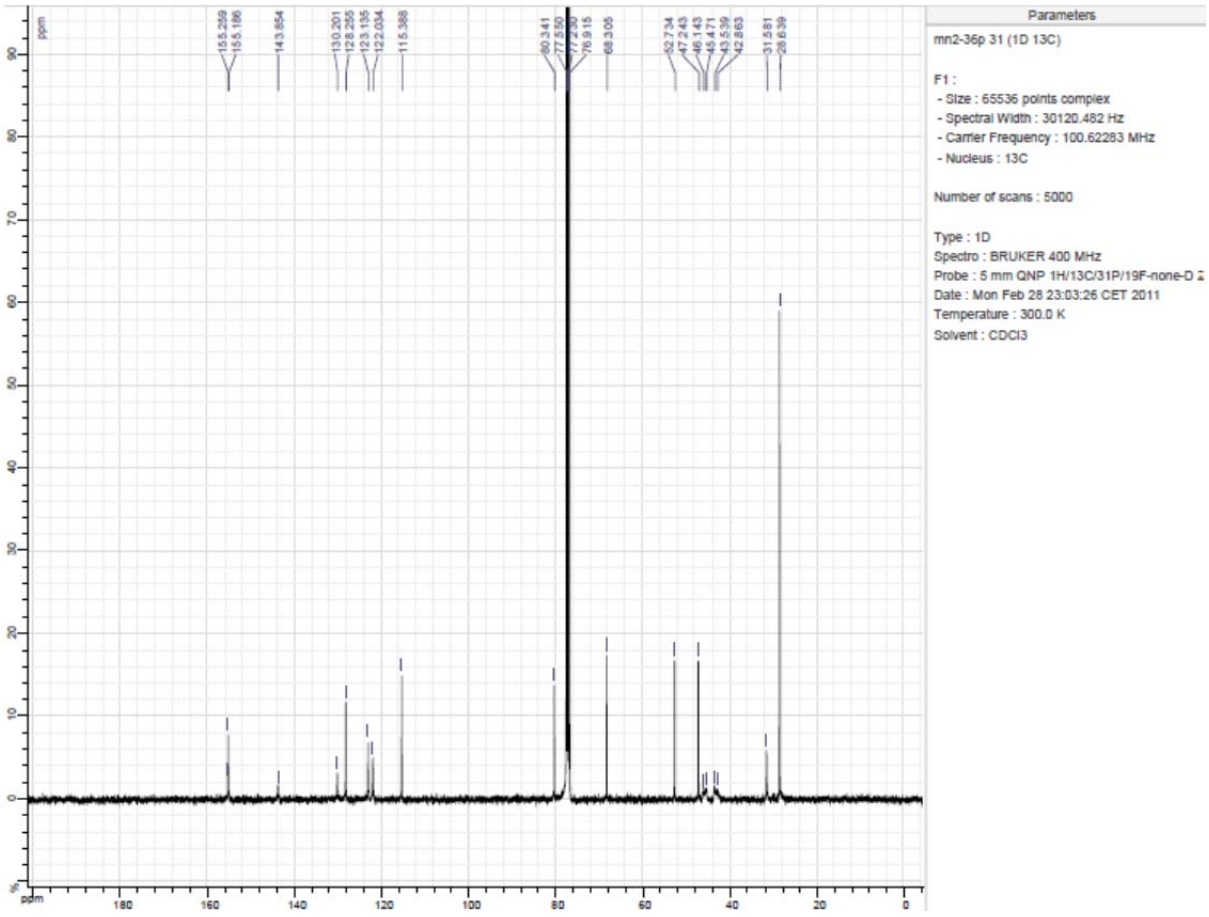
(4a*S*,9b*S*)-2-*tert*-Butyl 5-methyl 4,4a-dihydro-1*H*-pyrido[4,3-b]indole-2,5(3*H*,9b*H*)-dicarboxylate **2l**:

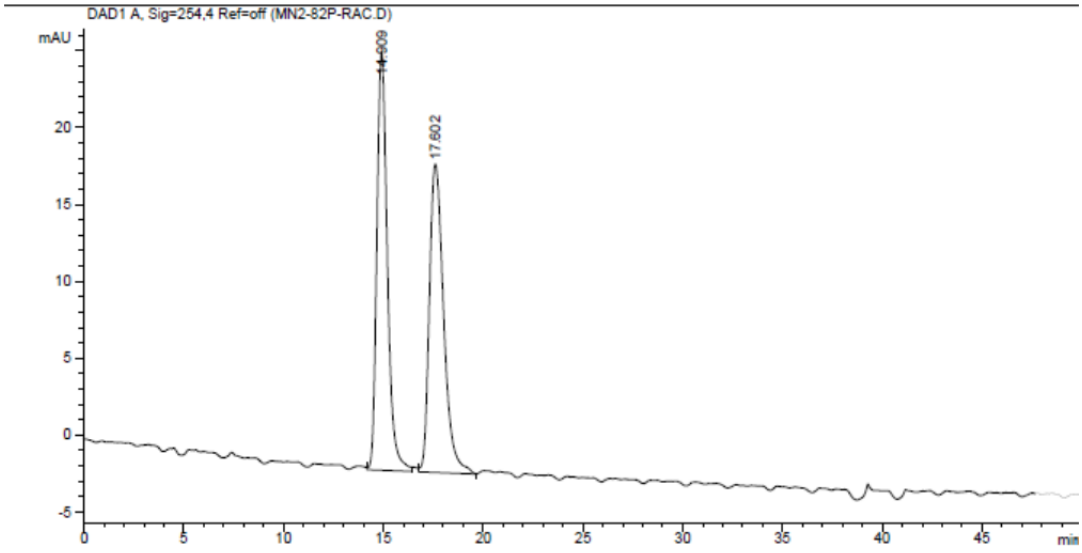


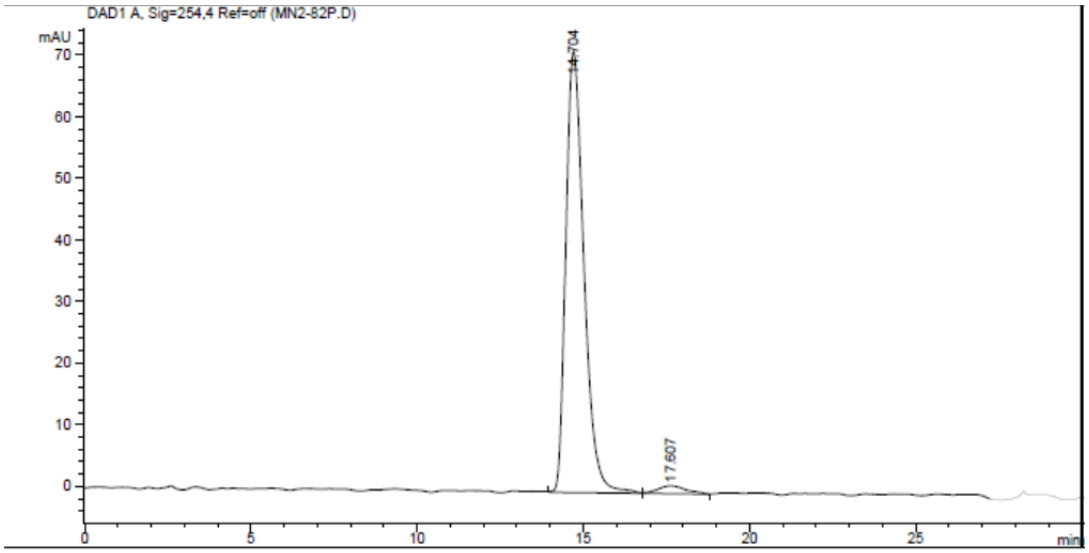
Colorless oil, 93% yield, 95% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 1.48 (s, 9H), 1.85 (qd, J = 13.2, 4.8 Hz, 1H), 2.70-3.00 (m, 4H), 3.51 (td, J = 11.6, 2.8 Hz, 1H), 3.84 (s, 3H), 4.20-5.00 (m, 2H), 6.99 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz): δ = 28.6, 31.6, 42.9, 43.5, 45.6, 46.1, 47.3, 52.7, 60.6, 68.3, 80.4, 115.4, 122.1, 123.1, 128.3, 130.2, 143.9, 155.3. IR (neat): υ = 621, 647, 730, 751, 801, 837, 862, 915, 976, 1018, 1044, 1090, 1127, 1165, 1201, 1224, 1261, 1321, 1342, 1363, 1392, 1444, 1477, 1607, 1689, 2865, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{18}H_{25}N_2O_4$ 333.1808, found 333.1809.



Supporting Information for Chem. Sci.





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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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   2  17.607 BV    0.7490   76.16730    1.28236   2.7304
```
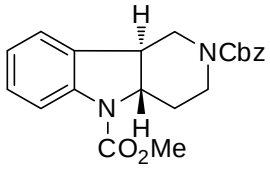
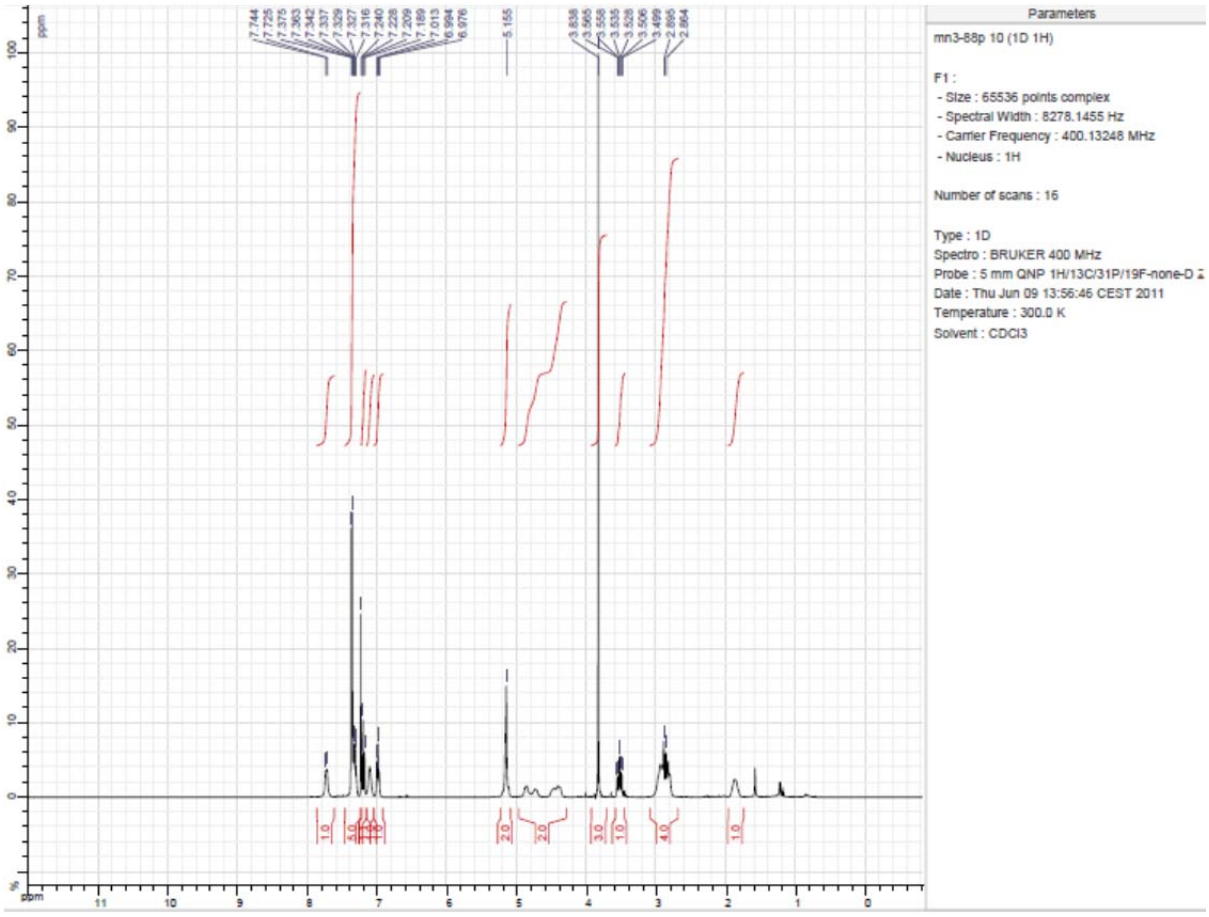

The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 99 : 1, 1.0 mL/min, 254 nm); ret. time = 17.0 min [major] and 20.5 min [minor]. $[\alpha]_D^{20}$ = -0.6 (*c* = 0.1 in CH_2Cl_2).

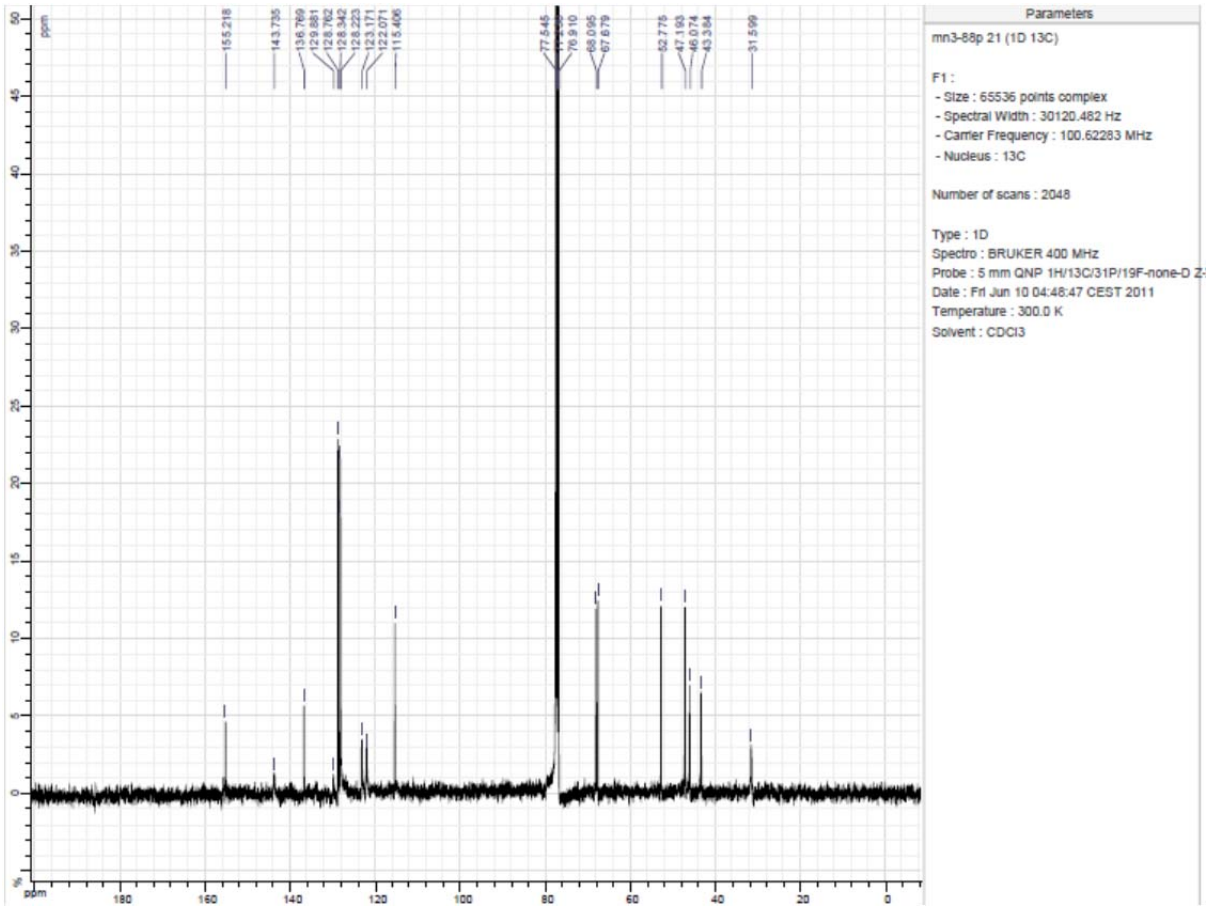
(4a*S*,9b*S*)-2-Benzyl 5-methyl 4,4a-dihydro-1*H*-pyrido[4,3-b]indole-2,5(3*H*,9b*H*)-dicarboxylate **2m**:

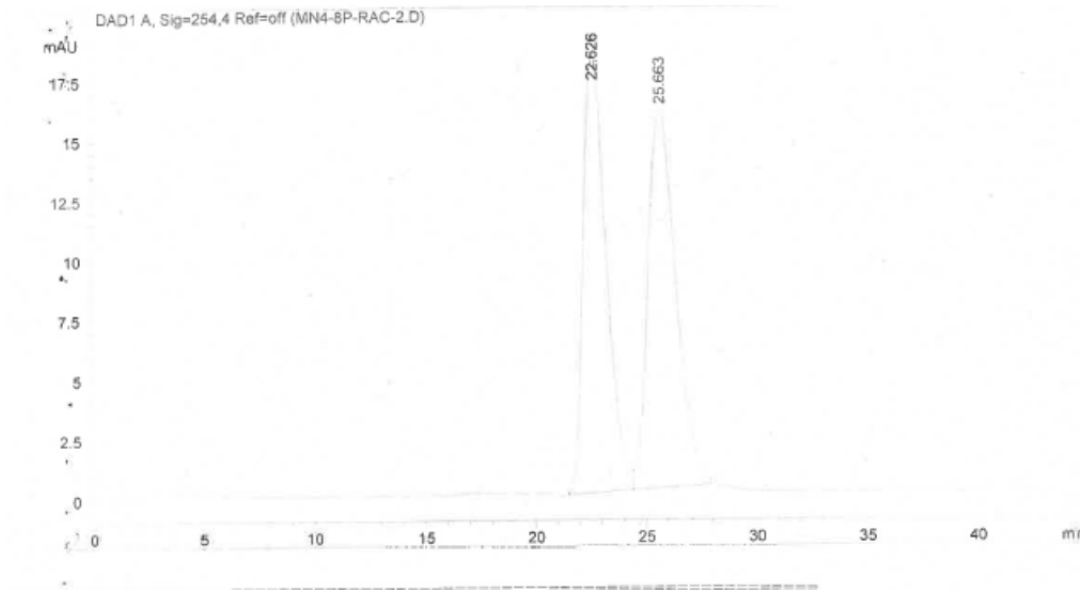


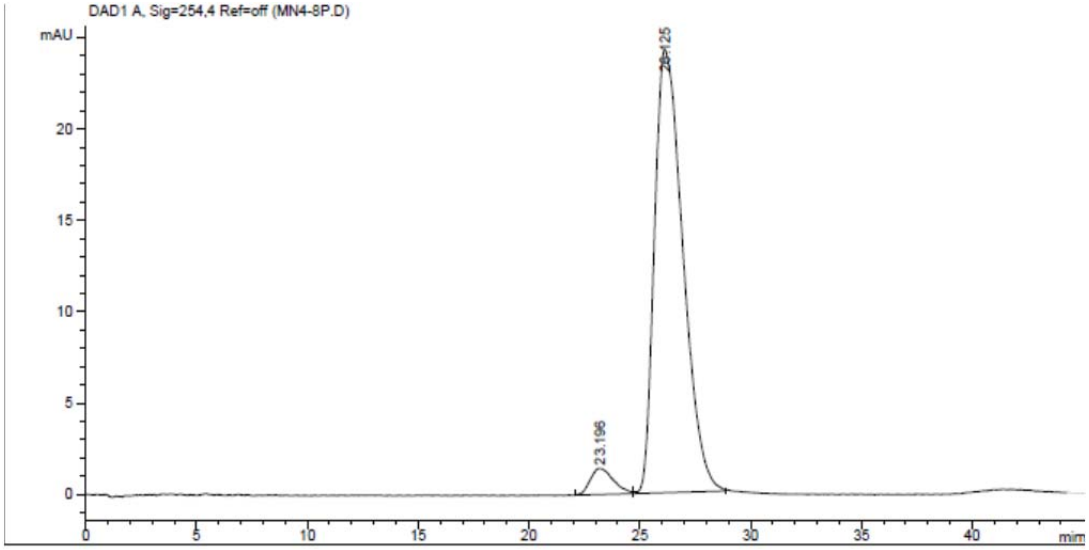
Orange oil, 55% yield, 91% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 1.76-1.98 (m, 1H), 2.70-3.10 (m, 4H), 3.53 (td, *J* = 12, 2.8 Hz, 1H), 3.84 (s, 3H), 4.30-4.98 (m, 2H), 5.10-5.24 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.26-7.47 (m, 5H), 7.73 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 31.6, 43.4, 46.1, 47.2, 52.8, 67.7, 68.1, 115.4, 122.1, 123.2, 128.2, 128.3, 128.8, 129.9, 136.8, 143.8, 155.2. IR (neat): υ = 730, 751, 862, 915, 976, 1018, 1044, 1090, 1127, 1165, 1201, 1224, 1261, 1321, 1342, 1363, 1392, 1443, 1477, 1607, 1689, 2865, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{18}H_{27}N_2O_4$ 367.1652, found 367.1652.

Supporting Information for Chem. Sci.







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Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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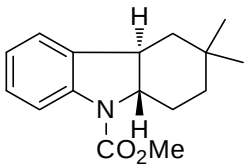
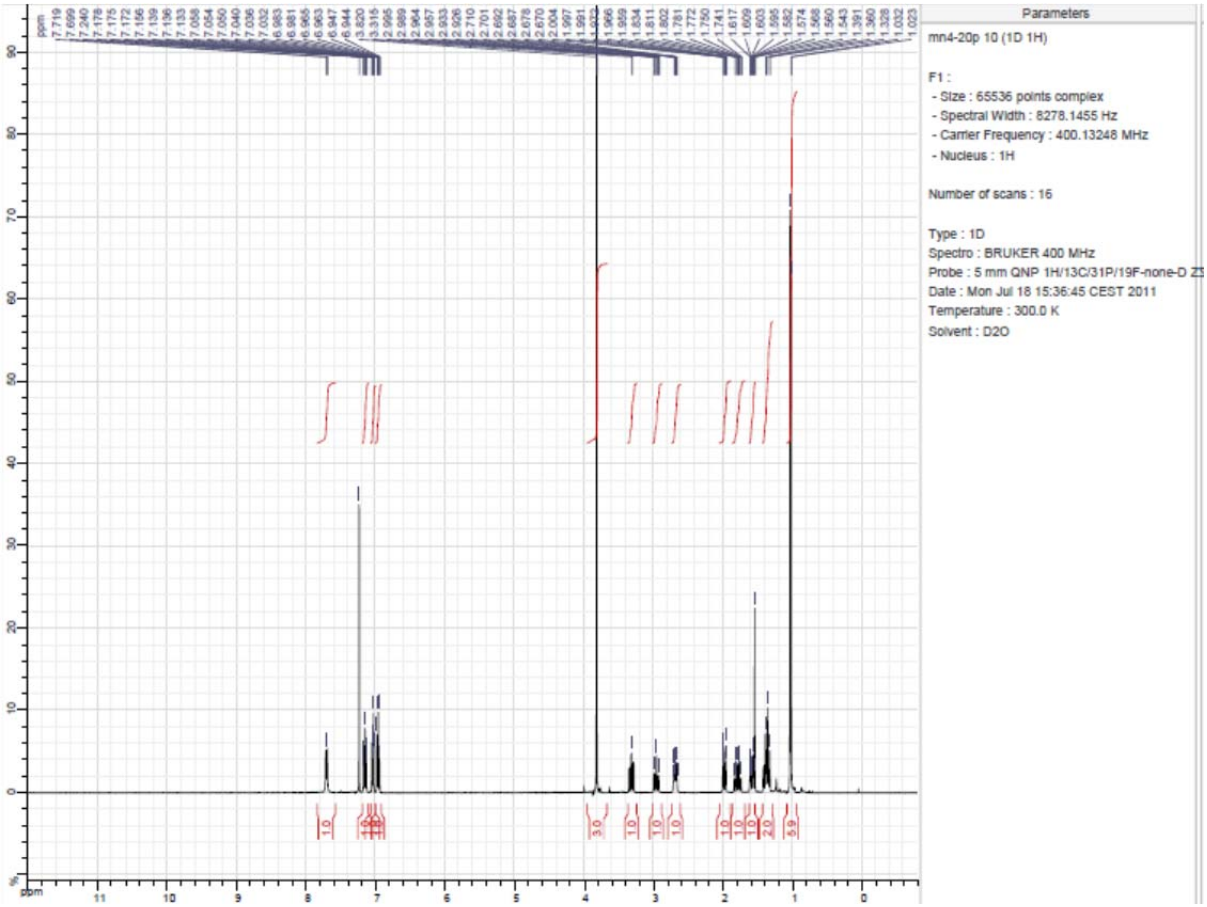
   2  26.125 VB    1.3499 2158.42944  24.26217  95.4757
```

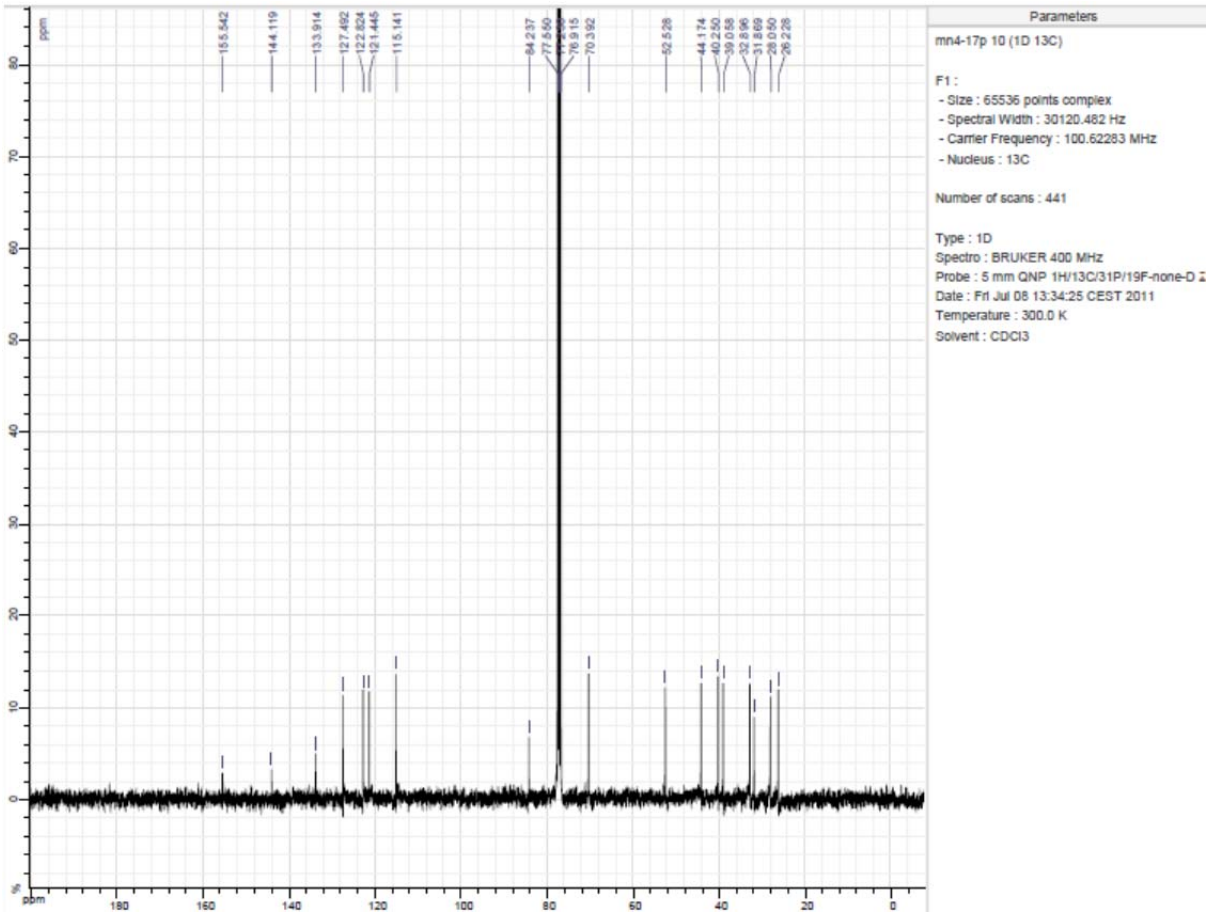
The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 95 : 5, 1.0 mL/min, 254 nm); ret. time = 23.6 min [major] and 26.7 min [minor]. $[\alpha]_D^{20}$ = +16 (*c* = 1.0 in CH_2Cl_2).

(4a*R*,9a*S*)-Methyl 3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-carbazole-9(9a*H*)-carboxylate **2n**:



Colorless oil, 39% yield, 92% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 1.03 (d, J = 3.6 Hz, 6H), 1.30-1.44 (m, 2H), 1.59 (dd, J = 14, 3.2 Hz, 1H), 1.79 (dd, J = 12.8, 3.6 Hz, 1H), 1.98 (td, J = 12.8, 2.8 Hz, 1H), 2.69 (dq, J = 12.8, 2.8 Hz, 1H), 2.96 (td, J = 12.4, 2.4 Hz, 1H), 3.82 (s, 3H), 6.96 (td, J = 7.2, 0.8 Hz, 1H), 7.05 (dt, J = 7.2, 1.6 Hz, 1H), 7.16 (tt, J = 7.6, 1.2 Hz, 1H), 7.71 (t, J = 8 Hz, 1H). ^{13}C NMR (100 MHz): δ = 26.2, 28.0, 31.9, 32.9, 39.1, 40.3, 44.2, 52.5, 70.4, 115.1, 121.4, 122.8, 127.5, 133.9, 144.1, 155.5. IR (neat): υ = 749, 793, 819, 861, 932, 966, 1020, 1047, 1068, 1086, 1112, 1128, 1154, 1197, 1231, 1255, 1279, 1314, 1336, 1362, 1387, 1441, 1459, 1476, 1606, 1706, 2852, 2912 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{22}NO_2$ 260.1650, found 260.1646.

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31.869
28.050
26.228
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- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 441
Type : 1D
Spectro : BRUKER 400 MHz
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Date : Fri Jul 08 13:34:25 CEST 2011
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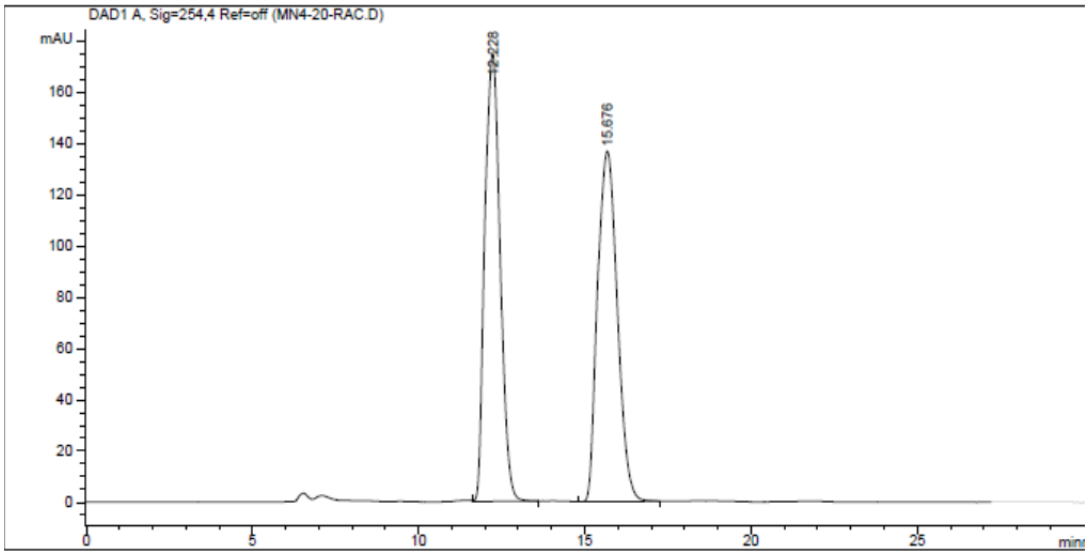
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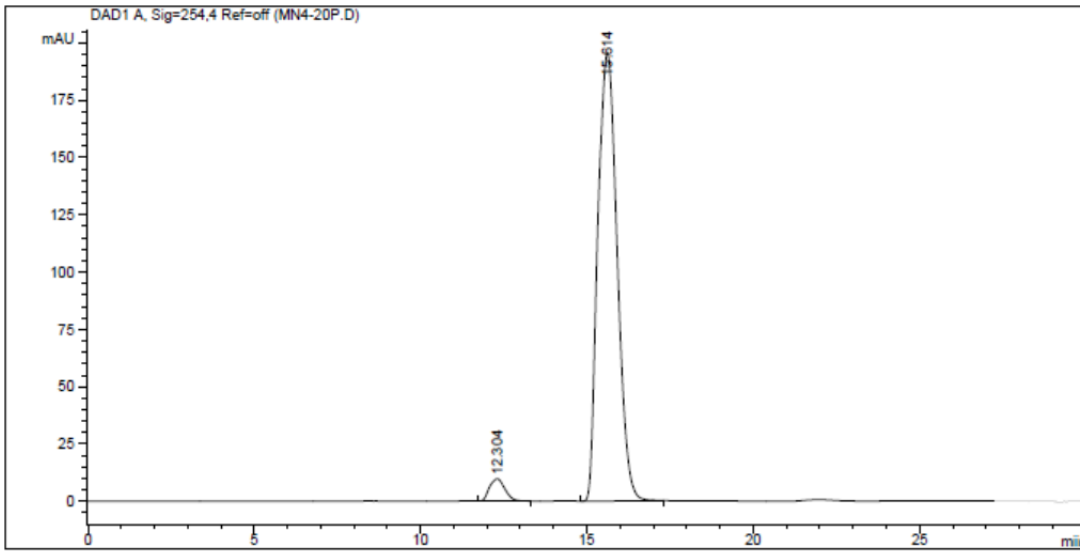
min

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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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   1  12.304 VB    0.5210  316.76120    9.80194   3.8585
   2  15.614 BB    0.6549 7892.76221  195.53145  96.1415
```
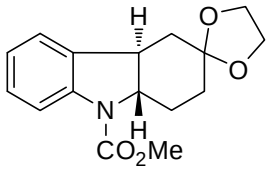
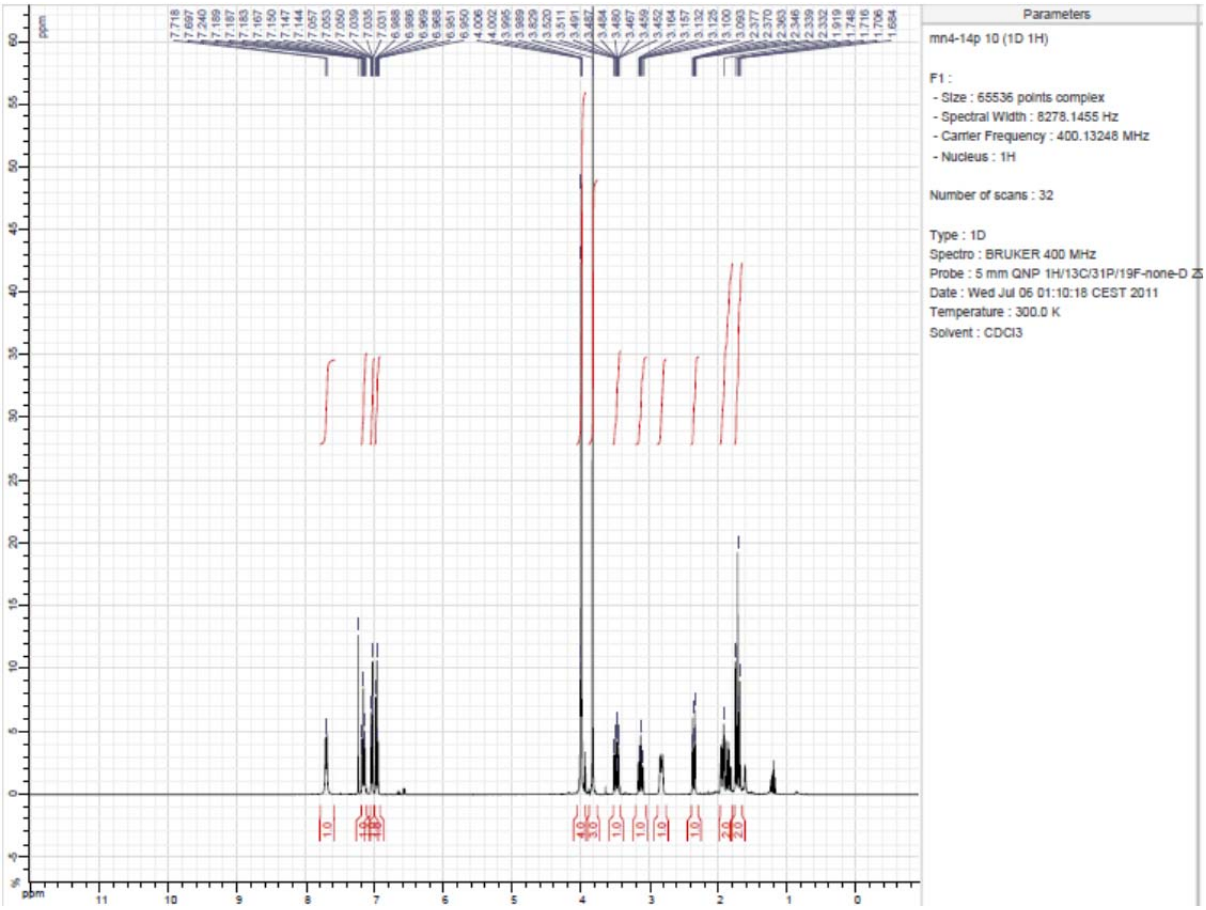

The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 12.2 min [major] and 15.7 min [minor]. $[\alpha]_D^{20}$ = -41.6 (*c* = 0.5 in CH_2Cl_2).

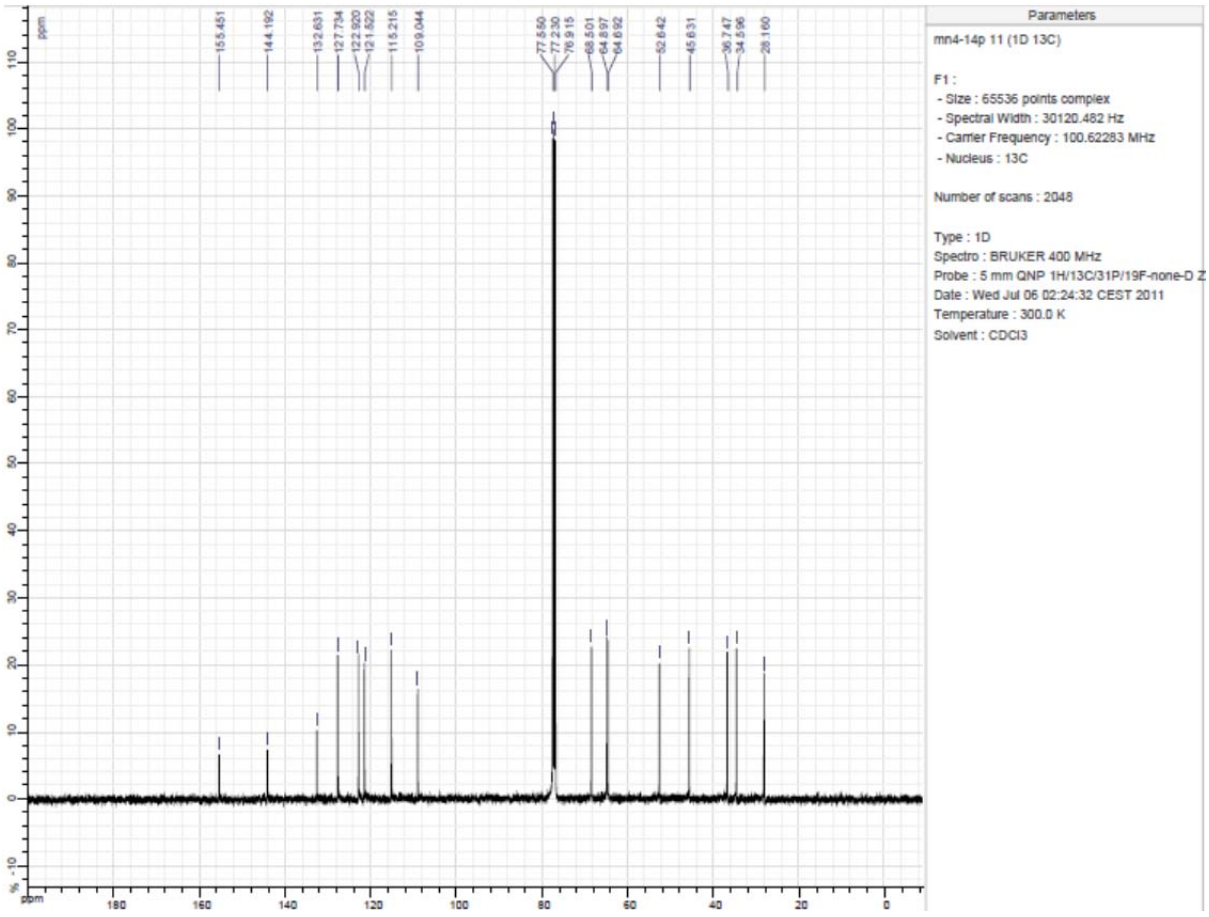
(4a*R*,9a*S*)-Methyl 1,4,4a,9a-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane]-9(2*H*)-carboxylate **2o**:

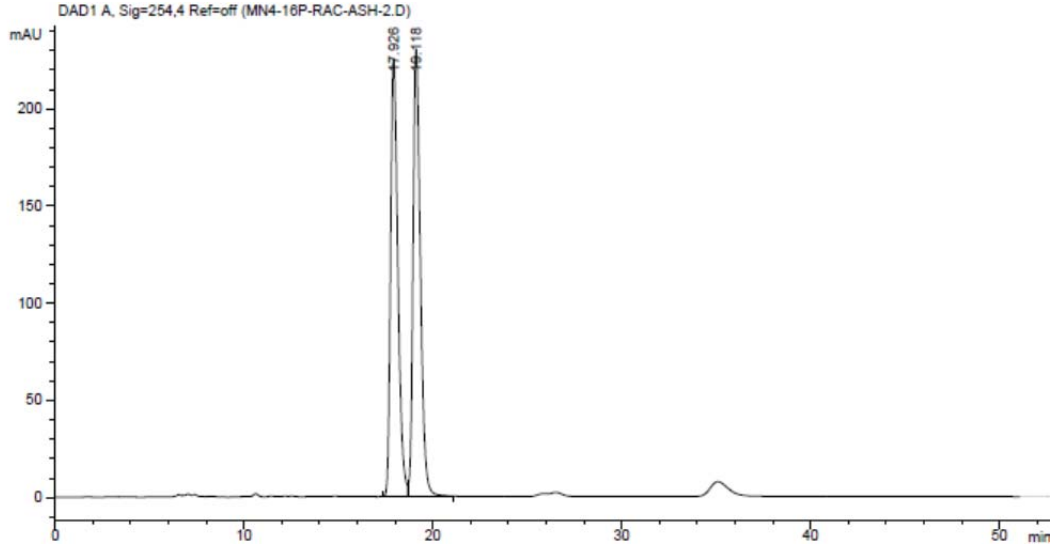


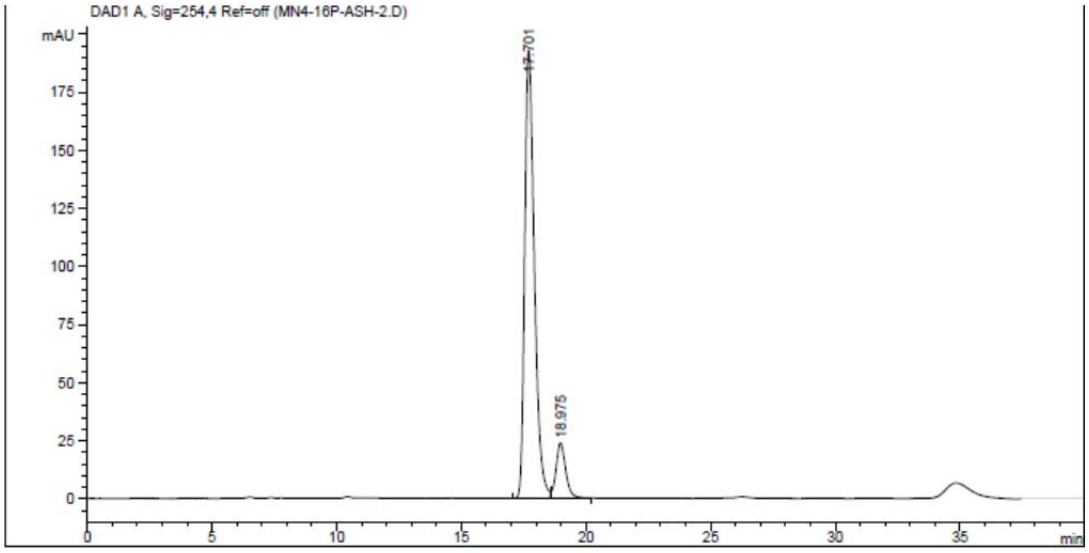
Colorless oil, 50% yield, 78% ee, ^{1}H NMR (400 MHz, $CDCl_3$): 1.66-1.77 (m, 2H), 1.80-1.95 (m, 2H), 2.35 (dd, J = 12.4, 2.8 Hz, 1H), 2.77-2.89 (m, 1H), 3.13 (td, J = 12.8, 2.8 Hz, 1H), 3.83 (s, 3H), 3.43-3.53 (m, 1H), 3.95-4.06 (m, 4H), 6.97 (td, J = 7.6, 0.8 Hz, 1H), 7.04 (t, J = 7.2, 1.6 Hz, 1H), 7.04 (dt, J = 7.2, 1.6 Hz, 1H), 7.17 (tt, J = 8, 0.8 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz): δ = 28.2, 34.6, 36.7, 45.6, 52.6, 64.7, 64.9, 68.5, 109.0, 115.2, 121.5, 122.9, 127.7, 132.6, 144.2, 155.5. IR (neat): υ = 752, 793, 817, 856, 887, 938, 995, 1014, 1022, 1036, 1060, 1087, 1108, 1125, 1144, 1202, 1225, 1263, 1282, 1319, 1339, 1364, 1388, 1442, 1460, 1476, 1606, 1705, 2884, 2953 cm^{-1}; ESI-HRMS calcd. for $C_{16}H_{20}NO_4$ 290.1386, found 290.1379.



Supporting Information for Chem. Sci.





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   2  18.975 VB    0.4131  646.55017   23.79040  11.0936
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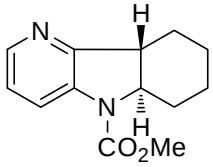
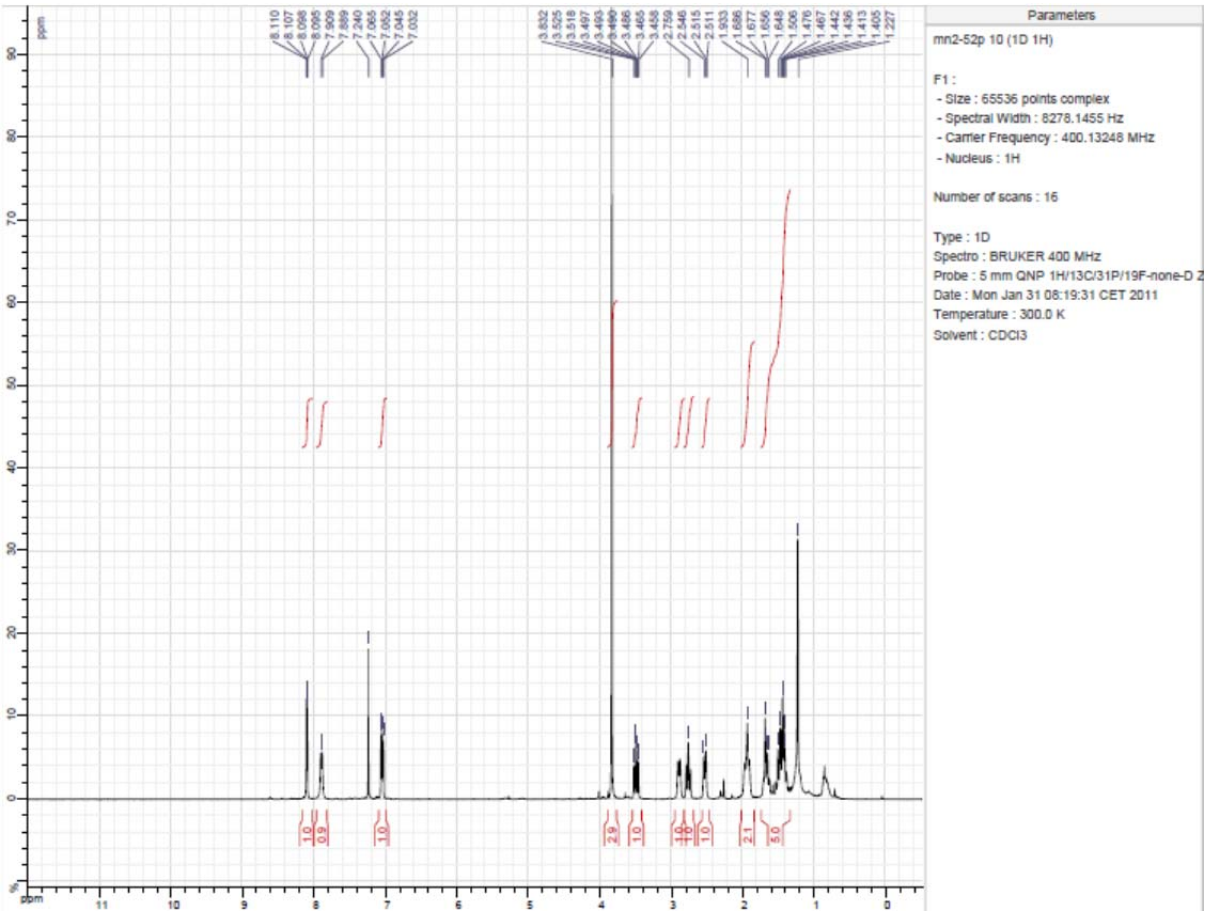
The enantiomer ratio was determined by HPLC: (chiral column: OD-H, *n*-hexane/2-propanol = 95 : 5, 1.0 mL/min, 254 nm); ret. time = 10.7 min [major] and 13.2 min [minor]. $[\alpha]_D^{20}$ = +30 (*c* = 0.5 in CH_2Cl_2).

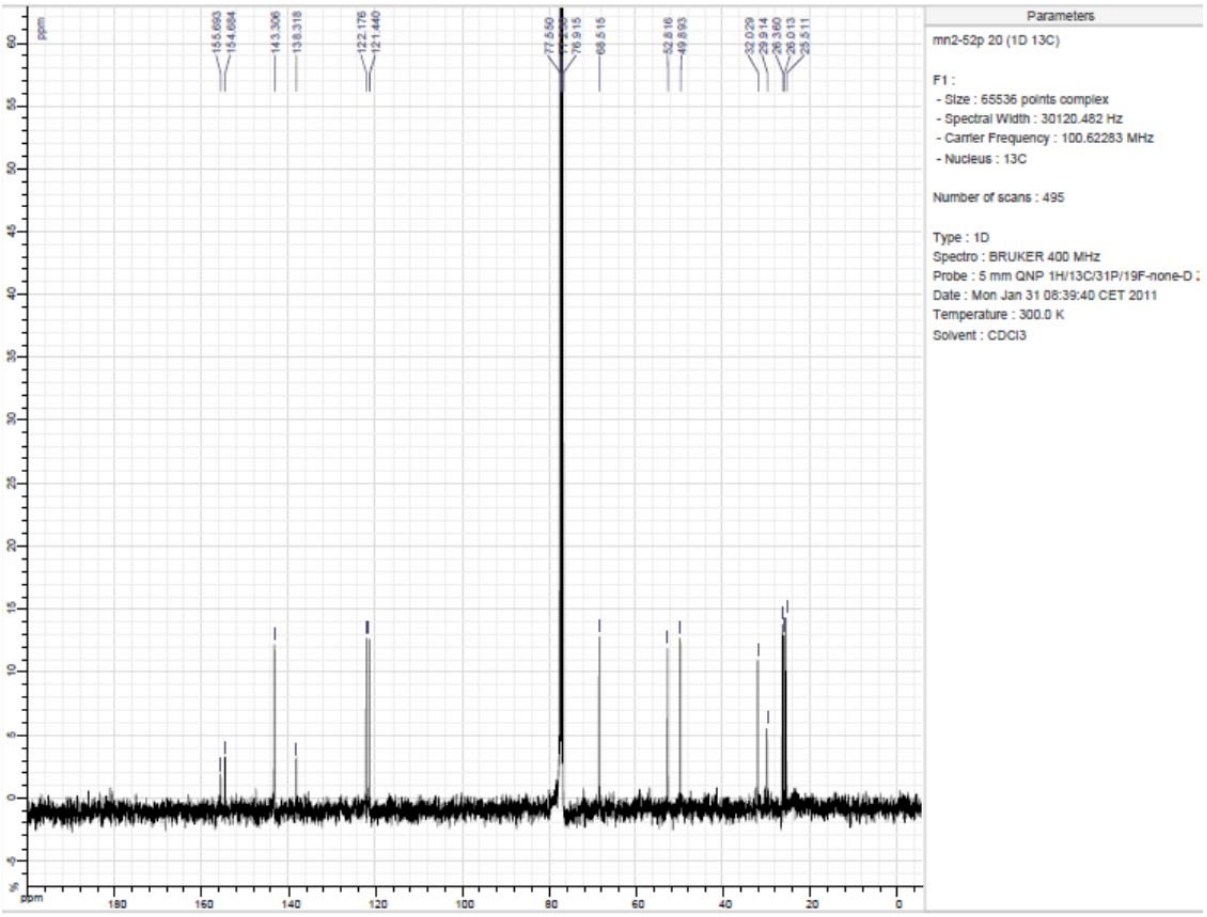
(5a*R*,9a*R*)-Methyl 5a,6,7,8,9,9a-hexahydro-5*H*-pyrido[3,2-b]indole-5-carboxylate **2p**:

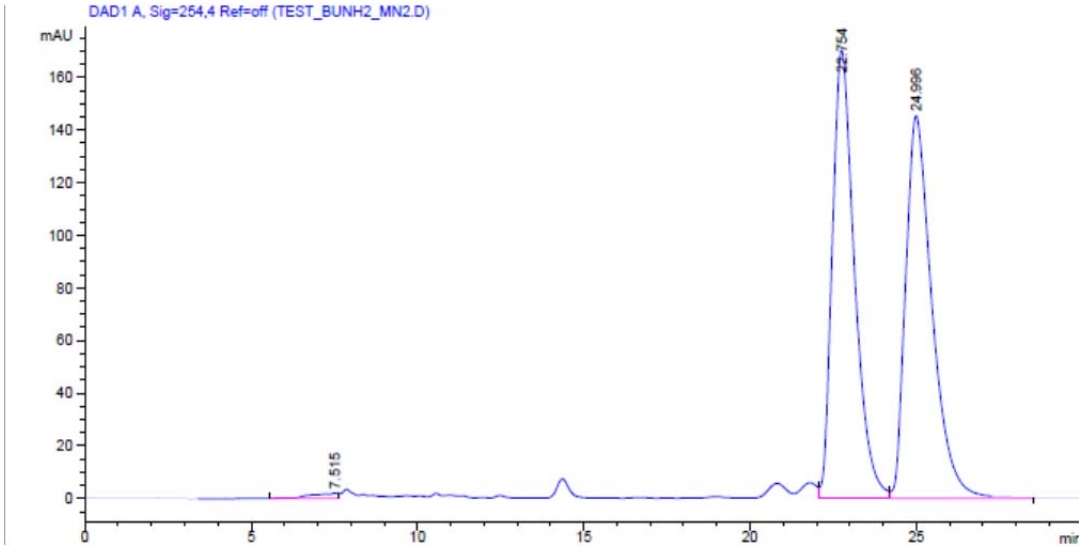


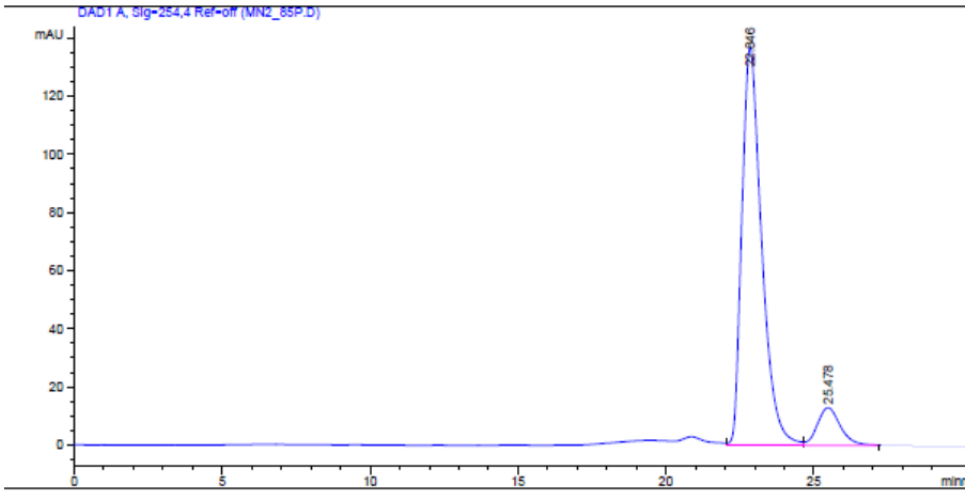
Light yellow solid, 77% yield, 80% ee, M. p. 90 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.35-1.74 (m, 5H), 1.84-2.02 (m, 2H), 2.47-2.57 (m, 1H), 2.69-2.82 (m, 1H), 2.82-2.95 (m, 1H), 3.48 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.83 (s, 3H), 7.05 (dd, *J* = 8, 5.2 Hz, 1H), 7.90 (d, *J* = 8 Hz, 1H), 8.10 (dd, *J* = 4.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.5, 26.0, 26.4, 29.9, 32.0, 49.9, 52.8, 68.5, 121.4, 122.2, 138.3, 143.3, 154.7, 155.7. IR (neat): υ = 741, 768, 794, 1031, 1063, 1116, 1147, 1205, 1273, 1305, 1335, 1363, 1427, 1445, 1592, 1715, 2857, 2929 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{17}N_2O_2$ 233.1284, found 233.1286.

Supporting Information for Chem. Sci.







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Totals :                  7088.16486  150.00695
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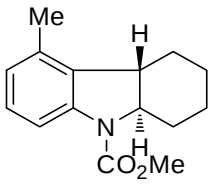
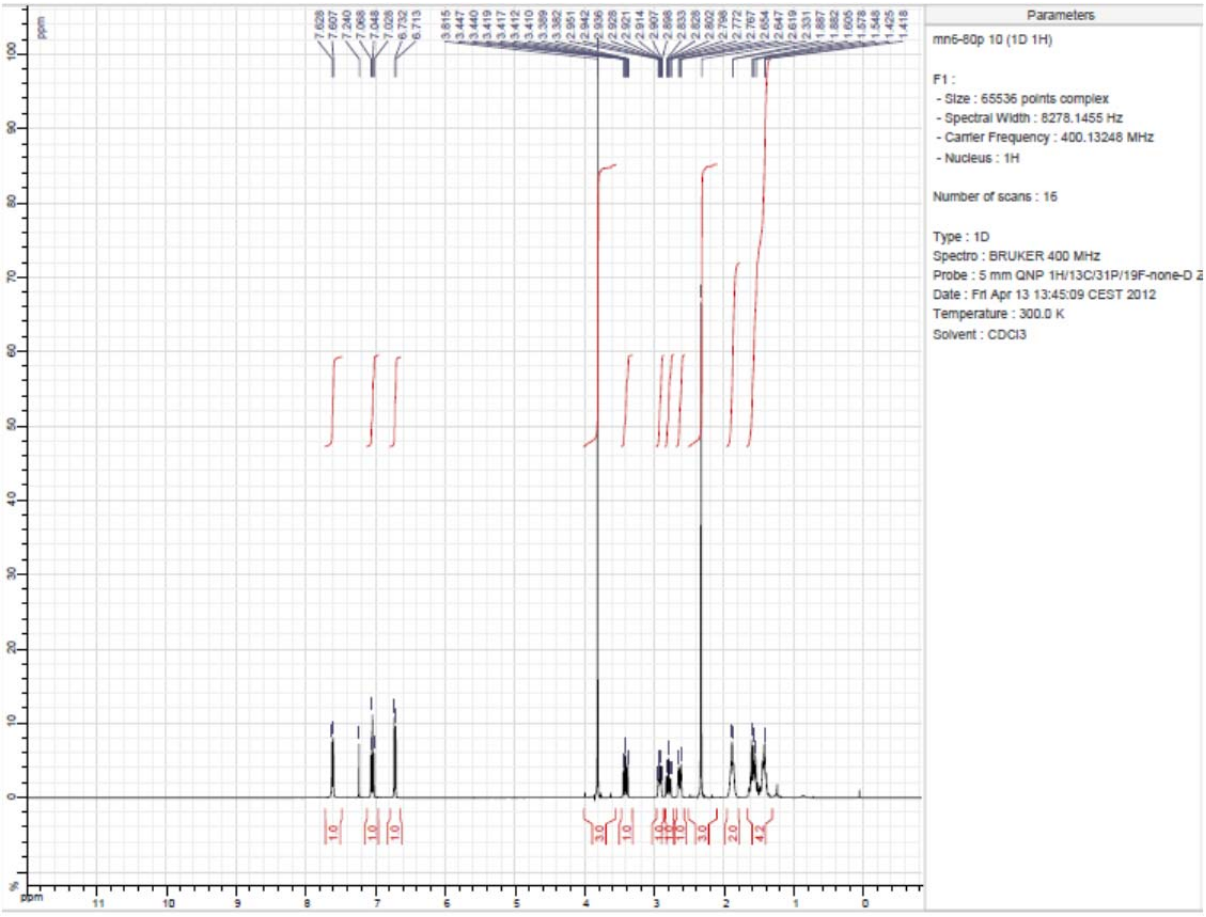
The enantiomer ratio was determined by HPLC: (chiral column: OD-H, hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 27.1 min [major] and 29.7 min [minor]. $[\alpha]_D^{20}$ = -11.4 (*c* = 0.1 in CH_2Cl_2).

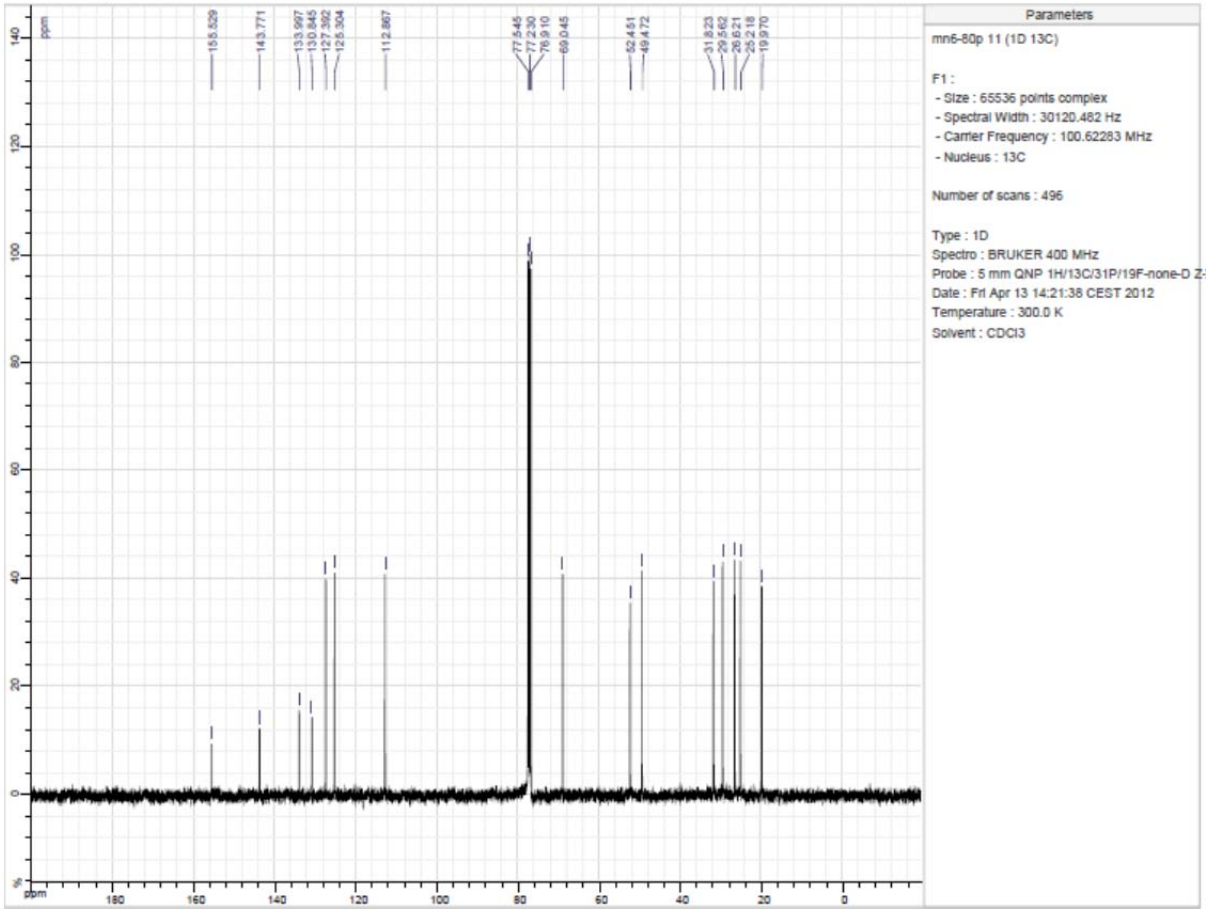
Methyl 5-methyl-2,3,4,4a-tetrahydro-1*H*-carbazole-9(9a*H*)-carboxylate **2r**:

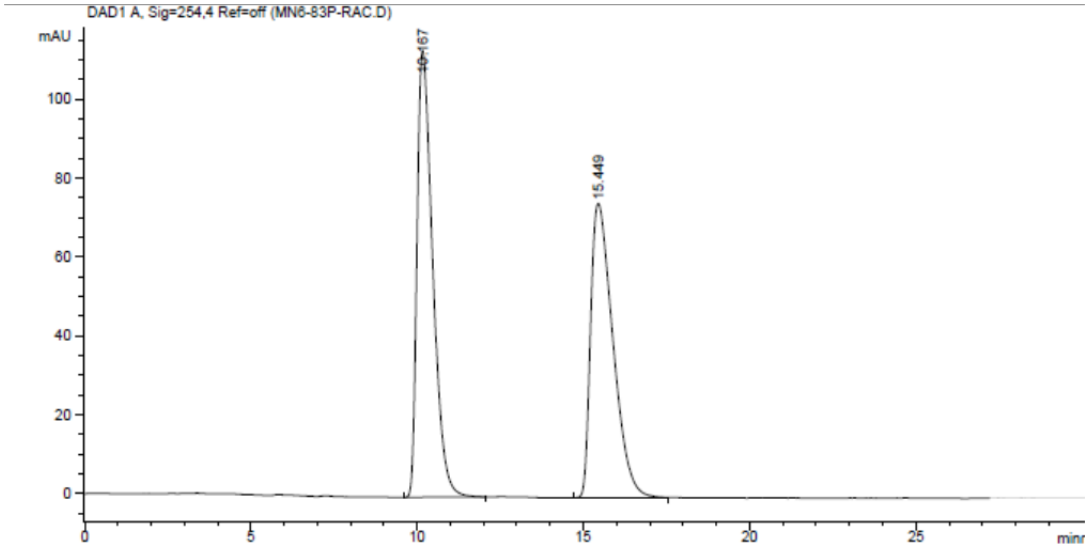


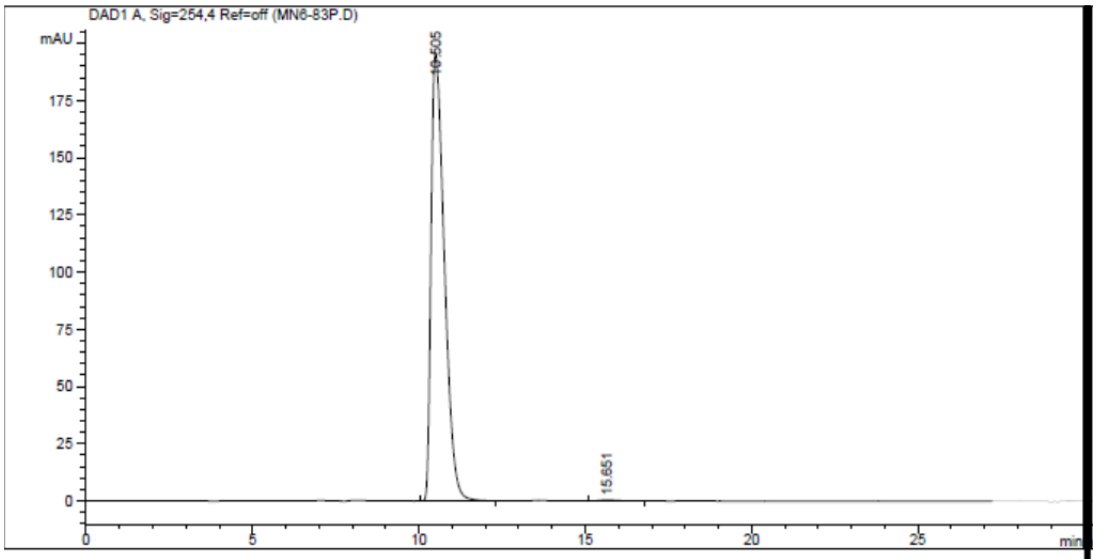
White solid, 18% yield, 99% ee, M. p. 67 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.32-1.68 (m, 4H), 1.80-1.97 (m, 2H), 2.33 (s, 3H), 2.58-2.69 (m, 1H), 2.80 (td, J = 12.4, 2 Hz, 1H), 2.88-2.98 (m, 1H), 3.41 (d, J = 11.6, 2.8 Hz, 1H), 3.82 (s, 3H), 6.72 (d, J = 7.6 Hz, 1H), 7.05 (t, J = 8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz): δ = 20.0, 25.2, 26.2, 29.6, 31.8, 49.5, 52.5, 69.0, 112.9, 125.3, 127.4, 130.8, 134.0, 143.8, 155.5. IR (neat): υ = 715, 776, 981, 1012, 1037, 1055, 1098, 1113, 1130, 1150, 1167, 1197, 1238, 1250, 1287, 1307, 1330, 1352, 1385, 1440, 1589, 1701, 2858, 2947 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{20}NO_2$ 246.1488, found 246.1492.



Supporting Information for Chem. Sci.





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Signal 1: DAD1 A, Sig=254,4 Ref=off

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   2  15.651 BB    0.4572   17.05798 4.63709e-1   0.3151
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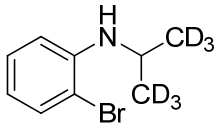
The enantiomer ratio was determined by HPLC: (chiral column: AD-H, *n*-hexane/2-propanol = 99 : 1, 0.5 mL/min, 254 nm); ret. time = 10.5 min [major] and 15.7 min [minor]. $[\alpha]_D^{20}$ = -78 (*c* = 1.0 in CH_2Cl_2).

3. KIE measurements

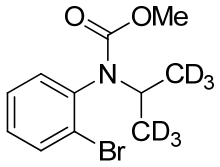
3.1. Intermolecular KIE

2-Bromo-*N*-isopropylaniline-d_6:[v]



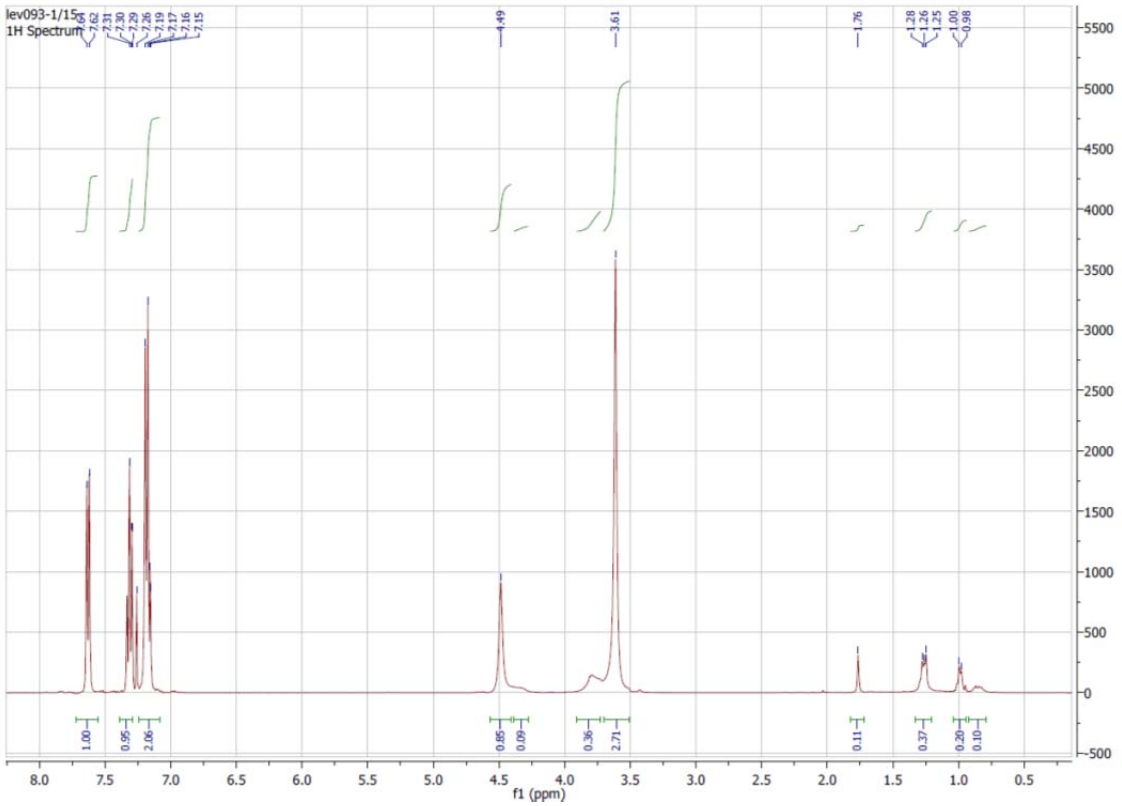
A round bottom flask was charged with a stirring bar and sodium triacetoxyborohydride (3.05 g, 14.4 mmol) and capped with a septum. Acetone-d_6 (923 µL, 14.4 mmol) was added via syringe to the flask followed by 2-iodoaniline (0.62 g, 3.6 mmol) dissolved in 1/1 THF/dichloromethane (12 mL). Two drops of CD_3COOD were introduced and the heterogeneous mixture was stirred for 28 h. The reaction was quenched with water (15 mL) and the resulting biphasic solution was extracted with dichloromethane (3 x 20 mL). The combined organic fractions were washed with brine, dried with $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by silica gel flash chromatography (pentane/ethyl acetate, 97/3) to give 0.51 g of the title compound as a clear oil (51 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 1.26 (m, 0.19H), 3.64 (s, 1H), 4.13 (br s, 1H), 6.51 (td, J = 7.6, 1.6 Hz, 1H), 6.63 (dd, J = 7.6, 1.6Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H).

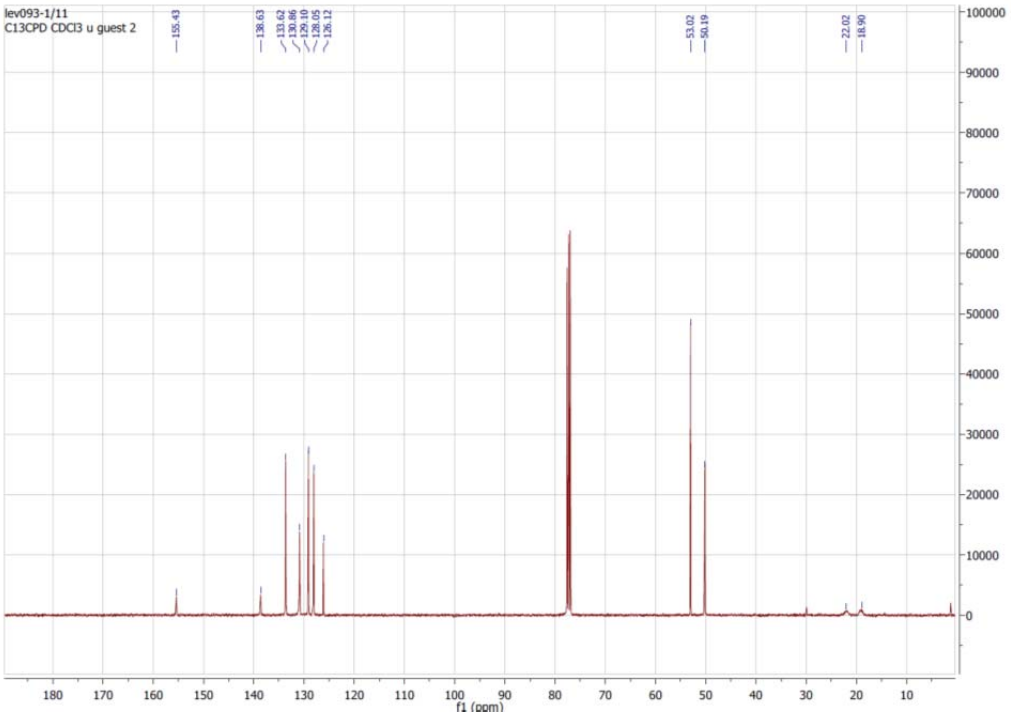
Methyl (2-bromophenyl)(isopropyl)carbamate **3a**-d_6:



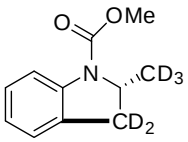
Prepared according to **GP2** from 2-bromo-*N*-isopropylaniline-d_6. Colorless oil, 0.44 g, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.00 (m, 0.2H), 1.36 (m, 0.37H), 3.61 (s, 3H), 4.36-4.42 (m, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.62 (d, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 18.9 (m), 22.0 (m), 50.5, 53.0, 126.1, 128.0, 129.1, 130.8, 133.6, 138.6, 155.4. MS (ESI, 70 eV): *m/z* (%) = 199 $(M\text{-}Br+H)^+$. Estimated D-content is ~94 %. ^{2}H NMR (500 MHz, $CDCl_3$): 1.01 (s, 3D), 1.30 (s, 3D).

Supporting Information for Chem. Sci.

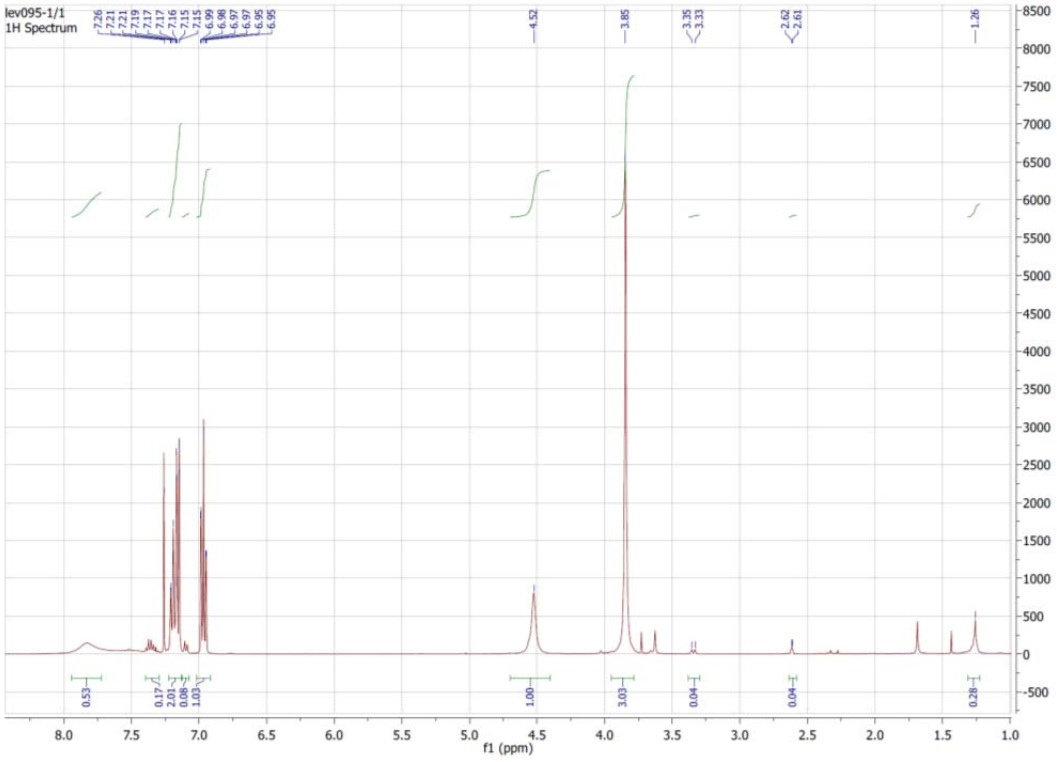




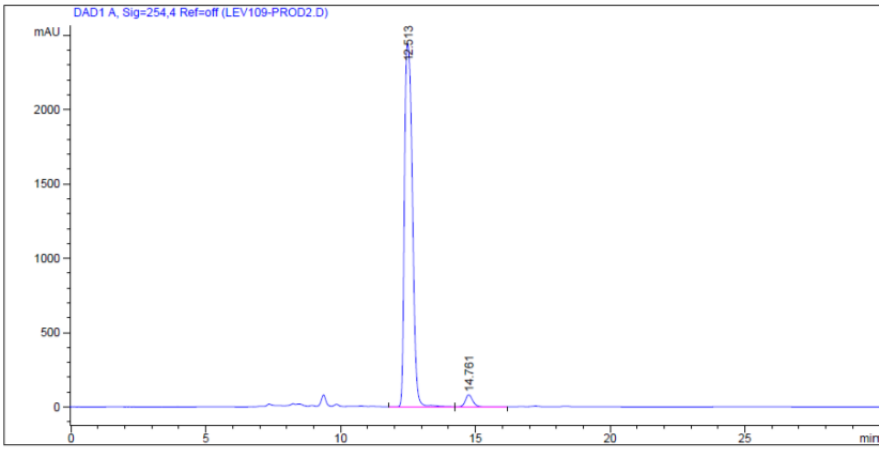
Racemic synthesis of indoline (*rac*)-7a-d_5 using 6 as a ligand:



Substrate **3a**-d_6 (57.0 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and **6**-HCl (8.5 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylene 2 mL was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 20 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; ethyl acetate : pentane = 1 : 30 as eluent) to afford indoline **7a**-d_5 in 76% yield (30.0 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.26 (0.28H), 2.62 (d, 0.04H), 3.34 (d, 0.04H), 3.83 (s, 3H), 4.40-4.65 (m, 1H), 6.57 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.44-8.10 (br d, 1H). ^{2}H NMR (500 MHz, $CDCl_3$): 1.29 (s, 3D), 2.63 (s, 1D), 3.37 (s, 1D). Estimated D-content is ~96 %. MS (ESI, 70 eV): *m/z* (%) = 197 $(M+H)^+$. HRMS calcd. for $C_{11}H_9D_5N_1O_2$ 197.1332, found 197.1336 (accuracy 1.6 ppm).



Asymmetric synthesis of indoline (*S*)-**7a**-d_5 was carried out according to **GP5** with 0.20 mmol of compound **3a**-d_6 using (*S*,*S*)-**8** as ligand. Usual work up gives 29 mg (74 %) of (*S*)-**7a**-d_5 as a colorless oil with ee 94%. The enantiomeric ratio was determined by HPLC: (chiral column: AS-H, *n*-hexane/ *i*-propanol = 99 : 1, 0.5 mL/min, 254 nm); t_R = 12.4 min [major] and 14.7 min [minor].

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   2  14.761 VB    0.3336 1666.32385   81.80379   3.2749

Totals :                  5.08824e4  2524.20979

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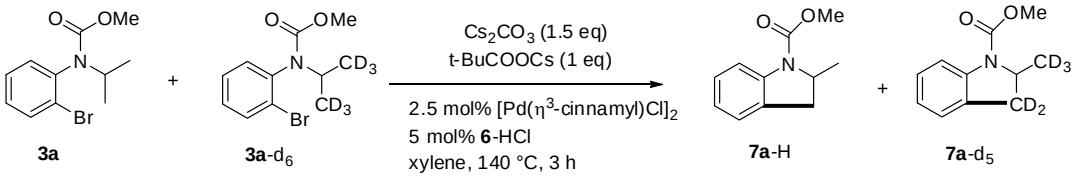
Kinetic isotope effect (KIE) measurements.

Carbamates **3a** (27.2 mg, 0.10 mmol) and **3a**-d_6 (27.8 mg, 0.10 mmol), cesium carbonate (97.5 mg, 0.30 mmol), cesium pivalate (46.8 mg, 0.2 mmol) [Pd(π-cinnamyl)Cl]$_2$ (2.6 mg, 0.005 mmol) and **6**-HCl (4.3 mg, 0.01 mmol) were placed in a dry Schlenk tube (20 mL). After the flask was evacuated and backfilled with nitrogen, dry, degassed xylene (2 mL) was added under nitrogen. The reaction mixture was stirred at 140 °C in the Schlenk tube for 3 hours, then cooled to room temperature, diluted with dichloromethane (10 mL) and then filtered through a pad of celite. Volatiles were removed under vacuum. Analysis by ^{1}H-NMR showed 20% conversion to product. Flash chromatography (silica gel; ethyl acetate : pentane = 1 : 10 as eluent) afforded **7a**/**7a**-$\boldsymbol{d_5}$ (8 mg, 20%) and recovered **3a**/**3a**-$\boldsymbol{d_6}$ (27 mg, 50%). The deuterium content in the starting mixture of substrates **3a**/**3a**-$\boldsymbol{d_6}$ and in product **7a**/**7a**-$\boldsymbol{d_5}$ was determined by ^{1}H NMR.



3a + **3a**-d_6 → **7a**-H + **7a**-d_5

20% conversion

run 1:	**[3a**-H]$_0$/**[3a**-d_6]$_0$ = 0.90	**7a**-H/**7a**-d_5 = 2.33	**KIE = 1.82**
run 2:	**[3a**-H]$_0$/**[3a**-d_6]$_0$ = 1.27	**7a**-H/**7a**-d_5 = 3.76	**KIE = 1.86**
run 3:	**[3a**-H]$_0$/**[3a**-d_6]$_0$ = 1.00	**7a**-H/**7a**-d_5 = 2.57	**KIE = 1.73**

KIE = 1.80

Scheme S1. Intermolecular KIE of C(sp^3)-H activation.

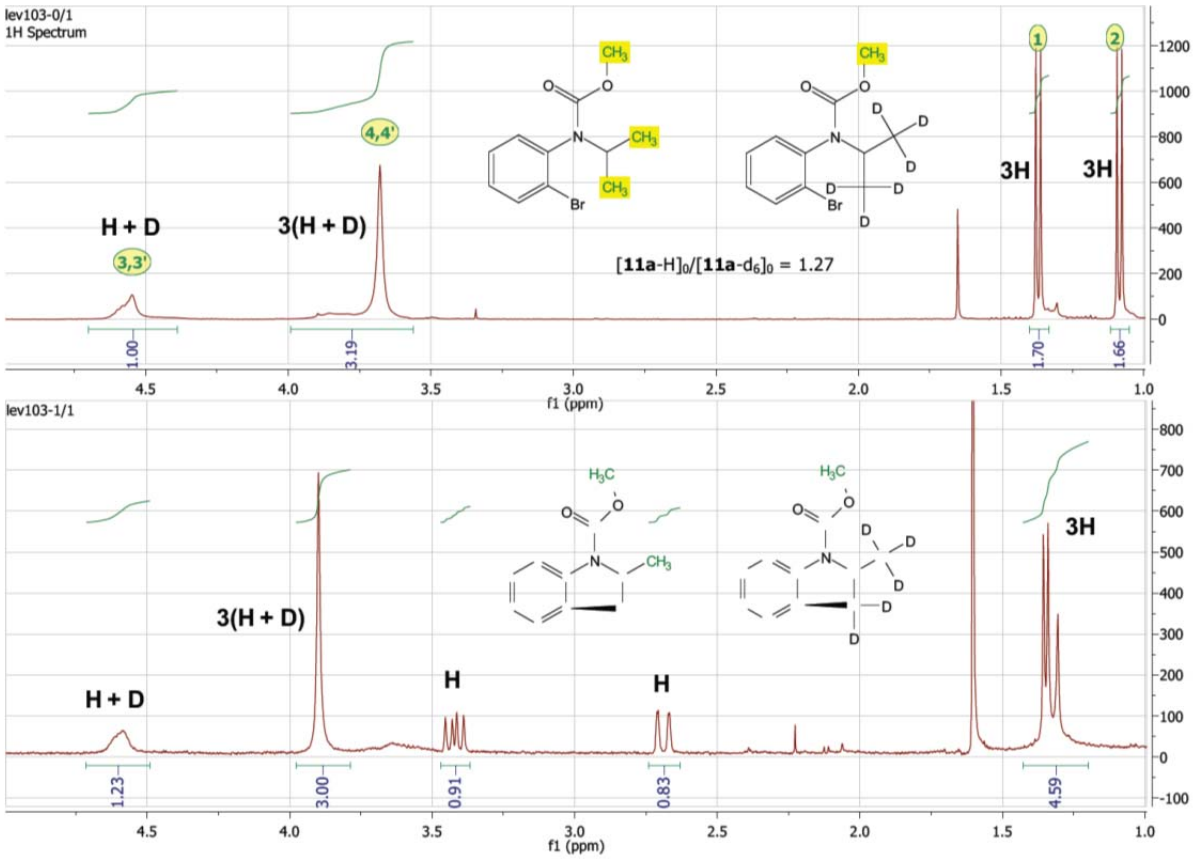


Figure S1. ^{1}H NMR spectra of KIE experiments: initial mixture of substrates **3a**-H/**3a**-d_6 (top), mixture of products **7a**-H/**7a**-d_5 after 3 h (bottom).

Calculation of KIE effect k_H/k_D.

Assuming first order kinetics in substrates **3a-H** and **3a-D**

$$3a_H \xrightarrow{k_H} 7a_H$$
$$3a_D \xrightarrow{k_D} 7a_D \qquad (1)$$

We can divide both kinetic laws to obtain equation (3) for KIE:

$$KIE = {k_H}/{k_D} \qquad (2)$$

$$KIE\,\frac{d[3a_D]}{[3a_D]} = \frac{d[3a_H]}{[3a_H]} \qquad (3)$$

Integration of eq. (3) gives eq. (4):

$$KIE = \frac{\ln([3a_H]/[3a_H]_0)}{\ln([3a_D]/[3a_D]_0)} \qquad (4)$$

Now we can express conversions of both substrates through the experimentally measured conversion:

$$y = \frac{[7a_H]+[7a_D]}{[3a_H]_0+[3a_D]_0} = \frac{[3a_H]_0+[3a_D]_0-[3a_H]+[3a_D]}{[3a_H]_0+[3a_D]_0} \qquad (5),$$

initial ratio of substrates:

$$c_0 = [3a_H]_0/[3a_D]_0 \qquad (6)$$

and actual ratio of products:

$$d = [7a_H]/[7a_D] \qquad (7)$$

From equations (5-7) we obtain:

$$[3a_H]/[3a_H]_0 = 1 - y\cdot\frac{1+1/c_0}{1+1/d} \qquad (8)$$

and

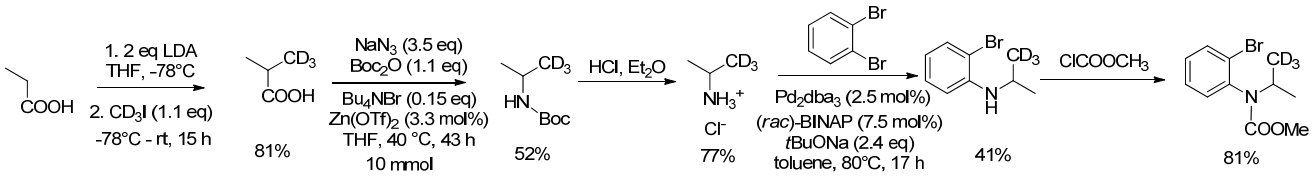
$$[3a_D]/[3a_D]_0 = 1 - y\cdot\frac{1+c_0}{1+d} \qquad (9)$$

Combining equations (4) with (8) and (9) gives the final equation (10) for KIE:

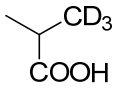
$$KIE = \frac{\ln\left[1 - y\cdot\frac{1+1/c_0}{1+1/d}\right]}{\ln\left[1 - y\cdot\frac{1+c_0}{1+d}\right]} \qquad (10)$$

3.2. Intramolecular KIE

3.2.1 Synthesis of substrate

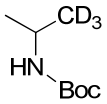


Isobutyric acid-d_3



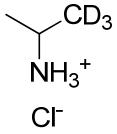
The LDA solution was prepared by dropwise addition of *n*BuLi solution (1.6 M in hexanes, 66 mmol) to the solution of *i*Pr$_2$NH (9.3 ml, 66 mmol) in 100 ml of THF at -78°C. After stirring for 30 min at 0°C, the mixture was cooled to -78°C and propionic acid (2.25 ml, 30 mmol) dissolved in THF (10 ml) was added dropwise. The reaction mixture was stirred for 30 min at -78°C and iodomethane-d_3 (2.1 ml, 33 mmol) was added. The mixture was stirred at rt overnight, poured into ice water (60 ml), and the organic layer separated. The aqueous layer was acidified with aqueous hydrogen chloride (2M) and extracted with diethyl ether (9x50 ml). The combined organic extract was washed with water (6 ml), aqueous sodium chloride (saturated; 6 ml), dried (MgSO,), and the solvent removed. The residual oil was distilled (60 °C at 3 mbar) to give isobutyric acid-d_3 as a liquid (2.20 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 2.62 (q, J = 7.0 Hz, 1H), 1.25 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz): δ = 18.9, 33.8, 183.9. ^{2}H NMR (500 MHz, $CDCl_3$): 1.19 (1D).

tert-butyl isopropylcarbamate-d_3



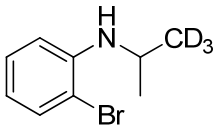
To a solution of sodium azide (2.27 g, 35.0 mmol), tetrabutylammonium bromide (484.0 mg, 1.5 mmol), zinc triflate (II) (120.0 mg, 330 µmol) and d_3-isobutyric acid (910 mg, 10 mmol) in THF (100 mL) was added di-*tert*-butyldicarbonate (2.53 mL, 11.0 mmol). The resulting mixture was then stirred at 40 °C for 43 h. After completion a 10% solution of $NaNO_2$ (30 mL) was added. The mixture was then diluted with ethyl acetate (30 mL), and the resulting mixture was stirred during 20 min at room temperature. The aqueous layer was extracted with ethyl acetate (3 x 40 mL) and the combined organic layers were washed with saturated NH_4Cl (2 x 30 mL), with saturated $NaHCO_3$ (2 x 30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude carbamate was purified by flash chromatography on silica gel to give 840 mg (52% yield) of product as white crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (s, 1H), 3.74 (s, 1H), 1.45 (s, 9H), 1.14 (d, J = 6.6 Hz, 3H).

Iso-propylamine-d_3 hydrochloride



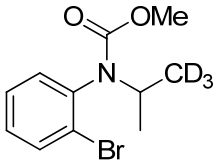
tert-butyl *iso*-propylcarbamate-d_3 (840 mg, 5.2 mmol) was dissolved in ethereal 2 M HCl (29 mL). The solution was stirred for 40 h, during which a precipitate was formed. The crystals were filtered off, washed with ether, and dried. This afforded the ammonium salt (395 mg, 77%) as yellowish solid. ^{1}H NMR (D_2O, 300 MHz): 3.36 (m, 1H), 1.18 (d, J = 7 Hz, 3H). NMR data were in agreement with a literature report for the *tert*-butyl *iso*-propylcarbamate.

2-Bromo-*N*-isopropylaniline-d_3:

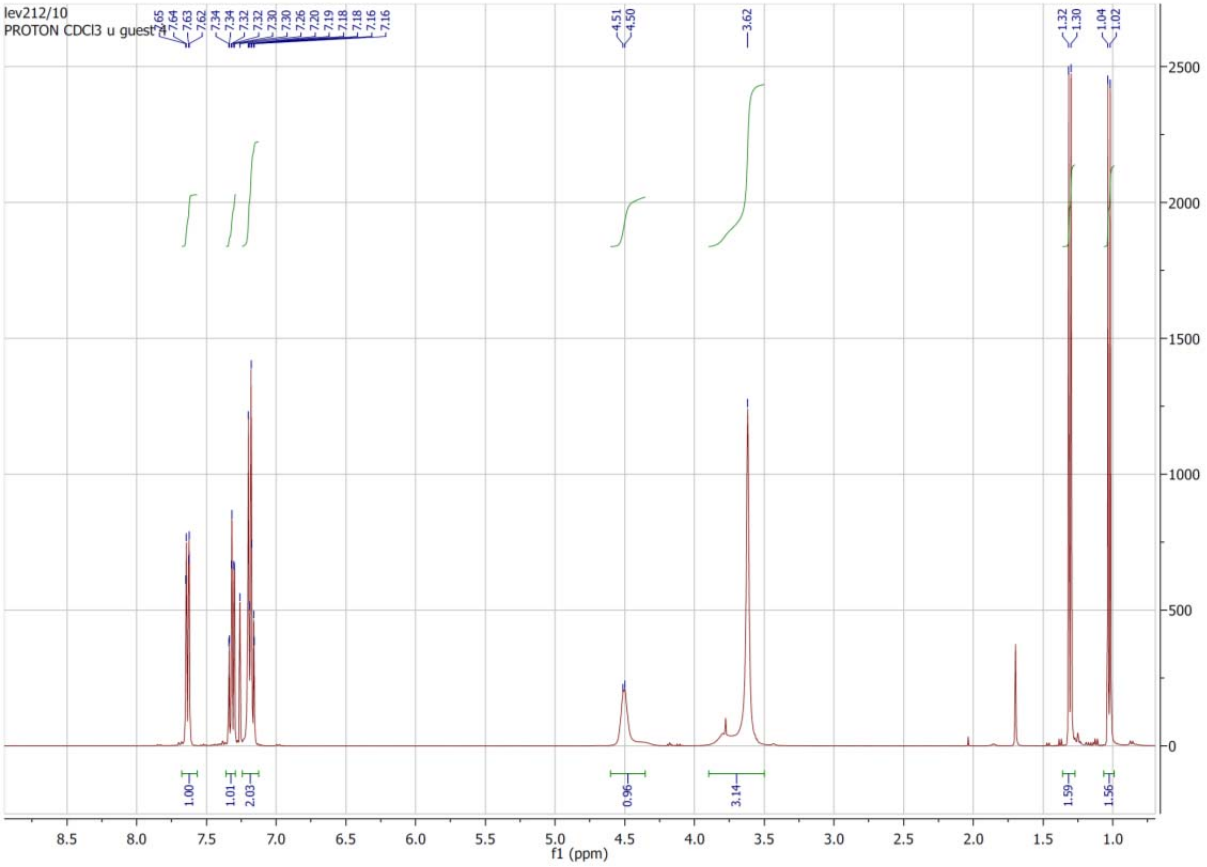


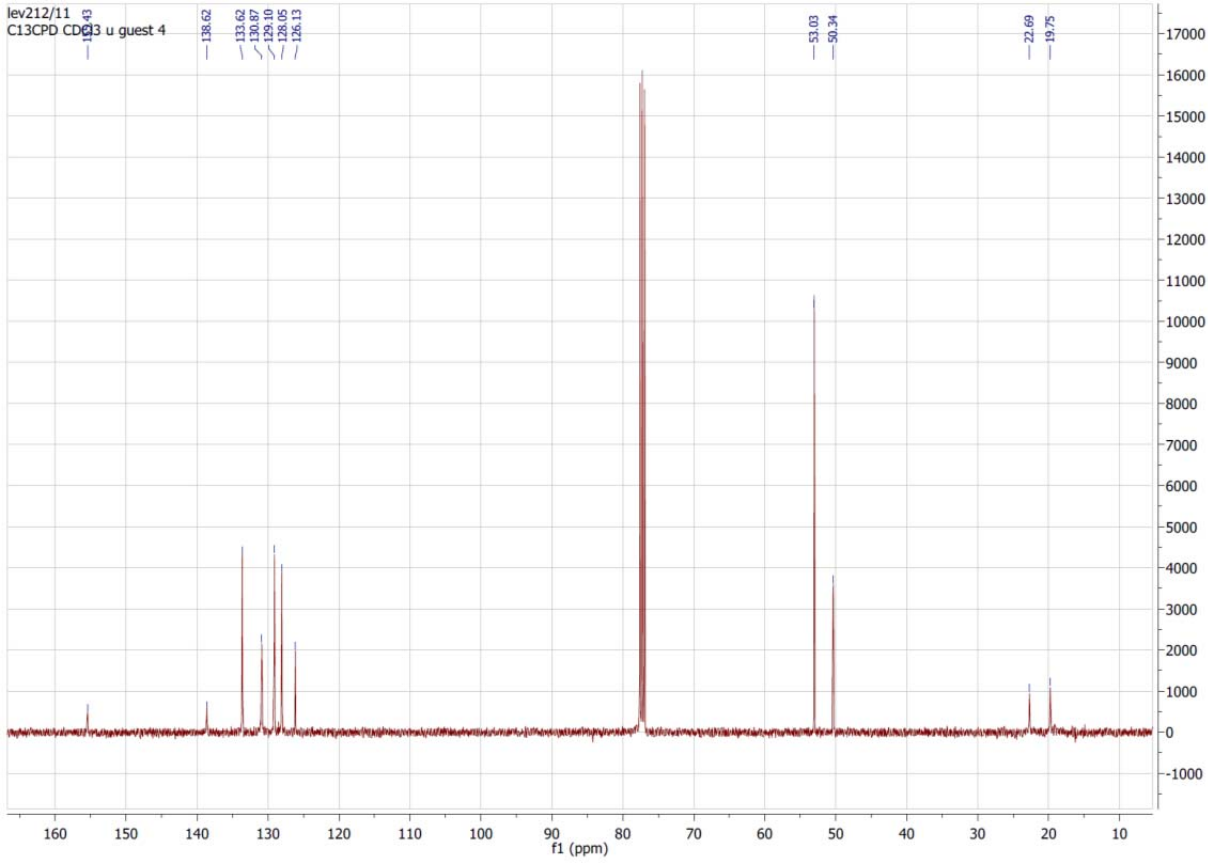
$Pd_2(dba)_3$ (103.5 mg, 2.5 mol%), *rac*-BINAP (186.9 mg, 7.5 mol%), and sodium *tert*-butoxide (922.6 mg, 9.6 mmol) were successfully filled into a microwave vial. After the vial was evacuated and backfilled with nitrogen, dry toluene (10 mL), isopropylamine-d_3 hydrochloride (395 mg. 4.0 mmol) and 1,2-dibromobenzene (944 mg, 4 mmol) were added under nitrogen. The vial was capped and the resulting reaction mixture was stirred at 80 °C for 17 hours. The reaction mixture was cooled down to room temperature and diluted with ethylacetate (10 ml) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under high vacuum. The residue was purified by flash column chromatography (silica gel; pentane as eluent) to afford 355 mg (41% yield) of product as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.27 (d, J = 6.4 Hz, 3H), 3.66 (d, J = 6.4 Hz, 1H), 4.17 (br s, 1H), 6.55 (td, J = 7.6, 1.5 Hz, 1H), 6.63 (dd, J = 7.6, 1.5 Hz, 1H), 7.18 (ddd, J = 8.5, 7.3, 1.5 Hz, 1H), 7.39 (dd, J = 7.9, 1.5 Hz, 1H). ^{13}C NMR (100 MHz): δ = 22.4 (hept, J = 19.2 Hz, CD_3), 23.1, 44.3, 110.0, 112.0, 117.4, 128.6, 132.7, 144.5. ^{2}H NMR (500 MHz, $CDCl_3$): 1.25 (s, 3D).

Methyl (2-bromophenyl)(isopropyl)carbamate-d_3 **3a**-d_3:



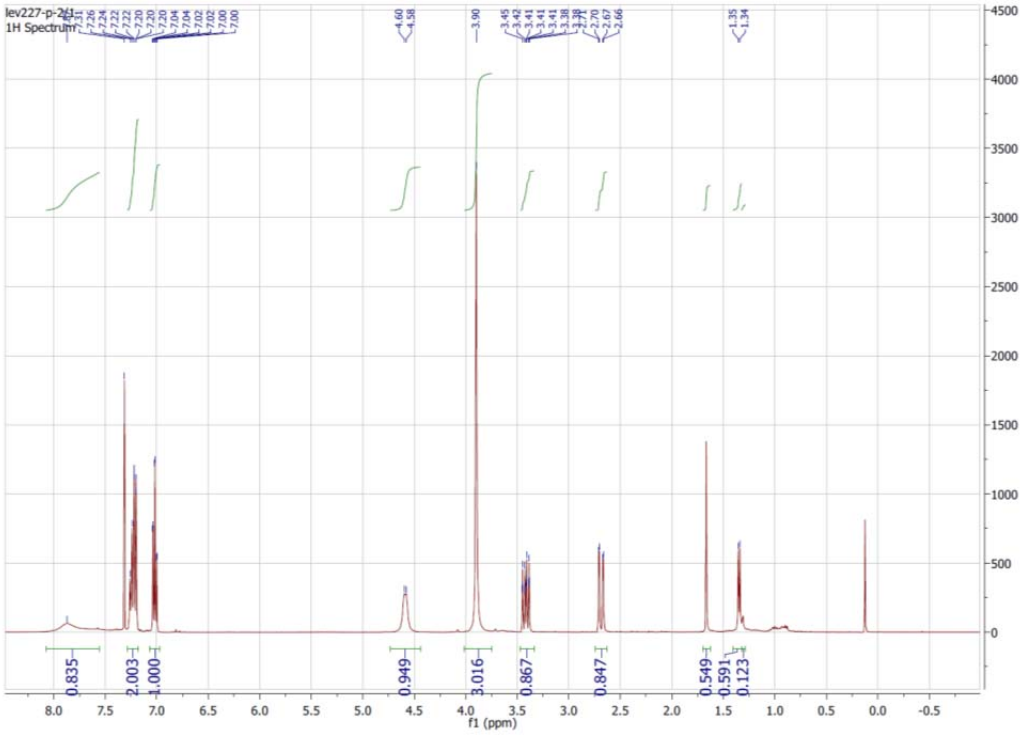
Colorless oil, 81% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.03 (d, J = 6.9 Hz, 1.5H), δ 1.31 (d, J = 6.6 Hz, 1.5H), 3.62 (s, 3H), 4.50 (m, 1H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.63 (d, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 19.8, 22.7, 50.3, 53.0, 126.1, 128.0, 129.1, 130.8, 133.6, 138.6, 155.4. ^{2}H NMR (500 MHz, $CDCl_3$): 1.00 (s, 1D), 1.28 (s, 1D). HRMS calcd. for $C_{12}H_{12}D_3BrN_1O_2$ 275.0468, found 275.0472 (accuracy 1.1 ppm).


lev212/10
PROTON CDCl3 u guest
7.65
7.64
7.63
7.62
7.34
7.34
7.32
7.32
7.30
7.30
7.26
7.20
7.19
7.18
7.18
7.16
7.16
7.16
4.51
4.50
3.62
1.32
1.30
1.04
1.02
1.00
1.01
2.03
0.96
3.14
1.59
1.56
f1 (ppm)

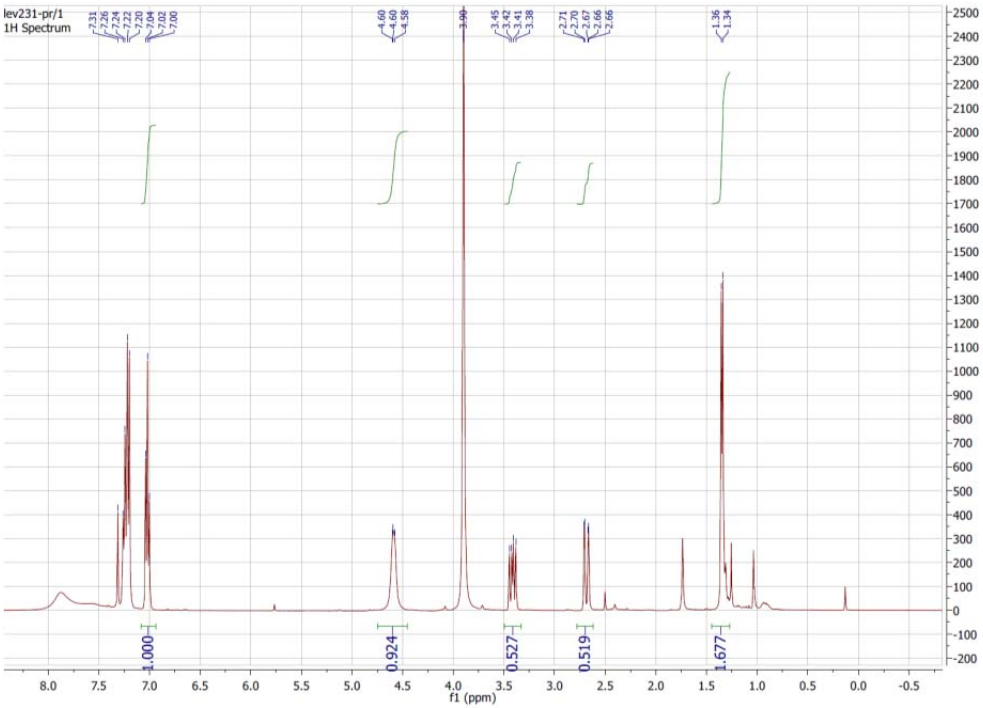

lev212/11
C13CPD CDCl3 u guest 4
138.62
133.62
130.87
129.10
128.05
126.13
53.03
50.34
22.69
19.75
f1 (ppm)

3.2.2 Kinetic isotope effect (KIE) measurement

Racemic C-H activation of carbamate **3a**-d_3 was carried out according to **GP4** with 0.20 mmol of substrate using **6** as a ligand. Usual work up gives 7.5 mg (39 %) of **7a**-d_3/d_2 as a colorless oil. KIE effect k_H/k_D = [H-act]/[D-act] = [**7a**-d_2]/[**7a**-d_3] = 5.5.

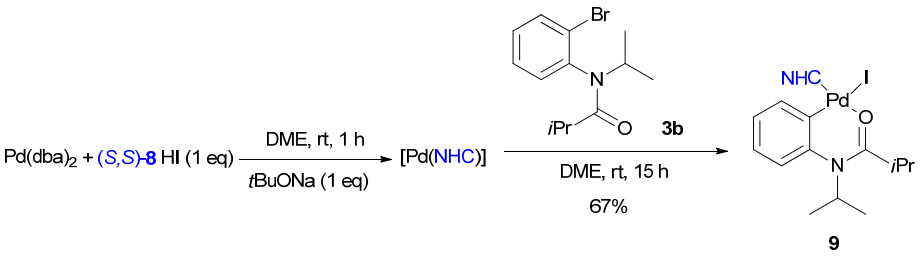


Asymmetric C-H activation of carbamate **3a**-d_3 was carried out according to **GP5** with 0.20 mmol of substrate using (*S*,*S*)-**8** as a ligand. Usual work up gives 33 mg (85 %) of (*S*)-**7a**-d_3/d_2 as a colorless oil. KIE effect k_H/k_D = [H-act]/[D-act] = 1.1.



4. Isolation of intermediates

4.1. Synthesis of complex 9



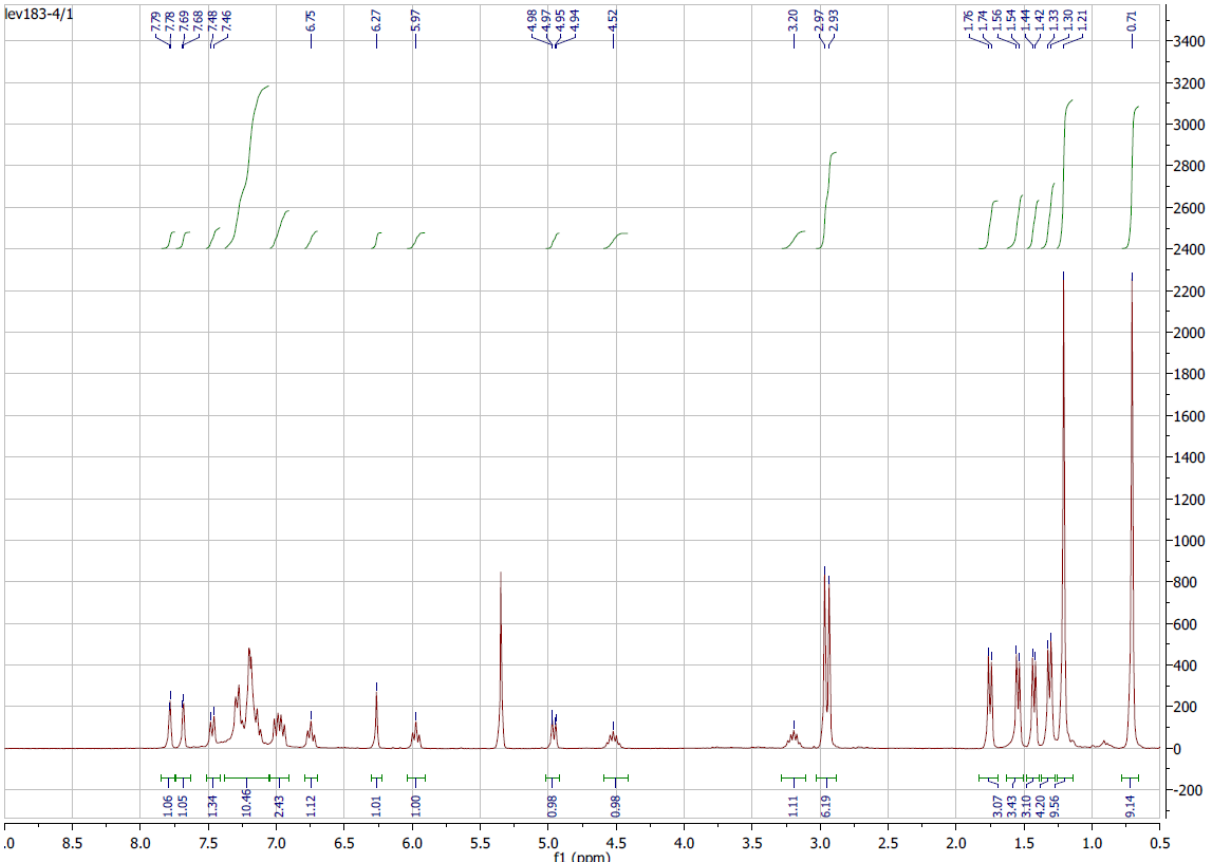
9

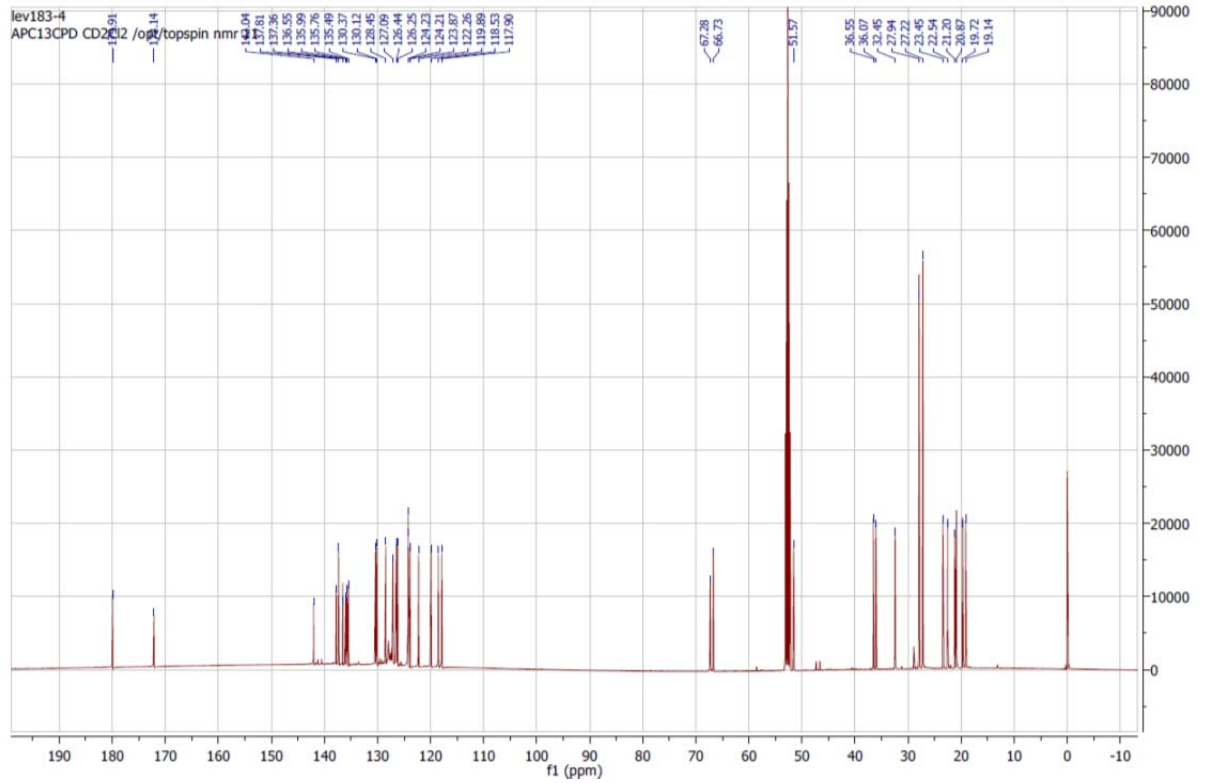
$Pd(dba)_2$ (115 mg, 0.2 mmol, 1.0 eq.), chiral carbene precursor (*S*,*S*)-**8**-HI (103.4 mg, 0.2 mmol, 1.0 eq.) and NaO*t*Bu (19.2 mg, 0.2 mmol, 1.0 eq.) were placed into a dried Schlenk tube under N_2. Dimethoxyethane (DME) (2 mL) (freshly distilled over Na and benzophenone) was added and the reaction mixture stirred for one hour at room temperature. Substrate **3b** (56.6 mg, 0.2 mmol, 1.0 eq.) was then added as a solution in DME (2 mL). The reaction was stirred at ambient temperature for 15 hours and then quenched with aq. NH_4Cl and filtered through celite. After evaporation of volatiles, the residue was purified by f.c. over SiO_2 (cyclohexane/EtOAc 5/1) followed by f.c. over SiO_2 (cyclohexane/CH_2Cl_2 gradient from 1/1 to 1/3) to give complex **9** (110 mg, 67%) as an off-white solid. The crystals suitable for X-ray analysis were obtained by diffusion of hexane into an etheral solution of complex.

(*S*,*S*)-**9:**

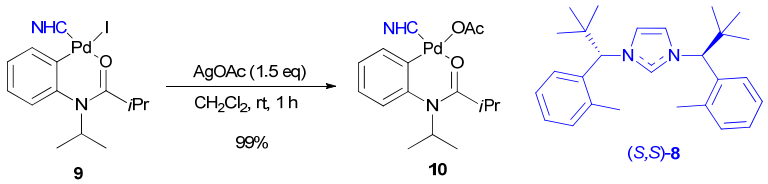
$[\alpha]_D^{22}$ = -125.0 (*c* = 1.0 in CH_2Cl_2), m.p. 230 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.11 – 7.05 (m, 3H), 7.02 (td, *J* = 7.5, 1.4 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.65 – 6.61 (m, 1H), 6.15 (s, 1H), 5.86 (td, *J* = 7.7, 1.3 Hz, 1H), 4.85 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.41 (hept, *J* = 6.9 Hz, 1H), 3.08 (hept, *J* = 6.6 Hz, 1H), 2.85 (s, 3H), 2.82 (s, 3H), 1.64 (d, *J* = 6.9 Hz, 3H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.09 (s, 9H), 0.59 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.91, 172.14, 142.04, 137.81, 137.36, 136.55, 135.99, 135.76, 135.49, 130.37, 130.12, 128.45, 127.09, 126.44, 126.25, 124.23, 124.21, 123.87, 122.26, 119.89, 118.53, 117.90, 67.28, 66.73, 51.57, 36.55, 36.07, 32.45, 27.94, 27.22, 23.45, 22.54, 21.20, 20.87, 19.72, 19.14. HRMS (EI): calcd. for $C_{40}H_{54}N_3OPd$ ($[M-I]^+$): 698.3296, found: 698.3274. IR (neat): υ = 2960 (m), 1672 (w), 1583 (s), 1551 (m), 1422 (s), 1364 (m), 1260 (m), 1227 (m), 1196 (m), 1162 (m), 1094 (m), 1027 (m), 745 (s) cm^{-1}.

Supporting Information for Chem. Sci.





4.2. Synthesis of complex 10



Complex **9** (58.0 mg, 0.07 mmol) and silver acetate (17.6 mg, 0.105 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry CH_2Cl_2 (1 mL) was added under nitrogen. The resulting reaction mixture was stirred at room temperature for 60 min. The reaction mixture was diluted with dichloromethane (2 mL) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was recrystallized from diethyl ether/hexane mixture to give complex **10** (20 mg, 38%) as an off-white solid.

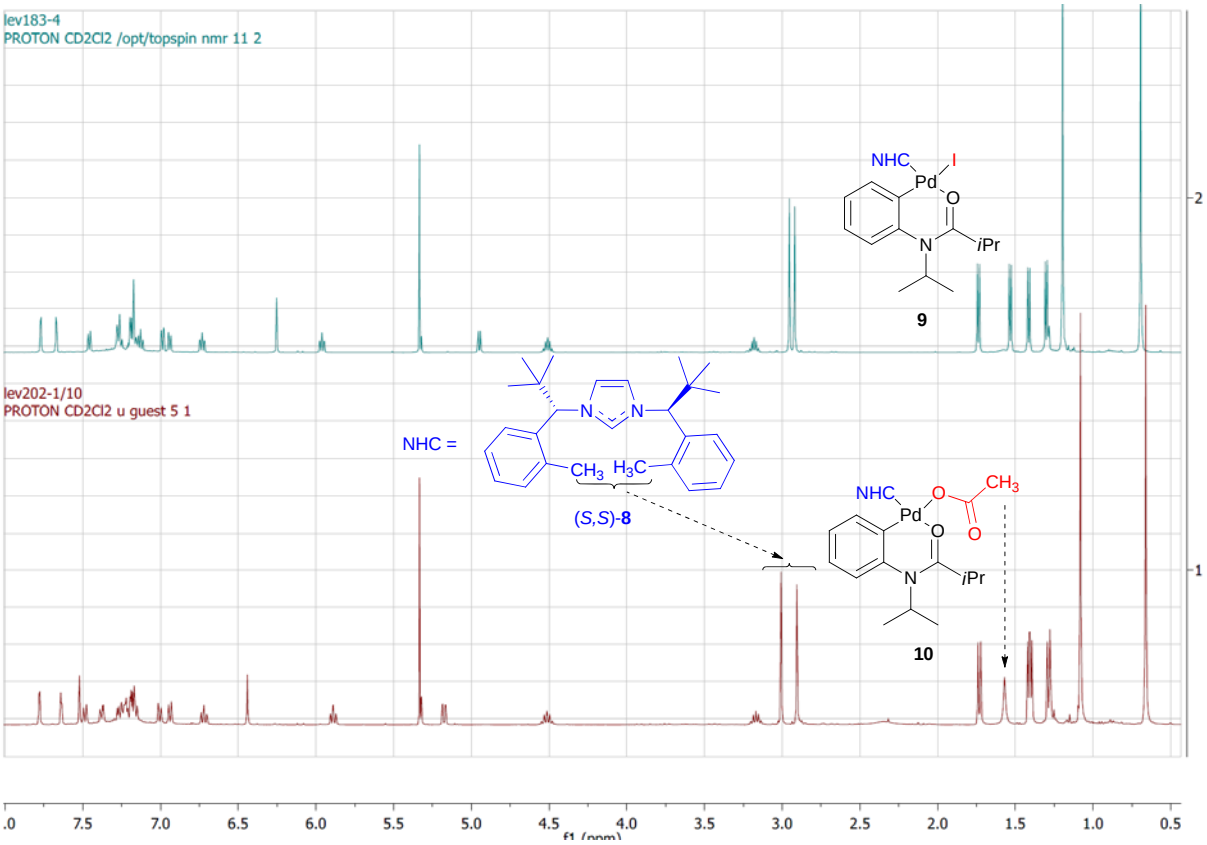
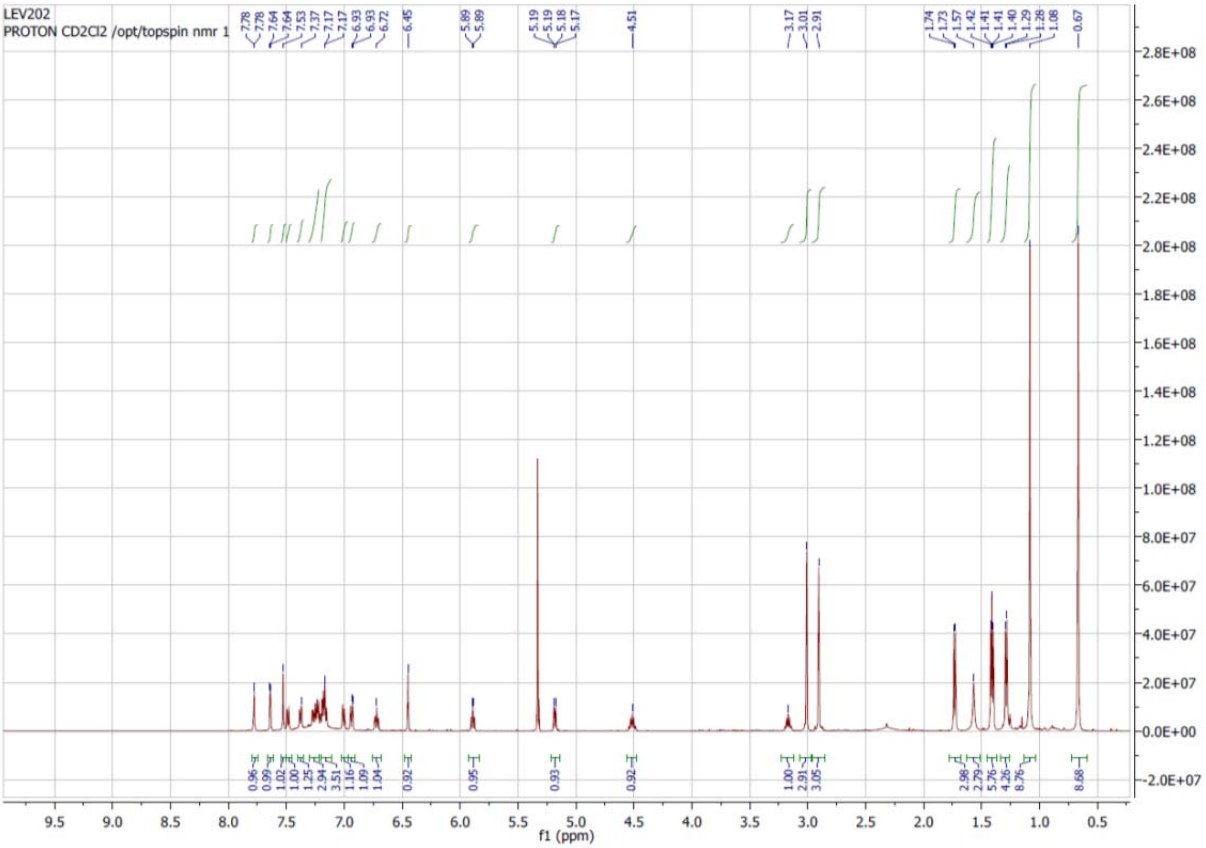


Figure S2. ^{1}H NMR spectra of complexes **9** and **10** recorded in CD_2Cl_2.

(*S,S*)-**10:**

$[\alpha]_D^{22}$ = -6.3 (*c* = 1.0 in CH_2Cl_2), m.p. 110 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (d, *J* = 2.2 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.52 (s, 1H), 7.49 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.29 – 7.21 (m, 2H), 7.18 (ddd, *J* = 7.8, 3.1, 1.7 Hz, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.94 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.72 (ddd, *J* = 8.2, 7.1, 1.6 Hz, 1H), 6.44 (s, 1H), 5.92 – 5.86 (m, 1H), 5.18 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.51 (hept, *J* = 6.9 Hz, 1H), 3.17 (hept, *J* = 6.6 Hz, 1H), 3.01 (s, 3H), 2.91 (s, 3H), 1.73 (d, *J* = 6.9 Hz, 3H), 1.57 (br s, 3H, $COCH_3$), 1.41 (d, *J* = 6.5 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.7 Hz, 3H), 1.08 (s, 9H), 0.66 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 181.54, 176.50, 173.73, 140.40, 139.81, 138.44, 137.83, 137.50, 137.35, 137.18, 131.61, 131.36, 128.89, 128.24, 127.62, 127.44, 125.51, 125.36, 124.71, 123.16, 120.91, 119.62, 119.29, 68.18, 67.89, 52.75, 37.42, 37.37, 33.53, 28.38, 27.87, 24.80, 24.64, 22.91, 22.42, 22.09, 20.75, 20.28. IR (neat): υ = 2965 (m), 1582 (s), 1548 (m), 1419 (m), 1368 (s), 1321 (m), 1260 (s), 1227 (m), 1196 (m), 1164 (m), 1093 (s), 1023 (m), 799 (s), 746 (vs) cm^{-1}.



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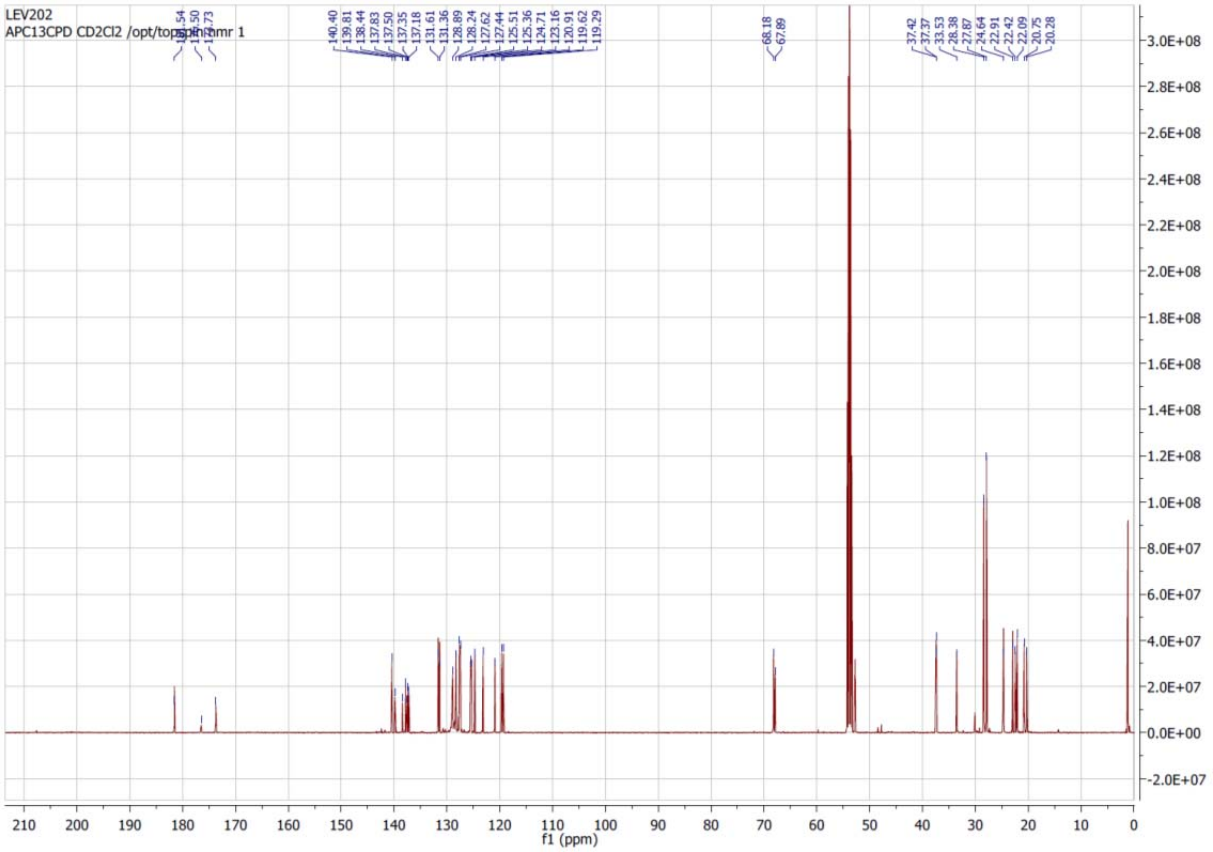


4.3. Catalytic and stoichiometric studies with complexes 9 and 10

Typical procedure for the catalytic reaction with complex 9 (Table 6, entry 3).

Amide **3b** (28.3 mg, 0.1 mmol), cesium carbonate (48.7 mg, 0.15 mmol) and cesium pivalate (23.4 mg, 0.1 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, a solution of complex **9** (0.005 mmol) in dry xylenes (1 mL) was added under nitrogen. A solution of cinnamylacetate (0.006 mmol) in dry xylenes (1 mL) was subsequently added. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; ethyl acetate/pentane mixtures as eluent) to afford product **7b** in 99% yield and 86% ee.

Typical procedure for the stoichiometric reaction with complex 9 (Table 7, entry 5).

Cesium carbonate (97.5 mg, 0.3 mmol, 15 eq) and cesium pivalate (46.8 mg, 0.2 mmol, 10 eq) were placed in a Schlenk flask. Solution of complex **9** (0.02 mmol, 1 eq) and hexamethylbenzene (0.003 mmol, 0.16 eq) in dry xylenes (1.0 ml) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and analysed by ^{1}H NMR and HPLC.

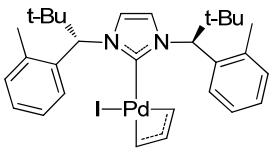
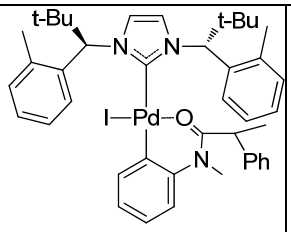
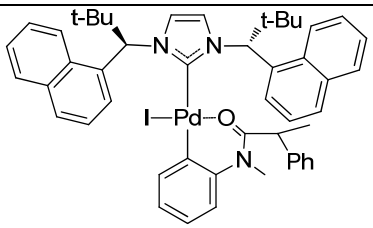
5. Computational details

Density functional [M06-L/LANL2DZ,6-31G(d,p)] calculations were used to examine important segments of the potential energy surface for the C(sp^3)-H arylation.[vi,vii] The geometry optimizations have been carried out using standard double-ζ basis sets (LANL2DZ) and effective core potentials (ECPs) for the heavy elements (Pd, Cl, Br, I). The 6-31G(d,p) basis set on other atoms (N, H, C, O) was used. Single point PCM calculations in xylene of all the gas phase optimized structures yielded the solvent corrected energy E_{solv}.[viii] The united atom topological model with UAHF radii was used. For the PCM calculations, the same level of theory as in the gas phase calculations was used. Thermochemical corrections to free energies (G_{298}) and enthalpies at 298.15 K (H_{298}), as well as at 413.15 K, have been calculated at the same level as that used for geometry optimization. Gas phase Gibbs free energy corrections G_{corr} were considered for each species and the total Gibbs free energy G of each optimized structure was taken as $G = E_{solv} + G_{corr}$. A frequency calculation was performed on all intermediates and transition states to verify minima and first order saddle points, respectively. Intrinsic reaction coordinate (irc) calculations were used to connect transition states **TS1-2, TS4-5** and **TS4-5$_{trans}$** with the corresponding intermediates **INT1**, **INT2'$_{Br}$** and **INT4**, **INT5**, and **INT4$_{trans}$**, **INT5$_{trans}$** respectively. The calculations were performed with the Gaussian09 package.[ix]

5.1. Methods screening: comparison with the known x-ray structures.

5.1.1 Basis set screening

Table S1.1. Basis set screening: RMSD values between x-ray and B3LYP/* optimized structures.

Basis set	 com_a	 com_b	 com_c	Averaged RMSD
bs1	0.24366	0.75605	0.32999	**0.44323**
bs2	0.24294	0.75840	0.50097	0.50077
bs3	0.25774	0.78206	0.45126	0.49702
bs4	0.25587	0.77405	0.34473	**0.45822**
Averaged	0.25005	0.76764	0.40674	

* Error terminations after 50 cycles (forces converged, displacement not).

Table S1.2. Basis set screening: computation times (in h) on 4p computers.

Basis set	com_a	com_b	com_c
bs1	17.0	38.0	47.0
bs2	16.0	38.0	45.5
bs3	27.0	61.0	67.5
bs4	32.0	70.0	67.0

Abbreviations:

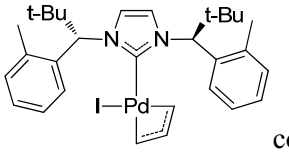
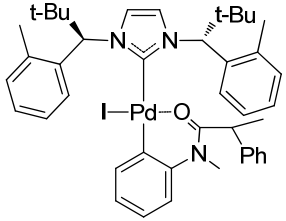
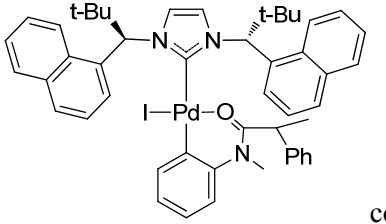
bs1: LANL2DZ(d) on Pd, I; 6-31G(d,p) on N, C, O; 6-31G(d) on H.

bs2: LANL2DZ on all atoms.

bs3: SDDAll on Pd, I (takes MWB28/46); 6-31G(d,p) on N, H, C, O.

bs4: MHF28 on Pd; MDF46 on I; 6-31G(d,p) on N, H, C, O.

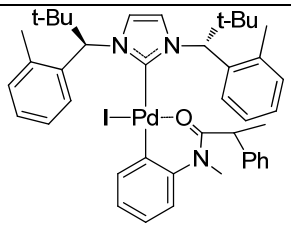
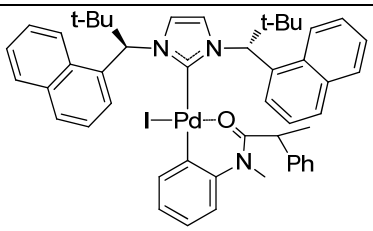
Table S1.3. Basis set screening: bond lengths in x-ray and B3LYP/* optimized structures.

Bond length, Å	 com_a			 com_b			 com_c		
	Pd-I	Pd-C(NHC)	Pd-C2(allyl)	Pd-I	Pd-C(NHC)	Pd-C(Ar)	Pd-I	Pd-C(NHC)	Pd-C(Ar)
x-ray	2.65001	2.04356	2.15581	2.71006	1.95116	1.98227	2.69555	1.96499	2.00388
bs1	2.74884	2.07369	2.21246	2.79824	2.00388	2.03295	2.81109	2.00737	2.03098
bs2	2.74088	2.06091	2.24734	2.79175	2.00474	2.04259	2.80092	2.00575	2.04409
bs3	2.73108	2.06351	2.19130	2.77802	1.99854	2.02754	2.78891	2.00029	2.02822
bs4	2.71472	2.10820	2.23199	2.76216	2.03548	2.05682	2.77225	2.03887	2.05455

Obtained data (Table S1.1) show that basis sets bs1 and bs4 show better performance in matching x-ray structures than bs2 and bs3 basis sets. Comparison of cpu times (Table S1.2) shows that employing bs4 basis set is much more time-consuming than basis set bs1 (*ca.* 2 times for studied systems). Examination of bond lengths between Pd and neighbouring atoms (Table S1.3) shows that Pd-I bond length is generally overestimated by more than 0.06 Å, whereas overestimation of Pd-C bonds is lower. Basis set bs4 shows worse performance for the latter.

5.1.2. DFT method screening

Table S1.4. DFT methods screening: RMSD values between x-ray and DFT optimized structures.

DFT	Basis set	 com_b	 com_c	Averaged RMSD
B3LYP	bs1	0.75605	0.32999	0.54302
	bs4	0.77405	0.34473	0.55939
B3PW91	bs1	0.71725	0.35383	0.53554
	bs4	0.73489	0.34511	0.54000
PBE1PBE	bs1	0.59119	0.26415	**0.42767**
	bs2	0.60274	0.26886	0.43580
	bs3	0.61079	0.27075	0.44077
	bs4	0.58665	0.25948	**0.42307**
M06-L	bs1	0.56572	0.41262	**0.48917**
	bs2	0.56916	0.42223	0.49570
	bs3	0.56203	0.41815	0.49009
	bs4	0.54766	0.41269	**0.48018**
B97-D	bs1	0.48066	0.53571	0.50819
	bs4	0.46017	0.52989	0.49503

Abbreviations:

bs1: LANL2DZ(d) on Pd, I; 6-31G(d,p) on N, C, O; 6-31G(d) on H.

bs4: MHF28 on Pd; MDF46 on I; 6-31G(d,p) on N, H, C, O.

*for M06-L and B97-D (in Gaussian 09):

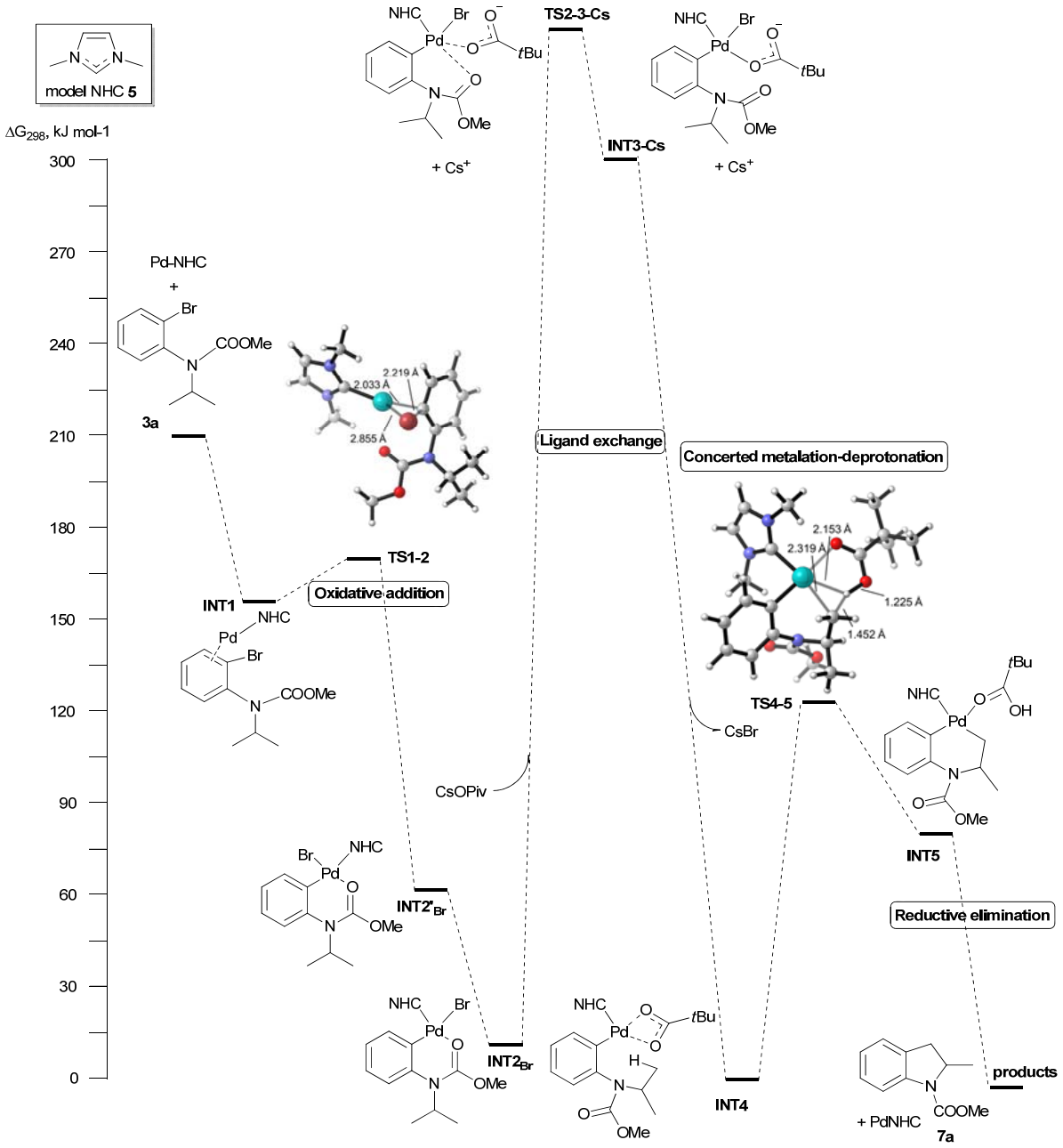
bs1: LANL2DZ on Pd, I; **bs4**: MHF28 on Pd; MWB46 on I;

From this comparison (Table S1.4) it can be seen that PBE1PBE and M06-L methods give the lowest RMSD among studied DFT methods. Combination of these two methods with basis sets bs1 and bs4 shows slightly better performance. Comparison of cpu times (Table S1.5) shows that M06-L method is less time-consuming than PBE1PBE. In conclusion, we chose M06-L/bs1 method for geometry optimization of studied Pd systems.

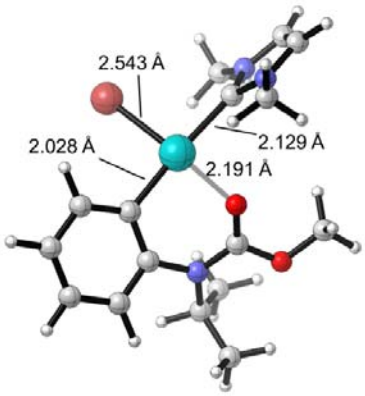
Table S1.5. DFT methods screening: cpu times (in h) pro SCF cycle.

DFT	Basis set	com_b	com_c
B3LYP	bs1	3.04	3.71
	bs4	5.55	5.34
B3PW91	bs1	3.14	3.00
	bs4	4.77	4.55
PBE1PBE	bs1	**2.93**	**3.50**
	bs2	**2.55**	**3.46**
	bs3	3.77	5.56
	bs4	5.29	6.31
M06-L	bs1	**2.34**	**3.03**
	bs2	**2.53**	**3.25**
	bs3	3.15	4.05
	bs4	3.64	2.82
B97-D	bs1	**1.47**	**2.46**
	bs4	**2.30**	**3.34**

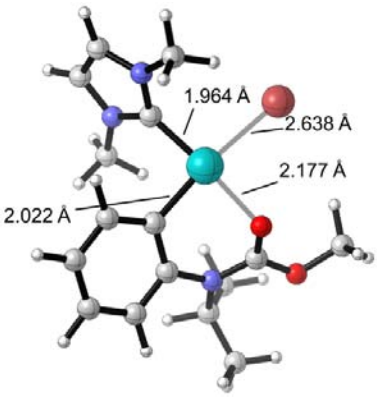
5.2. Catalytic cycle with model NHC 5



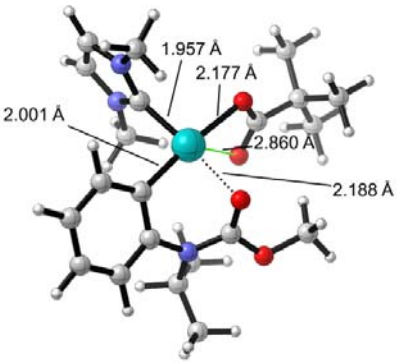
Supporting Information for Chem. Sci.



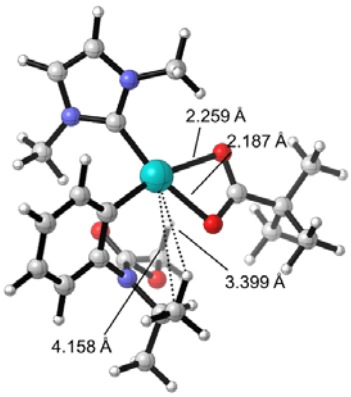
INT2'$_{Br}$



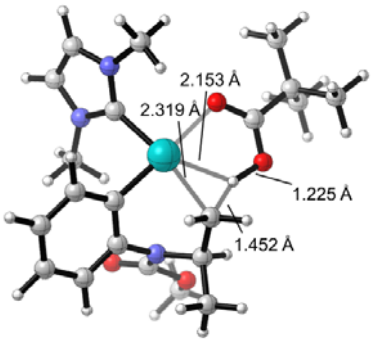
INT2$_{Br}$



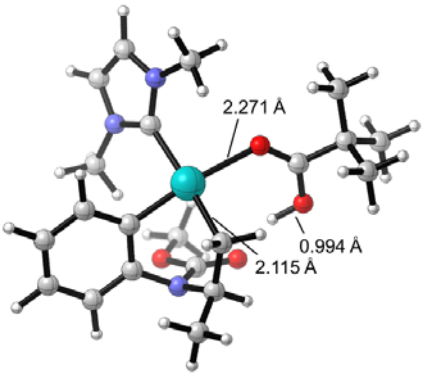
INT2$_{Piv}$



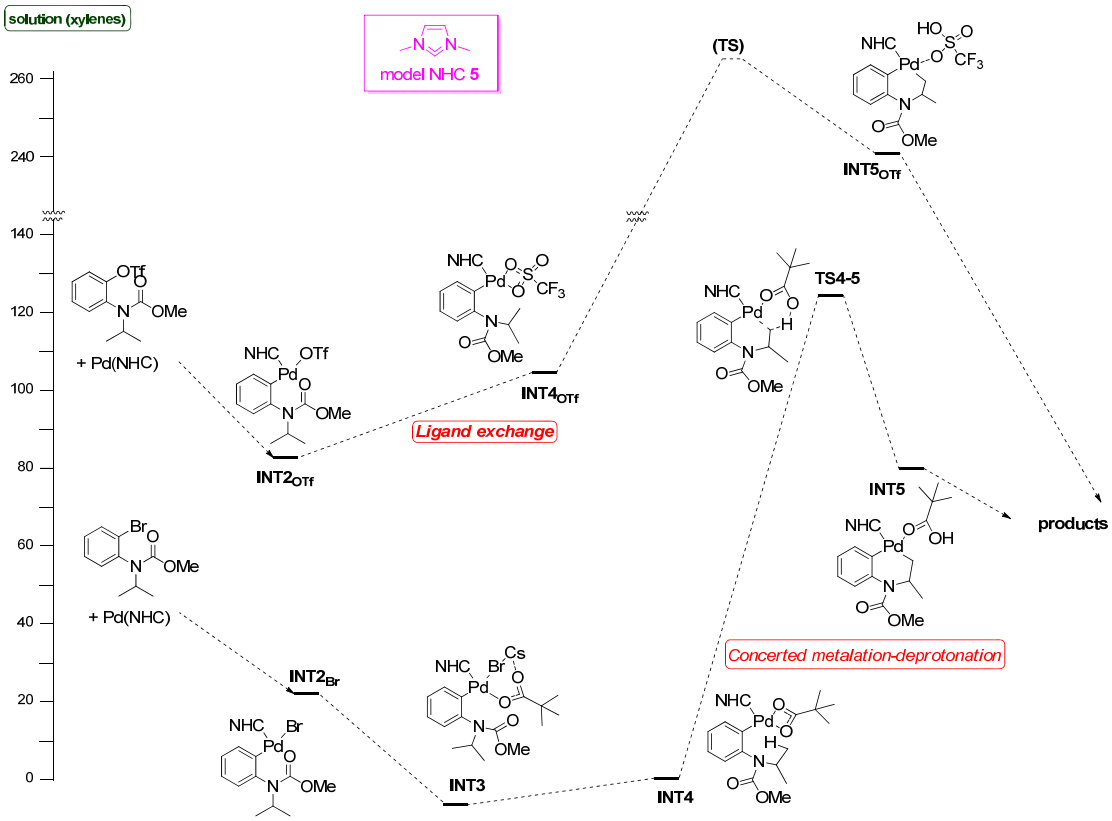
INT4



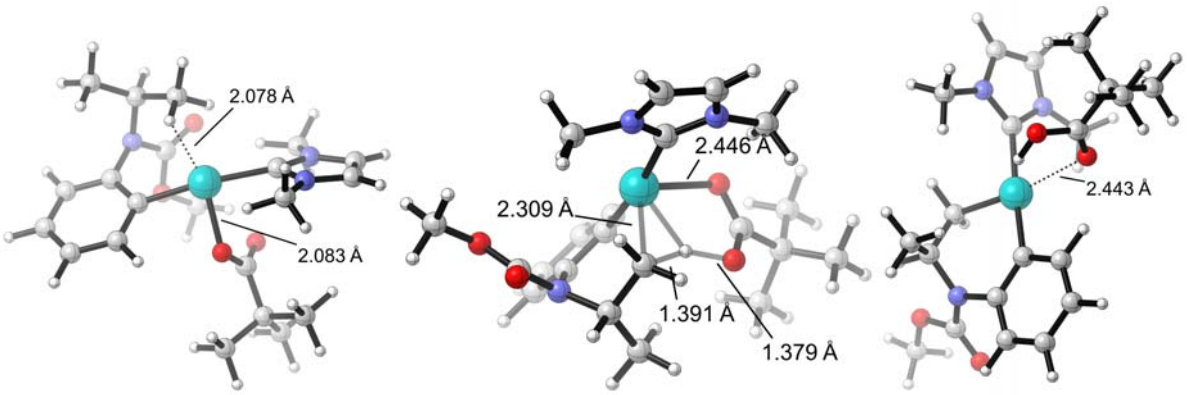
TS4-5



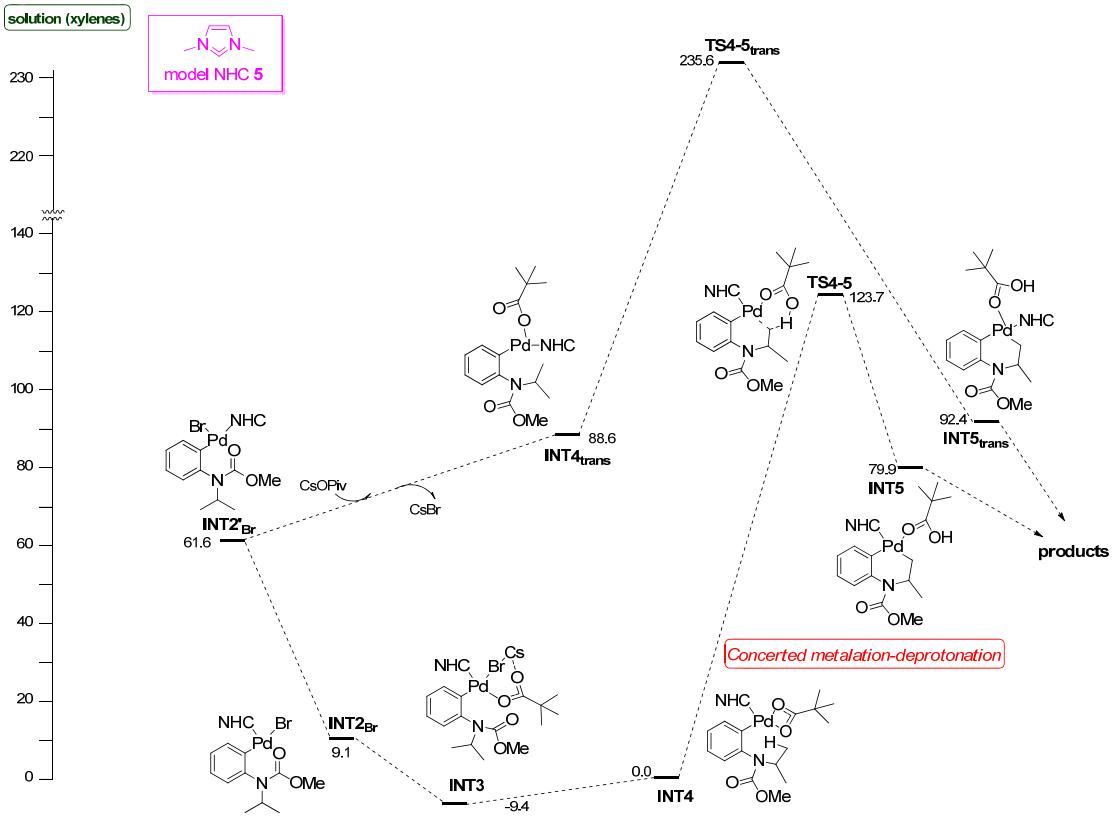
INT5



The Gibbs free energy profile (xylene, 298 K, kJ/mol) for the ligand exchange and CMD steps with triflate.



INT4$_{trans}$ **TS4-5$_{trans}$** **INT5$_{trans}$**



The Gibbs free energy profile (xylene, 298 K, kJ/mol) for the CMD steps with a *trans*-coodinated pivalate.

Table S2.1. Calculated energies of conformers at M06-L level with basis set bs1: LANL2DZ on Pd, I; 6-31G(d,p) on N, C, O, H. Solvent effects in xylenes are included by PCM single point calculations at the same level with UAHF radii. ΔG_{298} are free energies relative to complex **INT4**. Thermal corrections are calculated at 298 K.

	E_{tot}	H_{298}	G_{298}	ΔG_{298} gas phase	E_{tot}	G_{298}	ΔG_{298} solution
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	kJ/mol	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	kJ/mol
Cl	-14.999287	-14.996927	-15.014310		-15.077259	-15.092282	
Br	-13.226077	-13.223717	-13.242253		-13.296367	-13.312543	
I	-11.454416	-11.452056	-11.471264		-11.515958	-11.532806	
*t*BuCOO$^-$	-346.422035	-346.279783	-346.320994		-346.484501	-346.383460	
TfO$^-$	-961.447169	-961.411589	-961.451993		-961.501182	-961.506006	
CsCl	-34.883610	-34.879305	-34.908655		-34.917901	-34.942946	
CsBr	-33.099105	-33.094821	-33.125395		-33.134464	-33.160754	
CsI	-31.315034	-31.310764	-31.342232		-31.348778	-31.375976	
CsOpiv	-366.311144	-366.164811	-366.212981		-366.334942	-366.236779	
CsOAc	-248.376778	-248.319301	-248.360142		-248.402611	-248.385975	
Catalyst							
PdNHC	-431.5812952	-431.443468	-431.488227		-431.589308	-431.496240	
3a				240.6			210.1
1	-645.9077701	-645.655807	-645.715502		-645.915966	-645.723698	
2	-645.9096699	-645.657887	-645.719029		-645.918196	-645.727556	
Oxidative addition							
INT1				180.2			155.5
6pre	-1077.534616	-1077.144127	-1077.230273		-1077.548938	-1077.244595	
TS1-2				191.5			170.6
2	-1077.531418	-1077.141565	-1077.225956		-1077.544312	-1077.238850	
3	-1077.531066	-1077.141391	-1077.225297		-1077.543849	-1077.238080	
$INT2_{Br}$'				94.5			61.6
2.irc	-1077.570559	-1077.178671	-1077.262896		-1077.588019	-1077.280356	
1a	-1077.570778	-1077.178472	-1077.261894		-1077.588300	-1077.279417	
$INT2_{Cl}$	-1079.380985	-1078.988555	-1079.070962	0.0			
1	-1079.380985	-1078.988555	-1079.070962		-1079.399792	-1079.089769	-9.8
2	-1079.380647	-1078.988154	-1079.069299				
3	-1079.378967	-1078.986172	-1079.066505				

	E_{tot}	H_{298}	G_{298}	ΔG_{298} gas phase	E_{tot}	G_{298}	ΔG_{298} solution
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	kJ/mol	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	kJ/mol
4	-1079.379048	-1078.986307	-1079.067589				
7	-1079.378335	-1078.985658	-1079.065994				
8	-1079.378063	-1078.985450	-1079.065769				
9	-1079.376786	-1078.984146	-1079.065324				
10	-1079.374264	-1078.981522	-1079.062040				
11	-1079.376077	-1078.983628	-1079.063423				
12	-1079.373860	-1078.981095	-1079.061231				
13	-1079.373193	-1078.980526	-1079.062057				
14	-1079.372544	-1078.980280	-1079.061039				
$INT2_{Br}$	-1077.590985	-1077.198708	-1077.281585	45.5			
1	-1077.590810	-1077.198540	-1077.281585		-1077.609608	-1077.300383	9.1
2	-1077.590985	-1077.198708	-1077.281050				
3	-1077.589034	-1077.196508	-1077.279556				
4	-1077.590163	-1077.197475	-1077.280324				
7	-1077.589523	-1077.196770	-1077.278403				
8	-1077.589141	-1077.196311	-1077.277561				
9	-1077.586220	-1077.193956	-1077.276916				
$INT2_{I}$	-1075.805907	-1075.413316	-1075.497055	81.0			
1	-1075.805408	-1075.412868	-1075.497055		-1075.822966	-1075.514613	11.7
2	-1075.804955	-1075.412384	-1075.495538				
3	-1075.803118	-1075.410459	-1075.493659				
4	-1075.805907	-1075.413316	-1075.496735				
7	-1075.804211	-1075.411774	-1075.496587				
8	-1075.803271	-1075.411007	-1075.494055				
9	-1075.799524	-1075.407191	-1075.489643				
$INT2_{Ac}$	-1292.868040	-1292.421935	-1292.510838	14.3	-1292.885193	-1292.527992	2.8
4	-1292.868040	-1292.421935	-1292.510838		-1292.885193	-1292.527992	
7	-1292.866919	-1292.420640	-1292.508515		-1292.884894	-1292.526490	

	E_{tot}	H_{298}	G_{298}	ΔG_{298} gas phase	E_{tot}	G_{298}	ΔG_{298} solution
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	kJ/mol	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	kJ/mol
Ligand exchange							
TS2-3-Cs	-1424.055163	-1423.519921	-1423.619867	383.5	-1424.110187	-1423.674891	343.8
INT3-Cs	-1424.075190	-1423.538659	-1423.640504	329.3	-1424.127842	-1423.693156	295.9
4.1	-1424.066963	-1423.529961	-1423.631593		-1424.120140	-1423.684770	
4.2	-1424.075190	-1423.538659	-1423.640504		-1424.127842	-1423.693156	
INT3	-1443.945919	-1443.404646	-1443.511427	-28.2	-1443.978680	-1443.544188	-9.4
4.1	-1443.931202	-1443.391080	-1443.497215		-1443.969794	-1443.535807	
4.2	-1443.945919	-1443.404646	-1443.511427		-1443.978680	-1443.544188	
Triflate intermediates							
$INT2_{OTf}$	-2025.787686	-2025.359486	-2025.453034	146.0	-2025.805559	-2025.471242	84.7
4.2	-2025.787686	-2025.359486	-2025.453034		-2025.805559	-2025.470906	
7.2	-2025.786414	-2025.358311	-2025.453005		-2025.804652	-2025.471242	
$INT4_{OTf}$	-2025.779335	-2025.351031	-2025.445863	164.8	-2025.796286	-2025.462483	107.7
4.1	-2025.778263	-2025.350482	-2025.445863		-2025.794883	-2025.462483	
4.2	-2025.779335	-2025.351031	-2025.443583		-2025.796286	-2025.460533	
7.1	-2025.773919	-2025.346346	-2025.442425		-2025.792557	-2025.461063	
$INT5_{OTf}$				291.9			243.0
5	-2025.727516	-2025.302737	-2025.397457		-2025.741016	-2025.410957	
$INT2_{Piv}$	-1410.800979	-1410.265710	-1410.362073	40.9			
4	-1410.800979	-1410.265710	-1410.362073		-1410.817566	-1410.378660	6.0
7	-1410.799856	-1410.264589	-1410.360854				
8	-1410.799682	-1410.264299	-1410.360587				
1	-1410.795724	-1410.260006	-1410.356537				
2	-1410.794351	-1410.261473	-1410.355864				
3	-1410.790427	-1410.254902	-1410.348122				

	E_{tot}	H_{298}	G_{298}	ΔG_{298} gas phase	E_{tot}	G_{298}	ΔG_{298} solution
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	kJ/mol	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	kJ/mol
CMD step							
INT4	-1410.805447	-1410.269991	-1410.365784	31.1			
4	-1410.805447	-1410.269991	-1410.365784		-1410.819519	-1410.379856	0.0
7	-1410.804016	-1410.268634	-1410.364572				
13	-1410.796560	-1410.261295	-1410.358925				
9	-1410.804846	-1410.269462	-1410.364355				
10	-1410.801297	-1410.265529	-1410.359893				
1	-1410.801082	-1410.264911	-1410.358880				
12	-1410.800842	-1410.265905	-1410.361702				
8	-1410.800405	-1410.265029	-1410.359423				
11	-1410.797860	-1410.262552	-1410.358834				
2	-1410.795874	-1410.260924	-1410.358266				
6	-1410.795960	-1410.260629	-1410.356187				
3	-1410.794398	-1410.259172	-1410.355812				
14	-1410.787935	-1410.252626	-1410.347773				
15	-1410.795839	-1410.260278	-1410.355949				
TS4-5	-1410.771314	-1410.237042	-1410.335132	158.9			123.7
2	-1410.750553	-1410.220932	-1410.317116		-1410.766170	-1410.332733	
3	-1410.750511	-1410.221133	-1410.316874				
4	-1410.745658	-1410.216365	-1410.311034				
5	-1410.746741	-1410.217202	-1410.311518				
12	-1410.751961	-1410.222416	-1410.31513				
INT5	-1410.771314	-1410.237042	-1410.335132	111.6			79.9
1	-1410.758970	-1410.224242	-1410.320716				
2	-1410.757290	-1410.222549	-1410.320087				
3	-1410.765109	-1410.230734	-1410.329120				
4	-1410.763501	-1410.229327	-1410.323582				
5	-1410.771314	-1410.237042	-1410.335132		-1410.785617	-1410.349436	
6	-1410.754491	-1410.220556	-1410.315944				
7	-1410.768475	-1410.234014	-1410.330011				

	E_{tot}	H_{298}	G_{298}	ΔG_{298} gas phase	E_{tot}	G_{298}	ΔG_{298} solution
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	kJ/mol	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	kJ/mol
8	-1410.761112	-1410.226523	-1410.323962				
9	-1410.766453	-1410.231745	-1410.327567				
***t*BuCOOH**	-346.998629	-346.841854	-346.883859				
1	-346.998629	-346.841854	-346.883859				
2	-346.989291	-346.832621	-346.873620				
7a	-632.169651	-631.931316	-631.983489	57.9	-632.178399	-631.992237	-2.6
1	-632.1686878	-631.930229	-631.982258		-632.177413	-631.990984	
2	-632.1696514	-631.931316	-631.983489		-632.178399	-631.992237	
CMD step with *trans* pivalate							
$INT4_{trans}$	-1410.768643	-1410.234513	-1410.330335	93.1	-1410.784592	-1410.346094	88.6
12	-1410.768643	-1410.234513	-1410.330335		-1410.784402	-1410.346094	
22	-1410.767098	-1410.232374	-1410.328544		-1410.784592	-1410.346039	
2	-1410.764224	-1410.230941	-1410.325727		-1410.782202	-1410.343705	
4	-1410.765375	-1410.230925	-1410.326857		-1410.780808	-1410.342290	
1	-1410.759306	-1410.224670	-1410.320672		-1410.77796	-1410.339326	
3	-1410.754542	-1410.219945	-1410.316059		-1410.773136	-1410.334653	
$TS4\text{-}5_{trans}$	-1410.705905	-1410.177923	-1410.272157	245.8	-1410.723962	-1410.290122	235.6
3	-1410.705903	-1410.177923	-1410.272062		-1410.723962	-1410.290122	
4	-1410.705905	-1410.177877	-1410.272157		-1410.723836	-1410.290088	
1.qst3	-1410.702384	-1410.174472	-1410.269835		-1410.721120	-1410.288571	
2.qst3	-1410.692135	-1410.164484	-1410.261547		-1410.710865	-1410.280277	
2	-1410.689513	-1410.161562	-1410.258276		-1410.707771	-1410.276533	
$INT5_{trans}$	-1410.761830	-1410.226839	-1410.322815	112.8	-1410.783669	-1410.344653	92.4
1	-1410.761830	-1410.226839	-1410.322815		-1410.783669	-1410.344653	
2	-1410.758118	-1410.223528	-1410.321998		-1410.779738	-1410.343619	

Table S2.2. Calculated kinetic isotope effects for the CMD step with model NHC **5**.[a]

Ar 298 K:

	H_{298}	G_{298}	H_{298} (d_3)	G_{298} (d_3)	ΔH_{298} (D-H), kJ/mol	ΔG_{298} (D-H) , kJ/mol	$\Delta\Delta H_{298}$ (D-H) , kJ/mol	$\Delta\Delta G_{298}$ (D-H) , kJ/mol	k_H/k_D
3a	-645.658367	-645.719700	-645.667746	-645.729913	-24.6	-26.8			
INT4	-1410.272224	-1410.368008	-1410.281622	-1410.378236	-24.7	-26.9	0.0	0.0	**0.98**
TS4-5	-1410.222415	-1410.320244	-1410.230387	-1410.328848	-20.9	-22.6	3.7	4.2	**5.50**

At 413 K:

	H_{413}	G_{298}	H_{298} (d_3)	G_{298} (d_3)	ΔH_{298} (D-H), kJ/mol	ΔG_{298} (D-H) , kJ/mol	$\Delta\Delta H_{298}$ (D-H) , kJ/mol	$\Delta\Delta G_{298}$ (D-H) , kJ/mol	k_H/k_D
3a	-645.645912	-645.744797	-645.654985	-645.755982	-23.8	-29.4			
INT4	-1410.246833	-1410.409111	-1410.255887	-1410.419716	-23.8	-27.8	0.0	1.5	**1.56**
TS4-5	-1410.196908	-1410.362153	-1410.204466	-1410.371070	-19.8	-23.4	4.0	6.0	**5.66**

[a] *Int=ultrafine* keyword was used for the numerical integration in frequency analysis.

Formula for the KIE calculation:

ΔH_{298} (D-H) = H_{298} (d_3) - H_{298};

$\Delta\Delta H_{\mathbf{TS4\text{-}5}}$ (D-H) = $\Delta H_{\mathbf{TS4\text{-}5}}$ (D-H) - $\Delta H_{\mathbf{3a}}$ (D-H);

$k_H/k_D = \exp[-\Delta\Delta G_{\mathbf{TS4\text{-}5}}\text{ (D-H)}/RT]$

5.3. Catalytic cycle with chiral NHC 8

5.3.1 Ligand exchange step

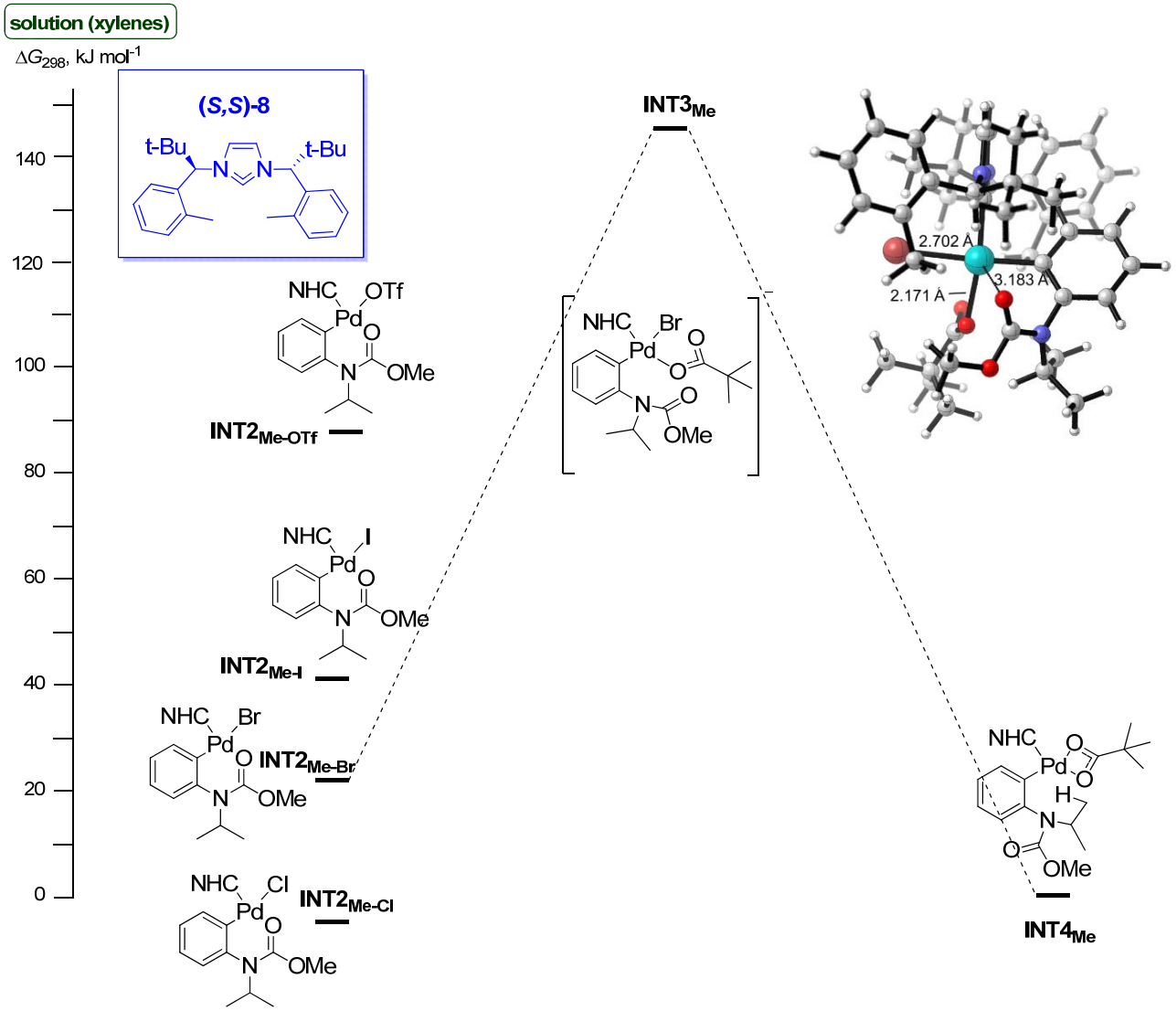
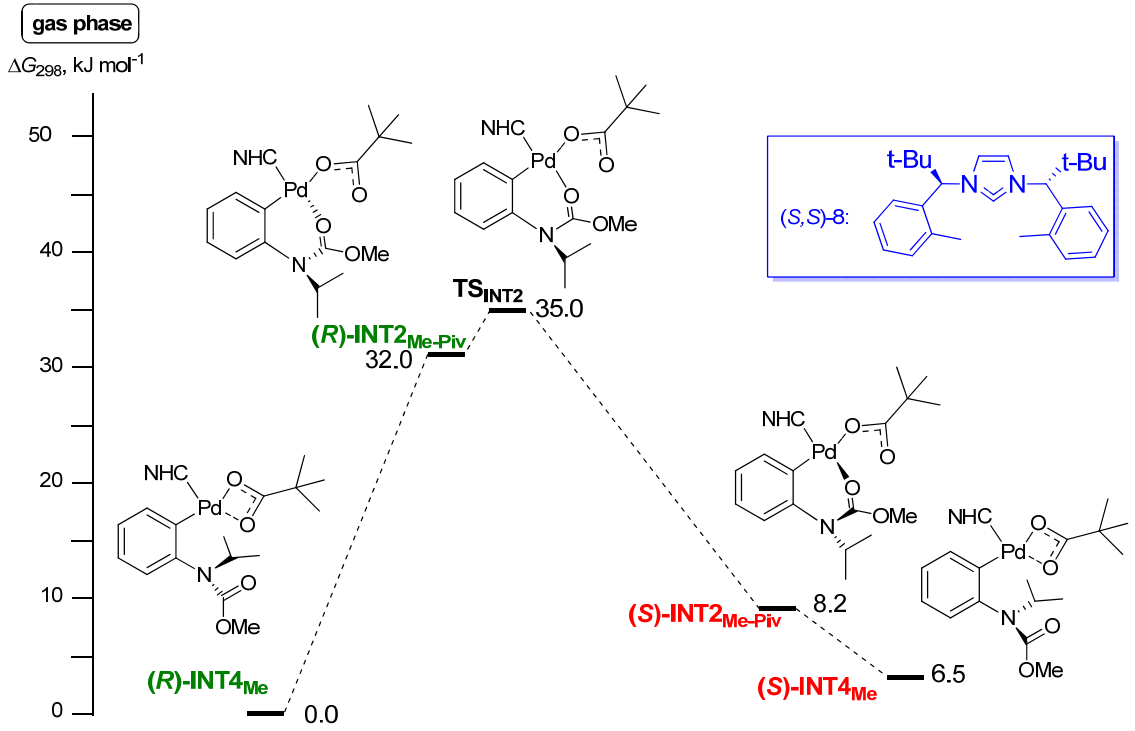


Table S3.1. Calculated energies of conformers at M06-L level with basis set bs1: LANL2DZ on Pd, I; 6-31G(d,p) on N, C, O; 6-31G(d) on H. Solvent effects in xylenes are included by PCM single point calculations at the same level with UAHF radii. Thermal corrections are calculated at 298 K and experimental temperature 413 K. The energies relative to complex **INT4$_{Me}$** are shown in bold.

	E_{tot}	H_{298}	G_{298}	E_{tot}	H_{298}	G_{298}	H_{413}	G_{413}	H_{413}	G_{413}
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1
INT2$_{Me-Cl}$										
(*R*)	-1934.547927	-1933.686619	-1933.811604	-1934.572484	-1933.711176	-1933.836161	-1933.647309	-1933.866222	-1933.671866	-1933.890779
(*S*)	-1934.563556	-1933.703381	-1933.828837	-1934.586866	-1933.726691	-1933.852147	-1933.663987	-1933.883652	-1933.687297	-1933.906962
	-1.5	**-10.3**	**-35.6**	**30.4**	**21.6**	**-3.7**	**-11.2**	**-45.2**	**20.6**	**-13.3**
INT2$_{Me-Br}$										
(*R*)	-1932.757482	-1931.896455	-1932.022622	-1932.782331	-1931.921303	-1932.047470	-1931.857101	-1932.077704	-1931.881949	-1932.102552
(*S*)	-1932.773537	-1931.913196	-1932.038938	-1932.797407	-1931.937066	-1932.062808	-1931.873796	-1932.093865	-1931.897666	-1932.117735
	42.7	**34.3**	**11.3**	**52.9**	**44.5**	**21.5**	**33.4**	**2.5**	**43.6**	**12.7**
INT2$_{Me-I}$										
(*R*)	-1930.971026	-1930.110266	-1930.238563	-1930.994970	-1930.134210	-1930.262507	-1930.070829	-1930.294483	-1930.094773	-1930.318427
(*S*)	-1930.987952	-1930.127874	-1930.253632	-1931.009502	-1930.149424	-1930.275182	-1930.088440	-1930.308573	-1930.109990	-1930.330123
	79.2	**70.2**	**48.8**	**72.6**	**63.5**	**42.2**	**69.3**	**40.8**	**62.7**	**34.1**
INT2$_{Me-OTf}$	-2880.966768	-2880.070115	-2880.207373	-2880.990597	-2880.093804	-2880.231062	-2880.025992	-2880.267525	-2880.049681	-2880.291214
(*R*)-1	-2880.954242	-2880.057993	-2880.195381	-2880.979420	-2880.083170	-2880.220558	-2880.013848	-2880.255586	-2880.039025	-2880.280763
(*R*)-2	-2880.959341	-2880.062306	-2880.198277	-2880.984290	-2880.087255	-2880.223226	-2880.018207	-2880.257927	-2880.043156	-2880.282876
(*S*)-1	-2880.966768	-2880.070115	-2880.207373	-2880.990457	-2880.093804	-2880.231062	-2880.025992	-2880.267525	-2880.049681	-2880.291214
(*S*)-2	-2880.966025	-2880.068814	-2880.205158	-2880.990597	-2880.093386	-2880.229730	-2880.024733	-2880.264950	-2880.049305	-2880.289522
	115.8	**115.6**	**119.7**	**83.4**	**83.5**	**87.7**	**115.6**	**121.3**	**83.5**	**89.2**
INT3$_{Me}$										
(*R*)	-2279.259791	-2278.254581	-2278.397138	-2279.312715	-2278.307505	-2278.450062	-2278.208143	-2278.459706	-2278.261067	-2278.512630
(*S*)	-2279.246893	-2278.241858	-2278.385144	-2279.299826	-2278.294791	-2278.438077	-2278.195369	-2278.448002	-2278.248302	-2278.500935
	281.5	**281.1**	**303.1**	**124.6**	**124.2**	**146.2**	**282.1**	**311.5**	**125.2**	**154.5**
INT2$_{Me-Piv}$	**κ^1-complexes**									
(*R*)-7	-2265.978340	-2264.973809	-2265.109606	-2266.001522	-2264.996991	-2265.132788	-2264.928584	-2265.169359	-2264.951766	-2265.192541
(*S*)-7.2	-2265.985639	-2264.981473	-2265.118834	-2266.007067	-2265.002901	-2265.140262	-2264.936210	-2265.179198	-2264.957638	-2265.200626
	0.3	**2.2**	**8.2**	**-3.6**	**-1.7**	**4.3**	**2.0**	**10.6**	**-1.9**	**6.7**

TS between κ^1-complexes										
TS_{INT2}	-2265.973497	-2264.971331	-2265.108869	-2265.996627	-2264.994461	-2265.131999	-2264.926254	-2265.169270	-2264.949384	-2265.192400
	32.2	**28.9**	**34.4**	**23.8**	**20.5**	**26.0**	**28.1**	**36.6**	**19.8**	**28.3**
$INT4_{Me}$	**κ^2-complexes**									
(*R*)-7	-2265.985751	-2264.982326	-2265.121965	-2266.005688	-2265.002263	-2265.141902	-2264.936975	-2265.183224	-2264.956912	-2265.203161
(*S*)-3	-2265.983788	-2264.980926	-2265.119487	-2266.002679	-2264.999817	-2265.138378	-2264.935527	-2265.180337	-2264.954418	-2265.199228
	0.0	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**

5.3.2 Interconversion of κ^2-complexes $INT4_{Me}$



5.3.3. CMD step (Figure 2).

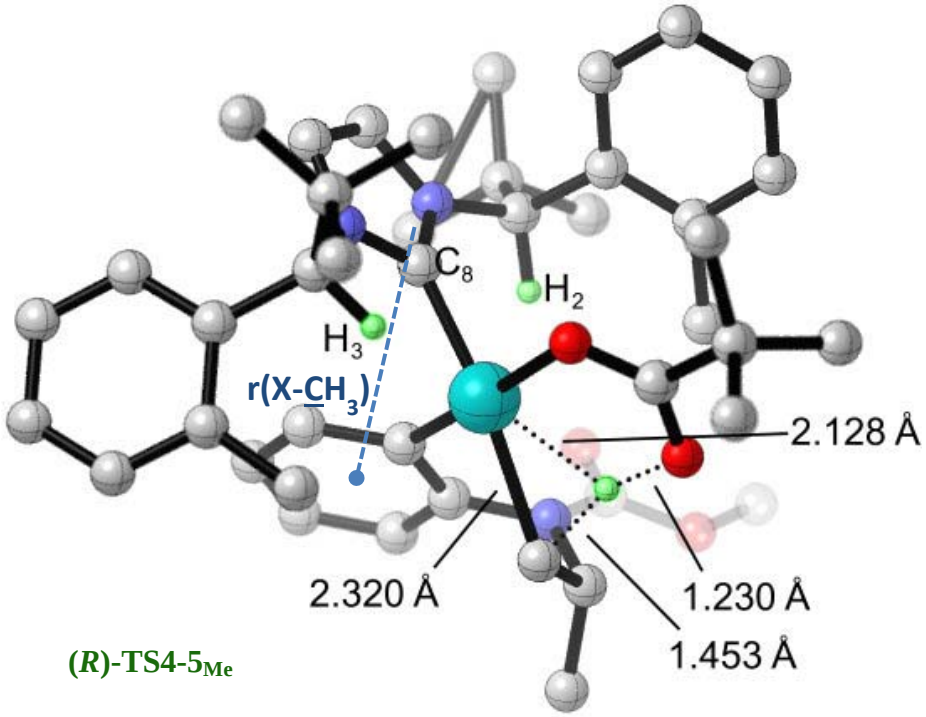
Table S3.2. Calculated energies of conformers at M06-L level with basis set bs1: LANL2DZ on Pd, I; 6-31G(d,p) on N, C, O; 6-31G(d) on H. Solvent effects in xylenes are included by PCM single point calculations at the same level with UAHF radii. Thermal corrections are calculated at 298 K and experimental temperature 413 K. Δ(S-R) denote the energy differences (kJ/mol) between the corresponding (*S*) and (*R*) species.

	E_{tot}	H_{298}	G_{298}	E_{tot}	H_{298}	G_{298}	H_{413}	G_{413}	H_{413}	G_{413}
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1
κ^2-complexes										
(*R*)-INT4$_{Me}$										
7	-2265.985751	-2264.982326	-2265.121965	-2266.005688	-2265.002263	-2265.141902	-2264.936975	-2265.183224	-2264.956912	-2265.203161
4	-2265.978216									
7.2	-2265.977862									
9	-2265.977715									
12	-2265.974975									
2	-2265.971011									
(*S*)-INT4$_{Me}$										
3	-2265.983788	-2264.980926	-2265.119487	-2266.002679	-2264.999817	-2265.138378	-2264.935527	-2265.180337	-2264.954418	-2265.199228
8	-2265.975478									
11	-2265.969863									
Δ(S-R), kJ/mol	**5.15**	**3.7**	**6.5**	**7.9**	**6.4**	**9.3**	**3.8**	**7.6**	**6.6**	**10.3**
Transition states										
(*R*)-TS4-5$_{Me}$										
2	-2265.938089	-2264.940347	-2265.077789	-2265.960481	-2264.962739	-2265.100181	-2264.895302	-2265.138145	-2264.917694	-2265.160537
3	-2265.937604	-2264.939256	-2265.075476	-2265.960528	-2264.962180	-2265.098400	-2264.894279	-2265.135347	-2264.917203	-2265.158271
(*S*)-TS4-5$_{Me}$										
6	-2265.930579	-2264.932962	-2265.070387	-2265.951659	-2264.954042	-2265.091467	-2264.887894	-2265.13074	-2264.908974	-2265.151820
5	-2265.927309	-2264.929599	-2265.065979	-2265.950009	-2264.952299	-2265.088679	-2264.884600	-2265.125916	-2264.907300	-2265.148616
4	-2265.926092	-2264.928404	-2265.064539	-2265.947694	-2264.950006	-2265.086141	-2264.883382	-2265.124385	-2264.904984	-2265.145987
Δ(S-R), kJ/mol	**19.7**	**19.4**	**19.4**	**23.3**	**22.8**	**22.9**	**19.4**	**19.4**	**22.9**	**22.9**
Relative to κ^2-complex										
$\Delta\Delta G^{\ddagger}$, kJ/mol	**14.6**	**15.7**	**12.9**	**15.4**	**16.4**	**13.6**	**15.6**	**11.9**	**16.3**	**12.6**

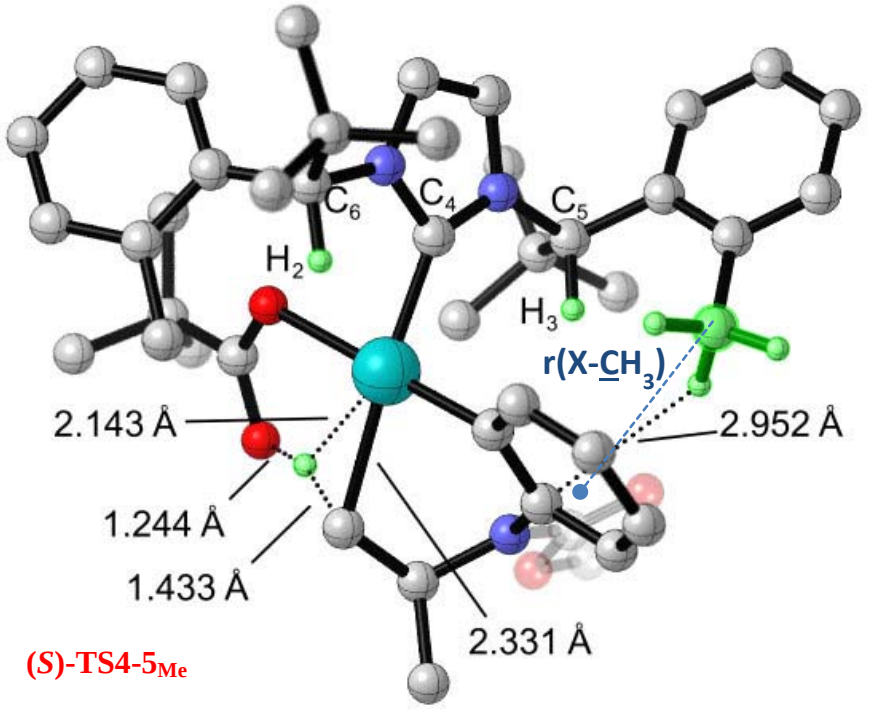
Table S3.3. Comparison of structural parameters and relative Gibbs free energies of diastereomeric intermediates **INT4$_{Me}$** and TSs **TS4-5$_{Me}$** with ligand (*S*,*S*)-**8**.

Structure	Distances, Å		Dihedral angles in NHC				ΔG_{298} [b], kJ/mol
	r(X-**C**H$_3$) [a]	r(X-**H**$_3$C) [a]	Pd-C$_4$-N-C$_5$	C$_4$-N-C$_5$-H$_3$	Pd-C$_4$-N-C$_6$	C$_4$-N-C$_6$-H$_2$	
INT4$_{Me}$							
R	3.733	2.944	-10.4	+15.8	+6.8	-3.0	0.0
S	3.460	2.506	-11.7	-18.8	+6.8	+38.4	9.3
TS4-5$_{Me}$							
R	3.918	2.978	-18.8	+36.7	+13.8	+5.7	109.5
S	3.367	2.667	-20.3	-17.5	+21.0	+9.9	132.4

[a] Distances between CH$_3$ group of *o*-methylphenyl (for (*S*)-species) or *t*-butyl (for (*R*)-species) of ligand (*S*,*S*)-**8** (highlighted green in Figure 2) and X – center of substrate benzene ring. [b] Relative Gibbs free energies calculated at 298 K in xylenes.



(*R*)-TS4-5$_{Me}$



(*S*)-TS4-5$_{Me}$

Structures of conformers for **TS4-5$_{Me}$**.

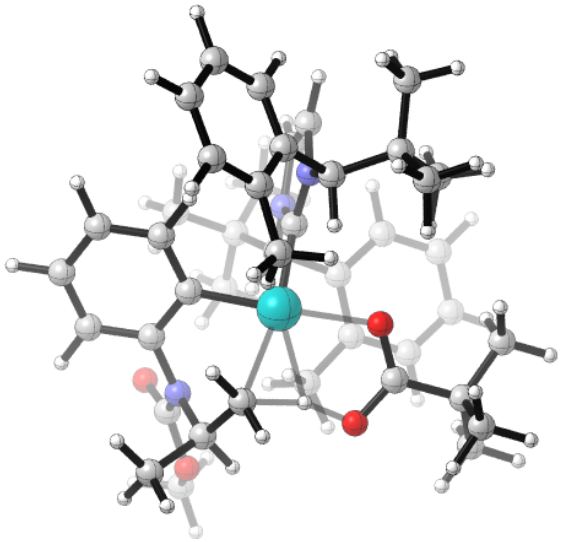
Several parameters were varied during conformational search:

1. Rotation of the carbamate $COOCH_3$ group: it leads to a small change in energy of 1–6 kJ/mol (compare two columns).

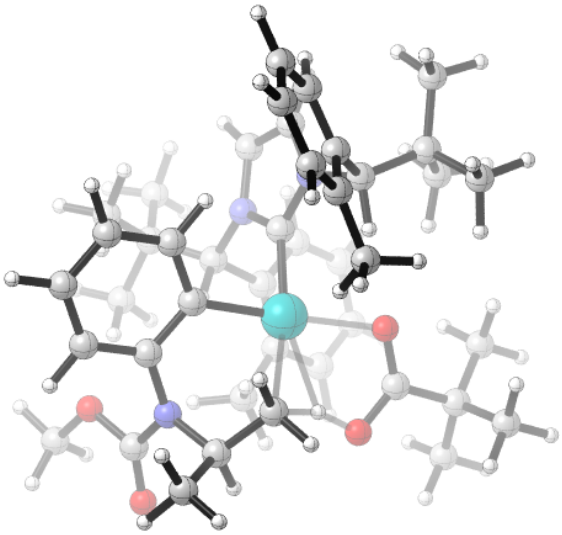
2. Allylic strain keeps (tBu)C-H and (Ar)C-CH_3 bonds in the NHC ligand coplanar (see Table S3.3). Rotating *o*-tolyl substituent to the sterically hindered side of NHC leads to a large energy increase (i.e., from 31.4 to 41.7 kJ/mol for (*S*)-TSs).

3. A position of the second, not activated methyl group of isopropyl, which lies ”on the open side of the complex” in the best conformations of (*R*)- and (*S*)-TSs (0.0 and 19.6 kJ/mol, respectively). This methyl group has a contact with the Me group of the NHC ligand in less stable, closed conformations of (*R*)- and (*S*)-TSs (59.1 and 31.4 kJ/mol, respectively).

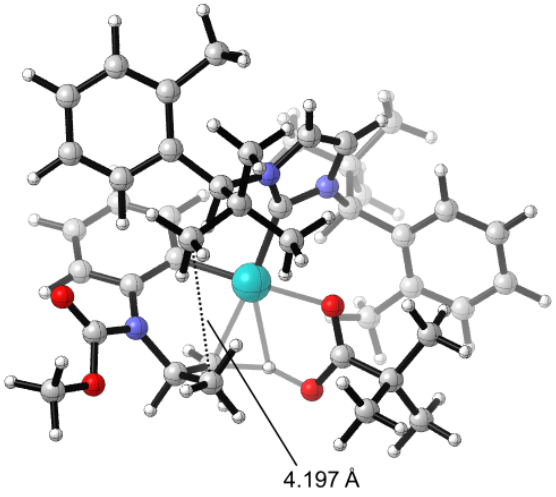
(*R*)-TS:



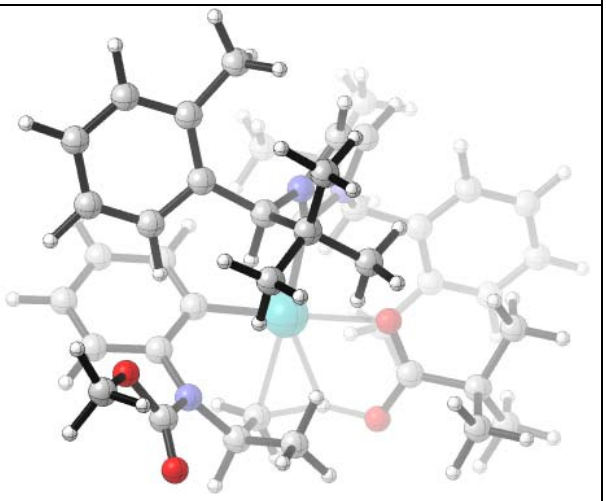
ΔE = 0.0 kJ/mol



ΔE = 1.3 kJ/mol



ΔE = 59.1 kJ/mol



ΔE = 56.4 kJ/mol

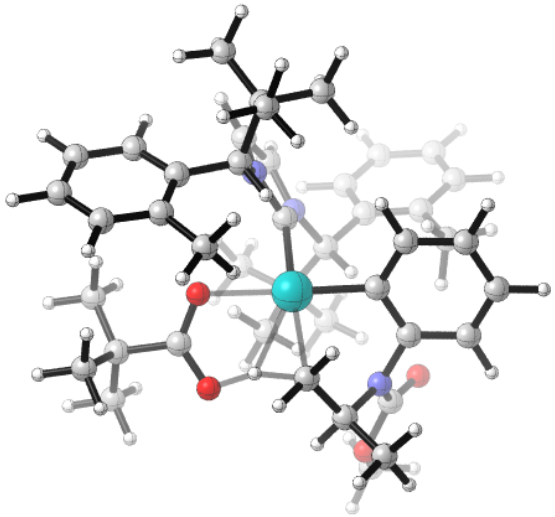
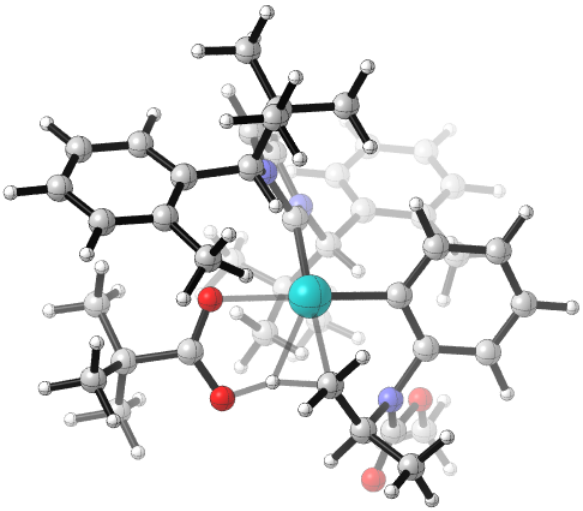
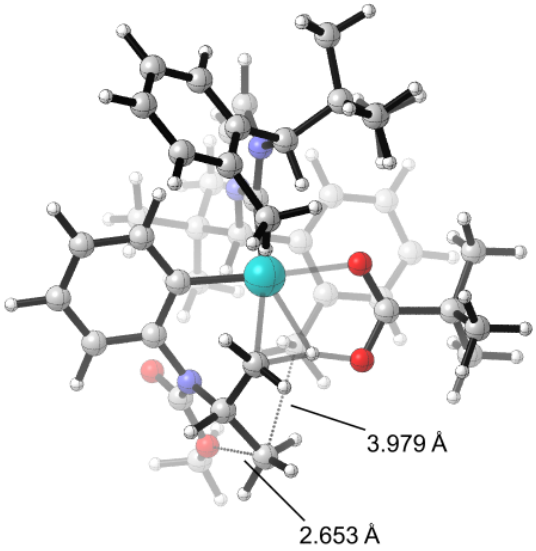
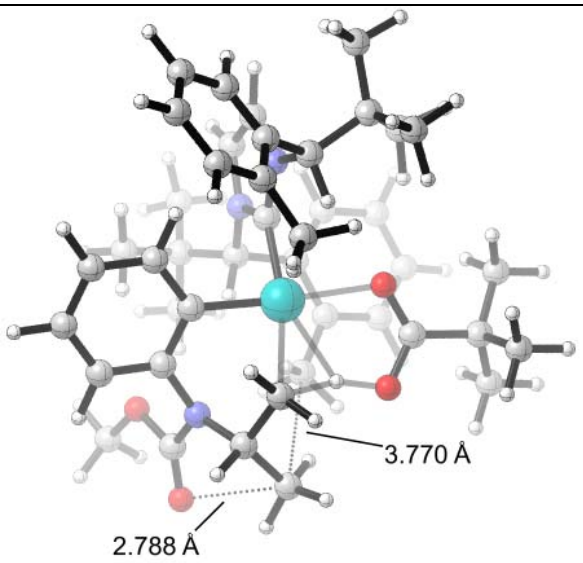
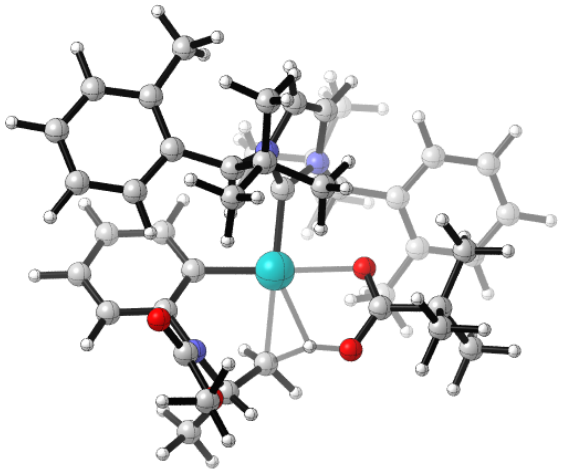
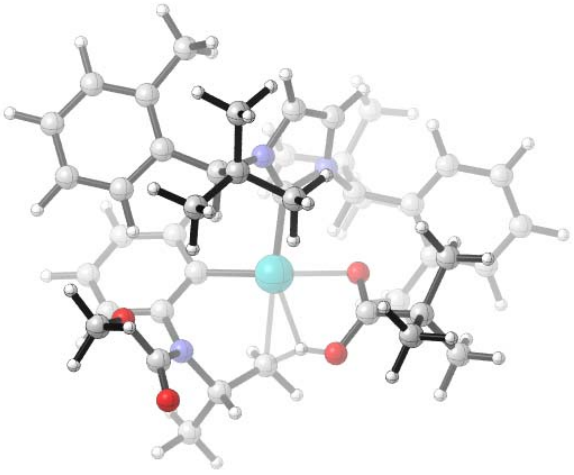
(*S*)-TS:	
 ΔE = 19.6 kJ/mol	 ΔE = 26.3 kJ/mol
 ΔE = 31.4 kJ/mol	 ΔE = 28.3 kJ/mol
 ΔE = 41.7 kJ/mol	 ΔE = 41.0 kJ/mol

Table S3.4. Calculated kinetic isotope effects for the CMD step with chiral NHC (*S*,*S*)-**8**.[a]

	H_{298}	G_{298}	H_{298} (d_3)	G_{298} (d_3)	ΔH_{298} (D-H)	ΔG_{298} (D-H)	$\Delta\Delta H_{298}$ (D-H), kJ/mol	$\Delta\Delta G_{298}$ (D-H), kJ/mol	k_H/k_D
3a	-645.658367	-645.719700	-645.667746	-645.729913	-24.6	-26.8			
INT4$_{Me}$									
R	-2264.940494	-2265.190657	-2264.958498	-2265.211784	-47.3	-55.5	0.1	0.1	**1.02**
S	-2264.937387	-2265.186947	-2264.955361	-2265.208057	-47.2	-55.4	0.2	0.1	**1.03**
TS4-5$_{Me}$									
R	-2264.898800	-2265.145003	-2264.915342	-2265.164462	-43.4	-51.1	3.9	4.4	**3.64**
S	-2264.889669	-2265.136254	-2264.906191	-2265.155696	-43.4	-51.0	4.0	4.5	**3.69**

[a] *Int=ultrafine* keyword was used for the numerical integration in frequency analysis.

Formula for the KIE calculation:

Formula for the KIE calculation:

ΔH_{298} (D-H) = H_{298} (d_3) - H_{298}.

$\Delta\Delta H_{\mathbf{TS4\text{-}5}}$ (D-H) = $\Delta H_{\mathbf{TS4\text{-}5}}$ (D-H) - $\Delta H_{\mathbf{3a}}$ (D-H).

$k_H/k_D = \exp[-\Delta\Delta G_{\mathbf{TS4\text{-}5}}\text{ (D-H)}/RT]$

5.4 Effects of ligands on the calculated activation barriers and enantioselectivities

Table S4.1. Relative Gibbs free energies of (*R*)- and (*S*)- intermediates **INT4** and TSs **TS4-5** with ligand **4** (Table 5, entry 2).

	E_{tot}	H_{298}	G_{298}	H_{413}	G_{413}	E_{tot}	H_{298}	G_{298}	H_{413}	**G_{413}**
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	**$PCM_{xylenes}$ M06-L/bs1**
κ^2-complexes **INT4**										
(*R*)-	-2494.612692	-2493.568547	-2493.712484	-2493.520481	-2493.775832	-2494.634632	-2493.590487	-2493.734424	-2493.542421	-2493.797772
(*S*)-	-2494.613997	-2493.570270	-2493.712851	-2493.522147	-2493.775686	-2494.635174	-2493.591447	-2493.734028	-2493.543324	-2493.796863
Δ(S-R), kJ/mol	**-3.4**	**-4.5**	**-1.0**	**-4.4**	**0.4**	**-1.4**	**-2.5**	**1.0**	**-2.4**	**2.4**
Transition states **TS4-5**										
(*R*)-	-2494.567658	-2493.529903	-2493.672759	-2493.482003	-2493.735659	-2494.590114	-2493.552358	-2493.695214	-2493.504458	-2493.758114
(*S*)-	-2494.562740	-2493.525501	-2493.667439	-2493.47761	-2493.729983	-2494.585061	-2493.547821	-2493.689759	-2493.499930	-2493.752303
Δ(S-R), kJ/mol	**12.9**	**11.6**	**14.0**	**11.5**	**14.9**	**13.3**	**11.9**	**14.3**	**11.9**	**15.3**
$\Delta G^{\ddagger}_{R}$, kJ/mol	**118.2**	**101.5**	**104.3**	**101.0**	**105.5**	**116.9**	**100.1**	**102.9**	**99.7**	**104.1**
Relative to κ^2-complex										
$\Delta\Delta G^{\ddagger}$, kJ/mol	**16.3**	**16.1**	**14.9**	**15.9**	**14.5**	**14.7**	**14.4**	**13.3**	**14.3**	**12.9**

Table S4.2. Relative Gibbs free energies of (*R*)- and (*S*)- intermediates **INT4** and TSs **TS4-5** with ligand **8'** (Table 5, entry 3).

	E_{tot}	H_{298}	G_{298}	H_{413}	G_{413}	E_{tot}	H_{298}	G_{298}	H_{413}	**G_{413}**
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	**$PCM_{xylenes}$ M06-L/bs1**
κ^2-complexes **INT4**										
(*R*)-	-2226.671259	-2225.697441	-2225.837017	-2225.653244	-2225.898063	-2226.690430	-2225.716613	-2225.856189	-2225.672416	-2225.917235
(*S*)-	-2226.673693	-2225.700001	-2225.836836	-2225.655810	-2225.896823	-2226.693376	-2225.719684	-2225.856519	-2225.675493	-2225.916506
Δ(S-R), kJ/mol	**-6.4**	**-6.7**	**0.5**	**-6.7**	**3.3**	**-7.7**	**-8.1**	**-0.9**	**-8.1**	**1.9**
Transition states **TS4-5**										
(*R*)-	-2226.621821	-2225.653749	-2225.787844	-2225.609859	-2225.846719	-2226.644117	-2225.676045	-2225.810140	-2225.632155	-2225.869015
(*S*)-	-2226.623475	-2225.654904	-2225.787601	-2225.611144	-2225.845913	-2226.643997	-2225.675426	-2225.808123	-2225.631666	-2225.866435
Δ(S-R), kJ/mol	**-4.3**	**-3.0**	**0.6**	**-3.4**	**2.1**	**0.3**	**1.6**	**5.3**	**1.3**	**6.8**
$\Delta G^{\ddagger}_{R}$, kJ/mol	**131.8**	**118.4**	**129.1**	**117.3**	**134.8**	**129.3**	**114.6**	**121.8**	**113.8**	**126.6**
Relative to κ^2-complex										
$\Delta\Delta G^{\ddagger}$, kJ/mol	**2.0**	**3.7**	**0.2**	**3.4**	**-1.1**	**8.0**	**9.7**	**6.2**	**9.4**	**4.9**

Table S4.3. Relative Gibbs free energies of (*R*)- and (*S*)- intermediates **INT4** and TSs **TS4-5** with ligand **8''** (Table 5, entry 4).

	E_{tot}	H_{298}	G_{298}	H_{413}	G_{413}	E_{tot}	H_{298}	G_{298}	H_{413}	**G_{413}**
Conformer	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	M06-L/bs1	M06-L/bs1	$PCM_{xylenes}$ M06-L/bs1	**$PCM_{xylenes}$ M06-L/bs1**
κ^2-complexes **INT4**										
(*R*)-	-2187.354727	-2186.410035	-2186.547531	-2186.367110	-2186.607564	-2187.375859	-2186.431166	-2186.568662	-2186.388241	-2186.628695
(*S*)-	-2187.356921	-2186.412442	-2186.546785	-2186.369514	-2186.605602	-2187.377095	-2186.432616	-2186.566959	-2186.389688	-2186.625776
Δ(S-R), kJ/mol	**-5.8**	**-6.3**	**2.0**	**-6.3**	**5.2**	**-3.2**	**-3.8**	**4.5**	**-3.8**	**7.7**
Transition states **TS4-5**										
(*R*)-	-2187.305333	-2186.367101	-2186.499466	-2186.324346	-2186.557488	-2187.329260	-2186.391029	-2186.523394	-2186.348274	-2186.581416
(*S*)-	-2187.308773	-2186.370554	-2186.502070	-2186.327843	-2186.559756	-2187.330321	-2186.392103	-2186.523619	-2186.349392	-2186.581305
Δ(S-R), kJ/mol	**-9.0**	**-9.1**	**-6.8**	**-9.2**	**-6.0**	**-2.8**	**-2.8**	**-0.6**	**-2.9**	**0.3**
$\Delta G^{\ddagger}_{R}$, kJ/mol	**126.4**	**110.0**	**119.4**	**109.4**	**125.5**	**122.8**	**106.4**	**118.3**	**105.8**	**124.1**
Relative to κ^2-complex										
$\Delta\Delta G^{\ddagger}$, kJ/mol	**-3.3**	**-2.7**	**-8.8**	**-2.9**	**-11.1**	**0.5**	**1.0**	**-5.1**	**0.9**	**-7.4**

5.5 Coordinates of all stationary points (the best conformers)

5.5.1 Catalytic cycle with model NHC 5.

3a.2
29 atoms
PCM Energy= -645.918196455
O 1.207841 -0.657310 -1.883788
N 0.839000 0.522085 0.051881
C 1.380337 1.078212 1.315789
C 1.602357 -0.203115 -0.828830
C -3.179660 1.302157 -0.988790
C -1.508578 -0.197952 -0.144925
C -0.508188 0.762817 -0.322218
C -2.832431 0.054767 -0.478029
C -2.205043 2.277798 -1.172276
C -0.881927 2.002496 -0.846374
H 2.089612 0.328524 1.679589
H -4.215471 1.503916 -1.245023
H -3.581611 -0.715216 -0.332853
H -2.471308 3.249174 -1.577971
H -0.104169 2.744361 -1.004696
C 0.280594 1.243019 2.349658
H 0.720955 1.556385 3.299815
H -0.443001 2.008931 2.052049
H -0.261851 0.308060 2.515130
C 2.128663 2.380832 1.071980
H 1.444798 3.168507 0.736584
H 2.605235 2.729961 1.993383
H 2.906481 2.249912 0.316082
O 2.872744 -0.344223 -0.363000
C 3.699138 -1.126457 -1.222908
H 4.669983 -1.180058 -0.731246
H 3.282854 -2.127542 -1.358161
H 3.794183 -0.658173 -2.205780
Br -1.051598 -1.950186 0.602165

INT1
45 atoms
PCM Energy= -1077.54893783
O -0.601225 1.836278 -0.327717
N -2.373713 0.386384 -0.650183
C -3.854241 0.233818 -0.687328
C -1.796665 1.606401 -0.428437
C 0.033498 -3.101928 -0.812084
C -0.780638 -1.163906 0.432367
C 0.041979 -2.326581 0.368914
C -0.726760 -2.719695 -1.902618
C -1.480712 -1.536933 -1.858093
H -4.236252 0.947886 0.048895
H 0.616171 -4.019516 -0.841124
H 0.455389 -2.736616 1.284699
H -0.729407 -3.321512 -2.806187
H -2.031021 -1.200265 -2.733218
C -4.278894 -1.158131 -0.256731
H -5.367385 -1.181225 -0.155450
H -3.993699 -1.918572 -0.989240
H -3.839481 -1.431289 0.706806
C -4.408761 0.601819 -2.055191
H -4.067326 -0.105419 -2.818744
H -5.503006 0.575214 -2.044937
H -4.095606 1.606332 -2.348609
O -2.738905 2.582646 -0.345334
C -2.200337 3.872252 -0.066856
H -3.057820 4.541302 -0.003224
H -1.648589 3.868367 0.876655
H -1.524410 4.194805 -0.863068
Br -1.388312 -0.531685 2.252397
C -1.533743 -0.759218 -0.709410
Pd 1.106261 -0.319174 0.156287
C 3.054388 0.334190 -0.157025
N 3.511529 1.624096 -0.165239
N 4.190939 -0.391571 -0.396614
C 4.871552 1.693876 -0.398159
C 2.654949 2.767640 0.064703
C 5.302216 0.416271 -0.547070
C 4.201191 -1.832755 -0.499457
H 5.407286 2.629723 -0.438409
H 2.781459 3.503153 -0.734438
H 1.618002 2.424247 0.073611
H 2.888199 3.241176 1.023188
H 6.286160 0.020432 -0.745925
H 3.178031 -2.174099 -0.319332
H 4.519905 -2.149359 -1.496962
H 4.871951 -2.270288 0.245440

TS1-2.2
45 atoms
PCM Energy= -1077.53141812
O 0.437098 1.828594 0.383218
N 2.417459 0.646905 0.287014
C 3.824343 0.617684 -0.203762
C 1.614961 1.726371 0.062610
C 0.815440 -2.887999 1.985755
C 0.813365 -1.228953 0.218426
C 0.331447 -2.438679 0.752660
C 1.794506 -2.165425 2.655745
C 2.292020 -0.980832 2.103792
H 3.804638 1.134254 -1.168913
H 0.437986 -3.818226 2.402170
H -0.358710 -3.040356 0.169632
H 2.180420 -2.516988 3.607709
H 3.039247 -0.396046 2.636005
C 4.299914 -0.804015 -0.437935
H 5.279207 -0.772605 -0.923489
H 4.408239 -1.357750 0.499214
H 3.613221 -1.356810 -1.084787
C 4.745740 1.375648 0.739967
H 4.811540 0.870844 1.709992
H 5.757254 1.429173 0.325155
H 4.391421 2.395720 0.903767
O 2.290494 2.723907 -0.561524
C 1.485139 3.861779 -0.860943
H 2.138825 4.551007 -1.394609
H 0.632898 3.582688 -1.484901
H 1.109523 4.326837 0.054360
Br 0.794989 -1.094908 -1.996771
C 1.841465 -0.513050 0.874167
Pd -1.006793 -0.333692 0.082743
C -3.003316 0.277293 0.165876
N -3.534270 1.389118 0.760658
N -4.110933 -0.363912 -0.321217
C -4.911354 1.432070 0.650689
C -2.727681 2.388680 1.426204
C -5.277775 0.320266 -0.034333
C -4.045364 -1.615672 -1.040114
H -5.501814 2.238151 1.058305
H -2.949499 2.415019 2.497103
H -1.677976 2.128960 1.277050
H -2.917277 3.378110 1.000484
H -6.249573 -0.033736 -0.341721
H -2.989100 -1.839282 -1.213027
H -4.495185 -2.426562 -0.459259
H -4.561041 -1.536562 -2.000974

INT2$_{Br}$'.1a
45 atoms
PCM Energy= -1077.58830046
Pd -0.506464 0.457012 -0.234756
O 0.500140 -1.301395 -1.068110
N 2.415693 -0.833833 0.133157
C 3.382649 -1.272623 1.178783
N -2.909047 -1.254937 -1.226690
C 1.459560 -1.646383 -0.352033
N -3.215189 -0.855384 0.852619
C 2.751320 3.184913 -1.110489
C -4.279742 -1.635131 0.440723
C -2.351652 -0.602700 -0.167858
C 1.311511 1.335073 -0.428588
C 2.463255 0.540072 -0.305964
C -4.086127 -1.890136 -0.877303
C 1.489474 2.660758 -0.839462
C 3.879281 2.379756 -0.989799
C 3.732368 1.056641 -0.595260
H 3.909428 -0.345461 1.421606
H 2.850742 4.224952 -1.412013
H -5.072012 -1.930628 1.110779
H -4.674883 -2.451675 -1.585757
H 0.616692 3.302855 -0.918142
H 4.869034 2.770566 -1.209085
H 4.605468 0.410744 -0.525195
C -2.330898 -1.268338 -2.554220
H -3.076916 -0.968143 -3.293785
H -1.499138 -0.562830 -2.569656
H -1.953310 -2.263813 -2.805573
C -3.051444 -0.355037 2.203508
H -2.094568 0.163392 2.260799
H -3.840870 0.360932 2.443838
H -3.079464 -1.183980 2.916038
C 4.405303 -2.273726 0.665483
H 5.182147 -2.425412 1.420691
H 3.950265 -3.241954 0.449589
H 4.888240 -1.912417 -0.246964
C 2.669372 -1.729267 2.442765
H 2.171154 -2.690910 2.305936
H 3.396258 -1.841087 3.252379
H 1.926335 -0.989771 2.754681
O 1.624614 -2.941978 -0.020209
C 0.564768 -3.804274 -0.442632
H 0.797351 -4.778190 -0.014278
H -0.401686 -3.444831 -0.078952
H 0.528816 -3.868741 -1.532444
Br -1.536970 2.546353 0.784037

INT2$_{Cl}$.1
45 atoms
PCM Energy= -1079.39979247
Pd -0.638266 -0.623059 -0.390269
O 1.259336 -1.277126 -1.257695
N 2.343490 0.331408 -0.015513
C 3.309768 0.656199 1.069072
N -3.548342 -0.099376 -0.036909
C 2.153472 -0.933884 -0.468208
N -2.406193 0.983372 1.431996
C -0.014151 3.552581 -1.399526
C -3.733228 1.310003 1.640087
C -2.278576 0.113682 0.394228
C 0.115534 1.214267 -0.699256
C 1.504225 1.382156 -0.522638
C -4.451171 0.628524 0.713205
C -0.616001 2.321164 -1.145222
C 1.358792 3.696393 -1.230390
C 2.113585 2.609465 -0.804998
H 3.109804 1.713937 1.266540
H -0.617061 4.394046 -1.731889
H -4.042726 1.971776 2.433003
H -5.513052 0.581192 0.532031
H -1.691360 2.221164 -1.285424
H 1.847655 4.643721 -1.438782
H 3.191733 2.708598 -0.697840
C -3.889162 -0.952561 -1.162695
H -3.734223 -0.418677 -2.104572
H -3.253458 -1.841654 -1.131822
H -4.937091 -1.243362 -1.079653
C -1.300170 1.517025 2.200145
H -0.436894 0.868380 2.049407
H -1.042798 2.524454 1.859882
H -1.565498 1.538743 3.259006
C 4.757803 0.524561 0.624762
H 5.422793 0.899646 1.408477
H 5.019732 -0.516541 0.428129
H 4.947537 1.101918 -0.284788
C 3.007686 -0.105562 2.352458
H 3.275989 -1.159974 2.276343
H 3.579238 0.329621 3.177468
H 1.945230 -0.040951 2.605425
O 3.043317 -1.818176 -0.003311
C 2.721615 -3.188826 -0.321312
H 3.401218 -3.785224 0.285437
H 1.676259 -3.402010 -0.081571
H 2.891164 -3.377590 -1.382979
Cl -1.283412 -2.992178 0.034311

INT2$_{Br}$.1
45 atoms
PCM Energy= -1077.60960795
Pd -0.600186 -0.299452 -0.374810
O 1.195802 -1.188578 -1.224381
N 2.507303 0.248012 0.014414
C 3.574423 0.417140 1.038495
N -3.411096 0.653899 -0.149774
C 2.160007 -0.970252 -0.476326
N -2.215173 1.468128 1.447167
C 0.597491 3.783020 -1.298296
C -3.483799 1.999536 1.589064
C -2.154887 0.637434 0.374510
C 0.414448 1.429691 -0.638003
C 1.811766 1.410181 -0.459725
C -4.235792 1.484215 0.583924
C -0.161372 2.637051 -1.062494
C 1.975633 3.739324 -1.128809
C 2.577586 2.555519 -0.721788
H 3.507902 1.479539 1.289212
H 0.111832 4.702984 -1.616912
H -3.736342 2.667616 2.396845
H -5.276881 1.616620 0.336156
H -1.239402 2.686017 -1.203682
H 2.587527 4.615456 -1.323546
H 3.659613 2.511155 -0.616373
C -3.806335 -0.075089 -1.340586
H -3.470703 0.453092 -2.236930
H -3.356124 -1.069648 -1.310958
H -4.893677 -0.164211 -1.357434
C -1.081550 1.787028 2.290513
H -0.343107 0.993408 2.176404
H -0.628436 2.734683 1.985604
H -1.400484 1.846326 3.332770
C 4.961411 0.142546 0.478153
H 5.720761 0.413598 1.217369
H 5.089925 -0.914632 0.233269
H 5.148702 0.726701 -0.427747
C 3.290040 -0.357154 2.319790
H 3.410990 -1.431675 2.185883
H 3.984882 -0.034547 3.101808
H 2.273814 -0.166246 2.671626
O 2.978109 -1.967374 -0.093683
C 2.514280 -3.286931 -0.456865
H 3.170397 -3.976346 0.071740
H 1.467645 -3.416554 -0.156906
H 2.593925 -3.432627 -1.535435
Br -1.601510 -2.697375 0.081173

INT2$_{I}$.1
45 atoms
PCM Energy= -1075.82296570
Pd -0.477883 0.001167 -0.403530
O 1.115655 -1.239010 -1.240112
N 2.681004 -0.095432 0.012324
C 3.754170 -0.151138 1.043575
N -2.973436 1.628860 -0.191632
C 2.111792 -1.214760 -0.501295
N -1.684173 1.972483 1.496643
C 1.518828 3.775603 -1.230952
C -2.781822 2.796729 1.660886
C -1.791449 1.244479 0.355152
C 0.868553 1.495219 -0.631577
C 2.231072 1.193765 -0.439834
C -3.593206 2.580178 0.595904
C 0.546336 2.797692 -1.030666
C 2.859631 3.456766 -1.048604
C 3.211180 2.168229 -0.664836
H 3.875844 0.899263 1.325545
H 1.228310 4.779743 -1.529940
H -2.892369 3.439417 2.519419
H -4.554404 2.995881 0.338854
H -0.500340 3.060261 -1.178584
H 3.634618 4.199448 -1.213843
H 4.261561 1.909780 -0.550142
C -3.480847 1.121028 -1.452515
H -2.984458 1.616282 -2.291876
H -3.290330 0.045435 -1.500946
H -4.554458 1.305038 -1.504309
C -0.542928 1.922056 2.386368
H -0.019716 0.981290 2.210297
H 0.142130 2.750145 2.181184
H -0.880509 1.967120 3.423517
C 5.080655 -0.650569 0.492330
H 5.864386 -0.529652 1.246035
H 5.027926 -1.707696 0.225562
H 5.377986 -0.089292 -0.398144
C 3.310981 -0.900165 2.292542
H 3.251665 -1.976491 2.127328
H 4.031698 -0.722344 3.095980
H 2.332548 -0.550796 2.633812
O 2.739079 -2.346731 -0.158067
C 2.041229 -3.545106 -0.550546
H 2.563169 -4.355190 -0.043974
H 0.992446 -3.494164 -0.247279
H 2.092521 -3.673871 -1.633052
I -2.114798 -2.213185 0.068593

INT2$_{Piv}$.4
60 atoms
PCM Energy= -1410.81756648
O -0.053968 -1.348966 -1.541361
N -1.608564 -1.968622 0.050451
C -1.907374 -2.819617 1.236462
N -0.110021 2.468161 1.658628
C -0.496185 -2.152517 -0.704389
N -0.197869 3.630365 -0.150453
C -4.376760 1.134639 -0.696943
C -0.206204 4.530189 0.901252
C -0.137163 2.353786 0.307128
C -2.044755 0.417754 -0.536078
C -2.502133 -0.882479 -0.245012
C -0.155914 3.795361 2.040845
C -3.011146 1.405686 -0.755595
C -4.809998 -0.157427 -0.421025
C -3.873169 -1.160854 -0.204500
H -2.742612 -2.290631 1.707680
H -5.097897 1.930806 -0.865200
H -0.235440 5.596565 0.744981
H -0.143455 4.094907 3.076559
H -2.688154 2.423366 -0.968320
H -5.869915 -0.391964 -0.382644
H -4.205594 -2.177953 -0.008145
C -0.078906 1.318834 2.547055
H -1.087877 0.913374 2.674446
H 0.564448 0.547553 2.107423
H 0.313623 1.628165 3.517064
C -0.206342 3.979933 -1.555048
H 0.718207 4.492830 -1.831251
H -0.284107 3.051044 -2.124606
H -1.060379 4.623153 -1.782092
C -0.754394 -2.824293 2.230748
H -1.093788 -3.256431 3.177006
H 0.094666 -3.409182 1.873983
H -0.394480 -1.809544 2.416922
C -2.383065 -4.217558 0.871051
H -1.576988 -4.812053 0.437732
H -2.738960 -4.732503 1.768774
H -3.206695 -4.185725 0.151687
O 0.075611 -3.345404 -0.507682
C 1.386955 -3.491213 -1.072305
H 1.650866 -4.536177 -0.914684
H 1.381220 -3.250343 -2.136298
H 2.077874 -2.830813 -0.542576
Pd -0.061509 0.654672 -0.661741
O 2.114002 0.682100 -0.749031
C 2.533202 -0.222803 0.057949
O 1.820394 -0.880410 0.848386
C 4.055226 -0.474074 -0.002820
C 4.450287 -1.598106 0.946538
C 4.769273 0.820894 0.393286
C 4.434831 -0.836463 -1.439988
H 3.966707 -2.541741 0.672931
H 5.535327 -1.755429 0.924512
H 4.150658 -1.372796 1.973287
H 4.473957 1.639056 -0.268634
H 4.524968 1.110381 1.421717
H 5.857185 0.697519 0.332782
H 4.147255 -0.038662 -2.128765
H 5.515467 -1.002534 -1.524622
H 3.932589 -1.755062 -1.766105

INT2$_{Ac}$.4
51 atoms
PCM Energy= -1292.88519312
O -1.293413 -0.683989 -1.540939
N -2.205504 0.733493 0.037670
C -3.105128 0.872417 1.217497
N 2.424002 0.146988 1.659216
C -2.171073 -0.398436 -0.710198
N 3.573572 0.344516 -0.149050
C 0.320810 4.034045 -0.720951
C 4.453562 0.526583 0.903887
C 2.318230 0.105360 0.307889
C 0.055116 1.609475 -0.548593
C -1.307806 1.815347 -0.260269
C 3.726007 0.406007 2.042968
C 0.843599 2.743365 -0.775672
C -1.029291 4.217363 -0.442997
C -1.838821 3.109676 -0.222327
H -2.754395 1.800664 1.680634
H 0.967122 4.891194 -0.894314
H 5.504011 0.713418 0.748765
H 4.016005 0.475793 3.079251
H 1.903589 2.613622 -0.988505
H -1.458371 5.214690 -0.405604
H -2.900197 3.246104 -0.026285
C 1.285374 -0.052070 2.539169
H 0.692236 0.866061 2.601383
H 0.661439 -0.854486 2.128319
H 1.644186 -0.323115 3.533322
C 3.929906 0.332936 -1.551974
H 4.532068 -0.547222 -1.790179
H 3.002465 0.294401 -2.127546
H 4.486950 1.236957 -1.810316
C -2.887308 -0.247118 2.225374
H -3.409698 -0.003195 3.155553
H -3.262741 -1.205455 1.864107
H -1.824448 -0.374780 2.443947
C -4.566834 1.060469 0.840397
H -4.987805 0.148509 0.414058
H -5.148019 1.319661 1.730653
H -4.690840 1.865622 0.110119
O -3.234750 -1.185959 -0.514245
C -3.111989 -2.523178 -1.024330
H -4.105594 -2.958164 -0.924260
H -2.800665 -2.512041 -2.069295
H -2.382753 -3.066482 -0.417967

Pd 0.664712 -0.293713 -0.656475
O 1.127209 -2.415541 -0.739961
C 0.314432 -3.002609 0.060407
O -0.474768 -2.435431 0.848358
C 0.317858 -4.517198 -0.027941
H -0.298975 -4.825348 -0.879217
H 1.322440 -4.905318 -0.208639
H -0.103336 -4.962502 0.875316

TS2-3-Cs
PCM Energy= -1424.11018696
O -0.594581 0.782657 -2.178737
N -1.941651 1.757022 -0.592163
C -3.159282 1.523971 0.232358
N 2.933845 -0.789249 1.500690
C -1.693102 0.932651 -1.642871
N 3.766173 0.639553 0.120753
C 1.009615 4.181224 1.183797
C 4.815656 0.178891 0.895034
C 2.595593 0.033980 0.475819
C 0.414966 1.992110 0.231707
C -0.862551 2.530134 -0.060191
C 4.286798 -0.723701 1.760528
C 1.320263 2.859866 0.863728
C -0.236217 4.698599 0.851933
C -1.156839 3.868477 0.223407
H -3.415564 0.479857 0.035605
H 1.748450 4.802749 1.687810
H 5.824628 0.539448 0.769929
H 4.746219 -1.307875 2.542617
H 2.306262 2.488095 1.134056
H -0.492542 5.732040 1.072838
H -2.137030 4.249527 -0.056511
C 1.996517 -1.726243 2.096873
H 1.014645 -1.250329 2.217241
H 1.877723 -2.582406 1.423903
H 2.389925 -2.050125 3.063525
C 3.887128 1.530076 -1.010210
H 2.880883 1.863744 -1.275896
H 4.512235 2.389670 -0.750532
H 4.318427 1.004148 -1.867459
C -4.319084 2.401188 -0.215738
H -5.235899 2.113248 0.311460
H -4.134551 3.459627 0.003164
H -4.495932 2.295897 -1.289756
C -2.866956 1.643965 1.717056
H -2.675800 2.678784 2.020943
H -3.740702 1.286950 2.273959
H -2.010694 1.021657 1.996697
O -2.802714 0.315011 -2.100330
C -2.492987 -0.843636 -2.885220
H -3.452927 -1.325199 -3.079703
H -2.008073 -0.563364 -3.823705
H -1.831759 -1.498876 -2.310331
Pd 0.858810 0.132793 -0.428796
O -1.001973 -1.081442 2.258545
O -1.381309 -0.987622 0.028307
C -1.534545 -1.466264 1.192679
C -2.504735 -2.685797 1.260349
C -2.701794 -3.143436 2.699264
H -3.118048 -2.337531 3.312472
H -3.379926 -4.007407 2.750844
H -1.746164 -3.422571 3.152369
C -1.887390 -3.808658 0.426839
H -1.701729 -3.466129 -0.595067
H -0.919707 -4.117260 0.840030
H -2.541372 -4.691699 0.398625
C -3.846927 -2.282849 0.651504
H -3.702264 -1.901222 -0.363967
H -4.541462 -3.133904 0.613077
H -4.327995 -1.491147 1.241692
Br 1.629623 -2.200408 -1.562412

INT3-Cs.4.2
61 atoms
PCM Energy= -1424.12784204
O -0.126301 1.511941 2.392586
N 1.242989 2.219253 0.686691
C 2.609237 2.200245 0.106847
N -3.310516 -1.224591 -0.849513
C 0.969772 1.560331 1.850530
N -3.507652 0.428663 0.515388
C -1.767284 3.363880 -2.017141
C -4.787710 0.067982 0.137337
C -2.580770 -0.366253 -0.083728
C -0.693940 1.577890 -0.715793
C 0.137394 2.571384 -0.153813
C -4.662487 -0.979468 -0.717300
C -1.638970 2.022750 -1.655787
C -0.959112 4.327043 -1.419988
C -0.010052 3.919707 -0.487582
H 3.042798 1.251393 0.427179
H -2.506876 3.655088 -2.762112
H -5.660806 0.581174 0.509396
H -5.405551 -1.570346 -1.229996
H -2.294953 1.292644 -2.129466
H -1.060495 5.379114 -1.677224
H 0.645199 4.645722 -0.007792
C -2.713414 -2.279285 -1.650191
H -1.710869 -1.963359 -1.956828
H -2.601974 -3.188084 -1.053150
H -3.342028 -2.460399 -2.526487
C -3.176044 1.554601 1.365514
H -2.128262 1.472090 1.666364
H -3.311647 2.494847 0.819829
H -3.818396 1.547478 2.250374
C 3.435394 3.348821 0.669025

H 4.469404 3.294585 0.308393
H 3.024787 4.318686 0.361768
H 3.454819 3.315606 1.762243
C 2.591952 2.203888 -1.411303
H 2.226736 3.151556 -1.822534
H 3.615131 2.052523 -1.773949
H 1.966950 1.395376 -1.798821
O 2.082591 0.992444 2.389076
C 1.776760 -0.067423 3.295163
H 2.740709 -0.434011 3.652335
H 1.170205 0.289522 4.132012
H 1.237775 -0.866213 2.770356
Pd -0.612397 -0.351269 -0.065528
O 1.041069 -1.617752 -2.093092
O 1.525183 -0.537565 -0.170638
C 1.802508 -1.307235 -1.165414
C 3.211484 -1.947672 -1.110743
C 3.757042 -2.099814 -2.526482
H 3.937548 -1.119667 -2.985481
H 4.707141 -2.650898 -2.525967
H 3.034871 -2.628659 -3.152800
C 3.001702 -3.327642 -0.478184
H 2.537654 -3.231352 0.509531
H 2.328115 -3.932558 -1.092770
H 3.957404 -3.859511 -0.374267
C 4.181171 -1.141106 -0.254314
H 3.779117 -0.983657 0.750535
H 5.146659 -1.659403 -0.171845
H 4.373608 -0.154036 -0.692329
Br -0.669897 -2.778528 1.164470

INT3.4.2
62 atoms
PCM Energy= -1443.97867988
O 2.682574 0.044589 1.962033
N 2.901003 -1.152067 0.009238
C 2.790962 -2.482351 -0.642791
N -0.648466 3.636347 -0.195623
C 2.710672 -1.014141 1.350036
N 1.260604 3.553258 0.782570
C 3.107642 2.024223 -2.741992
C 0.948131 4.889681 0.629286
C 0.277549 2.757395 0.286291
C 1.829763 0.852830 -1.005267
C 2.947108 0.015326 -0.814889
C -0.258095 4.945340 0.015737
C 1.945172 1.844055 -1.994547
C 4.220163 1.226362 -2.496733
C 4.129760 0.227134 -1.535510
H 2.035792 -3.020216 -0.060338
H 3.150246 2.800579 -3.503203
H 1.608686 5.671156 0.969609
H -0.870743 5.782988 -0.276905
H 1.100172 2.502710 -2.188805
H 5.144610 1.373098 -3.048740
H 4.977781 -0.423590 -1.330954
C -1.874998 3.244823 -0.842988
H -1.743521 2.204785 -1.155941
H -2.720770 3.307034 -0.149714
H -2.056295 3.879014 -1.715674
C 2.529134 3.078759 1.306625
H 2.486475 1.996068 1.440047
H 3.331685 3.319701 0.602442
H 2.729207 3.559719 2.266689
C 4.105715 -3.243471 -0.565004
H 3.978808 -4.264782 -0.940807
H 4.878625 -2.760862 -1.174046
H 4.462524 -3.302016 0.465930
C 2.278040 -2.373336 -2.068165
H 2.987947 -1.859996 -2.724482
H 2.129042 -3.382703 -2.464706
H 1.321341 -1.845201 -2.114282
O 2.595582 -2.215287 1.975530
C 2.174379 -2.095543 3.332945
H 2.078223 -3.117203 3.702007
H 2.908112 -1.542082 3.924223
H 1.211840 -1.578162 3.389427
Pd 0.194690 0.765385 0.203753
O -1.236556 -1.704513 -1.451535
O 0.111679 -1.380584 0.329047
C -0.671606 -2.075530 -0.399554
C -0.963675 -3.514882 0.101923
C -0.402889 -4.508633 -0.916432
H 0.692379 -4.489047 -0.928906
H -0.710121 -5.531932 -0.669069
H -0.757107 -4.270177 -1.924237
C -2.486036 -3.673999 0.161943
H -2.923317 -2.982255 0.894790
H -2.926626 -3.487675 -0.823798
H -2.760585 -4.688449 0.472026
C -0.377178 -3.772439 1.483414
H -0.754166 -3.046156 2.210353
H -0.640243 -4.780198 1.828773
H 0.711877 -3.683185 1.474797
Br -2.010751 0.884816 1.865174
-3.731232 -0.306241 -0.975638

INT2$_{OTf}$.7.2
52 atoms
PCM Energy= -2025.80465156
O -0.779309 -1.266991 -1.722846
N -2.280763 -1.461639 0.018453
C -2.598776 -2.241187 1.249788
N 0.274372 2.644822 1.338039
C -1.332633 -1.934767 -0.830392
N 1.357283 3.138411 -0.454653
C -4.099148 2.310280 -0.603339
C 1.751331 4.045542 0.509274
C 0.460569 2.258561 0.053155
C -2.078305 0.952790 -0.570541
C -2.858132 -0.171480 -0.228954
C 1.070144 3.731455 1.639676
C -2.719580 2.180477 -0.754328
C -4.863792 1.195047 -0.280709
C -4.245657 -0.038542 -0.108826
H -1.686330 -2.811067 1.442782
H -4.571161 3.279521 -0.741538
H 2.463552 4.828033 0.303307
H 1.075977 4.180416 2.619878
H -2.125154 3.054101 -1.009230
H -5.941540 1.275057 -0.173789
H -4.844705 -0.915613 0.116469
C -0.474592 1.868001 2.306755
H -1.451787 1.612062 1.891962
H 0.076275 0.951852 2.539640
H -0.605781 2.460651 3.212803
C 1.938240 3.018467 -1.777541
H 2.831320 2.391189 -1.738964
H 1.209540 2.541121 -2.435059
H 2.185434 4.009865 -2.161240
C -3.730396 -3.237600 1.045930
H -3.793933 -3.905361 1.910368
H -4.704142 -2.750035 0.940972
H -3.552867 -3.850430 0.159294
C -2.810913 -1.322130 2.437798
H -3.715047 -0.713692 2.348059
H -2.902034 -1.926477 3.344194
H -1.953579 -0.654592 2.561325
O -1.056884 -3.226354 -0.653053
C 0.107961 -3.690099 -1.360499
H 0.232970 -4.725319 -1.047944
H -0.053252 -3.630073 -2.438053
H 0.974531 -3.090881 -1.077482
Pd -0.144931 0.610448 -0.846883
O 2.007796 -0.084695 -0.958542
S 2.220878 -0.566467 0.457324
O 2.599709 0.490286 1.399926
O 1.193739 -1.525101 0.904562
C 3.738686 -1.588411 0.243414
F 4.128343 -2.075302 1.425250
F 3.500986 -2.619598 -0.581237
F 4.734875 -0.860011 -0.269072

INT4$_{OTf}$.4.1
52 atoms
PCM Energy= -2025.79488282
O 1.369138 -1.211612 2.126679
N 1.036073 -2.317534 0.133051
C 0.248593 -3.344799 -0.606214
N 0.675450 3.530583 0.092800
C 0.804902 -2.066846 1.455122
N 2.310276 2.453321 0.995899
C 3.634949 0.025265 -2.223703
C 2.650614 3.791815 1.013869
C 1.092652 2.279582 0.425125
C 1.656070 -0.112945 -0.813023
C 1.940027 -1.471284 -0.579773
C 1.622672 4.471157 0.444954
C 2.515747 0.617777 -1.639352
C 3.928209 -1.309213 -1.964009
C 3.081250 -2.047456 -1.144573
H -0.744877 -3.317596 -0.152317
H 4.278497 0.613731 -2.872919
H 3.576373 4.137817 1.444842
H 1.473079 5.525665 0.276805
H 2.308965 1.667010 -1.839508
H 4.808589 -1.776013 -2.396580
H 3.288863 -3.093838 -0.932659
C -0.576755 3.810890 -0.588012
H -0.470722 3.655814 -1.665307
H -1.351761 3.143730 -0.206886
H -0.861412 4.846262 -0.397201
C 3.154426 1.387184 1.512300
H 2.549756 0.489550 1.658644
H 3.957701 1.169520 0.802545
H 3.581055 1.703407 2.466171
C 0.844840 -4.731489 -0.418681
H 0.199943 -5.488430 -0.876250
H 1.830069 -4.808960 -0.892116
H 0.949914 -4.973145 0.641806
C 0.097150 -2.978515 -2.070919
H 1.047213 -3.032066 -2.612135
H -0.595747 -3.681982 -2.540534
H -0.310566 -1.971386 -2.186701
O -0.129256 -2.905686 1.960927
C -0.523707 -2.598255 3.296928
H -1.235418 -3.373774 3.576583
H 0.336279 -2.601230 3.970721
H -1.005297 -1.617210 3.342840
Pd 0.037399 0.657759 0.067192
O -2.026417 1.174100 0.978687
O -1.561479 -0.931454 -0.157190
S -2.647227 -0.085596 0.449674
O -3.609558 -0.764568 1.294703
C -3.586658 0.509709 -1.022484
F -2.762935 1.172360 -1.849933
F -4.559219 1.339329 -0.639964
F -4.119751 -0.517307 -1.681603

INT5$_{OTf}$.5
52 atoms
PCM Energy= -2025.74101551
O -0.026146 -2.897088 1.055860
N -1.853955 -1.965032 -0.002811
C -1.395129 -2.399153 -1.359776
N -0.328289 2.618208 1.335238
C -1.066581 -2.210232 1.059715
N 0.668106 3.384094 -0.395016
C -4.504444 1.296842 -0.092133
C 0.761694 4.365520 0.573691
C -0.001893 2.286314 0.056443
C -2.307069 0.361282 -0.552273
C -2.758423 -0.846467 -0.000730
C 0.126307 3.879688 1.669810
C -3.209242 1.431106 -0.591707
C -4.925633 0.090381 0.464469
C -4.049117 -0.989093 0.503136
H -0.684570 -3.204745 -1.154326
H -5.187353 2.142701 -0.133413
H 1.263688 5.305078 0.403001
H -0.035911 4.314115 2.643734
H -2.889241 2.387915 -0.998782
H -5.931942 -0.011707 0.860752
H -4.349656 -1.943720 0.929096
C -1.049978 1.737709 2.231902
H -2.089295 2.060082 2.346632
H -1.041639 0.734695 1.804706
H -0.558717 1.722292 3.208300
C 1.248028 3.467862 -1.718645
H 2.334928 3.356735 -1.677772
H 0.834681 2.653860 -2.317700
H 0.997505 4.424512 -2.183269
C -0.706767 -1.264930 -2.111606
H 0.297653 -1.563589 -2.436073
H -1.283891 -0.988873 -3.001585
C -2.592647 -2.972663 -2.098692
H -2.271669 -3.374524 -3.063279
H -3.080148 -3.773787 -1.533506
H -3.335737 -2.192593 -2.296374
O -1.532905 -1.667673 2.200260
C -0.682223 -1.849435 3.336165
H -1.183531 -1.331339 4.153288
H -0.567991 -2.909756 3.570863
H 0.303516 -1.415675 3.152055
Pd -0.372910 0.487617 -1.015195
O 2.067147 0.224452 -1.140433
O 1.920541 -2.140590 -0.339032
C 4.108643 -0.833454 0.108322
H 1.110739 -2.481988 0.223161
S 2.274960 -0.659246 0.012619
F 4.595644 -1.218693 -1.065661
F 4.435877 -1.722528 1.041114
F 4.618951 0.354387 0.432349
O 1.805695 -0.279000 1.335463

INT4.4
60 atoms
PCM Energy= -1410.81951907
O -0.030179 1.257874 2.243776
N 0.760226 2.190895 0.292892
C 1.950544 2.545653 -0.527351
N -2.795180 -2.476161 -0.200804
C 0.890328 1.607199 1.516378
N -3.213476 -0.789498 1.071538
C -2.989745 2.559567 -1.599692
C -4.322015 -1.612725 1.116311
C -2.259480 -1.309644 0.255709
C -1.262448 1.120735 -0.652257
C -0.550338 2.275164 -0.276458
C -4.060667 -2.674932 0.314231
C -2.484708 1.291403 -1.313944
C -2.287839 3.692725 -1.201547
C -1.073923 3.543507 -0.539599
H 2.697196 1.782276 -0.293904
H -3.936242 2.657608 -2.126505
H -5.180341 -1.378216 1.725208
H -4.645853 -3.548986 0.077287
H -3.055800 0.416259 -1.618117
H -2.680523 4.685824 -1.401193
H -0.507096 4.414544 -0.217946
C -2.123598 -3.365906 -1.130175
H -2.388497 -3.118230 -2.161882
H -1.044264 -3.263551 -1.000229
H -2.419271 -4.395304 -0.920108
C -3.096014 0.455487 1.813752
H -2.043646 0.739073 1.876961
H -3.653306 1.250686 1.310380
H -3.497035 0.306933 2.818672
C 2.489491 3.912709 -0.133716
H 3.422003 4.126092 -0.666472
H 1.777461 4.706793 -0.385155
H 2.693460 3.959779 0.939009
C 1.653245 2.450298 -2.012107
H 0.942581 3.214269 -2.343301
H 2.584612 2.596564 -2.567546
H 1.253576 1.466511 -2.268164
O 2.196097 1.471377 1.874938
C 2.369773 0.747896 3.089367
H 3.445704 0.713975 3.262441
H 1.862270 1.242645 3.921077
H 1.970739 -0.266770 2.990935
Pd -0.458783 -0.672435 -0.257281
O 0.935800 -2.437549 -0.047758
O 1.667980 -0.459316 -0.719085
C 1.886538 -1.677145 -0.411291
C 3.326556 -2.176582 -0.432510
C 3.368040 -3.699801 -0.415061
H 2.893374 -4.120364 -1.307047
H 4.405557 -4.050364 -0.386924
H 2.841791 -4.098314 0.455499
C 4.002809 -1.615780 0.826346
H 3.932779 -0.523651 0.851333
H 3.534359 -2.008696 1.735543
H 5.061235 -1.897517 0.844844
C 4.034718 -1.627298 -1.671259
H 3.985136 -0.535530 -1.696855
H 5.087613 -1.929475 -1.671407
H 3.578249 -2.003767 -2.592612

TS4-5
60 atoms
PCM Energy= -1410.76617022
C 4.426537 1.166329 -1.159622
C 3.550428 2.184251 -1.530096
C 2.173432 2.006636 -1.392495
C 1.651920 0.809813 -0.891573
C 3.921310 -0.032977 -0.670452
H 5.500107 1.303305 -1.255031
H 3.937828 3.122806 -1.919717
H 1.499784 2.817832 -1.663036
H 4.587566 -0.837500 -0.368179
H -1.002718 -1.539447 -0.987768
O -2.486658 0.176322 -0.287834
C -2.827055 -1.030500 -0.248328
O -2.032313 -2.001073 -0.510210
C -4.256010 -1.409926 0.135470
Pd -0.300750 0.461714 -0.617284
C -0.410217 2.175523 0.451111
N 0.357387 2.560842 1.504874
N -1.287479 3.199834 0.278103
C -0.032480 3.799159 1.975584
C 1.457075 1.784620 2.055563
C -1.073800 4.202648 1.205393
C -2.344279 3.201894 -0.713745
H 0.460214 4.276709 2.807424
H 1.283898 0.726648 1.863839
H 2.405743 2.061265 1.587748
H 1.511544 1.955133 3.132033
H -1.676792 5.096017 1.235510
H -2.111319 2.443030 -1.461193
H -3.304309 2.947820 -0.257423
H -2.405900 4.184914 -1.185703
C 2.542185 -0.209732 -0.535904
N 2.023048 -1.444888 -0.039717
C 1.256958 -2.302866 -0.977944
C 2.422284 -1.854209 1.199722
H 0.720783 -3.018076 -0.348448
C 2.226971 -3.057046 -1.879255
C 0.229318 -1.488520 -1.755067
O 3.038383 -1.175265 2.007364
O 2.029458 -3.135032 1.453022
H 1.686767 -3.708223 -2.573290
H 2.819460 -2.352640 -2.474217
H 2.914696 -3.676598 -1.294151

H 0.720581 -0.846729 -2.494967
H -0.343117 -2.187365 -2.381397
C 2.357246 -3.576697 2.765658
H 2.000445 -4.604484 2.829147
H 3.436165 -3.536053 2.936387
H 1.868257 -2.958999 3.523955
C -4.192988 -2.219584 1.435221
H -5.200888 -2.526848 1.734013
H -3.580995 -3.115878 1.306929
H -3.766353 -1.629734 2.253301
C -5.102262 -0.157804 0.334496
H -4.687783 0.479902 1.120348
H -5.150405 0.439371 -0.581065
H -6.123939 -0.433497 0.616314
C -4.844779 -2.281909 -0.976654
H -4.236956 -3.176072 -1.132904
H -5.861064 -2.592859 -0.712221
H -4.899216 -1.737349 -1.925249

INT5.5
60 atoms
PCM Energy= -1410.78561718
O 0.163615 -2.113386 1.932958
N -1.516864 -2.229565 0.345276
C -0.544787 -2.811622 -0.633040
N -1.372970 2.749584 0.843853
C -0.974597 -1.858468 1.537515
N 0.324531 3.326247 -0.321356
C -4.205045 0.345144 -1.617819
C -0.205194 4.492531 0.196240
C -0.380300 2.222730 0.067068
C -1.942228 -0.170688 -0.883223
C -2.458798 -1.324746 -0.269942
C -1.283808 4.126152 0.931308
C -2.844585 0.652981 -1.567283
C -4.696796 -0.788060 -0.973299
C -3.815561 -1.632229 -0.301816
H 0.122792 -3.415958 -0.011246
H -4.886006 0.997522 -2.161133
H 0.227042 5.461919 0.002939
H -1.985074 4.713994 1.503009
H -2.483763 1.556948 -2.055451
H -5.757730 -1.020822 -1.002219
H -4.166860 -2.531520 0.199113
C -2.440958 1.986346 1.460744
H -3.381145 2.130872 0.920763
H -2.189094 0.927340 1.425472
H -2.564977 2.305483 2.499391
C 1.493917 3.270991 -1.174023
H 2.411930 3.371365 -0.588593
H 1.508169 2.301548 -1.674423
H 1.448673 4.070428 -1.917308
C 0.256875 -1.727172 -1.347947
H 1.331731 -1.947795 -1.304129
H -0.017411 -1.684962 -2.408912
C -1.305135 -3.725300 -1.577597
H -0.601323 -4.247811 -2.231551
H -1.896082 -4.472044 -1.037200
H -1.983945 -3.150744 -2.216867
O -1.868449 -1.196289 2.315425
C -1.329389 -0.731876 3.550473
H -2.161896 -0.263382 4.075995
H -0.922644 -1.558004 4.137627
H -0.532744 0.000486 3.379209
Pd -0.004087 0.227726 -0.585322
O 2.236394 0.395737 -0.253188
O 2.600753 -1.492921 0.941940
C 2.984845 -0.460334 0.218573
C 4.482903 -0.450776 -0.050389
C 4.889248 0.907211 -0.611989
H 4.709715 1.706546 0.113649
H 5.955440 0.907047 -0.858866
H 4.323070 1.147073 -1.515639
C 4.735336 -1.546665 -1.098624
H 4.443216 -2.530227 -0.720428
H 4.174286 -1.352047 -2.018558
H 5.799655 -1.577885 -1.352561
C 5.269557 -0.764141 1.222152
H 4.990769 -1.736087 1.633804
H 6.341280 -0.777256 0.999109
H 5.099341 -0.008070 1.995358
H 1.617193 -1.540386 1.080448

***t*BuCOOH**.1
17 atoms
PCM Energy= -347.007126797
O -1.525166 1.244684 0.000000
O -1.597118 -1.002848 0.000000
C -0.939563 0.184553 0.000000
C 0.568764 -0.007487 0.000000
C 1.236710 1.362371 0.000000
H 0.950364 1.943585 0.880125
H 2.325180 1.247953 -0.000002
H 0.950361 1.943586 -0.880123
C 0.968522 -0.796886 -1.251996
H 0.499449 -1.783771 -1.267890
H 0.682565 -0.267433 -2.166543
H 2.054710 -0.932093 -1.272194
C 0.968522 -0.796886 1.251996
H 0.499446 -1.783770 1.267893
H 2.054709 -0.932096 1.272191
H 0.682569 -0.267429 2.166543
H -2.538821 -0.777206 0.000000

5.5.2 Catalytic cycle with chiral NHC 8

(*S*)-INT2$_{Me\text{-}Cl}$.s.1
95 atoms
PCM Energy= -1934.58686646
O -0.789460 -2.143059 -2.070886
N -2.373052 -2.512952 -0.440278
C -3.826034 -2.522410 -0.115119
C -1.972938 -2.265200 -1.711959
C 0.494341 -2.969403 2.632806
C -0.278748 -1.757834 0.660788
C -1.364501 -2.654532 0.573602
C 0.638165 -1.944639 1.700108
C -0.573702 -3.853733 2.527227
C -1.489609 -3.702669 1.491361
H -4.264648 -1.790089 -0.800666
H 1.226806 -3.079406 3.429233
H 1.489182 -1.271661 1.788077
H -0.691358 -4.670001 3.234239
H -2.307449 -4.410738 1.383692
C -4.088958 -2.036417 1.297972
H -5.154356 -1.814388 1.407529
H -3.817441 -2.771782 2.059358
H -3.525624 -1.122744 1.509867
C -4.465789 -3.872221 -0.403452
H -4.091636 -4.650478 0.268770
H -5.549725 -3.810977 -0.266594
H -4.271791 -4.183890 -1.432104
O -2.981339 -2.160878 -2.588715
C -2.572347 -1.685986 -3.888484
H -3.500985 -1.454334 -4.408094
H -1.933332 -0.802937 -3.792252
H -2.022085 -2.465715 -4.418082
Pd 0.024883 -0.489754 -0.870532
C 0.735331 0.920551 0.303731
N 2.042189 1.285095 0.362232
N 0.086810 1.704145 1.209145
C 3.070145 0.622646 -0.475229
C 2.212785 2.284530 1.299773
C -1.389931 1.741739 1.288413
C 0.990817 2.561382 1.816264
C 4.100888 1.611502 -1.104036
C 3.644254 -0.566510 0.270800
H 2.478457 0.260032 -1.322891
H 3.170224 2.729181 1.511517
C -1.958662 1.666963 2.740405
C -1.934161 2.851037 0.405272
H -1.670959 0.784141 0.833645
H 0.704455 3.300843 2.542524
C 5.251096 2.016646 -0.178883
C 4.712190 0.873985 -2.300319
C 3.369572 2.850570 -1.626159
C 3.621927 -1.860670 -0.288340
C 4.147466 -0.391007 1.564960
C -1.473585 0.366131 3.381777
C -1.607776 2.835570 3.666296
C -3.485740 1.637397 2.617557
C -2.808745 2.552872 -0.661228
C -1.557273 4.180464 0.619424
H 4.931337 2.576038 0.706055
H 5.937155 2.670440 -0.727648
H 5.822179 1.148936 0.164908
H 3.947002 0.638979 -3.047883
H 5.469130 1.502083 -2.780746
H 5.201420 -0.057276 -1.992588
H 2.488442 2.568243 -2.213357
H 4.040717 3.432847 -2.266270
H 3.036863 3.509467 -0.817871
C 3.046589 -2.154574 -1.641934
C 4.115583 -2.922074 0.480248
C 4.626591 -1.458093 2.314761
H 4.147194 0.605532 2.002863
H -1.894774 0.256474 4.386713
H -0.382408 0.339912 3.470998
H -1.766327 -0.511222 2.793497
H -2.202979 2.748844 4.581597
H -0.561786 2.829913 3.982902
H -1.845302 3.808026 3.224815
H -3.935213 1.473846 3.602027
H -3.876856 2.578814 2.219031
H -3.828777 0.829713 1.964142
C -3.281293 3.605357 -1.450678
C -3.215951 1.150385 -1.006352
C -2.037908 5.214198 -0.175462
H -0.850221 4.416014 1.409975
H 1.958383 -2.005566 -1.657271
H 3.452881 -1.516700 -2.431585
H 3.234960 -3.193581 -1.922436
C 4.610298 -2.735904 1.764749
H 4.088655 -3.922882 0.054205
H 5.007814 -1.291399 3.318428
C -2.911955 4.924033 -1.216034
H -3.945284 3.371615 -2.279986
H -2.336926 0.536765 -1.252171
H -3.875747 1.141684 -1.877992
H -3.743544 0.645180 -0.187821
H -1.722881 6.236307 0.014350
H 4.975507 -3.585661 2.335268
H -3.293455 5.717200 -1.852981
Cl 0.366509 0.862826 -2.946770

(*R*)-INT2$_{Me\text{-}Br}$.r.1
95 atoms
PCM Energy= -1932.78233080
O 0.182611 2.993248 0.544414
N -2.115743 3.035522 0.435017
C -3.281906 3.678518 -0.238993
C -0.876664 3.527251 0.183251
C -2.825559 -0.308440 2.941504
C -1.391758 0.779369 1.281799
C -2.257929 1.900959 1.312416
C -1.712054 -0.307548 2.103802
C -3.637878 0.816826 2.997493
C -3.344111 1.913814 2.195331
H -2.855386 4.087773 -1.157275
H -3.052551 -1.186530 3.541049
H -1.086207 -1.195833 2.064291
H -4.496912 0.852100 3.661530
H -3.973015 2.796214 2.252261
C -3.848642 4.853450 0.546878
H -4.550299 5.411213 -0.080919
H -4.392542 4.541963 1.442607
H -3.052810 5.537955 0.849121
C -4.333658 2.671260 -0.664138
H -4.869314 2.221173 0.175141
H -5.069243 3.180452 -1.293361
H -3.886580 1.865785 -1.253371
O -0.868679 4.678948 -0.497878
C 0.444008 5.088655 -0.934811
H 0.266672 5.903861 -1.634277
H 1.029686 5.437856 -0.082057
H 0.964387 4.253713 -1.413374
Pd 0.203579 0.874392 0.053786
C 0.529843 -1.072624 -0.109312
N -0.173976 -2.081285 -0.694837
N 1.733690 -1.614021 0.244046
C -1.551054 -1.911504 -1.212588
C 0.610698 -3.221887 -0.757177
C 2.719040 -0.890995 1.084560
C 1.792275 -2.931315 -0.164714
C -1.610252 -2.073798 -2.767306
C -2.569832 -2.726473 -0.423178
H -1.736583 -0.847201 -1.022276
H 0.296372 -4.132300 -1.233763
C 2.901470 -1.588509 2.475581
C 3.998766 -0.539774 0.352785
H 2.192184 0.045021 1.307842
H 2.650911 -3.559983 -0.010652
C -1.549506 -3.525844 -3.241987
C -2.941261 -1.481821 -3.236186
C -0.467440 -1.272890 -3.389135
C -3.778344 -2.149924 0.029511
C -2.338717 -4.078197 -0.132945
C 1.522112 -1.878123 3.067467
C 3.728493 -2.874701 2.436993
C 3.621740 -0.596280 3.392069
C 4.500586 0.779695 0.392918
C 4.706597 -1.508694 -0.364336
H -0.584615 -3.997461 -3.034789
H -1.677467 -3.554720 -4.329045
H -2.341011 -4.139263 -2.800092
H -3.026304 -0.424767 -2.958975
H -3.012405 -1.543757 -4.326557
H -3.798308 -2.020901 -2.817581
H -0.434542 -0.243324 -3.014580
H -0.582795 -1.236425 -4.477256
H 0.512844 -1.710620 -3.175502
C -4.175298 -0.730313 -0.234918
C -4.672555 -2.942910 0.759921
C -3.240330 -4.850933 0.587344
H -1.428081 -4.554771 -0.474525
H 1.619953 -2.252907 4.091659
H 0.974480 -2.632729 2.490988
H 0.909747 -0.969350 3.099912
H 3.901384 -3.221279 3.461393
H 3.221621 -3.693021 1.918067
H 4.707281 -2.717117 1.974343
H 3.786608 -1.048544 4.375098
H 4.597802 -0.305790 2.989182
H 3.026294 0.310188 3.541656
C 5.696243 1.055747 -0.277347
C 3.795963 1.908763 1.086499
C 5.887709 -1.211706 -1.033358
H 4.326473 -2.524124 -0.417173
H -3.335790 -0.036492 -0.154929
H -4.612643 -0.604916 -1.231600
H -4.925916 -0.404906 0.490467
C -4.420464 -4.277065 1.043945
H -5.590600 -2.480397 1.117478
H -3.015530 -5.894206 0.789746
C 6.389664 0.082455 -0.984826
H 6.072657 2.076267 -0.257069
H 2.749110 1.990866 0.771479
H 4.274517 2.859031 0.837017
H 3.810946 1.813512 2.177058
H 6.406475 -1.988155 -1.588213
H -5.136105 -4.860408 1.616686
H 7.309068 0.337638 -1.504825
Br 1.851778 1.395758 -1.961626

(*S*)-INT2$_{Me\text{-}Br}$.1
95 atoms
PCM Energy= -1932.79740716
O -0.972874 -1.864135 -2.115903
N -2.537873 -2.409289 -0.515287
C -3.988193 -2.431994 -0.175833
C -2.150778 -2.027832 -1.757154
C 0.300919 -3.188696 2.518457
C -0.431897 -1.788083 0.654683
C -1.526131 -2.660685 0.474663
C 0.462657 -2.080331 1.690485
C -0.766565 -4.054420 2.309567
C -1.667724 -3.793678 1.283077
H -4.421704 -1.626580 -0.776614
H 1.021524 -3.378475 3.310575
H 1.316892 -1.427030 1.854651
H -0.896742 -4.937566 2.928592
H -2.490675 -4.479005 1.097180
C -4.231088 -2.089730 1.282814
H -5.287570 -1.841754 1.419454
H -3.987841 -2.910779 1.961046
H -3.634117 -1.224265 1.585182
C -4.653406 -3.732895 -0.598814
H -4.288697 -4.585460 -0.017860
H -5.735034 -3.668146 -0.445916
H -4.473601 -3.935205 -1.656946
O -3.168611 -1.832075 -2.607721
C -2.769712 -1.212738 -3.848050
H -3.702297 -0.945693 -4.342866
H -2.150465 -0.331803 -3.652809
H -2.199976 -1.916544 -4.457093
Pd -0.068169 -0.389545 -0.759204
C 0.764653 0.793258 0.572001
N 2.100173 1.000784 0.712224
N 0.172076 1.458865 1.599192
C 3.084045 0.406984 -0.221744
C 2.341107 1.781430 1.826578
C -1.298837 1.624677 1.644453
C 1.137012 2.082485 2.371540
C 4.200720 1.403592 -0.665445
C 3.549631 -0.937880 0.302591
H 2.480996 0.246555 -1.122291
H 3.331119 2.073220 2.132831
C -1.896854 1.694412 3.081838
C -1.699355 2.743438 0.700651
H -1.658312 0.673238 1.231937
H 0.904081 2.683422 3.232067
C 5.362746 1.551657 0.319333
C 4.771530 0.838618 -1.971032
C 3.576505 2.768823 -0.963951
C 3.426820 -2.105983 -0.478017
C 4.060607 -1.036872 1.601604
C -1.352741 0.523878 3.903098
C -1.685701 3.019997 3.820407
C -3.412838 1.525382 2.930565
C -2.654725 2.540230 -0.314246
C -1.067977 3.986963 0.805415
H 5.073272 1.979374 1.284804
H 6.107388 2.231391 -0.107993
H 5.859311 0.596326 0.513153
H 4.000636 0.795971 -2.748327
H 5.581261 1.478514 -2.335894
H 5.183319 -0.167266 -1.828814
H 2.701992 2.665803 -1.616503
H 4.309130 3.408838 -1.466727
H 3.255163 3.288364 -0.055508
C 2.839188 -2.105081 -1.858214
C 3.836748 -3.322404 0.081224
C 4.458174 -2.254184 2.140794
H 4.128946 -0.139756 2.213784
H -1.863493 0.467672 4.870043
H -0.279578 0.615811 4.098665
H -1.505617 -0.429240 3.381386
H -2.235755 2.990273 4.766889
H -0.646039 3.232590 4.079066
H -2.068789 3.867608 3.245000
H -3.895238 1.573591 3.911814
H -3.846390 2.313559 2.305454
H -3.668785 0.558477 2.487212
C -2.953730 3.607132 -1.167941
C -3.325509 1.218005 -0.544489
C -1.375110 5.033477 -0.053541
H -0.301104 4.129022 1.564562
H 1.775621 -1.830495 -1.846408
H 3.328477 -1.397070 -2.533263
H 2.912563 -3.098122 -2.307965
C 4.346595 -3.407164 1.370269
H 3.736364 -4.225008 -0.517895
H 4.848089 -2.300248 3.153880
C -2.330314 4.841903 -1.046011
H -3.677538 3.446039 -1.963829
H -2.584862 0.413045 -0.663818
H -3.927010 1.246141 -1.457235
H -3.988368 0.926181 0.279278
H -0.864051 5.986837 0.045513
H 4.649369 -4.369853 1.773308
H -2.575554 5.644908 -1.735388
Br 0.365540 1.263848 -2.773134

(*S*)-INT2$_{Me\text{-}I}$.1
95 atoms
PCM Energy= -1931.00950201
O 1.001910 1.591264 -2.244974
N 2.594298 2.314673 -0.745040
C 4.048863 2.339171 -0.421756
C 2.184271 1.801410 -1.930296
C -0.143784 3.607727 2.199526
C 0.483003 1.939645 0.525697
C 1.606249 2.732890 0.210665
C -0.372261 2.406563 1.530688
C 0.949304 4.393537 1.851913
C 1.810384 3.959577 0.851426
H 4.451902 1.450561 -0.918558
H -0.831237 3.930402 2.978171
H -1.247999 1.819349 1.800251
H 1.129221 5.345681 2.342963
H 2.653327 4.579305 0.557128
C 4.292909 2.174683 1.067804
H 5.337666 1.894246 1.229822
H 4.096430 3.086355 1.636750
H 3.657297 1.385595 1.480361
C 4.752332 3.555596 -1.004752
H 4.417766 4.484165 -0.532628
H 5.831832 3.475497 -0.844035
H 4.575593 3.632578 -2.079622
O 3.189674 1.531071 -2.774835
C 2.781424 0.822857 -3.961127
H 3.709609 0.532756 -4.451073
H 2.178013 -0.050771 -3.698364
H 2.194545 1.476240 -4.609179
Pd 0.060864 0.360177 -0.681766
C -0.795426 -0.623299 0.790756
N -2.133634 -0.805938 0.956075
N -0.205939 -1.177720 1.885098
C -3.118308 -0.294006 -0.024835
C -2.376360 -1.456995 2.150695
C 1.264809 -1.329502 1.969381
C -1.173148 -1.705172 2.722918
C -4.310558 -1.266784 -0.291484
C -3.488822 1.135955 0.318707
H -2.542062 -0.294147 -0.957857
H -3.367289 -1.705398 2.490479
C 1.845600 -1.212920 3.411660
C 1.693909 -2.551087 1.178811
H 1.625236 -0.432538 1.451063
H -0.940758 -2.212133 3.642093
C -5.440360 -1.201674 0.739957
C -4.903388 -0.847511 -1.641723
C -3.790746 -2.700213 -0.423270
C -3.351831 2.173287 -0.626207
C -3.926939 1.443555 1.611778
C 1.303024 0.061159 4.061296
C 1.613344 -2.424530 4.321041
C 3.364826 -1.078433 3.257176
C 2.677325 -2.466991 0.173457
C 1.067910 -3.779038 1.418493
H -5.142189 -1.507114 1.748000
H -6.241334 -1.883049 0.433995
H -5.868433 -0.197492 0.811233
H -4.168298 -0.955862 -2.446876
H -5.762149 -1.480677 -1.886461
H -5.253899 0.190680 -1.624232
H -2.934434 -2.748309 -1.105578
H -4.581734 -3.344754 -0.820615
H -3.474563 -3.123039 0.535068
C -2.834038 1.949497 -2.016318
C -3.676758 3.476119 -0.229497
C -4.238271 2.744072 1.988358
H -4.005101 0.645194 2.347420
H 1.784989 0.230065 5.029891
H 0.222401 0.011179 4.230791
H 1.492688 0.937953 3.429433
H 2.190786 -2.292209 5.242113
H 0.574887 -2.560791 4.631945
H 1.952463 -3.352487 3.851491
H 3.832192 -0.970434 4.240797
H 3.799936 -1.959495 2.773295
H 3.634375 -0.197620 2.667058
C 3.012301 -3.630090 -0.527818
C 3.350906 -1.180905 -0.205843
C 1.412121 -4.922722 0.710048
H 0.275014 -3.832430 2.162245
H -1.802669 1.571351 -2.010069
H -3.422418 1.221789 -2.582894
H -2.832708 2.885331 -2.580059
C -4.113322 3.769178 1.056022
H -3.563395 4.278517 -0.955303
H -4.571325 2.953255 3.001253
C 2.399004 -4.847645 -0.267121
H 3.757315 -3.560475 -1.317595
H 2.627199 -0.359516 -0.302267
H 3.854379 -1.284628 -1.171505
H 4.104296 -0.863076 0.526384
H 0.904169 -5.861331 0.912019
H -4.347423 4.794203 1.330141
H 2.673663 -5.728303 -0.840478
I -0.375665 -1.692828 -2.532245

(*R*)-INT2$_{Me\text{-}OTf}$.2
102 atoms
PCM Energy= -2880.98429046
O -0.561693 2.457419 -1.474716
N 1.588593 3.140711 -1.002401
C 2.355610 4.109792 -0.166225
C 0.250693 3.338480 -1.144723
C 3.580170 -0.128237 -2.822064
C 1.659575 0.697119 -1.562903
C 2.204623 2.000162 -1.618788
C 2.366017 -0.344974 -2.174694
C 4.102030 1.158351 -2.886138
C 3.410641 2.211460 -2.299187
H 1.604423 4.496200 0.528684
H 4.111523 -0.963403 -3.271238
H 1.967505 -1.354972 -2.120874
H 5.040047 1.352451 -3.398568
H 3.805889 3.219500 -2.372957
C 2.907153 5.296694 -0.943447
H 3.245363 6.066183 -0.242733
H 3.765617 5.031204 -1.566806
H 2.137569 5.737784 -1.580038
C 3.404688 3.393608 0.661655
H 4.227435 3.003871 0.055100
H 3.825511 4.091538 1.390329
H 2.956735 2.557099 1.208639
O -0.118052 4.596712 -0.932044
C -1.540494 4.840295 -0.941687
H -1.639014 5.909720 -0.764676
H -1.959814 4.570955 -1.912677
H -2.028899 4.258643 -0.161063
C 0.122240 -1.395955 -0.101950
N 0.974764 -2.039715 0.743766
N -0.859465 -2.293697 -0.404560
C 2.140588 -1.370444 1.373521
C 0.496491 -3.316100 0.995488
C -1.902240 -2.022789 -1.426280
C -0.637477 -3.474923 0.273136
C 1.859634 -1.051461 2.878702
C 3.464857 -2.064547 1.078106
H 2.146789 -0.396958 0.869468
H 0.962393 -4.005649 1.673911
C -1.761752 -2.969402 -2.661781
C -3.295298 -1.885950 -0.846337
H -1.602283 -1.037814 -1.799757
H -1.281432 -4.332844 0.194841
C 1.825222 -2.293759 3.767970
C 2.976301 -0.132951 3.377110
C 0.527955 -0.310315 2.980869
C 4.587288 -1.323309 0.639417
C 3.625478 -3.445517 1.259511
C -0.300163 -2.980578 -3.110641
C -2.240558 -4.400927 -2.417595
C -2.615033 -2.368145 -3.781312
C -4.085841 -0.758339 -1.159355
C -3.811921 -2.853471 0.021047
H 0.980924 -2.948456 3.533420
H 1.698667 -1.987468 4.811377
H 2.752722 -2.872489 3.706765
H 2.995610 0.808240 2.817197
H 2.808248 0.116606 4.429163
H 3.962328 -0.603698 3.297573
H 0.488404 0.566630 2.321162
H 0.368900 0.041151 4.005043
H -0.325086 -0.943583 2.719994
C 4.594428 0.165494 0.470973
C 5.783148 -2.001336 0.372147
C 4.822481 -4.099808 0.996246
H 2.800986 -4.043769 1.624397
H -0.194330 -3.534194 -4.049162
H 0.353895 -3.456414 -2.370736
H 0.068112 -1.961224 -3.279411
H -2.215392 -4.956662 -3.360728
H -1.601170 -4.948841 -1.719195
H -3.269606 -4.427057 -2.046743
H -2.548044 -2.990745 -4.679013
H -3.669650 -2.305086 -3.493460
H -2.272600 -1.362264 -4.046714
C -5.354657 -0.656522 -0.579505
C -3.647067 0.350262 -2.071165
C -5.077665 -2.735313 0.583875
H -3.211066 -3.720574 0.278166
H 3.665600 0.558368 0.053088
H 4.762585 0.677225 1.425422
H 5.400037 0.469108 -0.202789
C 5.913816 -3.372124 0.540328
H 6.632467 -1.418734 0.021165
H 4.894950 -5.172733 1.149223
C -5.855992 -1.625462 0.279322
H -5.947525 0.229074 -0.796567
H -2.591859 0.614496 -1.955253
H -4.207856 1.259561 -1.849224
H -3.811147 0.099846 -3.125776
H -5.444708 -3.502899 1.259290
H 6.857259 -3.864322 0.321070
H -6.842044 -1.505994 0.719535
Pd -0.082002 0.509746 -0.640211
O -1.962725 0.455616 0.576859
S -2.334674 1.811727 1.122146
O -1.162846 2.621107 1.497594
O -3.407315 2.486681 0.386713
C -3.131159 1.330209 2.713061
F -3.576202 2.425244 3.339851
F -4.164131 0.513483 2.487667
F -2.267130 0.705768 3.525190

(*S*)-INT2$_{Me\text{-}OTf}$.2
102 atoms
PCM Energy= -2880.99059707
O -1.182830 0.315407 -2.463064
N -3.165245 -0.604807 -1.714361
C -4.607900 -0.320344 -1.466402
C -2.424345 0.309853 -2.397740
C -1.469093 -4.278952 -0.470348
C -1.282971 -1.851454 -0.650088
C -2.547235 -1.822165 -1.272427
C -0.761520 -3.096394 -0.272714
C -2.717041 -4.238614 -1.081595
C -3.238468 -3.019553 -1.495389
H -4.645061 0.768800 -1.361194
H -1.036983 -5.226043 -0.158049
H 0.228154 -3.148654 0.177295
H -3.277641 -5.151167 -1.262463
H -4.190759 -2.992427 -2.015953
C -5.066191 -0.916437 -0.146865
H -6.023414 -0.469010 0.134366
H -5.201497 -1.999785 -0.190683
H -4.343539 -0.702736 0.646470
C -5.510287 -0.695781 -2.633420
H -5.595202 -1.778459 -2.762549
H -6.518811 -0.309768 -2.456504
H -5.143152 -0.263420 -3.565877
O -3.161511 1.216399 -3.034595
C -2.415831 2.263691 -3.701334
H -3.171529 2.840673 -4.231530
H -1.885058 2.869737 -2.966172
H -1.693986 1.831539 -4.394951
C 0.620641 -0.762056 1.104977
N 1.905303 -1.169874 1.238080
N 0.029415 -0.963705 2.311911
C 2.878550 -1.017571 0.132012
C 2.117608 -1.645111 2.518797
C -1.268866 -0.301280 2.598569
C 0.948683 -1.502241 3.194120
C 4.162109 -0.241015 0.560363
C 3.066142 -2.331499 -0.597481
H 2.359704 -0.327851 -0.537963
H 3.064394 -2.034175 2.852880
C -2.127853 -0.986512 3.694933
C -0.995431 1.184845 2.758161
H -1.827605 -0.454451 1.667318
H 0.711670 -1.746278 4.214547
C 5.209787 -1.092541 1.278672
C 4.788801 0.287014 -0.734602
C 3.764401 0.956178 1.429992
C 2.816629 -2.419921 -1.983360
C 3.430325 -3.484666 0.105772
C -2.246657 -2.476344 3.366803
C -1.642673 -0.782273 5.133217
C -3.517981 -0.347833 3.607966
C -1.645153 2.148194 1.961191
C 0.012712 1.595197 3.639953
H 4.866848 -1.480588 2.243351
H 6.091346 -0.477987 1.489181
H 5.535908 -1.940418 0.668737
H 4.117563 0.991137 -1.237390
H 5.720570 0.816733 -0.512570
H 5.027723 -0.526083 -1.429847
H 2.952270 1.529751 0.970933
H 4.624115 1.622700 1.553947
H 3.437525 0.653953 2.431105
C 2.364176 -1.249470 -2.806712
C 2.956549 -3.667489 -2.602676
C 3.556518 -4.715999 -0.525873
H 3.607130 -3.422199 1.177227
H -2.939109 -2.966637 4.058724
H -1.284577 -2.994779 3.433538
H -2.623281 -2.626451 2.347113
H -2.380927 -1.205139 5.822470
H -0.693236 -1.272578 5.361665
H -1.537523 0.279720 5.372935
H -4.188803 -0.804839 4.342038
H -3.478167 0.727602 3.812215
H -3.964335 -0.489713 2.618406
C -1.250658 3.485888 2.084437
C -2.723999 1.813560 0.973770
C 0.379318 2.928387 3.757598
H 0.543257 0.846549 4.225976
H 1.341219 -0.945332 -2.545956
H 2.985300 -0.358439 -2.680529
H 2.362231 -1.503564 -3.869048
C 3.318213 -4.805866 -1.893138
H 2.761459 -3.738246 -3.670695
H 3.838330 -5.595205 0.046254
C -0.258043 3.881000 2.969191
H -1.713003 4.219920 1.429613
H -2.486241 0.915866 0.389778
H -2.846131 2.630967 0.258716
H -3.691895 1.634491 1.460418
H 1.170862 3.216257 4.443907
H 3.411281 -5.759395 -2.405833
H 0.039306 4.924680 3.017970
Pd -0.209725 -0.177528 -0.590862
O 1.138175 1.593393 -0.680198
S 0.665241 2.744039 -1.540281
O 0.960252 2.592608 -2.962938
O -0.671494 3.228714 -1.167347
C 1.829658 4.047934 -0.958533
F 1.672581 5.157757 -1.687373
F 1.622010 4.350951 0.327804
F 3.096963 3.630711 -1.090679

(*R*)-INT3$_{Me}$.r.1
PCM Energy= -2279.31271500
O -0.599192 -2.636138 1.748496
N 1.668145 -2.364174 1.980573
C 3.023832 -2.826108 1.603889
C 0.551306 -3.023817 1.581346
C 1.547062 1.525564 3.547022
C 1.052083 0.018087 1.660712
C 1.517606 -1.032541 2.479573
C 1.077938 1.291106 2.255657
C 1.977527 0.464794 4.335220
C 1.949585 -0.813958 3.791399
H 2.877561 -3.414716 0.698549
H 1.554202 2.543553 3.934238
H 0.718418 2.151246 1.702074
H 2.324061 0.623996 5.353840
H 2.267646 -1.674982 4.376481
C 3.616878 -3.715547 2.688345
H 4.574963 -4.134562 2.359378
H 3.801807 -3.148420 3.608697
H 2.945185 -4.545844 2.925071
C 3.943010 -1.665346 1.258723
H 4.193279 -1.061113 2.138033
H 4.877570 -2.064761 0.848253
H 3.493212 -1.009095 0.508560
O 0.850387 -4.230451 1.019395
C -0.203921 -4.754396 0.222482
H 0.138453 -5.733329 -0.118008
H -1.129263 -4.853016 0.798249
H -0.381107 -4.100301 -0.639059
O 2.665752 -0.427022 -1.981287
O 1.525626 -1.981262 -0.817330
C 2.345790 -1.599606 -1.734210
C 2.916393 -2.740343 -2.614457
C 4.175821 -2.259469 -3.326049
H 4.958338 -1.998819 -2.603890
H 4.569926 -3.041740 -3.988559
H 3.968638 -1.363906 -3.915451
C 1.832267 -3.078643 -3.642188
H 0.917915 -3.416602 -3.145097
H 1.563268 -2.198730 -4.234641
H 2.180593 -3.867744 -4.322674
C 3.231574 -3.987500 -1.792978
H 2.361300 -4.306712 -1.213136
H 3.538689 -4.812935 -2.449370
H 4.055185 -3.806112 -1.090860
Pd 0.276286 -0.304754 -0.233568
C -0.977174 1.208943 0.049063
N -0.756294 2.513692 -0.303126
N -2.223770 1.191763 0.604767
C 0.485770 2.956648 -0.973267
C -1.850441 3.290053 0.032394
C -2.875488 -0.071175 1.026910
C -2.764279 2.467671 0.600137
C 0.233351 3.651314 -2.355666
C 1.389184 3.747422 -0.036592
H 0.972664 2.000293 -1.207851
H -1.911316 4.344514 -0.178995
C -3.228210 -0.101924 2.549534
C -4.016648 -0.458310 0.096470
H -2.064472 -0.802630 0.911768
H -3.737117 2.700399 0.995368
C -0.089681 5.145129 -2.266608
C 1.533161 3.494300 -3.151499
C -0.891995 2.943242 -3.106258
C 2.730896 3.358356 0.172246
C 0.897738 4.860405 0.654855
C -1.980599 0.258144 3.351983
C -4.381787 0.816693 2.955358
C -3.617679 -1.542863 2.893035
C -4.055016 -1.741860 -0.493265
C -5.060825 0.430871 -0.179739
H -1.016400 5.347254 -1.717908
H -0.235438 5.536458 -3.279889
H 0.713607 5.721330 -1.797910
H 1.780402 2.436181 -3.293944
H 1.428350 3.955553 -4.139908
H 2.375477 3.981714 -2.646041
H -0.724866 1.863664 -3.173296
H -0.962858 3.348307 -4.122427
H -1.864013 3.090347 -2.622954
C 3.316191 2.131724 -0.449079
C 3.518325 4.123896 1.040886
C 1.692060 5.601270 1.522549
H -0.138422 5.156391 0.520348
H -2.185312 0.164783 4.425135
H -1.648847 1.284431 3.163521
H -1.153105 -0.412952 3.099975
H -4.586974 0.679824 4.023390
H -4.144401 1.876788 2.818745
H -5.305280 0.589326 2.413343
H -3.884190 -1.609433 3.954114
H -4.481772 -1.881307 2.309445
H -2.777950 -2.220547 2.711256
C -5.134649 -2.065175 -1.322884
C -2.982655 -2.760948 -0.276459
C -6.125525 0.092215 -1.007551
H -5.050894 1.424579 0.254558
H 2.711995 1.236879 -0.257684
H 3.384723 2.188122 -1.539424
H 4.321161 1.943667 -0.060935
C 3.019176 5.233203 1.711255
H 4.547740 3.811527 1.206553
H 1.272584 6.457274 2.045312
C -6.163794 -1.170350 -1.584725
H -5.146294 -3.050746 -1.784767
H -1.991644 -2.355001 -0.508046
H -3.145340 -3.626513 -0.925575
H -2.936934 -3.113972 0.758183
H -6.913648 0.816145 -1.198948
H 3.658549 5.797603 2.386030
H -6.983175 -1.455212 -2.240552

Br -0.990220 -0.724820 -2.583476

(*S*)-INT3$_{Me}$.s.1
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N -0.925468 -3.398868 0.741569
C -2.286913 -3.909801 1.060595
C -0.510748 -3.342579 -0.552578
C 0.814085 -1.172326 3.860582
C -0.058658 -1.202917 1.557776
C -0.226543 -2.598754 1.703024
C 0.439617 -0.529370 2.681797
C 0.722339 -2.557650 3.944592
C 0.201671 -3.256651 2.861153
H -2.931816 -3.536248 0.256001
H 1.188604 -0.588379 4.700341
H 0.521539 0.552151 2.629819
H 1.039669 -3.088723 4.838771
H 0.093261 -4.339689 2.903397
C -2.826610 -3.373700 2.374009
H -3.873344 -3.683374 2.462329
H -2.287006 -3.774355 3.237911
H -2.796119 -2.281823 2.411609
C -2.299540 -5.431693 1.033507
H -3.320543 -5.805448 1.171596
H -1.923299 -5.815449 0.082303
H -1.681375 -5.841160 1.841714
O -1.425641 -3.858778 -1.415251
C -1.231987 -3.422437 -2.759283
H -1.991909 -3.937281 -3.348939
H -1.382929 -2.338539 -2.818837
H -0.229497 -3.672138 -3.120477
O -3.418835 -0.302974 1.281254
O -2.282862 -1.207164 -0.453853
C -3.348939 -0.872878 0.182816
C -4.669733 -1.196317 -0.561714
C -5.585687 -1.988954 0.368719
H -5.666510 -1.485276 1.336561
H -6.589591 -2.092828 -0.063408
H -5.196894 -3.000764 0.544104
C -4.429145 -1.961614 -1.856611
H -3.784217 -1.387190 -2.527548
H -3.932240 -2.919703 -1.665092
H -5.381341 -2.162402 -2.366845
C -5.306558 0.162304 -0.872089
H -4.626186 0.780164 -1.470478
H -6.243328 0.034394 -1.430400
H -5.520504 0.697465 0.057792
Pd -0.512760 -0.104527 -0.093490
C 1.189973 1.017640 -0.079561
N 1.251468 2.344753 0.266475
N 2.398399 0.772750 -0.686167
C 2.433584 2.911661 -0.165822
C 0.226514 3.013442 1.088017
C 3.151560 1.930550 -0.757175
C 2.876910 -0.570886 -1.095555
H 2.686309 3.944845 0.004334
H -0.377190 2.168401 1.440622
C 0.833938 3.701156 2.371727
C -0.682847 3.929472 0.288521
H 4.139524 1.962777 -1.181058
H 2.117452 -1.237891 -0.671854
C 2.799175 -0.825407 -2.637128
C 4.226401 -0.885056 -0.453172
C 2.011504 2.905715 2.944014
C 1.297784 5.145316 2.152644
C -0.283410 3.738643 3.418347
C -0.148258 4.900828 -0.560833
C -2.082648 3.814942 0.404608
C 1.364409 -0.570200 -3.085626
C 3.718334 0.042497 -3.501916
C 3.150032 -2.298598 -2.863857
C 4.320315 -1.853944 0.571728
C 5.407656 -0.253000 -0.866984
H 1.774715 1.848319 3.084798
H 2.897367 2.956165 2.304432
H 2.285283 3.318074 3.921871
H 0.480818 5.792328 1.823320
H 1.686236 5.541555 3.097980
H 2.105232 5.231548 1.418499
H 0.071640 4.224436 4.334441
H -1.148713 4.303604 3.055607
H -0.620809 2.729153 3.679383
C -0.958770 5.775385 -1.273362
C -2.882458 4.714053 -0.308182
H 0.648377 -1.107044 -2.456832
H 1.095244 0.488321 -3.039410
H 1.230961 -0.905183 -4.121960
H 4.771968 -0.242592 -3.431617
H 3.426266 -0.079314 -4.551095
H 3.619024 1.109917 -3.272441
H 3.058820 -2.539331 -3.929590
H 4.178008 -2.524992 -2.556763
H 2.465370 -2.948450 -2.310964
C 5.577726 -2.149511 1.112075
C 6.647635 -0.551534 -0.312143
H 5.373384 0.490703 -1.654253
C -2.339583 5.687385 -1.136353
H -3.963108 4.610423 -0.231117
C 6.736387 -1.514853 0.684463
H 7.536071 -0.034011 -0.665732
H -2.991938 6.359726 -1.688785
H 7.696709 -1.768618 1.127501
H 0.929820 4.968192 -0.683239
H -0.512575 6.512991 -1.935603
H 5.632540 -2.900325 1.898490
C -2.734684 2.711871 1.174176
H -3.822270 2.759532 1.082922
H -2.432580 1.727897 0.792637
H -2.495213 2.711625 2.242466

C 3.120520 -2.549438 1.127265
H 2.457662 -1.841421 1.636675
H 2.499929 -3.027476 0.363536
H 3.414212 -3.305679 1.860364
Br -1.393175 1.427271 -2.169160

(*R*)-INT2$_{Me\text{-}Piv}$.7
PCM Energy= -2266.00152170
O -0.617000 2.539073 -1.466879
N 1.555978 3.136173 -0.989880
C 2.371283 4.009917 -0.099149
C 0.219745 3.360745 -1.062619
C 3.381867 -0.152180 -2.938825
C 1.533707 0.702303 -1.586936
C 2.116315 1.989714 -1.655545
C 2.190246 -0.345986 -2.242960
C 3.937272 1.120551 -3.007921
C 3.298801 2.183818 -2.378737
H 1.648452 4.388824 0.627893
H 3.872892 -0.994245 -3.420910
H 1.771596 -1.348288 -2.181320
H 4.858936 1.295717 -3.555976
H 3.717507 3.183159 -2.453000
C 2.974547 5.209977 -0.814232
H 3.374762 5.914756 -0.078794
H 3.799739 4.932119 -1.476447
H 2.217622 5.732163 -1.403604
C 3.390458 3.193865 0.670730
H 4.186979 2.802006 0.031107
H 3.851386 3.822154 1.437949
H 2.901089 2.348844 1.167192
O -0.127417 4.598671 -0.696773
C -1.538829 4.798495 -0.532755
H -1.646959 5.842141 -0.240946
H -2.067894 4.604127 -1.467916
H -1.908094 4.134269 0.251644
O -1.927345 0.690386 0.727617
O -0.765364 2.448458 1.513130
C -1.759451 1.692370 1.515128
C -2.931090 1.939951 2.486053
C -3.379676 0.613936 3.101831
H -2.585105 0.171422 3.713588
H -4.251181 0.766463 3.750049
H -3.645214 -0.104946 2.321547
C -4.089302 2.520325 1.667228
H -3.816539 3.475332 1.201648
H -4.387690 1.825277 0.876370
H -4.960107 2.703477 2.308045
C -2.514736 2.924074 3.571746
H -2.177806 3.869167 3.137201
H -3.351560 3.127676 4.250318
H -1.683089 2.528939 4.164239
Pd -0.168600 0.584367 -0.555921
C -0.066982 -1.322844 -0.040131
N 0.781951 -2.034359 0.756175
N -1.124727 -2.150119 -0.291103
C 2.007170 -1.445220 1.349176
C 0.233783 -3.279460 1.022654
C -2.190211 -1.798457 -1.259404
C -0.945551 -3.353238 0.362522
C 1.806400 -1.148023 2.872887
C 3.275185 -2.206401 0.980282
H 2.046859 -0.461407 0.866052
H 0.691134 -4.009870 1.663277
C -2.135273 -2.720518 -2.522598
C -3.556311 -1.622300 -0.625658
H -1.861157 -0.813810 -1.613628
H -1.645767 -4.167730 0.310393
C 1.737555 -2.405743 3.738685
C 2.991737 -0.304404 3.344456
C 0.525261 -0.331174 3.044906
C 4.412065 -1.522566 0.487931
C 3.364541 -3.597276 1.131361
C -0.689570 -2.787261 -3.017131
C -2.668783 -4.135642 -2.294043
C -2.990710 -2.063248 -3.607883
C -4.310392 -0.455229 -0.883768
C -4.098697 -2.600921 0.212620
H 0.843597 -3.002619 3.535958
H 1.684196 -2.115062 4.792833
H 2.622610 -3.039384 3.619228
H 3.040385 0.647725 2.805477
H 2.881045 -0.072023 4.408225
H 3.946111 -0.826165 3.214183
H 0.533918 0.576110 2.428281
H 0.414764 -0.023364 4.090901
H -0.370464 -0.899759 2.771730
C 4.493265 -0.033290 0.347662
C 5.547065 -2.264170 0.137622
C 4.503686 -4.315043 0.787984
H 2.526723 -4.153113 1.531982
H -0.640728 -3.317800 -3.973673
H -0.036755 -3.314688 -2.312170
H -0.278218 -1.781865 -3.167992
H -2.679086 -4.675278 -3.246891
H -2.042175 -4.721095 -1.614918
H -3.693298 -4.129456 -1.909793
H -2.999784 -2.687831 -4.506670
H -4.028137 -1.930504 -3.282325
H -2.588834 -1.084697 -3.890408
C -5.575594 -0.339292 -0.297523
C -3.815787 0.681141 -1.731265
C -5.353627 -2.460190 0.796944
H -3.528297 -3.498798 0.428004
H 3.582777 0.411741 -0.059085
H 4.688272 0.451055 1.311217
H 5.311097 0.242717 -0.322977
C 5.606065 -3.643483 0.276331
H 6.406306 -1.725723 -0.257355
H 4.521664 -5.393093 0.920161
C -6.101186 -1.319741 0.535317
H -6.151993 0.562905 -0.494099
H -2.851132 1.061691 -1.377602
H -4.524594 1.513273 -1.693198
H -3.699770 0.407813 -2.784621
H -5.737953 -3.238846 1.449723
H 6.503246 -4.185783 -0.008845
H -7.083639 -1.188559 0.980173

(*S*)-INT2$_{\text{Me-Piv}}$_7_2
PCM Energy= -2266.00706686
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N -2.138839 -2.508381 -1.379281
C -3.529583 -2.935081 -1.057003
C -1.938486 -1.567162 -2.339825
C 1.077249 -4.143066 0.821697
C -0.022768 -2.170467 -0.118187
C -1.011796 -3.020814 -0.652838
C 1.012277 -2.767006 0.615784
C 0.103748 -4.968350 0.269457
C -0.926984 -4.406230 -0.474912
H -4.131270 -2.034472 -1.215181
H 1.898581 -4.564001 1.397295
H 1.795199 -2.138058 1.037615
H 0.148780 -6.045972 0.399206
H -1.674211 -5.048523 -0.933450
C -3.672041 -3.326349 0.403871
H -4.732013 -3.317672 0.673363
H -3.280671 -4.323275 0.619367
H -3.149162 -2.616643 1.051492
C -4.046886 -4.009369 -2.002929
H -3.518205 -4.958436 -1.870827
H -5.107899 -4.196398 -1.810027
H -3.942567 -3.697940 -3.044152
O -3.041329 -1.298396 -3.046148
C -2.920232 -0.189298 -3.958801
H -3.900309 -0.106807 -4.426746
H -2.662520 0.715839 -3.402480
H -2.157362 -0.400617 -4.710558
O 0.332323 1.736560 -1.558002
O -1.910552 1.685652 -1.621394
C -0.820599 2.259862 -1.794736
C -0.793022 3.732753 -2.247663
C 0.428860 4.025482 -3.114647
H 0.438059 3.403523 -4.016128
H 0.430710 5.075189 -3.432207
H 1.357535 3.831155 -2.571340
C -0.730611 4.569263 -0.963544
H -1.604582 4.376664 -0.333141
H 0.162409 4.329311 -0.375524
H -0.705214 5.639807 -1.200171
C -2.073291 4.065257 -3.006806
H -2.952226 3.821865 -2.404876
H -2.103515 5.129971 -3.266145
H -2.142270 3.492357 -3.938515
Pd 0.031643 -0.258264 -0.723860
C 0.854321 0.333915 0.960976
N 2.144642 0.743692 1.083841
N 0.314487 0.424285 2.206115
C 3.066513 0.730991 -0.074468
C 2.411092 1.081850 2.396803
C -1.130732 0.202135 2.432454
C 1.264277 0.895020 3.096089
C 3.908722 2.036309 -0.211258
C 3.824646 -0.581575 -0.115009
H 2.374701 0.761960 -0.920921
H 3.371083 1.436563 2.731047
C -1.466788 -0.541918 3.761316
C -1.898949 1.486093 2.182307
H -1.383280 -0.511875 1.640511
H 1.059059 1.067723 4.137693
C 5.143050 2.104690 0.688399
C 4.389098 2.079228 -1.665414
C 2.991884 3.236989 0.031974
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C 4.512959 -1.019269 1.021955
C -0.600612 -1.798397 3.858274
C -1.338205 0.292735 5.039276
C -2.936450 -0.963603 3.659577
C -2.991222 1.524366 1.292753
C -1.508479 2.661279 2.836207
H 4.906342 2.124509 1.756643
H 5.692822 3.027954 0.476510
H 5.822970 1.266211 0.510128
H 3.540107 2.104628 -2.357944
H 4.990226 2.977779 -1.837709
H 5.012533 1.211479 -1.909969
H 2.059684 3.120804 -0.532897
H 3.484702 4.161543 -0.287359
H 2.728935 3.349417 1.089179
C 3.048120 -1.035457 -2.507594
C 4.461782 -2.634363 -1.208756
C 5.168842 -2.243173 1.053823
H 4.519835 -0.393159 1.911298
H -0.892005 -2.395564 4.728590
H 0.463306 -1.559219 3.959244
H -0.711247 -2.423941 2.964345
H -1.742187 -0.281193 5.879959
H -0.307389 0.536306 5.308294
H -1.906966 1.225038 4.976666
H -3.231543 -1.514536 4.558030
H -3.598870 -0.096656 3.563728
H -3.107011 -1.619015 2.799722
C -3.663826 2.740940 1.123254
C -3.467130 0.329302 0.521413
C -2.194610 3.855402 2.662949
H -0.640643 2.639449 3.492288
H 1.982132 -0.856571 -2.311696
H 3.434941 -0.124716 -2.975666
H 3.112765 -1.838437 -3.245484
C 5.141990 -3.057604 -0.073825
H 4.426811 -3.276838 -2.085875
H 5.693362 -2.557359 1.951882
C -3.288880 3.891574 1.803340
H -4.491567 2.776372 0.417953
H -2.632029 -0.263726 0.129709
H -4.050027 0.651140 -0.344295
H -4.095861 -0.331572 1.132293
H -1.871273 4.750802 3.186310
H 5.643070 -4.021929 -0.068403
H -3.832496 4.819099 1.643905

TS_{INT2}
PCM Energy= -2265.99662701
O 0.049632 2.753790 -0.553332
N 2.328454 2.848664 -0.908414
C 3.571152 3.602177 -0.552990
C 1.150579 3.307645 -0.417152
C 2.815797 -0.593050 -3.318061
C 1.586749 0.517867 -1.502737
C 2.360886 1.680610 -1.749064
C 1.874840 -0.606275 -2.291918
C 3.483350 0.588430 -3.613438
C 3.246015 1.713637 -2.834476
H 3.371068 3.965215 0.458223
H 3.006587 -1.496659 -3.891969
H 1.345695 -1.534875 -2.089974
H 4.184456 0.644512 -4.441200
H 3.761023 2.639873 -3.069223
C 3.781933 4.822387 -1.439726
H 4.607935 5.424535 -1.048498
H 4.036029 4.548937 -2.467988
H 2.889647 5.450887 -1.462137
C 4.807010 2.724888 -0.463413
H 5.216074 2.443221 -1.435529
H 5.581361 3.283736 0.069895
H 4.606205 1.809456 0.095086
O 1.256315 4.477718 0.225280
C 0.059514 4.888589 0.911188
H 0.328764 5.815076 1.416374
H -0.746606 5.063483 0.195301
H -0.236292 4.115173 1.624888
O -1.745005 0.902241 0.992413
O -0.228933 1.912525 2.310588
C -1.401034 1.627828 1.997619
C -2.594341 2.155754 2.820123
C -3.470746 0.975602 3.245933
H -2.925194 0.295005 3.909431
H -4.354652 1.330449 3.789857
H -3.804749 0.405945 2.373974
C -3.410419 3.078521 1.910601
H -2.801248 3.905700 1.525771
H -3.797575 2.518997 1.054154
H -4.257376 3.512167 2.455773
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H -1.491954 3.780485 3.760083
H -2.944214 3.270905 4.643982
H -1.470830 2.278321 4.673840
Pd 0.007983 0.613855 -0.251928
C -0.328414 -1.330851 -0.200601
N 0.257150 -2.316651 0.530832
N -1.336993 -1.933450 -0.894076
C 1.306619 -2.022755 1.527614
C -0.383087 -3.522057 0.298772
C -2.251446 -1.179134 -1.782092
C -1.376572 -3.281656 -0.589915
C 0.792061 -2.224295 2.991642
C 2.629982 -2.683036 1.192090
H 1.423914 -0.938239 1.412190
H -0.096379 -4.446087 0.768546
C -2.413750 -1.830247 -3.196275
C -3.552158 -0.837104 -1.077420
H -1.695052 -0.247290 -1.947302
H -2.086059 -3.963293 -1.024761
C 0.700157 -3.686588 3.427437
C 1.779812 -1.506040 3.914860
C -0.573268 -1.552649 3.135086
C 3.800291 -1.900479 1.098566
C 2.730567 -4.063004 0.982680
C -1.041846 -2.239901 -3.731108
C -3.372643 -3.023131 -3.249284
C -2.987462 -0.750687 -4.119544
C -4.043503 0.485134 -1.067165
C -4.281110 -1.837426 -0.428141
H -0.032642 -4.255646 2.846336
H 0.367589 -3.728249 4.469814
H 1.665529 -4.198812 3.371374
H 1.780575 -0.427561 3.722275
H 1.489813 -1.652177 4.960249
H 2.800398 -1.888191 3.797605
H -0.518939 -0.500268 2.842151
H -0.898289 -1.597331 4.180250
H -1.349053 -2.030981 2.526221
C 3.794422 -0.414064 1.291605
C 5.011708 -2.533319 0.801516
C 3.941852 -4.675602 0.682564
H 1.845793 -4.685945 1.061371
H -1.129653 -2.580062 -4.768254
H -0.596717 -3.055989 -3.151989
H -0.341116 -1.397703 -3.712249
H -3.472308 -3.353355 -4.288678
H -3.025725 -3.892819 -2.684270
H -4.370970 -2.760277 -2.888743
H -3.143393 -1.161419 -5.122109
H -3.952363 -0.379560 -3.758060
H -2.302482 0.098491 -4.213481
C -5.269004 0.730417 -0.437471
C -3.288165 1.644312 -1.647360
C -5.488593 -1.570772 0.207209
H -3.895329 -2.853898 -0.412677
H 3.152832 0.086967 0.555388
H 3.431010 -0.113984 2.279381
H 4.807206 -0.018289 1.182888
C 5.093869 -3.903889 0.592428
H 5.908869 -1.922256 0.728305
H 3.981017 -5.749716 0.525075
C -5.991317 -0.275326 0.193547
H -5.649411 1.750239 -0.431325
H -2.360764 1.818250 -1.087051
H -3.884741 2.558402 -1.581550
H -3.018676 1.506189 -2.698164
H -6.028609 -2.370518 0.705732
H 6.050438 -4.364391 0.360945
H -6.934972 -0.044670 0.680631

(*R*)-INT4$_{Me}$.7
PCM Energy= -2266.00568753
O 2.590345 -0.672916 -1.757750
N 1.574791 -2.701231 -1.395058
C 1.631342 -4.027976 -0.727958
C 2.613204 -1.827152 -1.346001
C -2.117716 -1.697497 -3.149188
C -0.475721 -1.298327 -1.379492
C 0.349394 -2.261613 -1.990107
C -1.707610 -1.033409 -1.994516
C -1.277087 -2.622827 -3.755777
C -0.043973 -2.892116 -3.174128
H 2.328555 -3.894974 0.102725
H -3.094548 -1.474479 -3.572999
H -2.388827 -0.305696 -1.563561
H -1.571935 -3.129261 -4.670661
H 0.639997 -3.603504 -3.630487
C 2.168689 -5.101754 -1.662678
H 2.320614 -6.039463 -1.118115
H 1.467670 -5.307433 -2.478621
H 3.126505 -4.800833 -2.094877
C 0.280943 -4.399394 -0.140115
H -0.474995 -4.570200 -0.914324
H 0.384369 -5.323693 0.436578
H -0.074188 -3.613131 0.531464
O 3.725773 -2.402358 -0.814815
C 4.824232 -1.510621 -0.670655
H 5.659811 -2.122235 -0.329623
H 5.067042 -1.024098 -1.619356
H 4.602286 -0.738568 0.072396
O 1.067576 -0.003453 2.362829
O 1.432423 -1.946725 1.373075
C 1.614838 -1.148804 2.350491
C 2.528075 -1.598957 3.483952
C 2.548793 -0.566662 4.603768
H 1.552304 -0.421182 5.030261
H 3.220300 -0.891263 5.406360
H 2.890600 0.405612 4.238389
C 3.932381 -1.774985 2.894316
H 3.916601 -2.480770 2.058293
H 4.329493 -0.820993 2.528079
H 4.621961 -2.151319 3.657863
C 2.025621 -2.950764 3.997909
H 1.987368 -3.683530 3.186595
H 2.690467 -3.331765 4.780727
H 1.020726 -2.866058 4.425329
Pd 0.166598 -0.451755 0.349709
C -0.865415 1.154082 -0.172084
N -2.158062 1.416891 0.168289
N -0.466360 2.188439 -0.957297
C -2.892970 0.553415 1.117915
C -2.564416 2.604504 -0.411895
C 0.951868 2.348497 -1.368195
C -1.507515 3.086577 -1.111872
C -3.108715 1.250489 2.496063
C -4.098564 -0.108793 0.479836
H -2.150031 -0.227644 1.318300
H -3.552604 3.013713 -0.294920
C 1.152957 2.513160 -2.903755
C 1.628516 3.378390 -0.476405
H 1.373014 1.360057 -1.147147
H -1.428385 3.983554 -1.700852
C -4.222019 2.297018 2.502028
C -3.471939 0.146185 3.491706
C -1.791487 1.897800 2.929589
C -4.172282 -1.517879 0.410773
C -5.129313 0.647522 -0.089153
C 0.417407 1.375852 -3.613133
C 0.701996 3.856598 -3.478397
C 2.656630 2.365657 -3.159792
C 2.751454 3.023521 0.300966
C 1.136930 4.686037 -0.385931
H -4.026321 3.122414 1.809238
H -4.296186 2.740123 3.500737
H -5.198079 1.864575 2.261974
H -2.649992 -0.570960 3.600109
H -3.667678 0.575155 4.479338
H -4.369547 -0.401441 3.182254
H -0.954874 1.190965 2.884721
H -1.875426 2.257774 3.960308
H -1.530979 2.758226 2.302827
C -3.110611 -2.410616 0.982009
C -5.265064 -2.100311 -0.238991
C -6.208755 0.050597 -0.731061
H -5.096432 1.731099 -0.031736
H 0.626957 1.407825 -4.687695
H -0.668363 1.445701 -3.484950
H 0.741447 0.402557 -3.229059
H 0.940477 3.884116 -4.546888
H -0.378781 4.012619 -3.401763
H 1.214398 4.702283 -3.010027
H 2.861893 2.468914 -4.230410
H 3.232671 3.137389 -2.636091
H 3.011447 1.380905 -2.841793
C 3.330772 3.994262 1.125558
C 3.346833 1.649978 0.273901
C 1.723855 5.637147 0.440697
H 0.270224 4.976382 -0.971503
H -2.131064 -2.222592 0.524084
H -2.986351 -2.273821 2.061906
H -3.355149 -3.461532 0.808774
C -6.274131 -1.335215 -0.810826
H -5.310448 -3.185323 -0.301508
H -6.989691 0.668097 -1.165655
C 2.831655 5.287890 1.203672
H 4.193996 3.712640 1.724941
H 2.613204 0.876060 0.531349
H 4.171620 1.579020 0.989822
H 3.729111 1.380249 -0.715807
H 1.314176 6.642329 0.486664
H -7.106062 -1.819679 -1.314245
H 3.302106 6.015733 1.859127

(*S*)-INT4$_{Me}$.3
PCM Energy= -2266.00267859
O 1.149618 -2.740018 -0.443369
N -0.214056 -3.081566 1.376719
C -1.434598 -3.744161 1.912550
C 0.192834 -3.283953 0.097084
C 1.599399 -0.229117 3.900860
C 0.367838 -0.708944 1.842709
C 0.451912 -2.081104 2.156153
C 0.959988 0.193621 2.735686
C 1.693918 -1.586713 4.184284
C 1.124883 -2.502975 3.305640
H -2.094932 -3.858751 1.050214
H 2.036728 0.506151 4.572612
H 0.932954 1.258544 2.514295
H 2.209940 -1.933700 5.075059
H 1.193859 -3.570932 3.500545
C -2.146328 -2.860042 2.919559
H -3.101239 -3.323936 3.184382
H -1.567781 -2.733293 3.840427
H -2.350156 -1.874468 2.493950
C -1.107884 -5.118314 2.477792
H -2.025873 -5.640068 2.767200
H -0.588106 -5.732996 1.738121
H -0.477395 -5.043254 3.370549
O -0.573347 -4.207459 -0.543414
C -0.212285 -4.391201 -1.908525
H -0.931754 -5.104675 -2.310989
H -0.266521 -3.446335 -2.460092
H 0.804992 -4.782418 -1.999715
O -2.058345 -0.096925 -1.576652
O -2.260425 -1.587559 0.044200
C -2.614874 -1.125434 -1.093488
C -3.717614 -1.827330 -1.880701
C -4.952824 -0.920647 -1.868908
H -4.722571 0.059879 -2.296706
H -5.762278 -1.374613 -2.451594
H -5.321519 -0.768591 -0.847769
C -4.049816 -3.177008 -1.252634
H -3.171271 -3.829684 -1.224912
H -4.398744 -3.059715 -0.222124
H -4.836547 -3.679578 -1.826609
C -3.238183 -2.007389 -3.322624
H -2.356730 -2.657080 -3.370848
H -4.024454 -2.465689 -3.932768
H -2.966977 -1.044790 -3.763003
Pd -0.601666 -0.165432 0.172394
C 0.696617 1.315934 -0.094378
N 0.424540 2.613029 0.234482
N 1.880662 1.350658 -0.765385
C 1.408193 3.446704 -0.266220
C -0.821244 2.966136 0.957045
C 2.320125 2.656823 -0.882955
C 2.596830 0.146616 -1.271689
H 1.403388 4.513621 -0.129745
H -0.937348 2.135060 1.663836
C -0.718206 4.246755 1.843709
C -1.998031 2.950652 0.000381
H 3.256256 2.913398 -1.348822
H 2.153984 -0.669770 -0.689436
C 2.233044 -0.189590 -2.755838
C 4.080931 0.232905 -0.938776
C 0.538108 4.190752 2.716449
C -0.784548 5.567275 1.070260
C -1.932712 4.220393 2.779487
C -1.874353 3.609685 -1.228116
C -3.202374 2.288086 0.309707
C 0.721046 -0.385947 -2.854977
C 2.634970 0.872111 -3.783747
C 2.919379 -1.517267 -3.088153
C 4.618055 -0.553573 0.104933
C 4.948219 1.079992 -1.643213
H 0.562469 3.268333 3.307815
H 1.468158 4.241844 2.144431
H 0.538313 5.029395 3.420291
H -1.711065 5.644219 0.494567
H -0.765229 6.400118 1.780905
H 0.044433 5.727443 0.376166
H -1.904947 5.084895 3.450062
H -2.872549 4.263031 2.219732
H -1.940053 3.317236 3.399186
C -2.922741 3.661934 -2.136005
C -4.251638 2.366341 -0.613150
H 0.370980 -1.122205 -2.123733
H 0.160984 0.540272 -2.688842
H 0.458919 -0.748862 -3.855887
H 3.702741 0.859148 -4.014571
H 2.107455 0.677217 -4.723472
H 2.352999 1.883808 -3.467149
H 2.660297 -1.825422 -4.106969
H 4.009906 -1.436927 -3.030018
H 2.589743 -2.304573 -2.401658
C 5.986747 -0.462694 0.381790
C 6.305700 1.159207 -1.351593
H 4.563251 1.698945 -2.445628
C -4.127512 3.043554 -1.818313
H -5.182348 1.852555 -0.380139
C 6.831821 0.377135 -0.331537
H 6.943046 1.827258 -1.924137
H -4.961729 3.070469 -2.514490
H 7.890341 0.421077 -0.089691
H -0.925955 4.083846 -1.477038
H -2.797435 4.177500 -3.083975
H 6.389156 -1.074591 1.186645
C -3.411616 1.474551 1.555013
H -4.199312 0.733378 1.391684
H -2.514395 0.916204 1.845153
H -3.711990 2.085130 2.414059
C 3.776642 -1.470018 0.935990
H 2.973452 -0.930183 1.447676
H 3.279960 -2.244374 0.344144
H 4.382178 -1.960257 1.702615

(*R*)-TS4-5$_{Me}$.2
PCM Energy= -2265.96048096
C -0.420631 -4.908542 0.035409
C 0.780655 -4.277947 0.351022
C 0.933850 -2.912457 0.119117
C -0.103041 -2.152961 -0.437088
C -1.455709 -4.171994 -0.526543
H -0.550728 -5.971345 0.220044
H 1.601188 -4.845264 0.784325
H 1.875212 -2.432228 0.382724
H -2.403881 -4.643537 -0.772976
H -1.016433 0.523052 -2.534635
O 0.391238 1.967596 -1.314779
C -0.519026 2.428621 -2.046666
O -1.386657 1.691868 -2.637819
C -0.593118 3.930491 -2.309627
C -1.301788 -2.801826 -0.760218
N -2.369420 -2.060431 -1.357755
C -2.181656 -1.528683 -2.732970
C -3.594637 -2.120332 -0.761718
H -2.947259 -0.756288 -2.853917
C -2.430610 -2.641856 -3.743377
C -0.818592 -0.871201 -2.891734
O -3.828677 -2.603050 0.336870
O -4.557501 -1.538138 -1.532234
H -2.316869 -2.269846 -4.766177
H -1.709048 -3.454111 -3.600154
H -3.439540 -3.054497 -3.639939
H -0.024161 -1.626702 -2.901594
H -0.768723 -0.443299 -3.902885
C -5.836258 -1.499958 -0.908033
H -6.506591 -1.045482 -1.637112
H -6.177845 -2.504754 -0.647185
H -5.812673 -0.898350 0.006633
C -2.052909 4.383227 -2.321880
H -2.111967 5.449456 -2.565446
H -2.634218 3.824396 -3.058560
H -2.517116 4.237850 -1.340763
C 0.190199 4.691272 -1.244653
H -0.174730 4.455948 -0.238909
H 1.254203 4.441321 -1.277329
H 0.087783 5.770015 -1.403931
C 0.031195 4.168281 -3.691082
H -0.519290 3.634032 -4.470698
H 0.014193 5.236709 -3.930733
H 1.074599 3.835542 -3.715710
Pd 0.086361 -0.198230 -0.864052
C 0.861065 0.019704 0.993848
N 2.177862 0.154180 1.298503
N 0.219195 -0.104470 2.185053
C 3.172384 0.454766 0.250396
C 2.360704 0.103495 2.668333
C -1.261590 -0.021870 2.243270
C 1.131510 -0.049680 3.222642
C 3.870809 1.834456 0.474351
C 4.069557 -0.732488 -0.032467
H 2.532894 0.610804 -0.624092
H 3.324427 0.188318 3.141227
C -1.918744 -0.850982 3.387498
C -1.665905 1.440887 2.160910
H -1.568921 -0.522639 1.316035
H 0.853461 -0.123625 4.258918
C 5.038045 1.799589 1.460313
C 4.411153 2.268169 -0.891736
C 2.824537 2.851453 0.939379
C 4.137102 -1.277125 -1.332224
C 4.803457 -1.337041 0.993875
C -1.395254 -2.286434 3.309383
C -1.736837 -0.280706 4.798426
C -3.427763 -0.867528 3.114175
C -2.605767 1.887960 1.208909
C -1.080590 2.371729 3.025883
H 4.731298 1.515330 2.472249
H 5.477078 2.799896 1.537400
H 5.827483 1.114357 1.137628
H 3.594692 2.412759 -1.609319
H 4.949857 3.217078 -0.803603
H 5.106955 1.528742 -1.305322
H 1.925337 2.808276 0.315980
H 3.236423 3.864730 0.880150
H 2.520461 2.680162 1.977784
C 3.334757 -0.730991 -2.476034
C 4.949435 -2.395549 -1.546921
C 5.597523 -2.454445 0.764412
H 4.749624 -0.932441 2.001051
H -1.910995 -2.914443 4.043272
H -0.320826 -2.350008 3.513264
H -1.577389 -2.713780 2.316014
H -2.358406 -0.857111 5.491295
H -0.716852 -0.343795 5.185621
H -2.061898 0.762293 4.861291
H -3.932031 -1.438171 3.900651
H -3.848759 0.144730 3.122274
H -3.662258 -1.349757 2.160966
C -2.953800 3.243984 1.205851
C -3.222081 0.974328 0.194245
C -1.424057 3.718366 2.994211
H -0.327094 2.034074 3.735244
H 2.255940 -0.794772 -2.272072
H 3.549589 0.323255 -2.681081
H 3.532839 -1.293966 -3.391158
C 5.673018 -2.985833 -0.518160
H 4.996758 -2.816685 -2.548934
H 6.150845 -2.904909 1.583442
C -2.379300 4.156282 2.083116
H -3.695903 3.583494 0.485830
H -2.453273 0.437919 -0.379009
H -3.829037 1.533764 -0.523239
H -3.858101 0.208860 0.651876
H -0.950601 4.416545 3.678668
H 6.287523 -3.859336 -0.717342
H -2.668282 5.203103 2.046364

(*S*)-TS4-5$_{Me}$.6
PCM Energy= -2265.95165941
O 4.162808 -1.555961 0.123400
N 2.304789 -2.329820 1.234133
C 1.324427 -3.421425 1.469000
C 3.328556 -2.424877 0.342484
C 2.074417 0.822228 4.014566
C 1.159999 -0.358960 2.096944
C 2.269526 -1.212738 2.126687
C 1.068504 0.643478 3.066081
C 3.198259 -0.001182 3.999755
C 3.288088 -1.027396 3.065173
H 1.316143 -4.008747 0.547061
H 1.983220 1.610038 4.758686
H 0.196778 1.294015 3.079966
H 3.993674 0.141597 4.725823
H 4.147725 -1.693548 3.049083
C -0.075610 -2.861598 1.684349
H -0.768833 -3.708309 1.787676
H -0.153822 -2.357920 2.654196
C 1.808726 -4.296562 2.617667
H 1.110804 -5.119641 2.798029
H 2.793803 -4.723834 2.402114
H 1.881562 -3.710991 3.541083
O 3.310066 -3.614504 -0.319128
C 4.285064 -3.708545 -1.352585
H 4.213856 -4.727322 -1.732624
H 4.074497 -2.993930 -2.154680
H 5.288269 -3.510888 -0.967925
O -1.902939 -1.115254 -0.712504
O -1.162876 -3.222293 -0.680955
C -1.898591 -2.289012 -1.158880
C -2.830945 -2.653645 -2.310544
C -3.334314 -1.386649 -2.994194
H -2.505167 -0.806733 -3.415084
H -4.014931 -1.646722 -3.812386
H -3.864505 -0.739817 -2.290553
C -4.009140 -3.421595 -1.697950
H -3.667836 -4.332213 -1.197180
H -4.542405 -2.800962 -0.968619
H -4.720435 -3.704759 -2.481340
C -2.092306 -3.545849 -3.308104
H -1.714133 -4.450603 -2.827021
H -2.766723 -3.837682 -4.120404
H -1.241041 -3.020559 -3.755014
H -0.659855 -2.805251 0.377091
Pd -0.272275 -0.731935 0.757380
C -0.289499 1.140003 -0.064821
N 0.527211 1.682149 -1.012931
N -1.387294 1.951311 -0.037212
C 1.882174 1.177386 -1.369250
C -0.062257 2.803638 -1.570990
C -2.475132 1.765652 0.942641
C -1.260702 2.969629 -0.962680
C 1.870986 0.205799 -2.599339
C 2.868824 2.335229 -1.430003
H 2.154126 0.544772 -0.515210
H 0.427460 3.403890 -2.319102
C -2.727239 3.041075 1.821998
C -3.728825 1.166740 0.332599
H -2.038668 1.024583 1.624163
H -2.002505 3.737582 -1.099851
C 1.159670 0.741529 -3.845840
C 3.325559 -0.137903 -2.929036
C 1.139814 -1.076423 -2.194997
C 3.764943 2.560035 -0.362710
C 2.919013 3.193442 -2.536154
C -1.394500 3.690634 2.197269
C -3.632085 4.096292 1.181120
C -3.419109 2.556416 3.099843
C -4.313837 0.010565 0.888871
C -4.333689 1.762427 -0.777640
H 0.162607 1.132442 -3.613625
H 1.019162 -0.081429 -4.555438
H 1.725316 1.511759 -4.375541
H 3.850545 -0.522018 -2.046096
H 3.354167 -0.911213 -3.705079
H 3.876530 0.730377 -3.302137
H 1.520278 -1.495076 -1.255939
H 1.255192 -1.838388 -2.974708
H 0.069364 -0.894461 -2.062640
C 3.779237 1.706943 0.866317
C 4.670295 3.623573 -0.460538
C 3.819999 4.249005 -2.612685
H 2.241986 3.037725 -3.369370
H -1.554593 4.453039 2.966254
H -0.916350 4.179034 1.342816
H -0.683322 2.960077 2.594558
H -3.769747 4.922041 1.887148
H -3.210733 4.534394 0.270924
H -4.621080 3.698113 0.939759
H -3.637014 3.403387 3.758124
H -4.369378 2.058079 2.878138
H -2.785186 1.856547 3.656646
C -5.503844 -0.469455 0.331616
C -3.690647 -0.752966 2.019611
C -5.512110 1.266230 -1.325315
H -3.874037 2.637142 -1.230648
H 2.809020 1.707180 1.375975
H 4.013335 0.657520 0.651312
H 4.521232 2.072080 1.580708
C 4.707709 4.463865 -1.565537
H 5.360987 3.786676 0.364238
H 3.828343 4.891460 -3.488545
C -6.108219 0.145678 -0.758517
H -5.954505 -1.361069 0.763973
H -2.655865 -1.038530 1.784928
H -4.249597 -1.671667 2.216699
H -3.658390 -0.183471 2.954644
H -5.955817 1.752435 -2.189510
H 5.424421 5.279738 -1.607243
H -7.029870 -0.256621 -1.169919

5.5.3 Effects of ligands

(*R*)-INT4 with NHC **4**
116 atoms
PCM Energy= -2494.63463153
O -1.745586 1.737975 -2.032758
N 0.059873 3.062371 -1.507405
C 0.547545 4.277001 -0.803444
C -1.264330 2.779171 -1.597469
C 3.013760 0.382543 -2.853457
C 1.164558 0.841006 -1.318711
C 0.998074 2.082262 -1.961166
C 2.175892 0.003644 -1.806856
C 2.829704 1.607585 -3.482825
C 1.812614 2.443134 -3.039172
H -0.201501 4.474192 -0.032591
H 3.802576 -0.293905 -3.176028
H 2.341856 -0.971657 -1.361072
H 3.459898 1.907612 -4.315335
H 1.630833 3.399456 -3.524043
C 0.631562 5.473686 -1.738609
H 0.879683 6.379675 -1.176042
H 1.409657 5.335507 -2.497158
H -0.321646 5.639980 -2.246745
C 1.862863 3.998661 -0.098688
H 2.681950 3.824410 -0.804547
H 2.127848 4.861522 0.520426
H 1.771887 3.121198 0.548233
O -2.027801 3.822178 -1.176413
C -3.424582 3.561303 -1.224314
H -3.907793 4.461217 -0.843134
H -3.754225 3.354005 -2.246066
H -3.684182 2.701292 -0.600072
O -1.274763 0.553196 2.160236
O -0.530075 2.371949 1.146986
C -1.186639 1.814984 2.089946
C -1.826676 2.717558 3.139382
C -2.657148 1.899923 4.119895
H -2.042597 1.162204 4.642376
H -3.117492 2.556798 4.866353
H -3.450781 1.350841 3.604321
C -2.698180 3.760746 2.433851
H -2.129884 4.301984 1.672163
H -3.559398 3.295838 1.940145
H -3.088125 4.482567 3.160023
C -0.684420 3.437238 3.867544
H -0.080010 4.015222 3.161366
H -1.084703 4.121482 4.623669
H -0.025746 2.724916 4.376361
Pd -0.019590 0.420338 0.273094
C 0.187427 -1.502552 -0.171215
N 1.147241 -2.337597 0.319956
N -0.572844 -2.260421 -1.004889
C 2.130908 -1.865768 1.318336
C 0.982747 -3.606089 -0.206556
C -1.828561 -1.742301 -1.603584
C -0.093186 -3.557481 -1.030460
C 1.898070 -2.479822 2.731520
H 1.825793 -0.821685 1.427357
H 1.623965 -4.436155 0.033509
C -1.855771 -1.756367 -3.161457
H -1.772011 -0.678146 -1.359035
H -0.544030 -4.339800 -1.615770
C 2.324059 -3.940936 2.863644
C 2.722391 -1.638532 3.709685
C 0.413972 -2.344817 3.078233
C -0.605065 -1.037879 -3.669214
C -1.938557 -3.134513 -3.818685
C -3.094603 -0.949981 -3.565953
H 1.768644 -4.600702 2.188385
H 2.113827 -4.287340 3.880858
H 3.395026 -4.076925 2.686814
H 2.407518 -0.588904 3.695076
H 2.590526 -2.009700 4.730847
H 3.791915 -1.673357 3.476087
H 0.053780 -1.317249 2.950316
H 0.246298 -2.635626 4.120428
H -0.211946 -2.990662 2.452837
H -0.637428 -0.963588 -4.761439
H 0.312425 -1.573515 -3.400920
H -0.538471 -0.025347 -3.259038
H -1.923650 -3.004119 -4.906029
H -1.085365 -3.777426 -3.575422
H -2.863371 -3.663989 -3.573963
H -3.140802 -0.862235 -4.656279
H -4.018323 -1.435513 -3.231891
H -3.057988 0.060227 -3.146305
C 3.548403 -1.892013 0.782386
C 4.307349 -0.678694 0.676974
C 4.114824 -3.073719 0.340941
C 3.834057 0.595207 1.092208
C 5.615429 -0.736185 0.086536
C 5.401786 -3.125487 -0.224999
H 3.555770 -3.999877 0.422574
C 4.594540 1.729637 0.932385
H 2.842484 0.703193 1.523394
C 6.368758 0.453159 -0.065866
C 6.136028 -1.974560 -0.354134
H 5.801514 -4.077654 -0.561359
C 5.873556 1.664685 0.346536
H 4.197880 2.687271 1.257236
H 7.354499 0.381379 -0.520526
H 7.129091 -1.993046 -0.797942
H 6.460753 2.570154 0.222086
C -3.020531 -2.356036 -0.887615
C -3.889295 -1.550659 -0.079959
C -3.261705 -3.716031 -0.969948
C -3.736416 -0.149429 0.096519
C -4.977537 -2.190790 0.609696
C -4.332692 -4.334924 -0.300470
H -2.607356 -4.342817 -1.565540

C -4.589102 0.557173 0.912651
H -2.937505 0.392265 -0.405438
C -5.837523 -1.425207 1.432791
C -5.177478 -3.583375 0.474641
H -4.479460 -5.406556 -0.401186
C -5.648399 -0.075381 1.590071
H -4.436546 1.625579 1.046621
H -6.649558 -1.937417 1.944235
H -6.008243 -4.044238 1.004546
H -6.305616 0.504141 2.232622

(*S*)-INT4 with NHC **4**
116 atoms
PCM Energy= -2494.63517390
O -1.495456 -2.556011 0.573382
N -0.215049 -2.986934 -1.289422
C 0.936612 -3.734990 -1.861796
C -0.632662 -3.200603 -0.013990
C -1.804141 0.156079 -3.611472
C -0.567792 -0.549822 -1.622130
C -0.779368 -1.887414 -2.013622
C -1.117327 0.451423 -2.434544
C -1.990863 -1.167700 -3.991173
C -1.487675 -2.181140 -3.182339
H 1.567273 -3.977250 -1.003870
H -2.205865 0.964801 -4.217961
H -1.010331 1.495561 -2.145234
H -2.538836 -1.414325 -4.896306
H -1.641613 -3.225827 -3.445406
C 1.748336 -2.849866 -2.788919
H 2.666266 -3.375040 -3.070943
H 1.204702 -2.603136 -3.707135
H 2.026887 -1.921320 -2.283244
C 0.486133 -5.024307 -2.531246
H 1.354450 -5.612633 -2.845148
H -0.106679 -5.636022 -1.846192
H -0.114451 -4.824370 -3.425541
O -0.005654 -4.262235 0.556835
C -0.388038 -4.482908 1.910311
H 0.258734 -5.282012 2.273750
H -0.249025 -3.578296 2.511430
H -1.438084 -4.781033 1.980369
O 2.046188 -0.266447 1.700727
O 1.962478 -1.893028 0.204452
C 2.409289 -1.412961 1.298338
C 3.343077 -2.248363 2.169965
C 4.644857 -1.476033 2.393379
H 4.438818 -0.481104 2.798323
H 5.287063 -2.014998 3.099309
H 5.199102 -1.352665 1.457524
C 3.621253 -3.593373 1.509230
H 2.695940 -4.160497 1.366274
H 4.074491 -3.457934 0.521928
H 4.303626 -4.189377 2.125626
C 2.647983 -2.445996 3.521837
H 1.706436 -2.995711 3.410446
H 3.290581 -3.018261 4.200232
H 2.420499 -1.481362 3.983738
Pd 0.554918 -0.194211 0.007904
C -0.430017 1.484048 0.355723
N 0.071829 2.719337 0.068350
N -1.526906 1.699179 1.130522
C -0.676050 3.692569 0.704842
C 1.234965 2.853919 -0.840510
C -1.676562 3.055668 1.362766
C -2.447846 0.604444 1.544910
H -0.462261 4.744881 0.632499
H 1.052553 2.052393 -1.562102
C 1.257038 4.159836 -1.693847
H -2.486543 3.466443 1.939142
H -2.099596 -0.234138 0.935046
C -2.209736 0.121839 3.010702
C -0.107380 4.381074 -2.352123
C 1.700027 5.412803 -0.934560
C 2.279439 3.923436 -2.813068
C -0.756008 -0.336072 3.135900
C -2.480205 1.173369 4.087721
C -3.122545 -1.087516 3.228959
H -0.417177 3.495546 -2.919137
H -0.901341 4.609970 -1.636565
H -0.048562 5.216505 -3.057291
H 2.706314 5.294454 -0.523648
H 1.720382 6.263060 -1.624016
H 1.039607 5.692551 -0.109110
H 2.329563 4.803800 -3.461251
H 3.282871 3.739656 -2.417777
H 2.000886 3.066744 -3.436535
H -0.519331 -1.099319 2.385048
H -0.038855 0.481484 3.011158
H -0.588828 -0.772483 4.127613
H -3.545385 1.381606 4.217830
H -2.109425 0.805327 5.050041
H -1.956102 2.115615 3.886639
H -2.950487 -1.508067 4.225630
H -4.180944 -0.814830 3.159006
H -2.914945 -1.868878 2.489945
C -3.882545 0.940170 1.163918
C -4.552230 0.213408 0.122932
C -4.574357 1.952430 1.808679
C -3.963288 -0.865637 -0.584566
C -5.899414 0.576945 -0.222872
C -5.893941 2.303425 1.466473
H -4.102855 2.501260 2.615804
C -4.653507 -1.535143 -1.568972
H -2.959037 -1.200725 -0.352396
C -6.574906 -0.129017 -1.247383
C -6.543565 1.629961 0.464104
H -6.388979 3.107270 2.003907
C -5.968137 -1.166059 -1.912279
H -4.165576 -2.357370 -2.085319
H -7.592834 0.168607 -1.490836
H -7.563183 1.888373 0.186145

H -6.498762 -1.701972 -2.694635
C 2.523261 2.547691 -0.106052
C 3.466240 1.609425 -0.631182
C 2.793138 3.185436 1.088100
C 3.255142 0.845118 -1.811171
C 4.692228 1.399283 0.082939
C 3.990980 2.965089 1.791742
H 2.053956 3.870022 1.500711
C 4.195691 -0.050427 -2.263829
H 2.328835 0.940454 -2.370441
C 5.644603 0.479618 -0.420918
C 4.929072 2.098011 1.289108
H 4.166820 3.485021 2.729128
C 5.406240 -0.235737 -1.568455
H 3.996090 -0.625832 -3.163444
H 6.569655 0.342911 0.136035
H 5.862511 1.918319 1.818930
H 6.142227 -0.944071 -1.937972

(*R*)-TS4-5 with NHC **4**
116 atoms
PCM Energy= -2494.59011363
C -0.025650 -5.000533 0.318649
C 0.987733 -4.237931 0.894889
C 1.032793 -2.861457 0.683122
C 0.075105 -2.221504 -0.112696
C -0.977576 -4.382941 -0.483040
H -0.072245 -6.073094 0.486315
H 1.745646 -4.711967 1.514850
H 1.824796 -2.277679 1.149144
H -1.780547 -4.957142 -0.938490
H -0.331172 0.372974 -2.529481
O 0.420954 1.946078 -0.899941
C -0.001857 2.321545 -2.022128
O -0.523246 1.528074 -2.881179
C 0.205774 3.772342 -2.451691
C -0.927459 -3.002413 -0.698917
N -1.893598 -2.378251 -1.549105
C -1.437370 -1.799929 -2.838809
C -3.209144 -2.551022 -1.242878
H -2.202742 -1.070143 -3.123286
C -1.385958 -2.903221 -3.890453
C -0.112469 -1.068458 -2.685212
O -3.640946 -3.056114 -0.216457
O -4.024643 -2.045945 -2.215575
H -1.076119 -2.501224 -4.860022
H -0.660028 -3.670811 -3.599241
H -2.363144 -3.380489 -4.015898
H 0.700098 -1.770083 -2.464979
H 0.160301 -0.694372 -3.682994
C -5.404494 -2.064666 -1.858909
H -5.938210 -1.679606 -2.727991
H -5.736668 -3.077909 -1.621882
H -5.592867 -1.425623 -0.989850
C -0.910506 4.233082 -3.385453
H -0.703595 5.247982 -3.742043
H -1.001062 3.572268 -4.250227
H -1.875232 4.244516 -2.869555
C 0.290218 4.680039 -1.228131
H -0.618578 4.612197 -0.619878
H 1.135111 4.409230 -0.589038
H 0.417038 5.721868 -1.541628
C 1.543555 3.791047 -3.208352
H 1.505883 3.146881 -4.092497
H 1.773625 4.809515 -3.538766
H 2.368657 3.451580 -2.571554
Pd 0.144550 -0.255383 -0.526770
C 0.449214 0.012428 1.461956
N 1.639090 0.329684 2.029010
N -0.379798 -0.292050 2.494661
C 2.735076 0.830126 1.177392
C 1.568843 0.196918 3.404160
C -1.840291 -0.295002 2.221487
C 0.294983 -0.177615 3.695475
C 3.311037 2.197471 1.646820
H 2.188616 1.077088 0.267620
H 2.406557 0.372919 4.058814
C -2.717141 -1.128881 3.188043
H -1.887958 -0.830989 1.266804
H -0.159900 -0.380508 4.650091
C 4.323789 2.103660 2.786987
C 4.009698 2.798023 0.422274
C 2.144508 3.109899 2.039591
C -2.127228 -2.537411 3.281958
C -2.914809 -0.525034 4.580800
C -4.102819 -1.213670 2.534059
H 3.889429 1.712174 3.712800
H 4.706761 3.102746 3.020659
H 5.179042 1.474903 2.521481
H 3.289020 2.967694 -0.386973
H 4.462710 3.761955 0.675404
H 4.801230 2.144230 0.039540
H 1.348656 3.079226 1.284885
H 2.491653 4.144576 2.132451
H 1.702371 2.821949 2.999256
H -2.786204 -3.184255 3.870028
H -1.140669 -2.545890 3.758166
H -2.022359 -2.981938 2.285466
H -3.590942 -1.168937 5.152757
H -1.997892 -0.437253 5.170889
H -3.374543 0.466428 4.527329
H -4.776407 -1.793263 3.173571
H -4.545179 -0.219265 2.403717
H -4.061322 -1.713569 1.561303
C 3.713140 -0.275481 0.851944
C 3.968429 -0.636996 -0.509436
C 4.299883 -1.005977 1.867491
C 3.406329 0.038830 -1.627134
C 4.822066 -1.761095 -0.772184
C 5.140917 -2.102781 1.604768

H 4.083419 -0.745597 2.901340
C 3.670911 -0.365128 -2.914658
H 2.747380 0.889215 -1.480678
C 5.072145 -2.148222 -2.111669
C 5.393831 -2.473685 0.307228
H 5.578671 -2.655056 2.431343
C 4.510692 -1.468848 -3.164623
H 3.215638 0.170979 -3.743787
H 5.720728 -3.003786 -2.287323
H 6.032995 -3.325656 0.086650
H 4.709394 -1.779477 -4.186450
C -2.234516 1.158729 2.002806
C -2.788291 1.603162 0.762810
C -1.922606 2.093468 2.972635
C -3.129657 0.730182 -0.303843
C -2.978919 3.011553 0.558927
C -2.135094 3.470250 2.779278
H -1.459739 1.760625 3.899439
C -3.619580 1.210304 -1.496504
H -3.008403 -0.340446 -0.181523
C -3.483767 3.471191 -0.682227
C -2.648146 3.921893 1.588606
H -1.873911 4.169595 3.568717
C -3.796649 2.594214 -1.691814
H -3.859994 0.510700 -2.292465
H -3.614111 4.543682 -0.818572
H -2.800000 4.985047 1.412909
H -4.171798 2.963719 -2.642344

(*S*)-TS4-5 with NHC **4**
116 atoms
PCM Energy= -2494.56274049
O 2.362332 2.500621 0.913517
N 1.395694 3.237616 -1.044043
C 0.116951 3.747553 -1.605565
C 1.580461 3.226544 0.312491
C 3.146637 0.048461 -3.175120
C 1.403456 0.846545 -1.670902
C 1.976077 2.127907 -1.753666
C 2.030382 -0.190060 -2.372812
C 3.673930 1.330994 -3.278439
C 3.090733 2.367606 -2.555609
H -0.171793 4.579791 -0.960793
H 3.609366 -0.777235 -3.710620
H 1.646085 -1.204062 -2.292432
H 4.547611 1.520628 -3.895869
H 3.493763 3.377593 -2.593667
C -0.950420 2.661001 -1.526232
H -1.953433 3.104381 -1.599554
H -0.891308 2.019481 -2.417197
C 0.345045 4.275693 -3.011277
H -0.585563 4.694704 -3.404602
H 1.110389 5.058301 -3.031767
H 0.660013 3.474389 -3.688075
O 0.822032 4.158860 0.936627
C 0.920359 4.129164 2.356537
H 0.264398 4.923461 2.711738
H 0.582005 3.165378 2.749836
H 1.948735 4.301571 2.684494
O -1.986539 0.449385 0.839922
O -1.855350 2.679355 0.967201
C -2.289234 1.542294 1.376420
C -3.228778 1.563146 2.578462
C -3.535278 0.142467 3.038563
H -2.624175 -0.388824 3.331287
H -4.209628 0.166122 3.901415
H -4.012488 -0.438690 2.244453
C -4.520270 2.266013 2.146158
H -4.314435 3.278002 1.787067
H -5.023989 1.712782 1.346251
H -5.210271 2.333126 2.994267
C -2.562051 2.360084 3.703265
H -2.338713 3.380382 3.381397
H -3.224959 2.406355 4.573785
H -1.624139 1.891368 4.022556
H -1.305899 2.508169 -0.112969
Pd -0.267856 0.649056 -0.563287
C 0.090066 -1.275402 -0.007765
N 1.035935 -1.870301 0.770306
N -0.860727 -2.232385 -0.227678
C 2.188047 -1.116415 1.333293
C 0.668883 -3.178724 1.038238
C -2.015358 -1.993105 -1.118387
C -0.508735 -3.406555 0.409583
C 1.926306 -0.692384 2.816552
H 2.149339 -0.181586 0.764013
H 1.253284 -3.852104 1.636206
C -1.970105 -2.882458 -2.405735
H -1.803998 -0.982223 -1.478138
H -1.094422 -4.307731 0.364138
C 1.845680 -1.866222 3.791124
C 3.072214 0.228774 3.242200
C 0.615358 0.094014 2.871088
C -0.593560 -2.724339 -3.050573
C -2.251920 -4.364933 -2.161219
C -3.028857 -2.346977 -3.373568
H 1.045866 -2.569749 3.535054
H 1.622731 -1.486079 4.793572
H 2.790853 -2.413010 3.857494
H 3.132862 1.110878 2.598427
H 2.903502 0.571147 4.268955
H 4.036977 -0.288387 3.219594
H 0.635305 0.930847 2.160667
H 0.470274 0.502061 3.878587
H -0.256989 -0.524018 2.630477
H -0.560415 -3.250904 -4.009720
H 0.203126 -3.134894 -2.420246
H -0.362588 -1.668885 -3.237105
H -2.314650 -4.883579 -3.123444
H -1.454532 -4.855958 -1.596292
H -3.202612 -4.524240 -1.643021
H -2.977260 -2.896728 -4.318573

H -4.042591 -2.458465 -2.977061
H -2.871685 -1.286504 -3.598065
C -3.354385 -1.972285 -0.408156
C -4.287053 -0.911359 -0.662274
C -3.731424 -2.997625 0.437051
C -3.990348 0.237912 -1.443353
C -5.599572 -0.992251 -0.085862
C -5.006329 -3.051604 1.032527
H -3.033048 -3.798326 0.656373
C -4.928478 1.217130 -1.672068
H -2.992428 0.380999 -1.848224
C -6.548427 0.025210 -0.355915
C -5.931433 -2.077109 0.759186
H -5.252851 -3.877375 1.693501
C -6.229086 1.105923 -1.140181
H -4.658943 2.086875 -2.264832
H -7.538924 -0.067307 0.084287
H -6.928288 -2.115268 1.192325
H -6.964816 1.880802 -1.335228
C 3.525581 -1.794975 1.075903
C 4.590122 -1.073860 0.434739
C 3.775039 -3.091362 1.493274
C 4.497309 0.289330 0.056354
C 5.840329 -1.743332 0.198075
C 4.998715 -3.744491 1.253264
H 3.023895 -3.639617 2.047195
C 5.564117 0.947002 -0.511344
H 3.588915 0.857339 0.220572
C 6.905282 -1.042793 -0.417632
C 6.009560 -3.086491 0.602892
H 5.131863 -4.767550 1.593233
C 6.777543 0.280066 -0.763663
H 5.451202 1.995219 -0.774938
H 7.836697 -1.577059 -0.593495
H 6.961940 -3.575208 0.408967
H 7.607604 0.810235 -1.222819

(*R*)-INT4 with NHC **8'**
107 atoms
PCM Energy= -2226.69043019
O 2.789892 0.045194 -1.593031
N 2.069809 -2.136208 -1.609820
C 2.289128 -3.531861 -1.142594
C 2.939298 -1.138890 -1.308817
C -1.621645 -1.450584 -3.514011
C -0.173068 -1.078477 -1.581428
C 0.837382 -1.792534 -2.253696
C -1.398589 -0.920875 -2.243888
C -0.601790 -2.122684 -4.177977
C 0.624725 -2.286156 -3.543345
H 2.827421 -3.433412 -0.196639
H -2.595135 -1.323130 -3.982264
H -2.218492 -0.393909 -1.760384
H -0.755802 -2.519132 -5.177669
H 1.439331 -2.810260 -4.037631
C 3.142082 -4.311371 -2.131873
H 3.381982 -5.302370 -1.732953
H 2.615307 -4.457293 -3.081489
H 4.081683 -3.790443 -2.334565
C 0.972169 -4.225107 -0.842655
H 0.372252 -4.389778 -1.743711
H 1.180447 -5.201938 -0.395705
H 0.383506 -3.641664 -0.130222
O 4.045793 -1.604708 -0.670567
C 4.916902 -0.574267 -0.220352
H 5.774130 -1.081826 0.222268
H 5.231962 0.068051 -1.046827
H 4.422163 0.045605 0.536036
O 0.869823 -0.196346 2.431922
O 1.518297 -1.929024 1.221127
C 1.513357 -1.283994 2.321612
C 2.319922 -1.842028 3.488170
C 2.029748 -1.057560 4.761784
H 0.972206 -1.121391 5.035333
H 2.622555 -1.452150 5.594462
H 2.268798 0.001372 4.635663
C 3.803515 -1.722314 3.118739
H 4.021757 -2.262192 2.191812
H 4.091886 -0.673627 2.980766
H 4.427674 -2.137817 3.917681
C 1.961649 -3.319122 3.666742
H 2.146483 -3.879009 2.745599
H 2.559792 -3.761811 4.470751
H 0.905312 -3.443444 3.929154
Pd 0.206451 -0.424705 0.294145
C -0.963059 1.121664 -0.101964
N -2.260235 1.260684 0.285194
N -0.644651 2.266894 -0.756816
C -2.932689 0.222656 1.093522
C -2.741159 2.495228 -0.111826
C 0.747106 2.529370 -1.183014
C -1.726951 3.127602 -0.755193
C -3.281001 0.717990 2.530728
C -4.028485 -0.474060 0.311857
H -2.118803 -0.496650 1.241572
H -3.743921 2.831138 0.089081
C 0.894330 3.051978 -2.640423
C 1.475891 3.305630 -0.108214
H 1.187788 1.525992 -1.206238
H -1.695240 4.108549 -1.196883
C -4.537539 1.583124 2.615342
C -3.499288 -0.538666 3.378367
C -2.082058 1.487787 3.089338
C -3.956120 -1.864844 0.078226
C -5.094706 0.248517 -0.234170
C 0.240077 2.036843 -3.578184
C 0.315537 4.445720 -2.891372
C 2.398728 3.100184 -2.931372
C 2.682705 2.789459 0.374595
C 0.989718 4.497338 0.437483
H -4.446777 2.517877 2.051441
H -4.710592 1.866320 3.658887
H -5.428947 1.053129 2.266540
H -2.583098 -1.138721 3.432929
H -3.774785 -0.264194 4.401468
H -4.301494 -1.167822 2.975283
H -1.154516 0.910806 3.003414
H -2.245189 1.711597 4.148738
H -1.930357 2.441601 2.571692
C -2.830232 -2.711215 0.595064
C -4.957558 -2.465626 -0.692054
C -6.079329 -0.365125 -0.999777
H -5.161571 1.318667 -0.061461
H 0.375662 2.341509 -4.621532
H -0.836588 1.943881 -3.396136
H 0.686818 1.044277 -3.450550
H 0.659950 4.810465 -3.864957
H -0.777797 4.451856 -2.932962
H 0.647259 5.171642 -2.141119
H 2.560065 3.335178 -3.988604
H 2.898795 3.872352 -2.337535
H 2.874858 2.139056 -2.715494
C 3.389908 3.452577 1.372603
C 1.696141 5.161100 1.436511
H 0.040144 4.906461 0.099362
H -1.859537 -2.374582 0.207120
H -2.756252 -2.688560 1.687883
H -2.960198 -3.753602 0.294062
C -6.009103 -1.734000 -1.230363
H -4.894824 -3.535686 -0.878091
H -6.893049 0.224916 -1.411794
C 2.899569 4.641976 1.906057
H 4.322897 3.032853 1.741280
H 1.302132 6.084701 1.852021
H -6.768018 -2.231237 -1.828180
H 3.446984 5.157689 2.690117
H 3.048036 1.853740 -0.046073

(*S*)-INT4 with NHC **8'**
107 atoms
PCM Energy= -2226.69337591
O -2.542809 1.639556 -0.795295
N -1.948461 2.459200 1.265027
C -1.407144 3.594083 2.057123
C -2.178682 2.558752 -0.069021
C -2.432474 -1.250992 3.206638
C -1.188736 0.123485 1.611402
C -2.100075 1.167807 1.867960
C -1.393024 -1.084353 2.293132
C -3.324337 -0.211427 3.444062
C -3.155537 0.991423 2.766461
H -0.788965 4.160219 1.356000
H -2.549740 -2.203420 3.718455
H -0.729184 -1.926695 2.111788
H -4.148485 -0.334505 4.141309
H -3.848651 1.816141 2.918644
C -0.501233 3.095547 3.168240
H -0.028414 3.953091 3.655867
H -1.054957 2.538546 3.931099
H 0.285998 2.450405 2.768529
C -2.528052 4.479042 2.580818
H -2.117433 5.365844 3.074560
H -3.176078 4.813356 1.766476
H -3.142189 3.947688 3.316540
O -1.994383 3.823267 -0.531377
C -2.133181 3.929539 -1.943950
H -1.895378 4.964993 -2.188728
H -1.443574 3.250524 -2.456848
H -3.150920 3.686151 -2.261563
O 1.839524 1.318527 -1.106488
O 0.751777 2.628995 0.304145
C 1.557460 2.477102 -0.672066
C 2.186434 3.694488 -1.341196
C 3.700300 3.624407 -1.117227
H 4.105117 2.686345 -1.508187
H 4.200039 4.457546 -1.623746
H 3.947825 3.686756 -0.051237
C 1.620230 4.983421 -0.756323
H 0.535038 5.037705 -0.887025
H 1.819586 5.052512 0.317046
H 2.072077 5.852958 -1.246819
C 1.897540 3.608984 -2.842595
H 0.821610 3.661390 -3.045002
H 2.377543 4.439370 -3.371954
H 2.269463 2.667136 -3.253954
Pd 0.295435 0.462057 0.280644
C 0.238584 -1.461622 -0.150434
N 1.147064 -2.406187 0.220126
N -0.669132 -2.103754 -0.925801
C 0.811844 -3.626215 -0.343110
C 2.339733 -2.039053 1.017170
C -0.329420 -3.436674 -1.051748
C -1.838023 -1.415205 -1.516915
H 1.386208 -4.522825 -0.187138
H 1.965485 -1.222621 1.648503
C 2.814307 -3.146743 2.009297
C 3.420176 -1.487166 0.107248
H -0.928725 -4.137115 -1.609144
H -1.838802 -0.447793 -1.004758
C -1.618035 -1.063629 -3.018158
C -3.133051 -2.093449 -1.124033
C 1.617024 -3.705664 2.781204
C 3.618391 -4.280818 1.366764
C 3.743839 -2.460408 3.016666
C 3.772041 -2.203096 -1.041646
C 4.068239 -0.268550 0.385999
C -0.418361 -0.116262 -3.107173
C -1.366379 -2.273741 -3.916336
C -2.867977 -0.320963 -3.496613
C -3.955018 -1.402660 -0.225618
C -3.557278 -3.346572 -1.584053
H 1.040866 -2.899642 3.249848
H 0.931428 -4.281100 2.152651
H 1.964869 -4.369951 3.579011
H 4.511666 -3.901242 0.863017
H 3.946069 -4.974229 2.148216
H 3.058443 -4.873523 0.638589
H 4.115628 -3.192413 3.740486
H 4.612011 -2.011549 2.522875
H 3.220001 -1.677385 3.575226
C 4.773663 -1.761450 -1.896176
C 5.086861 0.150788 -0.477095
H -0.574782 0.767686 -2.476593
H 0.518519 -0.584192 -2.783064
H -0.278773 0.221029 -4.140548
H -2.224802 -2.951210 -3.955993
H -1.183301 -1.934341 -4.941621
H -0.482215 -2.842437 -3.607873
H -2.716874 0.038188 -4.520406
H -3.749599 -0.970120 -3.496064
H -3.076336 0.541769 -2.855797
C -5.160740 -1.945153 0.204862
C -4.765598 -3.889542 -1.154365
H -2.952250 -3.910155 -2.289453
C 5.445831 -0.579549 -1.602427
H 5.589611 1.092021 -0.262584
C -5.571099 -3.191701 -0.258581
H -5.078658 -4.862279 -1.524679
H 6.235037 -0.218195 -2.256173
H -6.512871 -3.619300 0.074795
H 3.239578 -3.123994 -1.274895
H 5.026130 -2.336226 -2.782569
H -5.776901 -1.389830 0.907521
C 3.682301 0.618804 1.532522
H 4.168266 1.593425 1.438833
H 2.598756 0.799837 1.554626
H 3.962486 0.207752 2.508178
H -3.633768 -0.424375 0.128519

(*R*)-TS4-5 with NHC **8'**
107 atoms
PCM Energy= -2226.64411680
C -1.185423 -4.612327 -1.306102
C 0.097851 -4.279548 -0.879368
C 0.446908 -2.943820 -0.687420
C -0.474025 -1.916794 -0.926444
C -2.111541 -3.605130 -1.549052
H -1.465384 -5.652005 -1.452520
H 0.833741 -5.058179 -0.691112
H 1.452208 -2.705449 -0.344258
H -3.122814 -3.843703 -1.868357
H -0.859153 1.371457 -2.207999
O 0.726381 2.151845 -0.610757
C 0.059894 2.954785 -1.308820
O -0.903844 2.594893 -2.072835
C 0.449521 4.431611 -1.348073
C -1.759738 -2.266285 -1.356806
N -2.713558 -1.230531 -1.610338
C -2.482923 -0.311004 -2.755593
C -3.914769 -1.303382 -0.969282
H -3.069107 0.587317 -2.534936
C -3.017246 -0.955834 -4.029419
C -1.019841 0.091069 -2.863877
O -4.208510 -2.101547 -0.091414
O -4.768908 -0.329504 -1.401313
H -2.884893 -0.288874 -4.886875
H -2.475952 -1.885060 -4.241426
H -4.083455 -1.188811 -3.941332
H -0.397093 -0.768875 -3.133835
H -0.928605 0.743301 -3.744149
C -5.988303 -0.274615 -0.667759
H -6.610992 0.455692 -1.184130
H -6.478503 -1.250396 -0.642933
H -5.810651 0.049135 0.363579
C -0.796329 5.307446 -1.466175
H -0.508256 6.360693 -1.552786
H -1.389193 5.034860 -2.341673
H -1.434576 5.205341 -0.583036
C 1.254826 4.807357 -0.109490
H 0.685124 4.617193 0.805919
H 2.180549 4.228996 -0.047167
H 1.514964 5.870804 -0.138348
C 1.316700 4.605384 -2.603902
H 0.756600 4.348333 -3.507550
H 1.648590 5.645599 -2.689695
H 2.208851 3.970637 -2.561077
Pd -0.001142 0.034031 -0.778471
C 0.736393 -0.398257 1.052032
N 2.040756 -0.486700 1.411235
N 0.023790 -0.774154 2.146879
C 3.105375 -0.051227 0.484708
C 2.148094 -0.932732 2.716896
C -1.445559 -0.543769 2.154630
C 0.882978 -1.100038 3.180847
C 4.052691 1.018930 1.109728
C 3.764252 -1.235256 -0.190865
H 2.532087 0.494339 -0.270841
H 3.091226 -1.089917 3.212739
C -2.228409 -1.247571 3.294971
C -1.679871 0.948291 2.031051
H -1.792830 -1.009823 1.220897
H 0.548770 -1.446798 4.142190
C 5.151608 0.447319 2.006205
C 4.727046 1.735224 -0.063937
C 3.210217 2.035370 1.885857
C 3.787646 -1.332505 -1.597983
C 4.300372 -2.277038 0.572884
C -1.931254 -2.748641 3.249847
C -1.985984 -0.659476 4.689444
C -3.719746 -1.051811 2.990722
C -2.549586 1.433106 1.051231
C -0.996112 1.862170 2.837100
H 4.761142 -0.062690 2.892482
H 5.784065 1.264030 2.369994
H 5.793354 -0.255519 1.466550
H 3.986046 2.246112 -0.689652
H 5.429685 2.489447 0.304653
H 5.290239 1.037553 -0.694477
H 2.351130 2.367147 1.292027
H 3.816572 2.912898 2.135323
H 2.829022 1.620497 2.824973
C 3.167302 -0.298066 -2.490956
C 4.365070 -2.467988 -2.176530
C 4.862071 -3.401640 -0.019500
H 4.261493 -2.215608 1.657966
H -2.576453 -3.281599 3.955756
H -0.895484 -2.993242 3.502027
H -2.131045 -3.146689 2.248177
H -2.621703 -1.181281 5.412357
H -0.959446 -0.740465 5.054682
H -2.259796 0.399710 4.719283
H -4.314726 -1.567029 3.751883
H -3.996899 0.007442 3.015716
H -3.992445 -1.460970 2.013774
C -2.751835 2.800982 0.893015
C -1.195617 3.229895 2.682251
H -0.282233 1.497246 3.574422
H 2.084441 -0.216186 -2.312076
H 3.582578 0.703945 -2.340207
H 3.309555 -0.560578 -3.541980
C 4.896951 -3.494927 -1.406722
H 4.376243 -2.547273 -3.261435
H 5.265669 -4.198174 0.599148
C -2.079557 3.702625 1.713927
H -3.414579 3.159010 0.109103
H -0.653316 3.929724 3.313136
H 5.330153 -4.367236 -1.888389
H -2.232612 4.772388 1.594187
H -3.047853 0.729056 0.387443

(*S*)-TS4-5 with NHC **8'**
107 atoms
PCM Energy= -2226.64399686
O 3.013501 1.986240 0.480085
N 2.263722 2.380941 -1.656640
C 1.211348 3.047846 -2.465506
C 2.441331 2.695940 -0.338152
C 3.170923 -1.598113 -2.698930
C 1.604323 0.007109 -1.741805
C 2.548056 1.015120 -2.000069
C 1.950387 -1.304221 -2.092048
C 4.087765 -0.583617 -2.957161
C 3.771700 0.724367 -2.603145
H 1.142560 4.061915 -2.066396
H 3.409644 -2.628050 -2.953775
H 1.264238 -2.119191 -1.873929
H 5.043881 -0.807561 -3.422699
H 4.469757 1.540098 -2.777637
C -0.132312 2.347585 -2.276805
H -0.955122 3.021597 -2.554037
H -0.225792 1.525792 -3.000740
C 1.657430 3.118459 -3.916248
H 0.907740 3.648190 -4.510959
H 2.614621 3.639194 -4.022866
H 1.768154 2.114757 -4.340790
O 1.944639 3.919879 -0.034629
C 2.049369 4.264934 1.342011
H 1.605523 5.256256 1.430260
H 1.498868 3.555454 1.968607
H 3.093093 4.279325 1.667008
O -1.885772 1.176678 0.372247
O -1.049512 3.227692 0.052606
C -1.843215 2.402168 0.634893
C -2.807471 2.986782 1.664586
C -3.306748 1.893628 2.603778
H -2.485795 1.461956 3.185076
H -4.035755 2.309445 3.307687
H -3.782529 1.082843 2.046504
C -3.989860 3.563908 0.873934
H -3.656967 4.313035 0.149082
H -4.522236 2.770622 0.337068
H -4.701350 4.040694 1.556549
C -2.115894 4.101005 2.449378
H -1.767457 4.896119 1.786335
H -2.809582 4.532601 3.178685
H -1.247685 3.719200 2.998407
H -0.556627 2.656038 -0.900020
Pd -0.117888 0.540421 -0.830203
C -0.144061 -1.208656 0.187619
N 0.714957 -1.684225 1.125419
N -1.096567 -2.173684 0.040955
C 1.865658 -0.900392 1.630079
C 0.315648 -2.936410 1.550897
C -2.232337 -2.002850 -0.892328
C -0.819916 -3.244147 0.876317
C 1.541096 -0.208110 2.990464
C 3.162881 -1.673973 1.536705
H 1.948940 -0.080648 0.907115
H 0.867547 -3.506018 2.279121
C -2.404789 -3.192754 -1.889736
C -3.496935 -1.578736 -0.169174
H -1.890998 -1.163709 -1.509787
H -1.433049 -4.126889 0.927173
C 1.132249 -1.172253 4.104173
C 2.783535 0.570140 3.429631
C 0.394912 0.776387 2.747107
C 4.118364 -1.195674 0.632474
C 3.474617 -2.811392 2.292695
C -1.050764 -3.520281 -2.516795
C -3.014814 -4.456771 -1.280210
C -3.347531 -2.708648 -2.995616
C -4.270547 -0.484373 -0.611592
C -3.908488 -2.281435 0.968063
H 0.239969 -1.753095 3.847630
H 0.892161 -0.600314 5.006978
H 1.937738 -1.862433 4.373523
H 3.123841 1.247556 2.641234
H 2.548765 1.165268 4.319246
H 3.609207 -0.101018 3.686849
H 0.649508 1.477423 1.940746
H 0.193611 1.356221 3.656301
H -0.533605 0.271218 2.458121
C 5.342354 -1.837864 0.479041
C 4.699832 -3.454727 2.138794
H 2.770336 -3.206059 3.019803
H -1.165977 -4.287223 -3.289542
H -0.335485 -3.898632 -1.778867
H -0.609757 -2.634473 -2.988117
H -3.231119 -5.173012 -2.079780
H -2.341027 -4.967624 -0.586976
H -3.956363 -4.249981 -0.762691
H -3.474791 -3.491915 -3.749414
H -4.338908 -2.461129 -2.601551
H -2.946758 -1.823047 -3.500558
C -5.437043 -0.168173 0.096710
C -3.910166 0.366182 -1.796060
C -5.066647 -1.950571 1.659808
H -3.302679 -3.107575 1.330233
C 5.637441 -2.971577 1.229974
H 6.063501 -1.447984 -0.234544
H 4.922244 -4.335186 2.735821
C -5.843279 -0.887376 1.214192
H -6.030806 0.679815 -0.240861
H -2.830046 0.499121 -1.915263
H -4.340382 1.366034 -1.687269
H -4.297900 -0.048048 -2.733574
H -5.355645 -2.517946 2.539673
H 6.592776 -3.476083 1.112215
H -6.751257 -0.607398 1.741242
H 3.890036 -0.300816 0.055407

(*R*)-INT4 with NHC **8''**
104 atoms
PCM Energy= -2187.37585882
O 2.705563 0.087040 -1.624434
N 2.090478 -2.124739 -1.554209
C 2.378954 -3.490253 -1.038557
C 2.911242 -1.076176 -1.292575
C -1.619172 -1.611446 -3.480443
C -0.192639 -1.159223 -1.548850
C 0.841084 -1.857060 -2.202495
C -1.417187 -1.047976 -2.221185
C -0.580974 -2.277740 -4.121239
C 0.646654 -2.392595 -3.478244
H 2.895622 -3.333195 -0.088505
H -2.591581 -1.516074 -3.958630
H -2.250634 -0.526080 -1.756970
H -0.720452 -2.703758 -5.110822
H 1.477810 -2.905804 -3.956707
C 3.287603 -4.251960 -1.991510
H 3.577419 -5.214529 -1.557575
H 2.782122 -4.457799 -2.941668
H 4.199055 -3.686216 -2.201351
C 1.097360 -4.245760 -0.737655
H 0.532580 -4.482153 -1.645159
H 1.350553 -5.189175 -0.244453
H 0.455398 -3.669459 -0.066333
O 4.037012 -1.462239 -0.634860
C 4.852293 -0.372963 -0.220324
H 5.737117 -0.819114 0.234016
H 5.130063 0.259828 -1.067364
H 4.326821 0.242695 0.518859
O 0.790151 -0.135833 2.441231
O 1.548920 -1.860903 1.284665
C 1.496936 -1.187282 2.366249
C 2.326526 -1.656672 3.555612
C 1.951025 -0.873567 4.807982
H 0.894309 -1.009694 5.058088
H 2.550074 -1.210441 5.661184
H 2.115976 0.197616 4.668843
C 3.800167 -1.419795 3.203050
H 4.077526 -1.968786 2.297544
H 3.998804 -0.355120 3.033473
H 4.445526 -1.754501 4.022702
C 2.091455 -3.154357 3.761654
H 2.332994 -3.715493 2.854612
H 2.715675 -3.528233 4.580714
H 1.046862 -3.362165 4.017039
Pd 0.161746 -0.451278 0.310566
C -1.073066 1.034971 -0.106027
N -2.364586 1.121945 0.309869
N -0.827574 2.174293 -0.801116
C -2.963287 0.065907 1.146052
C -2.920438 2.313656 -0.116854
C 0.546231 2.489704 -1.250731
C -1.953929 2.977724 -0.802107
C -3.385648 0.567622 2.557254
C -3.967344 -0.755350 0.371984
H -2.099300 -0.588320 1.327690
H -3.937763 2.595890 0.095376
C 0.654734 2.994299 -2.716716
C 1.257316 3.311583 -0.198162
H 1.027962 1.504805 -1.261324
H -1.982928 3.945657 -1.272752
C -4.700814 1.345577 2.575191
C -3.546051 -0.683397 3.426526
C -2.256999 1.428456 3.128364
C -3.756280 -2.134187 0.269687
C -5.067044 -0.198959 -0.289898
C 0.037176 1.936551 -3.631456
C 0.011076 4.357287 -2.978886
C 2.152208 3.104506 -3.026644
C 2.496889 2.855103 0.261607
C 0.729100 4.484808 0.347706
H -4.640471 2.291704 2.026863
H -4.957801 1.602413 3.608052
H -5.530301 0.760052 2.166225
H -2.607721 -1.248836 3.478047
H -3.819954 -0.401904 4.448024
H -4.325226 -1.351094 3.043351
H -1.294714 0.904574 3.100187
H -2.474535 1.685389 4.170128
H -2.140892 2.366733 2.574405
C -4.616514 -2.937951 -0.470742
C -5.926679 -0.999678 -1.035975
H -5.252997 0.870931 -0.235822
H 0.143133 2.232787 -4.680648
H -1.030879 1.793450 -3.432040
H 0.533552 0.968946 -3.496581
H 0.331975 4.727633 -3.958291
H -1.081580 4.312114 -3.012630
H 0.313490 5.104830 -2.237389
H 2.290522 3.323914 -4.090468
H 2.623455 3.910799 -2.455191
H 2.674339 2.170542 -2.797192
C 3.195298 3.558580 1.237335
C 1.427384 5.189262 1.324874
H -0.246224 4.845653 0.027205
C -5.703993 -2.371117 -1.128810
H -4.426667 -4.004835 -0.546218
H -6.771768 -0.548559 -1.548757
C 2.663312 4.729251 1.771659
H 4.154842 3.185791 1.587901
H 1.001329 6.098016 1.741689
H -6.372305 -2.993375 -1.717142
H 3.203625 5.276674 2.539051
H 2.896075 1.934002 -0.160499
H -2.885403 -2.571227 0.756314

(*S*)-INT4 with NHC **8'**
107 atoms
PCM Energy= -2226.69337591
O -2.542809 1.639556 -0.795295
N -1.948461 2.459200 1.265027
C -1.407144 3.594083 2.057123
C -2.178682 2.558752 -0.069021
C -2.432474 -1.250992 3.206638
C -1.188736 0.123485 1.611402
C -2.100075 1.167807 1.867960
C -1.393024 -1.084353 2.293132
C -3.324337 -0.211427 3.444062
C -3.155537 0.991423 2.766461
H -0.788965 4.160219 1.356000
H -2.549740 -2.203420 3.718455
H -0.729184 -1.926695 2.111788
H -4.148485 -0.334505 4.141309
H -3.848651 1.816141 2.918644
C -0.501233 3.095547 3.168240
H -0.028414 3.953091 3.655867
H -1.054957 2.538546 3.931099
H 0.285998 2.450405 2.768529
C -2.528052 4.479042 2.580818
H -2.117433 5.365844 3.074560
H -3.176078 4.813356 1.766476
H -3.142189 3.947688 3.316540
O -1.994383 3.823267 -0.531377
C -2.133181 3.929539 -1.943950
H -1.895378 4.964993 -2.188728
H -1.443574 3.250524 -2.456848
H -3.150920 3.686151 -2.261563
O 1.839524 1.318527 -1.106488
O 0.751777 2.628995 0.304145
C 1.557460 2.477102 -0.672066
C 2.186434 3.694488 -1.341196
C 3.700300 3.624407 -1.117227
H 4.105117 2.686345 -1.508187
H 4.200039 4.457546 -1.623746
H 3.947825 3.686756 -0.051237
C 1.620230 4.983421 -0.756323
H 0.535038 5.037705 -0.887025
H 1.819586 5.052512 0.317046
H 2.072077 5.852958 -1.246819
C 1.897540 3.608984 -2.842595
H 0.821610 3.661390 -3.045002
H 2.377543 4.439370 -3.371954
H 2.269463 2.667136 -3.253954
Pd 0.295435 0.462057 0.280644
C 0.238584 -1.461622 -0.150434
N 1.147064 -2.406187 0.220126
N -0.669132 -2.103754 -0.925801
C 0.811844 -3.626215 -0.343110
C 2.339733 -2.039053 1.017170
C -0.329420 -3.436674 -1.051748
C -1.838023 -1.415205 -1.516915
H 1.386208 -4.522825 -0.187138
H 1.965485 -1.222621 1.648503
C 2.814307 -3.146743 2.009297
C 3.420176 -1.487166 0.107248
H -0.928725 -4.137115 -1.609144
H -1.838802 -0.447793 -1.004758
C -1.618035 -1.063629 -3.018158
C -3.133051 -2.093449 -1.124033
C 1.617024 -3.705664 2.781204
C 3.618391 -4.280818 1.366764
C 3.743839 -2.460408 3.016666
C 3.772041 -2.203096 -1.041646
C 4.068239 -0.268550 0.385999
C -0.418361 -0.116262 -3.107173
C -1.366379 -2.273741 -3.916336
C -2.867977 -0.320963 -3.496613
C -3.955018 -1.402660 -0.225618
C -3.557278 -3.346572 -1.584053
H 1.040866 -2.899642 3.249848
H 0.931428 -4.281100 2.152651
H 1.964869 -4.369951 3.579011
H 4.511666 -3.901242 0.863017
H 3.946069 -4.974229 2.148216
H 3.058443 -4.873523 0.638589
H 4.115628 -3.192413 3.740486
H 4.612011 -2.011549 2.522875
H 3.220001 -1.677385 3.575226
C 4.773663 -1.761450 -1.896176
C 5.086861 0.150788 -0.477095
H -0.574782 0.767686 -2.476593
H 0.518519 -0.584192 -2.783064
H -0.278773 0.221029 -4.140548
H -2.224802 -2.951210 -3.955993
H -1.183301 -1.934341 -4.941621
H -0.482215 -2.842437 -3.607873
H -2.716874 0.038188 -4.520406
H -3.749599 -0.970120 -3.496064
H -3.076336 0.541769 -2.855797
C -5.160740 -1.945153 0.204862
C -4.765598 -3.889542 -1.154365
H -2.952250 -3.910155 -2.289453
C 5.445831 -0.579549 -1.602427
H 5.589611 1.092021 -0.262584
C -5.571099 -3.191701 -0.258581
H -5.078658 -4.862279 -1.524679
H 6.235037 -0.218195 -2.256173
H -6.512871 -3.619300 0.074795
H 3.239578 -3.123994 -1.274895
H 5.026130 -2.336226 -2.782569
H -5.776901 -1.389830 0.907521
C 3.682301 0.618804 1.532522
H 4.168266 1.593425 1.438833
H 2.598756 0.799837 1.554626
H 3.962486 0.207752 2.508178
H -3.633768 -0.424375 0.128519

(*R*)-TS4-5 with NHC **8''**
104 atoms
PCM Energy= -2187.32926025
C -1.001004 -4.662641 -1.286839
C 0.283097 -4.287464 -0.899055
C 0.598738 -2.939990 -0.733300
C -0.356712 -1.941960 -0.959093
C -1.962012 -3.685241 -1.514125
H -1.254551 -5.711704 -1.413106
H 1.045707 -5.042500 -0.721697
H 1.605931 -2.669088 -0.421783
H -2.974889 -3.955571 -1.801469
H -0.925176 1.317795 -2.239896
O 0.657152 2.184842 -0.696487
C -0.085484 2.948370 -1.361060
O -1.048982 2.531703 -2.096344
C 0.194308 4.450482 -1.390814
C -1.643839 -2.334870 -1.346571
N -2.636821 -1.332403 -1.581939
C -2.470357 -0.425961 -2.748011
C -3.809778 -1.429772 -0.894738
H -3.085980 0.452423 -2.528392
C -3.008260 -1.113866 -3.997453
C -1.026640 0.030946 -2.894184
O -4.042036 -2.217671 0.010702
O -4.713589 -0.496172 -1.314292
H -2.922375 -0.457534 -4.868894
H -2.436047 -2.024874 -4.207144
H -4.062168 -1.386836 -3.879586
H -0.374938 -0.804860 -3.170644
H -0.979109 0.681747 -3.778585
C -5.909066 -0.473463 -0.540842
H -6.574845 0.225539 -1.046528
H -6.362223 -1.465815 -0.485474
H -5.710188 -0.127969 0.479490
C -1.118359 5.233005 -1.409020
H -0.913775 6.305593 -1.496776
H -1.746559 4.928436 -2.248777
H -1.686947 5.073678 -0.487668
C 1.047295 4.861439 -0.195873
H 0.569547 4.578437 0.747686
H 2.030369 4.383229 -0.222883
H 1.195903 5.946578 -0.196123
C 0.960729 4.718492 -2.694353
H 0.364169 4.436642 -3.566586
H 1.202338 5.783838 -2.773518
H 1.900980 4.157577 -2.724320
Pd 0.045729 0.026788 -0.838028
C 0.854787 -0.371899 0.970850
N 2.174448 -0.427122 1.276092
N 0.199615 -0.766634 2.094884
C 3.182124 0.033640 0.306062
C 2.349879 -0.865232 2.576616
C -1.276515 -0.592816 2.160379
C 1.109814 -1.068266 3.092217
C 4.079532 1.182722 0.857275
C 3.892066 -1.125334 -0.352805
H 2.556970 0.504910 -0.462293
H 3.316819 -0.993010 3.033546
C -1.986969 -1.328298 3.328044
C -1.575176 0.887899 2.054443
H -1.641766 -1.071242 1.239500
H 0.824730 -1.422959 4.066600
C 5.236563 0.697460 1.729186
C 4.660328 1.897887 -0.366829
C 3.201825 2.166320 1.635990
C 3.949951 -1.171710 -1.748783
C 4.456153 -2.178439 0.374079
C -1.639985 -2.817585 3.261892
C -1.708644 -0.739072 4.715561
C -3.495751 -1.182056 3.087464
C -2.498903 1.340309 1.109492
C -0.908970 1.824596 2.849010
H 4.897681 0.217767 2.653054
H 5.853671 1.550963 2.028775
H 5.880989 -0.008146 1.195572
H 3.861817 2.297739 -1.003100
H 5.290906 2.735972 -0.053145
H 5.276907 1.227552 -0.975447
H 2.310925 2.440220 1.060066
H 3.766170 3.079101 1.855676
H 2.867806 1.746454 2.591153
C 4.557049 -2.238759 -2.404139
C 5.056340 -3.250757 -0.278243
H 4.410851 -2.173740 1.460530
H -2.223957 -3.373418 4.002539
H -0.582939 -3.024945 3.452046
H -1.883410 -3.221205 2.272371
H -2.293719 -1.288583 5.460302
H -0.665682 -0.782520 5.038068
H -2.020901 0.308621 4.764491
H -4.040414 -1.729409 3.863667
H -3.808073 -0.133702 3.141285
H -3.793643 -1.585451 2.115473
C -2.772967 2.698167 0.976601
C -1.182092 3.182167 2.721431
H -0.154813 1.486496 3.558490
C 5.108991 -3.283770 -1.669538
H 4.582593 -2.260812 -3.489880
H 5.481771 -4.064586 0.302553
C -2.121356 3.621609 1.790288
H -3.476998 3.033227 0.218754
H -0.655713 3.900592 3.344814
H 5.573670 -4.123718 -2.177924
H -2.333888 4.683475 1.693661
H -2.983701 0.619244 0.454185
H 3.491175 -0.368126 -2.322575

(*S*)-TS4-5 with NHC **8''**
104 atoms
PCM Energy= -2187.33032129
O 3.003782 1.852832 0.789718
N 2.415016 2.441356 -1.351098
C 1.451297 3.211283 -2.176370
C 2.506714 2.643000 -0.002871
C 3.282990 -1.468107 -2.657562
C 1.695651 0.105098 -1.683044
C 2.684015 1.098931 -1.787111
C 2.028789 -1.183770 -2.118068
C 4.244975 -0.467960 -2.761483
C 3.940863 0.816358 -2.321726
H 1.372208 4.185956 -1.690991
H 3.510494 -2.480560 -2.983366
H 1.302280 -1.987870 -2.025045
H 5.226533 -0.685800 -3.173892
H 4.672879 1.619087 -2.376503
C 0.081871 2.538185 -2.164950
H -0.698459 3.258037 -2.447471
H 0.032878 1.786315 -2.965046
C 2.020415 3.403473 -3.572306
H 1.336363 4.008952 -4.173804
H 2.994073 3.903888 -3.548159
H 2.145717 2.441606 -4.081360
O 2.018984 3.851894 0.368629
C 2.022229 4.071778 1.774300
H 1.588633 5.061220 1.917127
H 1.412451 3.322718 2.289644
H 3.037584 4.033250 2.178259
O -1.973901 1.211970 0.136584
O -0.991994 3.221224 0.171771
C -1.884777 2.386898 0.568695
C -2.907958 2.895029 1.581368
C -3.448698 1.734472 2.413342
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H -4.232536 2.093719 3.089253
H -3.869824 0.950379 1.779206
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H -3.688131 4.341288 0.139889
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H -4.819393 3.911797 1.435214
C -2.277019 3.953552 2.483887
H -1.898468 4.798519 1.904189
H -3.017108 4.325253 3.200628
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H -0.444615 2.734476 -0.800297
Pd -0.088414 0.620994 -0.890581
C -0.260926 -1.185036 0.017639
N 0.556701 -1.806637 0.908007
N -1.285183 -2.058372 -0.204132
C 1.695496 -1.117337 1.556292
C 0.068243 -3.063277 1.212195
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C -1.083373 -3.224777 0.515019
C 1.290656 -0.552436 2.955146
C 2.978657 -1.914898 1.480142
H 1.849238 -0.232894 0.927927
H 0.569639 -3.741516 1.881288
C -2.581615 -2.681762 -2.290038
C -3.699293 -1.460677 -0.292163
H -2.117419 -0.752235 -1.499423
H -1.750087 -4.068669 0.471382
C 0.834836 -1.617917 3.951558
C 2.504784 0.179354 3.533023
C 0.151831 0.450416 2.747397
C 4.026186 -1.353118 0.740557
C 3.195220 -3.150809 2.103351
C -1.213878 -2.865324 -2.946162
C -3.168301 -4.044343 -1.920319
C -3.521428 -2.005748 -3.291807
C -4.508071 -0.385854 -0.679349
C -4.124067 -2.251132 0.778619
H -0.051504 -2.161785 3.608029
H 0.565963 -1.136629 4.898206
H 1.626649 -2.338898 4.177296
H 2.875419 0.941448 2.842257
H 2.225359 0.668139 4.473181
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H 0.431364 1.218033 2.012582
H -0.085352 0.950128 3.694453
H -0.765135 -0.028698 2.382571
C 5.245869 -2.009137 0.615458
C 4.414791 -3.810162 1.974441
H 2.419436 -3.611046 2.708596
H -1.311490 -3.429882 -3.879072
H -0.523987 -3.415552 -2.297363
H -0.752045 -1.899099 -3.183103
H -3.383585 -4.611934 -2.831509
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H -3.149286 -1.016640 -3.583107
C -5.711732 -0.122966 -0.034880
C -5.321716 -1.981564 1.437386
H -3.515749 -3.082421 1.121844
C 5.443822 -3.243104 1.228031
H 6.040022 -1.552354 0.030475
H 4.560156 -4.769552 2.463966
C -6.123794 -0.921473 1.029541
H -6.319546 0.720289 -0.352466
H -5.625456 -2.605815 2.273166
H 6.394818 -3.759808 1.129323
H -7.057797 -0.711440 1.543090
H 3.872367 -0.383401 0.269679
H -4.169190 0.264893 -1.482828

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