Supporting Information

Nontraditional Fragment Couplings of Alcohols and Carboxylic Acids: C(sp^3)–C(sp^3) Cross-Coupling via Radical Sorting

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1) General information

Commercial reagents were used without prior purification unless otherwise indicated. All solvents were purified according to the method of Grubbs.[1] $Ir(dF(Me)ppy)_2(dtbbpy)PF_6$ was prepared according to literature procedure.[2] $Ni(TMHD)_2$ was purchased from Strem Chemicals and used as received. Iodomesitylene diacetate was purchased from TCI and used as received. Iodosylmesitylene was prepared according to literature procedure.[3] Alcohol activation *N*-heterocyclic carbene reagents **NHC-1** and **NHC-2** were prepared according to literature procedures.[4] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporating using a temperature-controlled water bath. Crude reaction mixtures containing high boiling solvents (e.g., DMSO) were concentrated on a GeneVac HT-4X Centrifugal Vacuum Evaporator Series II machine at 40 ºC under 1.5 mbar for 10–16 hours.

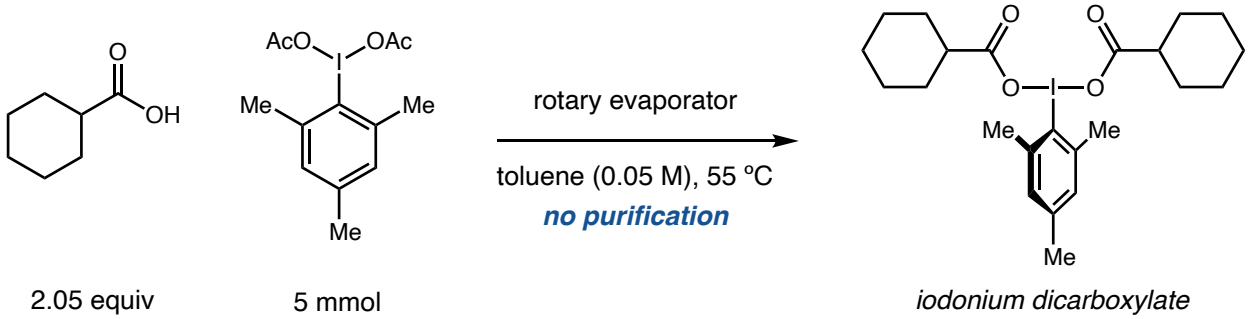
Chromatographic purification of products was performed on an automated Teledyne ISCO Combi*Flash*® NextGen 300+ system using RediSep Rf Gold® Silica Gel Disposable Flash Columns (20–40 microns). Reverse phase chromatography was performed on a Teledyne ISCO ACCQPrep® HP150 system using Waters XBridge BEH C18 OBD Prep Column (30 mm × 150 mm, 130 Å, 5 μm) with 0.1% ammonium hydroxide buffered water and acetonitrile solutions. Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm or Supelco 0.20 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching, $KMnO_4$ stain, *p*-anisaldehyde, or iodine stains.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III NMR 500 MHz instrument or a Bruker NanoBay Avance III HD NMR 400 MHz instrument, and are internally referenced to the residual proteo-solvent signals (7.26 ppm and 77.16 ppm, respectively, for $CDCl_3$; 5.32 ppm and 53.84 ppm, respectively, for CD_2Cl_2; 2.50 ppm and 39.52 ppm, respectively, for DMSO-d_6). ^{19}F NMR spectra were recorded on a Bruker NanoBay Avance III HD NMR 400 MHz and are reported unreferenced. Data for ^1H and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, b = broad), coupling constant (Hz), and integration. Peaks assigned to minor diastereomers and minor rotamers are enclosed in curly braces and square brackets, respectively. Data for ^{13}C NMR are reported in terms of chemical shift; multiplicity and coupling constants are included only in the case of coupling with ^{19}F nuclei. Quantitative ^{13}C NMR were taken with a relaxation delay of 28 s.

Liquid chromatography (LC) analysis was performed on an Agilent 1200 or Agilent 1290 Infinity II LC system. Chiral high performance liquid chromatography (HPLC) was performed on an Aiglent 1260 Infinity system using chiral columns as noted. Infrared (IR) spectroscopy was performed on a Thermo Nicolet 6700 FTIR spectrometer with diamond Smart Orbit ATR accessory, and spectra are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Princeton University Mass Spectral Facility on Agilent 6220 ESI-TOF LC/MS or Agilent 7200 GC-QTOF systems.

2) Synthesis of iodonium dicarboxylates (without purification)

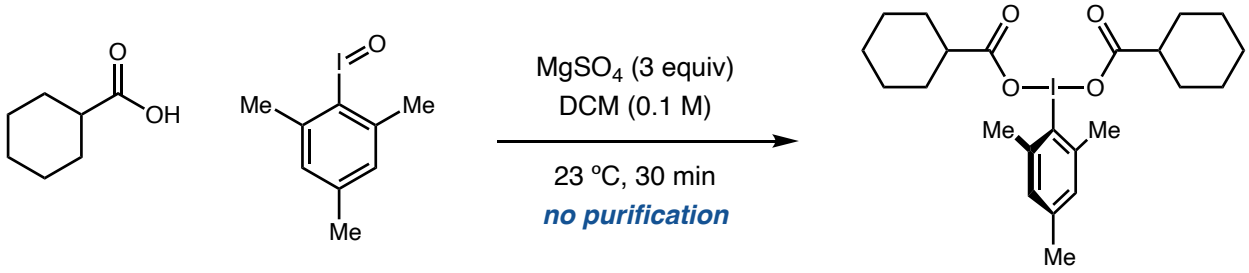
General procedure A – Exchange with Iodomesitylene Diacetate[5]:



2.05 equiv 5 mmol *iodonium dicarboxylate*

To a 250 mL round-bottom flask was added iodomesitylene diacetate (1.82 g, 5.0 mmol, 1.0 equiv), carboxylic acid (10.25 mmol, 2.05 equiv), and toluene (100 mL, 0.05 M). The solution was sonicated until homogeneous, and the solvent (along with the displaced acetic acid) was removed via rotary evaporator at 55 ºC. The residue was redissolved in a second portion of toluene (75 mL), and the evaporation step was repeated. This evaporation process was repeated with twice more with toluene (2 × 50 mL), and finally once with DCM (50 mL; this last step aids in the removal of residual toluene). For volatile carboxylic acids (e.g., methoxyacetic acid), excess carboxylic acid (up to 4.0 equiv) can be employed, and any unreacted starting material removed via high vacuum following the last evaporation from DCM.

General procedure B – Addition to Iodosylmesitylene:

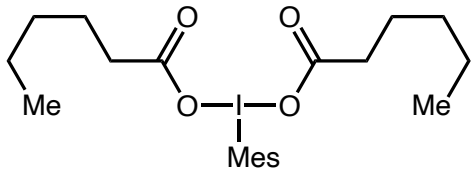


2.0 equiv 5 mmol *iodonium dicarboxylate*

To a 100 mL round-bottom flask was added iodosomesitylene (1.31 g, 5.0 mmol, 1.0 equiv), carboxylic acid (10.0 mmol, 2.0 equiv), and DCM (50 mL). The mixture was sonicated until homogenous, typically resulting in a slightly cloudy solution due to liberation of water. To this mixture magnesium sulfate (1.81 g, 15 mmol, 3 equiv) was added, and the reaction was stirred at room temperature for 30 minutes. The solids were filtered away, and the filtrate concentrated in vacuo to provide the title compound.

Use & Storage: The products obtained via either general procedure A or general procedure B are typically generated in >95% yield. After further removal of residual solvent under high vacuum, these iodonium dicarboxylates can be directly used in the cross-coupling of alcohols and carboxylic acids without purification. In general, these reagents can be stored in a capped vial under air at room temperature for 1–2 weeks. If stored in a capped vial at –20 ºC, usage can be prolonged to at least 1–2 months without appreciable loss in reagent efficiency.

Experimental Data for Iodonium Dicarboxylates



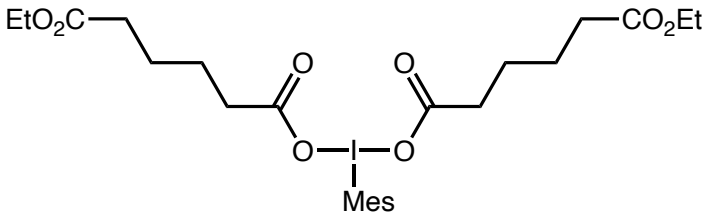
iodomesitylene dihexanoate (SI-1): According to general procedure B using hexanoic acid, the title compound was isolated as a clear colorless oil.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.13 (s, 2H), 2.70 (s, 6H), 2.37 (s, 3H), 2.21 (t, *J* = 7.5 Hz, 4H), 1.53 (p, *J* = 7.4 Hz, 4H), 1.36 – 1.16 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 6H)

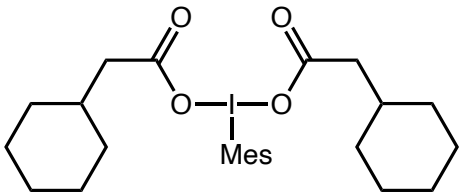
^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.27, 143.53, 141.75, 129.61, 129.15, 34.26, 31.78, 26.80, 25.85, 22.73, 21.26, 14.13.

IR (film) ν_{max} 3053, 2955, 2930, 2864, 1646, 1457, 1361, 1262, 1178, 732, 641, 539 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{33}INaO_4^+$ ([M+Na]$^+$) 499.1316, found 499.1321.



iodomesitylene bis(6-ethoxy-6-oxohexanoate): According to general procedure A using 6-ethoxy-6-oxohexanoic acid, the title compound was isolated as a clear colorless oil. Characterization data were consistent with literature values.[5a]



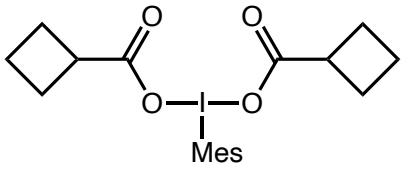
iodomesitylene bis(2-cyclohexylacetate) (SI-2): According to general procedure B using cyclohexylacetic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.11 (s, 2H), 2.67 (s, 6H), 2.35 (s, 3H), 2.07 (d, *J* = 7.1 Hz, 4H), 1.67 – 1.57 (m, 12H), 1.26 – 1.15 (m, 4H), 1.15 – 1.04 (m, 2H), 0.87 (qd, *J* = 13.2, 3.4 Hz, 4H).

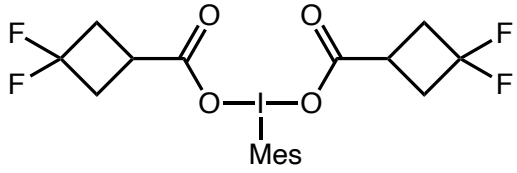
^{13}C NMR (126 MHz, CD_2Cl_2) δ 178.58, 143.56, 141.73, 129.72, 129.12, 42.24, 36.00, 33.34, 26.80, 26.58, 26.48, 21.28.

IR (film) ν_{max} 2919, 2848, 1645, 1446, 1348, 1288, 1227, 1168, 1112, 848, 710, 633, 500 cm^{-1}.

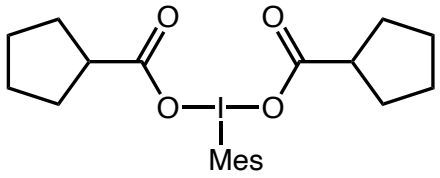
HRMS (ESI-TOF) *m/z* calcd. for $C_{25}H_{37}INaO_4^+$ ($[M+Na]^+$) 551.1629, found 551.1624.



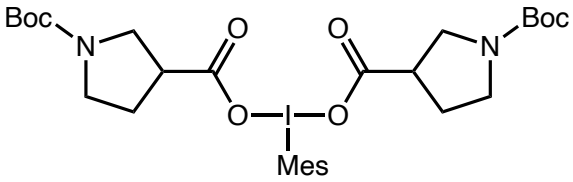
iodomesitylene dicyclobutanecarboxylate: According to general procedure A using cyclobutanecarboxlic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



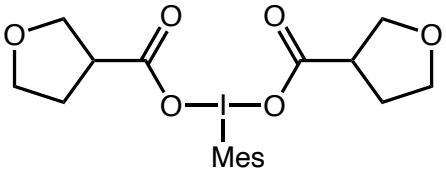
iodomesitylene bis(3,3-difluorocyclobutane-1-carboxylate): According to general procedure A using 3,3-difluorocyclobutane-1-carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5b]



iodomesitylene dicyclopentanecarboxylate: According to general procedure A using cyclopentanecarboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



iodomesitylene bis(1-(*tert*-butoxycarbonyl)pyrrolidine-3-carboxylate): According to general procedure A using 1-(*tert*-butoxycarbonyl)pyrrolidine-3-carboxylic acid, the title compound was isolated as a white foaming solid. Characterization data were consistent with literature values.[5b]



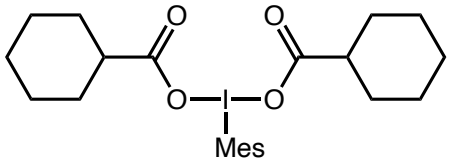
iodomesitylene bis(tetrahydrofuran-3-carboxylate) (SI-3): According to general procedure B using tetrahydrofuran-3-carboxylic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.12 (s, 2H), 3.82 – 3.75 (m, 2H), 3.78 – 3.70 (m, 4H), 3.70 – 3.62 (m, 2H), 2.97 (tt, *J* = 8.3, 6.0 Hz, 2H), 2.67 (s, 6H), 2.36 (s, 3H), 2.07 – 1.92 (m, 4H).

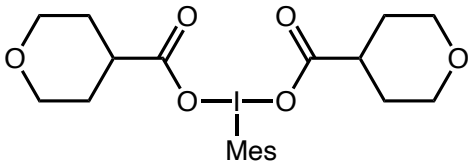
^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.13, 143.86, 141.80, 129.66, 129.27, 70.97, 68.39, 43.80, 30.48, 26.76, 21.26.

IR (film) ν_{max} 2955, 2863, 1647, 1450, 1351, 1177, 1062, 994, 957, 909, 851, 703, 492 cm^{-1}.

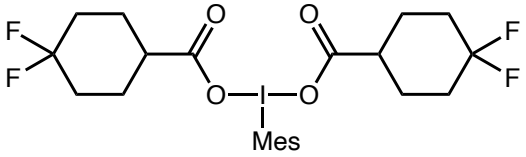
HRMS (ESI-TOF) *m*/*z* calcd. for $C_{19}H_{25}INaO_6^+$ ([M+Na]$^+$) 499.0588, found 499.0591.



iodomesitylene dicyclohexanecarboxylate: According to general procedure A using cyclohexane carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



iodomesitylene bis(tetrahydro-2*H*-pyran-4-carboxylate): According to general procedure A using tetrahydro-2*H*-pyran-4-carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



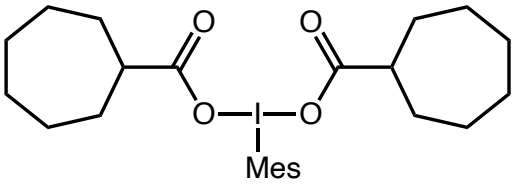
iodomesitylene bis(4,4-difluorocyclohexane-1-carboxylate) (SI-4): According to general procedure A using 4,4-difluorocyclohexane-1-carboxylic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.12 (s, 2H), 2.67 (s, 6H), 2.36 (s, 3H), 2.36 – 2.28 (m, 2H), 2.03 – 1.89 (m, 4H), 1.88 – 1.79 (m, 4H), 1.77 – 1.61 (m, 8H).

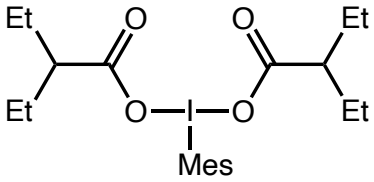
^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.59, 143.87, 141.81, 129.79, 129.31, 125.84, 123.46 (t, J = 240.7 Hz), 40.84, 32.93 (t, J = 24.3 Hz), 26.79, 26.11 (apparent dd, J = 7.1, 3.1 Hz), 21.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -94.49 (d, J = 235.7 Hz), -99.45 (d, J = 235.7 Hz).

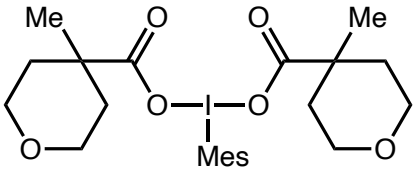
IR (film) ν_{max} 2953, 1649, 1449, 1364, 1315, 1258, 1203, 1097, 953, 853, 780, 710, 680, 591, 542, 493, 418 cm^{-1}.



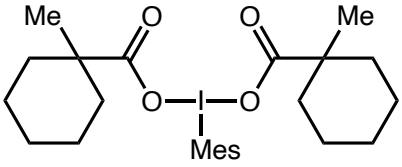
iodomesitylene dicycloheptanecarboxylate: According to general procedure A using cycloheptanecarboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



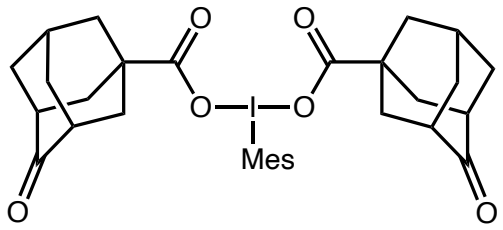
iodomesitylene bis(2-ethylbutanoate): According to general procedure A using 2-ethylbutanoic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



iodomesitylene bis(4-methyltetrahydro-2*H*-pyran-4-carboxylate): According to general procedure A using 4-methyltetrahydro-2*H*-pyran-4-carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5b]



iodomesitylene bis(1-methylcyclohexane-1-carboxylate): According to general procedure A using 1-methylcyclohexane-1-carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5b]



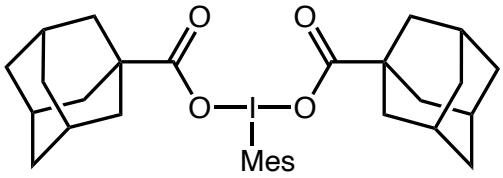
iodomesitylene bis(4-oxoadamantane-1-carboxylate) (SI-5): According to general procedure B using 4-oxoadamantane-1-carboxylic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.09 (s, 2H), 2.64 (s, 6H), 2.41 (t, *J* = 3.1 Hz, 4H), 2.33 (s, 3H), 2.06 (apparent p, *J* = 3.1 Hz, 2H), 2.02 (d, *J* = 2.9 Hz, 8H), 1.97 – 1.91 (m, 8H), 1.89 – 1.83 (m, 4H).

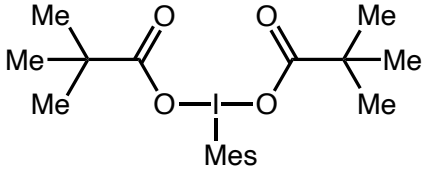
^{13}C NMR (126 MHz, CD_2Cl_2) δ 216.29, 180.87, 143.42, 141.66, 129.45, 129.13, 46.35, 41.01, 40.97, 38.57, 38.47, 27.89, 26.53, 21.20.

IR (film) ν_{max} 3054, 2929, 2860, 1719, 1640, 1451, 1311, 1232, 1068, 789, 730, 662, 538 cm^{-1}.

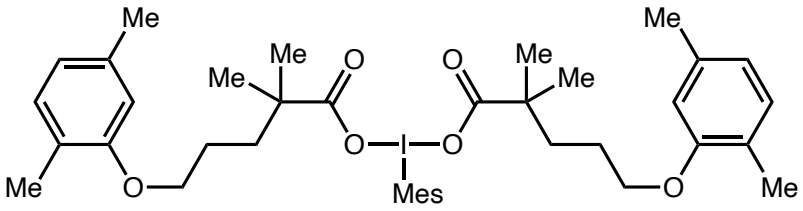
HRMS (ESI-TOF) *m*/*z* calcd. for $C_{31}H_{37}INaO_6^+$ ([M+Na]$^+$) 655.1527, found 655.1527.



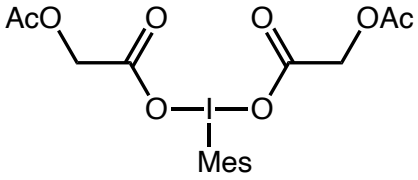
iodomesitylene bis(adamantane-1-carboxylate): According to general procedure A using adamantane-1-carboxylic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5a]



iodomesitylene dipivalate: According to general procedure A using pivalic acid, the title compound was isolated as a white solid. Characterization data were consistent with literature values.[5b]



iodomesitylene bis(5-(2,5-dimethylphenoxy)-2,2,-dimethylpentanoate): According to general procedure A using 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid, the title compound was isolated as a viscous waxy oil. Characterization data were consistent with literature values.[5b]



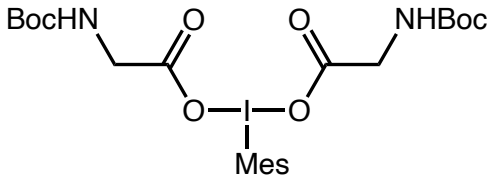
iodomesitylene bis(2-acetoxyacetate) (SI-6): According to general procedure B using 2-acetoxyacetic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.13 (s, 2H), 4.43 (s, 4H), 2.69 (s, 6H), 2.36 (s, 3H), 2.03 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.49, 170.45, 144.37, 141.90, 130.54, 129.30, 60.10, 26.72, 21.23, 20.53.

IR (film) ν_{max} 3057, 2952, 1745, 1678, 1422, 1375, 1269, 1191, 1065, 846, 729, 661, 535, 418 cm^{-1}.

HRMS (ESI-TOF) *m/z* calcd. for $C_{17}H_{21}INaO_8^+$ ($[M+Na]^+$) 503.0173, found 503.0178.



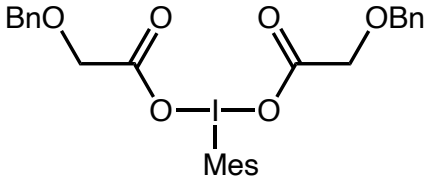
iodomesitylene bis((*tert*-butoxycarbonyl)glycinate) (SI-7): According to general procedure B using *N*-Boc glycine, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.12 (s, 2H), 5.26 (t, *J* = 5.7 Hz, 2H), 3.71 (d, *J* = 5.7 Hz, 4H), 2.68 (s, 6H), 2.35 (s, 3H), 1.37 (s, 18H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.23, 155.97, 144.21, 141.93, 129.33 (doubled peaks), 79.69, 41.97, 28.37, 26.86, 21.27.

IR (film) ν_{max} 3353, 2978, 2931, 1699, 1505, 1366, 1219, 1157, 1051, 950, 857, 731, 706, 601, 485 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{23}H_{35}IN_2NaO_8^+$ ($[M+Na]^+$) 617.1330, found 617.1332.

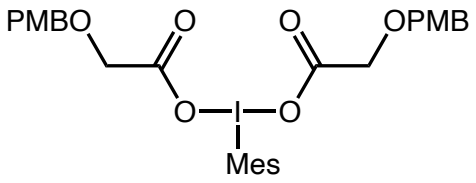


iodomesitylene bis(2-(benzyloxy)acetate) (SI-8): According to general procedure B using 2-benzyloxyacetic acid, the title compound was isolated as a pale yellow solid. This reagent is immediately used upon preparation, as it decomposes presumably via oxidative debenzylation.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.41 – 7.28 (m, 10H), 7.16 (s, 2H), 4.54 (s, 4H), 4.04 (s, 4H), 2.75 (s, 6H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.45, 144.19, 141.86, 137.97, 130.10, 129.34, 128.64, 128.33, 128.10, 73.30, 67.03, 26.93, 21.28.

IR (film) ν_{max} 3030, 2917, 2865, 1672, 1452, 1200, 1106, 1020, 950, 700, 611, 542, 416 cm^{-1}.

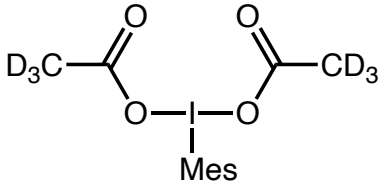


iodomesitylene bis(2-(4-methoxybenzyloxy)acetate) (SI-9): According to general procedure B using 2-(4-methoxybenzyloxy)acetic acid, the title compound was isolated as a white solid. This reagent is immediately used upon preparation, as it decomposes presumably via oxidative debenzylation.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.20 (d, *J* = 8.7 Hz, 4H), 7.15 (s, 2H), 6.85 (d, *J* = 8.7 Hz, 4H), 4.44 (s, 4H), 3.98 (s, 4H), 3.78 (s, 6H), 2.72 (s, 6H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.57, 159.74, 144.18, 141.87, 130.03, 129.33, 113.95, 72.93, 66.73, 55.50, 26.94, 21.28.

IR (film) ν_{max} 2944, 2914, 2839, 1726, 1604, 1512, 1456, 1245, 1105, 1028, 946, 819, 513 cm^{-1}.

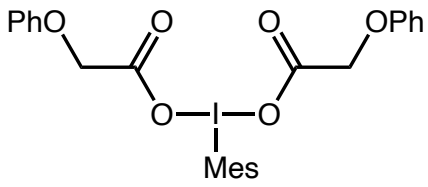


iodomesitylene bis(2-acetoxyacetate) (SI-10): According to general procedure B using d_4-acetic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.13 (s, 2H), 2.67 (s, 6H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.79, 141.83, 129.33, 129.23, 26.87, 21.29, 19.77 (hept, *J* = 19.6 Hz).

IR (film) ν_{max} 2980, 2923, 2856, 1637, 1455, 1282, 1078, 1034, 849, 825, 738, 633, 570, 536, 456 cm^{-1}.



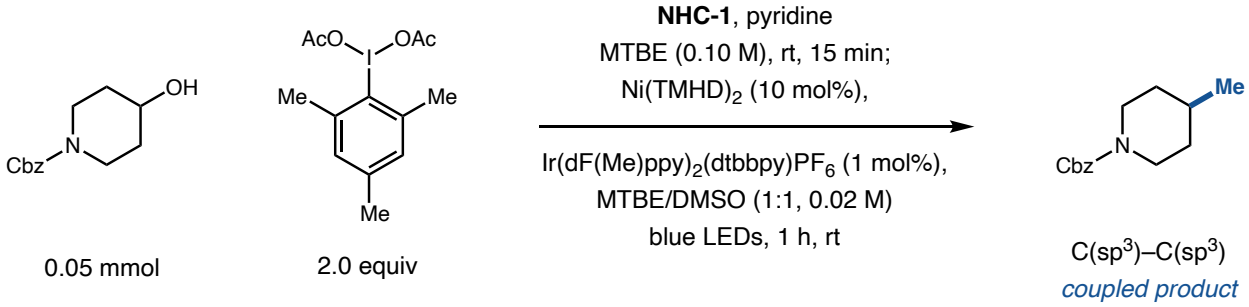
iodomesitylene bis(2-acetoxyacetate) (SI-11): According to general procedure B using d_4-acetic acid, the title compound was isolated as a white solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.23 (t, *J* = 8.0 Hz, 4H), 7.09 (s, 2H), 6.95 (t, *J* = 7.3 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 4H), 4.51 (s, 4H), 2.60 (s, 6H), 2.38 (s, 3H), .

^{13}C NMR (126 MHz, CD_2Cl_2) δ 173.69, 158.28, 144.39, 142.01, 130.70, 129.83, 129.41, 121.71, 114.72, 64.78, 26.74, 21.33.

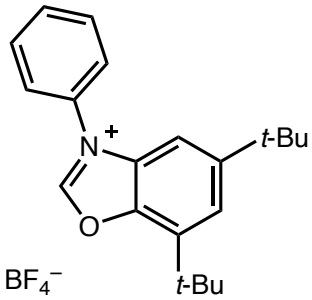
IR (film) ν_{max} 3035, 2922, 2857, 1670, 1593, 1491, 1295, 1194, 1070, 845, 754, 716, 691, 591, 418 cm^{-1}.

3) Reaction optimization and control experiments

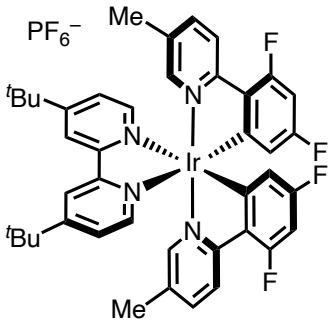


Stock solution 1 (Alcohol): To an oven dried vial equipped with a stir bar was added NHC-1 precursor salt (1.10 equiv) and alcohol substrate (1.00 equiv). The vial was placed under nitrogen atmosphere, and separately degassed anhydrous MTBE (0.10 M). Pyridine (1.05 equiv) was added in one portion, and the suspension was stirred at room temperature under nitrogen atmosphere. After 15 minutes, the resulting suspension was syringe filtered to remove pyridinium salts and unreacted NHC precursor to prepare a 0.1 M stock solution in MTBE. Note this solution was typically prepared on >0.20 mmol scale for reproducible results.

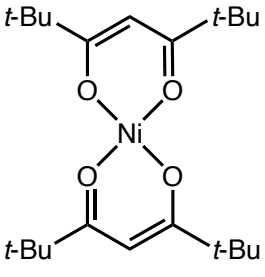
Example procedure: To an oven dried vial equipped with a stir bar was added iridium photocatalyst (0.01 equiv), nickel catalyst (0.10 equiv), and iodomesitylene diacetate (2.0 equiv). The vial was placed under nitrogen atmosphere, and separately degassed DMSO (1.25 mL) and MTBE (0.75 mL) were added in one portion. The pre-activated alcohol–NHC adduct was added via syringe (0.5 mL stock solution 1, 0.10 M, 0.05 mmol, 1.0 equiv), and the vial was sealed with parafilm and subsequently irradiated in the integrated photoreactor for 1 hour (100% intensity, 5200 rpm fans, 500 rpm stirring), after which the reaction was quenched by exposure to air for 10 minutes with stirring. Water-immiscible solvents were removed by GeneVac (e.g., MTBE), acetanilide was added as a solution in acetonitrile (1.0 mL, 25 mM, 0.025 mmol, 0.5 equiv), and a 0.1 mL aliquot of the resulting mixture was removed, filtered through celite, diluted in acetonitrile and analyzed via uHPLC analysis (Waters Acquity BEH C18 1.7 µm column, 3.0 × 50 mm, 5–100% MeCN/H_2O with 0.40 mM 1:1 formate/formic acid buffer) monitoring absorption at 195 nm.



NHC-1



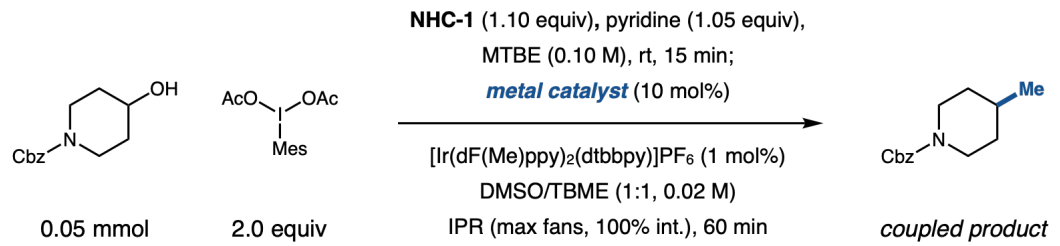
Ir(dF(Me)ppy)$_2$(dtbbpy)PF$_6$



Ni(TMHD)$_2$

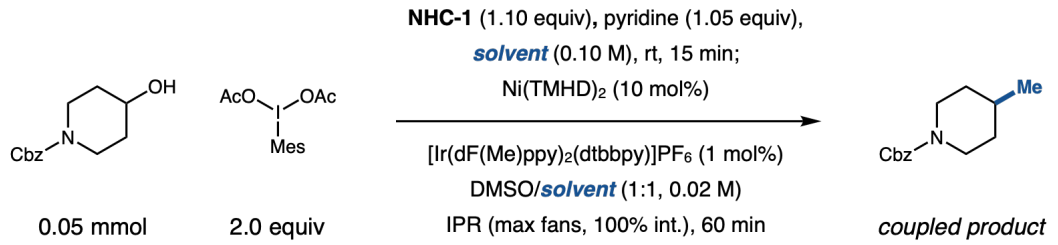
The above procedure was modified as necessary to screen the desired variables. If additives were required (e.g., quinuclidine), there were either added as a solid before the addition of solvents or as a solution in DMSO before the addition of stock solution 1. The amount of added DMSO was adjusted to account for stock solution volumes. If both the nickel catalyst and iridium photocatalyst were held constant, a single stock solution in DMSO containing both components was prepared.

Assay calibration: Varying ratios of independently prepared benzyl 4-methylpiperidine-1-carboxylate and acetanilide were combined and subjected to ^{1}H NMR and uHPLC analysis to determine the relative response factor (RRF). The actual compound ratio (determined by ^{1}H NMR) was plotted as a function of compound relative area (determined by uHPLC) to determine the RRF as the slope of the linear best fit. The RRF values for the recovered alcohol starting material ("alcohol") and proto-dehydroxylation byproduct ("alkane") were calculated in a similar fashion.



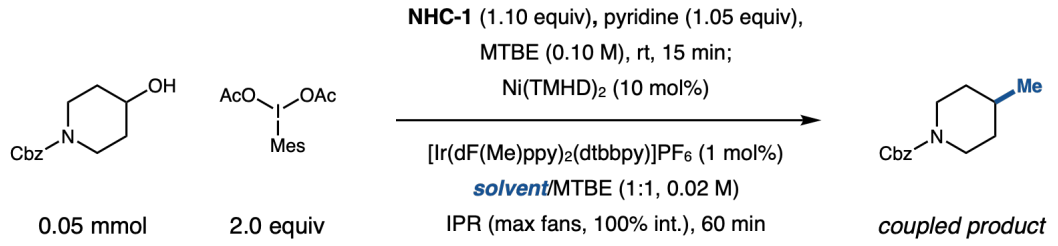
metal catalyst	yield	alcohol	alkane
$Ni(TMHD)_2$	75%	9%	3%
$Ni(acac)_2$	73%	9%	3%
$NiCl_2$•dtbbpy	24%	10%	7%
$Cu(OAc)_2$•tBu_3terpy	53%	12%	9%
$Cu(TMHD)_2$	68%	10%	4%

Table S1. Effect of Metal Catalyst



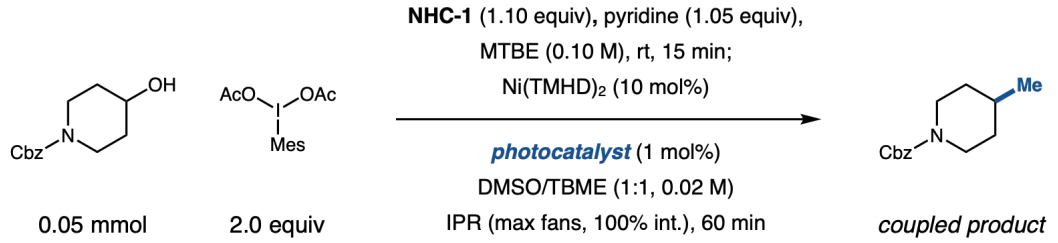
alcohol condensation solvent	yield	alcohol	alkane
MTBE	76%	9%	3%
CPME	63%	8%	10%
THF	6%	55%	22%
PhF	34%	28%	4%
$PhCF_3$	52%	14%	3%

Table S2. Effect of Condensation Solvent



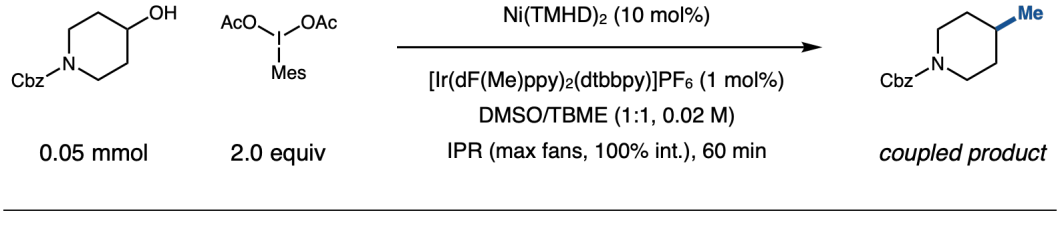
catalysis co-solvent	yield	alcohol	alkane
DMSO	76%	9%	3%
DMA	69%	9%	5%
NMP	64%	9%	17%
MeCN	38%	9%	13%
acetone	42%	9%	15%

Table S3. Effect of Catalysis Co-Solvent



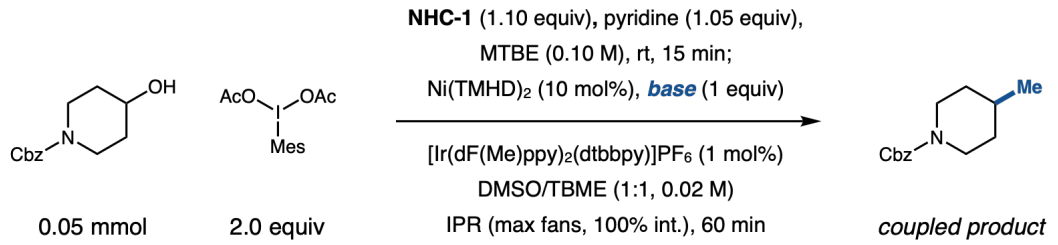
photocatalyst	yield	alcohol	alkane
$[Ir(ppy)_2(dtbbpy)][PF_6]$	68%	8%	4%
$[Ir(F(Me)ppy)_2(dtbbpy)][PF_6]$	62%	9%	3%
$[Ir(dF(Me)ppy)_2(dtbbpy)][PF_6]$	75%	9%	3%
$[Ir(dF(F)ppy)_2(dtbbpy)][PF_6]$	68%	8%	3%
$[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$	66%	8%	3%

Table S4. Effect of Iridium Photocatalyst



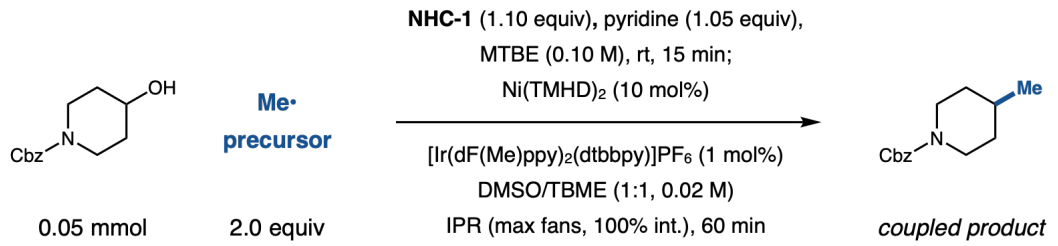
base (condensation)	yield	alcohol	alkane
pyridine	76%	9%	3%
2,6-lutidine	66%	11%	2%
4-OMe-pyridine	70%	10%	3%
DBU	50%	32%	2%
N-Me-imidazole	62%	16%	3%

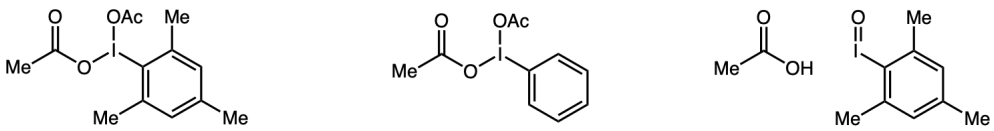
Table S5. Effect of Base in Alcohol Condensation



base (cross-coupling)	yield	alcohol	alkane
none	75%	9%	3%
NaOAc	66%	8%	3%
NaOBz	66%	10%	4%
quinuclidine	66%	8%	3%
DBU	75%	3%	20%

Table S6. Effect of Base in Cross-Coupling

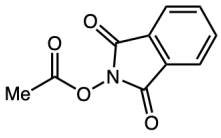




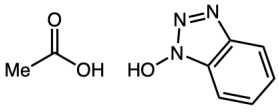
76% yield
9% alcohol, 3% alkane

71% yield
8% alcohol, 2% alkane

44% yield
18% alcohol, 11% alkane

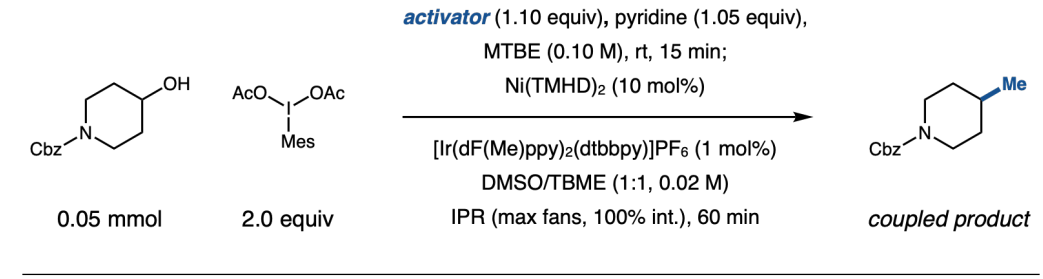


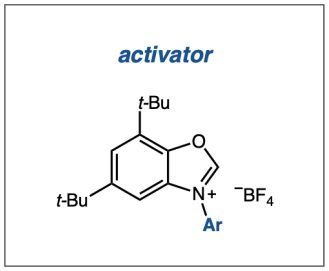
34% yield
11% alcohol, 8% alkane



0% yield
96% alcohol, 2% alkane

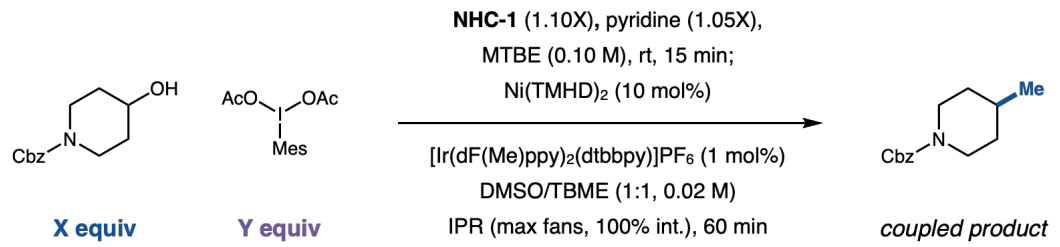
Table S7. Effect of Carboxylate Activating Group





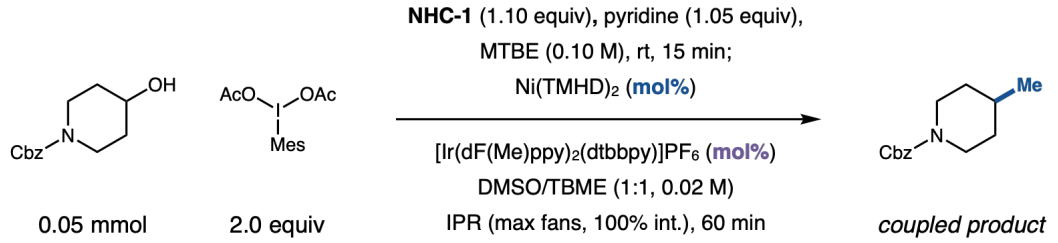
Ar	yield	alcohol	alkane
p-OMe-Ph	60%	18%	2%
3,5-dMe-Ph	66%	12%	3%
Ph	76%	9%	3%
m,p-dCl-Ph	66%	10%	3%
p-CF_3-Ph	74%	9%	3%

Table S8. Effect of Alcohol Activating Group



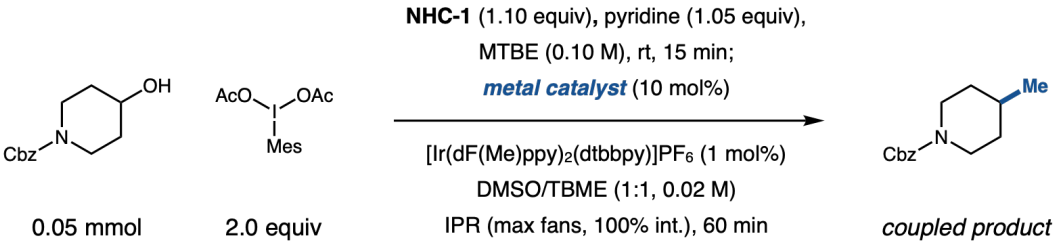
X equiv	Y equiv	yield	alcohol	alkane
1	2	75%	9%	3%
1	1.5	71%	11%	4%
1	1	67%	11%	10%
1.5	1	68%	29%	15%
2	1	61%	72%	15%

Table S9. Effect of Stoichiometry



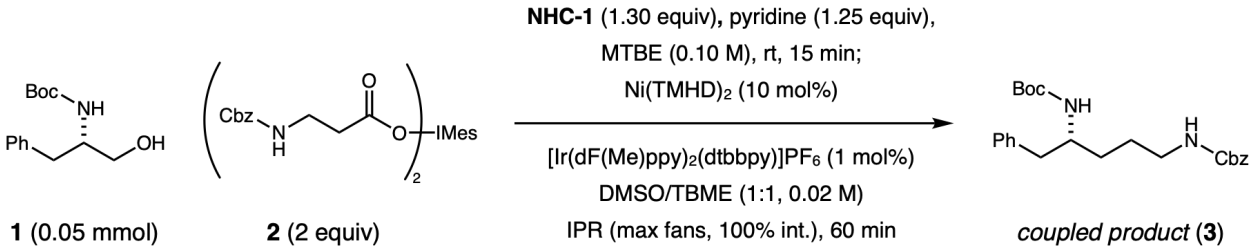
Ni mol%	Ir mol%	yield	alcohol	alkane
5	1	55%	10%	5%
10	1	75%	9%	3%
20	1	71%	10%	1%
10	2	66%	9%	3%
10	3	62%	10%	3%

Table S10. Effect of Catalyst Loadings



metal catalyst	yield	alcohol	alkane
$Ni(TMHD)_2$	76%	9%	3%
$Ni(acac)_2$	73%	9%	3%
$NiCl_2$•dtbbpy	24%	10%	7%
$Cu(OAc)_2$•tBu_3terpy	53%	12%	9%
$Cu(TMHD)_2$	68%	10%	4%

Table S11. Control Experiments



control conditions	yield (3)	1	2	4	5	6	7
as above	36%	3%	0%	12%	8%	174%	85%
no nickel catalyst	16%	5%	0%	41%	12%	196%	77%

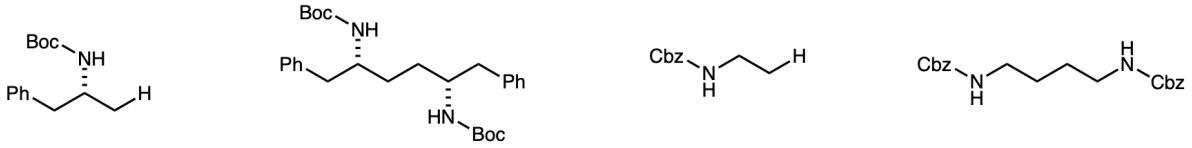
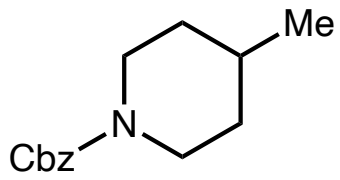


Table S12. Product distribution for primary–primary cross-coupling

As noted in reference 35 of the main text, it seems that β-amino substrates generally display excellent reactivity as model substrates in the combinations demonstrated in the main text. We hypothesize that the N–H moiety (or its carbamate protecting group) can support recognition by the nickel catalyst **12** and preferentially stabilize the resulting Ni–alkyl aintermediate through transitory chelation. To control for these effects and to determine the role of the nickel catalyst in its ability to distinguish between and cross-couple alkyl radicals, we selected the two β-amino substrates **1** and **2** as shown above (**Table S12**). While the overall reaction does appear to be less heteroselective for the formation of product **3** (36% yield) under our standard conditions, the selectivity of the transformation does change as a result of nickel catalyzed radical sorting. Comparing the ratio of the desired product **3** to the homodimerization of the limiting alcohol reagent **5** in the presence (4.5:1) and absence (1.3:1) of the catalyst **12**, we hypothesize that the nickel catalyst plays a role in modulating the selectivity of cross-coupling even with two similar β-substituted NH-moieties on both acid and alcohol components.

Synthesis & characterization of model substrate for reaction optimization



benzyl 4-methylpiperidine-1-carboxylate: The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene diacetate (364.2 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) to provide the title compound as a pale yellow oil (88.3 mg, 76% yield).

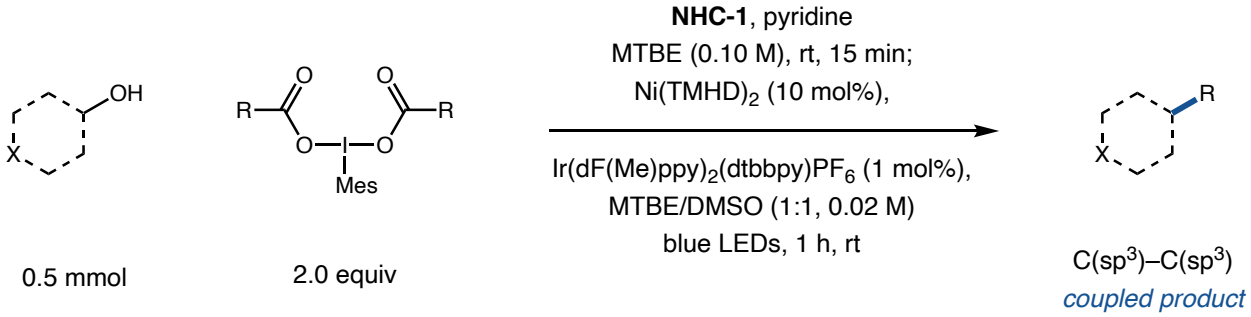
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.13 (s, 2H), 4.15 (bs, 2H), 2.76 (bs, 2H), 1.68 – 1.57 (m, 2H), 1.56 – 1.47 (m, 1H), 1.17 – 1.05 (m, 2H), 0.94 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.33, 137.04, 128.47, 127.90, 127.82, 66.91, 44.27, 33.96, 30.90, 21.90.

IR (film) ν_{max} 3357, 3065, 3031, 2924, 2850, 1693, 1468, 1302, 1275, 1229, 1150, 1085, 1015, 751, 697 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{20}NO_2^+$ ($[M+H]^+$) 234.1489, found 234.1489.

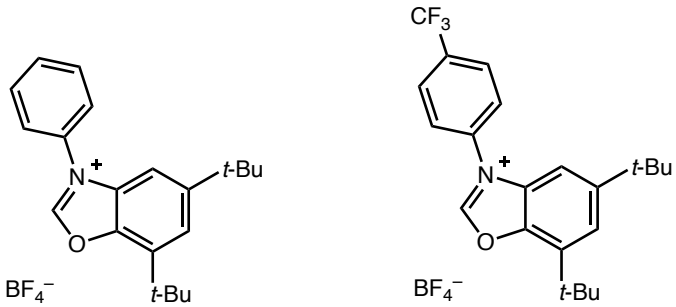
4) General procedure for cross-coupling of alcohols and carboxylic acids



Stock solution 1 (Alcohol)

For 1° or 2° alcohol substrates: To an oven dried 40 mL vial equipped with a stir bar was added **NHC-1** (1.10 equiv), alcohol substrate (1.00 equiv), and separately degassed anhydrous MTBE (0.10 M). Freshly distilled pyridine (1.05 equiv) was added dropwise, and the suspension was stirred at room temperature under nitrogen atmosphere. After 15 minutes, the resulting light pink suspension was syringe filtered to remove pyridinium salts and unreacted NHC precursor.

For 3° alcohol substrates: To an oven dried 40 mL vial equipped with a stir bar was added **NHC-2** (1.10 equiv), alcohol substrate (1.00 equiv), and separately degassed anhydrous $PhCF_3$ (0.10 M). At –25 ºC, freshly distilled pyridine (1.05 equiv) was added dropwise, and the suspension was stirred under nitrogen atmosphere, gradually warming to 0 ºC over the course of 6 h. The resulting light pink suspension was syringe filtered to remove pyridinium salts and unreacted NHC precursor, and $PhCF_3$ was removed under reduced pressure by rotary evaporator. The residue was redissolved in separately degassed anhydrous MTBE (0.10 M).



NHC-1 **NHC-2**

Stock solution 2 (Acid): To an oven dried 40 mL vial equipped with a X-shaped stir bar was added iodonium dicarboxylate (2.0 equiv), and the vial was sealed and placed under inert nitrogen atmosphere by evacuation and back-filling three times. Separately degassed anhydrous

DMSO/MTBE (1:1, 0.067 M) were added via syringe, and the resulting solution was sonicated until homogeneous.

Procedure: To an oven dried 40 mL vial equipped with a stir bar was added iridium photocatalyst (5.0 μmol, 0.01 equiv), nickel catalyst (50 μmol, 0.10 equiv), and anhydrous DMSO (5.0 mL), and the resulting solution was sparged with nitrogen for 15 minutes. The pre-activated alcohol–NHC adduct was added by syringe (5 mL stock solution 1, 0.10 M, 0.50 mmol, 1.0 equiv), the vial was sealed with parafilm and placed in the integrated photoreactor.

Upon irradiation (100% intensity, 5200 rpm fans, 500 rpm stirring), the iodonium dicarboxylate (15 mL stock solution 2, 0.067 M, 1.00 mmol, 2.0 equiv) was added, typically over the course of five minutes under nitrogen atmosphere (vide infra). The reaction mixture (0.02 M, 1:1 MTBE/DMSO) was further irradiated for 1 hour, and the reaction was quenched by exposure to air with stirring for 10 minutes. The crude reaction mixture was directly concentrated by GeneVac to remove both methyl *tert*-butyl ether and dimethylsulfoxide solvents. The residue was resuspended in 10 mL dichloromethane, the mixture was carefully concentrated in the presence of 5 g of silica gel, and directly purified by automated flash chromatography via dry loading.

5) Additional examples and limitations of alcohol and carboxylic acid substrates

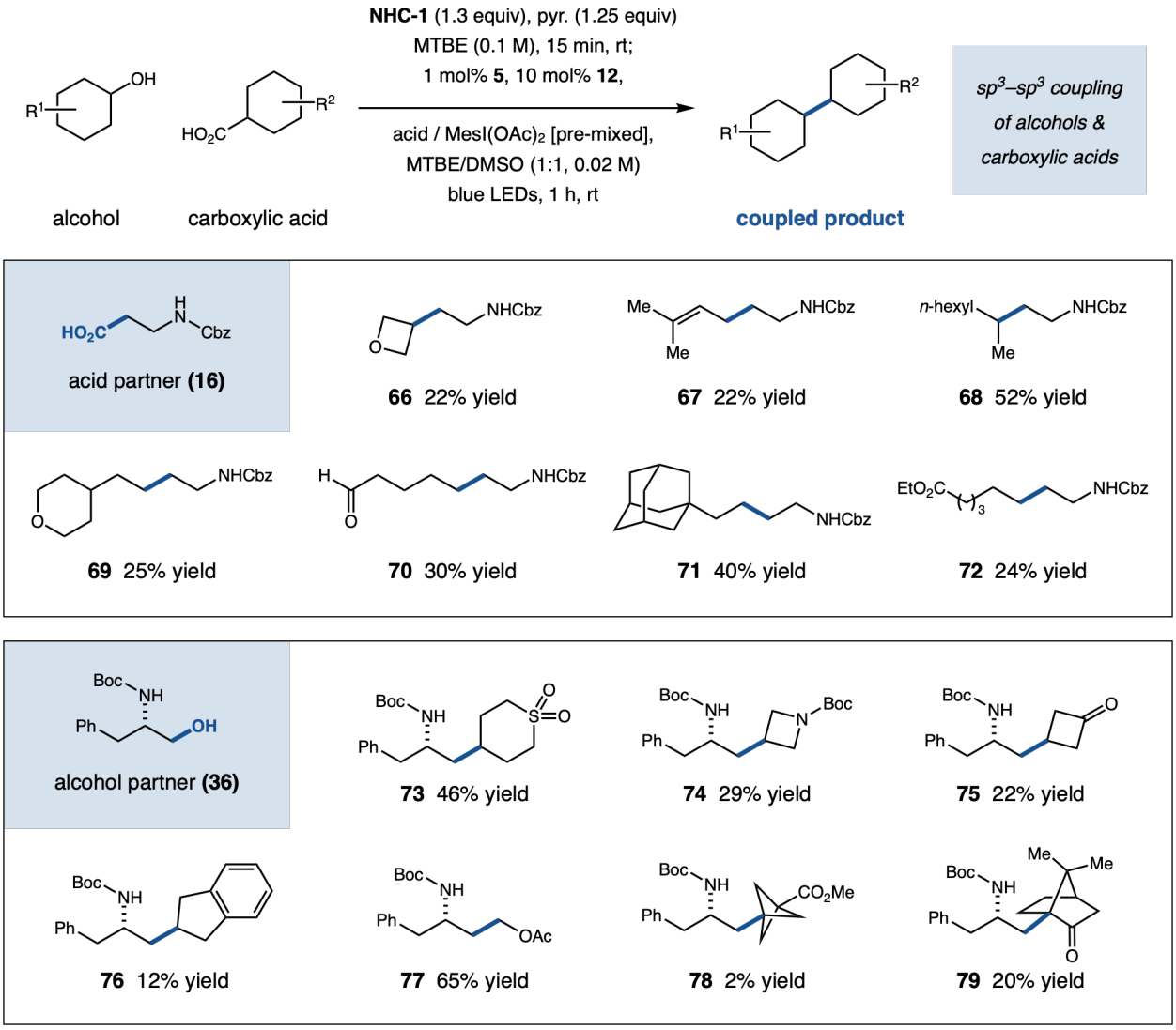


Table S13. Additional examples of alcohols and carboxylic acid substrates. To rapidly evaluate the efficiency of our reaction, an array of substrates were subjected to our optimized conditions and the crude reactions analyzed via NMR and HPLC-MS to obtain preliminary yields (based on ^{1}H NMR or starting material absorbance versus an internal standard) and confirm hits by ESI mass-spectrometry.

To illustrate further examples and limitations of our approach, **Table S13** contains additional alcohol and carboxylic acid substrates for which the C(sp^3)–C(sp^3) cross-coupling reaction was achieved in lower efficiency. Radicals derived from strained cyclic alcohols (**66**, 22% yield) and stabilized allylic systems (**67**, 22% yield) are less-reactive under our optimized conditions, while primary substrates (**69–72**, 24–40% yield) tend to suffer from lower reaction efficiencies due to competing homodimerization pathways. Additional carboxylic acid substrates such as sulfones (**73**, 46% yield) and strained 4-membered cyclic acids are competent, and the

corresponding products can be obtained in low yields (**74** and **75**, 29% and 22% yield, respectively). Indane-based carboxylic acid **76** suffers from oxidative elimination to the alkene, resulting in highly inefficient cross-coupling (12% yield). Formal homologation of alcohol **36** to the acetate-protected derivative can be achieved in good yield (**77**, 65% yield). However, strained caged tertiary carboxylic acids leading to radicals with high *s*-character are coupled inefficiently (**78** and **79**, 2% and 20% yield, respectively).

In the context of deoxymethylation (**Table S14**), cyclic secondary alcohols with 4–6 members undergo efficient cross-coupling with $MesI(OAc)_2$ to access methylated products in good yields (**80–83**, 52–69% yield). Simple acyclic alcohols work well for deoxymethylation (**84**, 54% yield), although more polar substrates can suffer from partial insolubility for the alcohol condensation with **NHC-1** (**85** and **86**, 14% and 31% yield, respectively). Primary alcohols can also be methylated in reasonable yields (**87–89**, 49–66% yield), as the primary radical can be presumably distinguished from the methyl radical by nickel catalyst **12**.

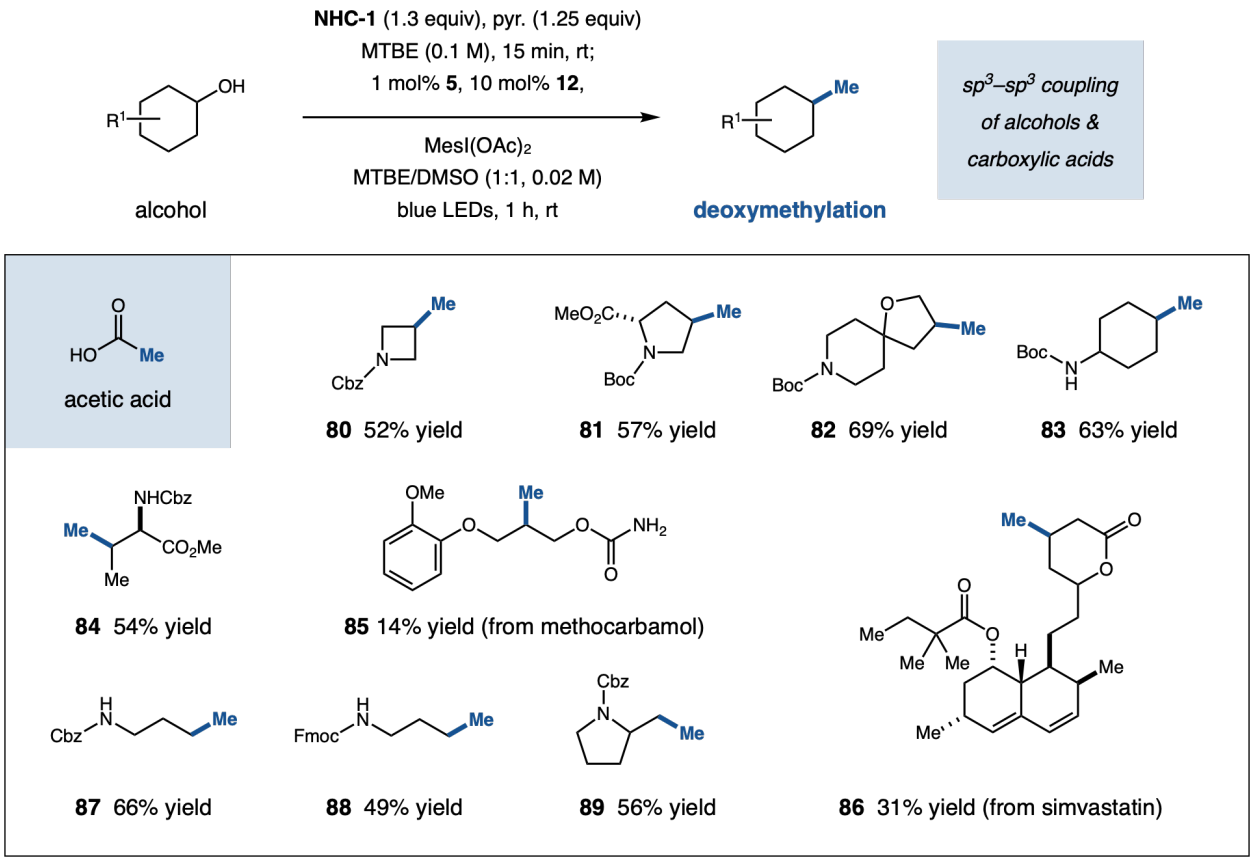
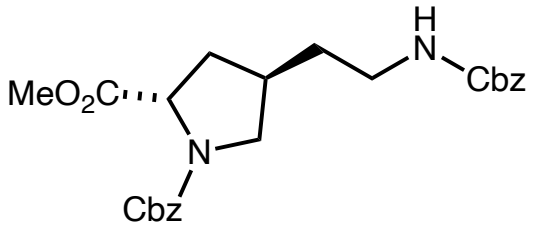
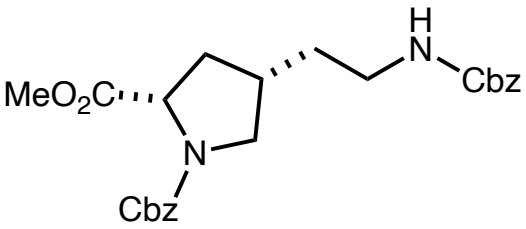


Table S14. Additional examples of deoxymethylation. To rapidly evaluate the efficiency of our reaction, an array of substrates were subjected to our optimized conditions and the crude reactions analyzed via NMR and HPLC-MS to obtain preliminary yields (based on ^{1}H NMR or starting material absorbance versus an internal standard) and confirm hits by ESI mass-spectrometry.

6) Experimental data for C(sp^3)–(Csp^3) cross-coupled products



major diastereomer (**17a**)



minor diastereomer (**17b**)

1-benzyl 2-methyl (2*S*)-4-(2-(((benzyloxy)carbonyl)amino)ethyl)pyrrolidine-1,2-dicarboxylate (17): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), Z-L-*trans*-hydroxyproline methyl ester (139.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 45–70% MeCN/H$_2$O with 0.1% NH$_4$OH) to provide the title compound as a clear colorless oil (111.9 mg, 51% yield). The diastereomer ratio was assigned as 2.7:1 by NMR and UHPLC analysis of the crude reaction mixture. Structural assignment was confirmed via isolation of major diastereomer **17a** (see spectra below).

Isolated mixture – **17a**/**17b** (2.7:1)

^{1}H NMR (500 MHz, CDCl$_3$) mixture of rotamers and diastereomers: 7.38 – 7.25 (m, 10H), 5.19 – 4.97 (m, 5H), 4.44 – 4.23 (m, 1H), 3.89 – 3.77 (m, 1H), 3.74 – 3.51 (m, 3H), 3.20 – 3.11 (m, 2H), 3.09 – 2.98 (m, 1H), 2.49 – 2.44 (m, 1H), 2.18 – 2.05 (m, 1H), 1.91 – 1.78 (m, 1H), 1.62 – 1.46 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) mixture of rotamers and diastereomers: 173.23, 173.07, 173.01, 172.88, 156.44, 156.40, 154.73, 154.59, 154.12, 154.02, 136.53, 136.50, 136.39, 136.37, 128.51, 128.47, 128.39, 128.14, 128.12, 128.11, 128.09, 128.05, 128.03, 127.98, 127.94, 127.92, 127.81, 127.70, 67.09, 67.07, 66.95, 66.63, 66.61, 59.22, 59.04, 58.92, 58.73, 52.31, 52.26, 52.16, 52.04, 52.00, 51.58, 39.67, 39.65, 39.59, 36.89, 36.45, 35.94, 35.55, 34.94, 34.03, 33.17, 33.13, 32.98, 32.85.

IR (film) ν_{max} 3337, 3033, 2946, 2874, 1693, 1527, 1415, 1352, 1244, 1201, 1121, 1013, 733, 697, 612 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{24}H_{28}N_2NaO_6^+$ ($[M+Na]^+$) 463.1840, found 463.1842.

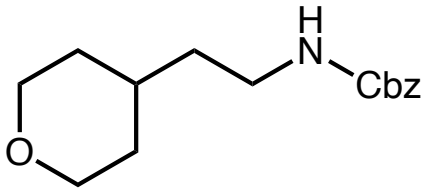
Major diastereomer – **17a**

^{1}H NMR (500 MHz, $CDCl_3$) mixture of rotamers (resonances for minor rotamer are enclosed in square brackets): δ 7.37 – 7.27 (m, 10H), 5.19 – 5.01 (m, 4H), 4.78 – 4.68 (m, 1H), 4.45 – 4.34 (m, 1H), 3.86 – 3.77 (m, 1H), 3.73 (s, 3H) [3.60], 3.19 (p, *J* = 7.2 Hz, 2H), 3.06 (dt, *J* = 24.4, 9.7 Hz, 1H), 2.34 (hept, *J* = 8.4 Hz, 1H), 2.18 – 2.12 (m, 1H), 1.93 – 1.81 (m, 1H), 1.67 – 1.51 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers: δ 173.14, 173.03, 156.43, 154.88, 154.27, 136.68, 136.66, 136.53, 128.71, 128.63, 128.55, 128.35, 128.33, 128.30, 128.19, 128.13, 128.10, 127.91, 67.29, 67.14, 66.91, 59.19, 58.89, 52.51, 52.33, 52.16, 51.74, 39.89, 39.86, 36.66, 35.76, 35.12, 34.22, 33.43.

IR (film) ν_{max} 3338, 3023, 2948, 2878, 1700, 1530, 1418, 1352, 1249, 1206, 1127, 1022, 744, 699, 613 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{24}H_{28}N_2NaO_6^+$ ($[M+Na]^+$) 463.1840, found 463.1840.



benzyl (2-(tetrahydro-2*H*-pyran-4-yl)ethyl)carbamate (18): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), tetrahydro-2*H*-pyran-4-ol (51.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

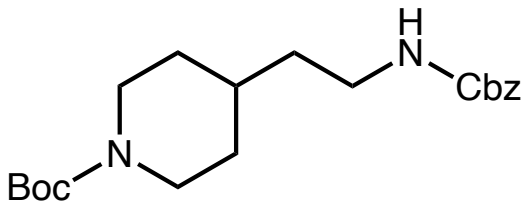
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–50% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 20–65% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (81.5 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.08 (s, 2H), 4.86 (bs, 1H), 3.93 (dd, *J* = 11.7, 4.6 Hz, 2H), 3.34 (t, *J* = 11.7 Hz, 2H), 3.22 (q, *J* = 6.4 Hz, 2H), 1.62 – 1.48 (m, 3H), 1.43 (q, *J* = 6.5 Hz, 2H), 1.27 (qd, *J* = 12.3, 4.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.46, 136.65, 128.58, 128.18 (2C), 67.97, 66.67, 38.32, 37.04, 32.91, 32.46.

IR (film) ν_{max} 3378, 3065, 3031, 2926, 2842, 1694, 1528, 1454, 1234, 1125, 1089, 1014, 979, 738, 697 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{22}NO_3^+$ ($[M+H]^+$) 264.1594, found 264.1595.



***tert*-butyl 4-(2-((benzyloxycarbonyl)amino)ethyl)piperidine-1-carboxylate (19):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *tert*-butyl 4-hydroxypiperidine-1-carboxylate (100.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

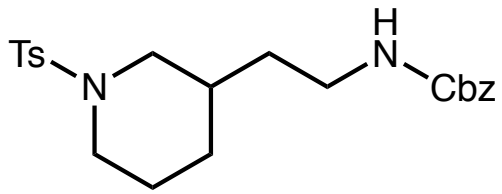
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–50% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 40–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (111.6 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 5.07 (s, 2H), 4.92 (t, *J* = 6.0 Hz, 1H), 4.04 (bs, 1H), 3.21 (q, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 13.1 Hz, 2H), 1.62 (d, *J* = 13.1 Hz, 2H), 1.43 (s, 9H), 1.07 (qd, *J* = 11.9, 4.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.45, 154.87, 136.65, 128.55, 128.15, 79.31, 66.62, 43.89 (broad), 38.52, 36.64, 33.45, 31.96, 28.50.

IR (film) ν_{max} 3339, 3067, 3031, 2974, 2927, 2851, 1689, 1671, 1530, 1423, 1365, 1243, 1168, 1144, 742, 698 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{23}N_2O_2^+$ ($[M+H–Boc]^+$) 263.1754, found 263.1756.



(±)-benzyl (2-(1-tosylpiperidin-3-yl)ethyl)carbamate (20): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), (±)-1-tosylpiperidin-3-ol (127.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

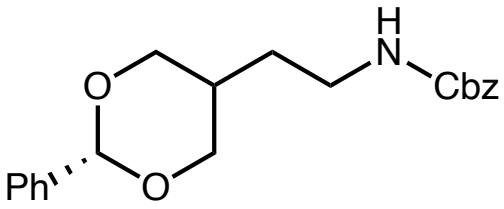
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–50% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–75% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (130.8 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.32 – 7.28 (m, 3H), 5.08 (s, 2H), 4.91 (t, *J* = 5.8 Hz, 1H), 3.53 (dt, *J* = 10.9, 5.6 Hz, 2H), 3.20 (q, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 2.31 (t, *J* = 11.1 Hz, 1H), 2.03 (t, *J* = 11.1 Hz, 1H), 1.77 – 1.63 (m, 3H), 1.61 – 1.51 (m, 1H), 1.40 (ddt, *J* = 41.4, 13.8, 6.9 Hz, 2H), 0.87 (q, *J* = 10.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.43, 143.49, 136.61, 133.18, 129.69, 128.58, 128.16, 128.14, 127.69, 66.68, 51.54, 46.76, 38.49, 33.66, 33.06, 29.69, 24.27, 21.59.

IR (film) ν_{max} 3378, 2934, 2851, 1704, 1522, 1452, 1335, 1244, 1162, 1096, 908, 726, 652, 583, 547 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{22}H_{29}N_2O_4S^+$ ($[M+H]^+$) 417.1843, found 417.1843.



benzyl (2-(2-phenyl-1,3-dioxan-5-yl)ethyl)carbamate (21): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *cis*-1,3-*O*-benzylidineglycerol (90.1 mg, 0.50 mmol, 1.0 equiv), NHC-1 (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

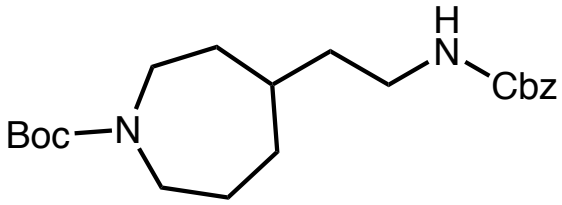
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–50% ethyl acetate/hexanes gradient to provide the title compound as a yellow oil (133.0 mg, 78% yield). The diastereomer ratio was assigned as 8:1 *trans/cis* by NMR analysis of the crude reaction mixture via comparison to the spectral data of analogous compounds.[6]

^{1}H NMR (500 MHz, $CDCl_3$) diastereomeric mixture (*cis* diastereomer in curly braces): δ 7.45 – 7.47 (m, 2H), 7.40 – 7.31 (m, 8H), 5.51 (s, 1H) {5.42}, 5.11 (s, 2H), 4.98 (t, *J* = 6.1 Hz, 1H), 4.24 (dd, *J* = 11.4, 4.6 Hz, 1H), 4.13 – 4.05 (m, 2H), 3.56 (t, *J* = 11.1 Hz, 1H), 3.34 (q, *J* = 6.7 Hz, 2H) {3.17 (q, *J* = 6.9 Hz)}, 2.22 – 2.11 (m, 1H) {1.52 (t, *J* = 7.6 Hz)}, 1.29 (q, *J* = 7.2 Hz, 2H) {2.01 (q, *J* = 7.0 Hz)}.

^{13}C NMR (126 MHz, $CDCl_3$) diastereomeric mixture: δ 156.62, 156.40, 138.52, 138.31, 136.64, 136.52, 129.00, 128.98, 128.62, 128.59, 128.37, 128.35, 128.24, 128.22, 128.18, 128.15, 126.11, 126.06, 102.03, 101.58, 72.09, 70.50, 66.80, 66.68, 39.04, 38.29, 32.03, 31.67, 30.16, 28.60.

IR (film) ν_{max} 3338, 3063, 3035, 2954, 2853, 1704, 1529, 1456, 1387, 1246, 1133, 1099, 1009, 750, 698 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{23}NNaO_4^+$ ($[M+Na]^+$) 364.1519, found 364.1518.



(±)-*tert*-butyl 3-(2-((benzyloxycarbonyl)amino)ethyl)azepane-1-carboxylate (22): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), (±)-*tert*-butyl 4-hydroxyazepane-1-carboxylate (107.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

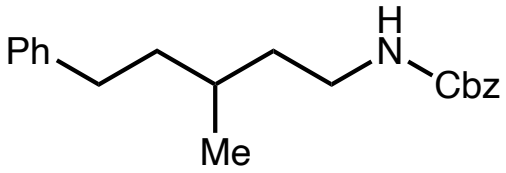
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–60% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 55–75% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (128.5 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.35 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 5.06 (s, 2H), 4.91 (t, J = 6.1 Hz, 1H), 3.59 – 3.44 (m, 1H), 3.42 – 3.22 (m, 2H), 3.22 – 3.04 (m, 3H), 1.85 – 1.73 (m, 2H), 1.73 – 1.64 (m, 1H), 1.56 – 1.36 (m, 4H), 1.43 (s, 9H), 1.33 – 1.21 (m, 1H), 1.15 (q, J = 10.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 156.44, 155.63, 136.66, 128.52, 128.13, 128.10, 79.06, 66.57, 46.71 [46.15], 45.10 [44.84], 39.08, 37.37, 36.56 [36.12], 34.69, 33.22 [32.90], 28.55, 26.92 (broad).

IR (film) ν_{max} 3328, 2970, 2925, 2870, 1672, 1531, 1415, 1364, 1244, 1162, 1023, 913, 730, 696, 457 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{32}N_2NaO_4^+$ ($[M+Na]^+$) 399.2254, found 399.2255.



(±)-benzyl (3-methyl-5-phenylpentyl)carbamate (23): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), (±)-4-phenyl-butan-2-ol (76.6 μL, 75.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

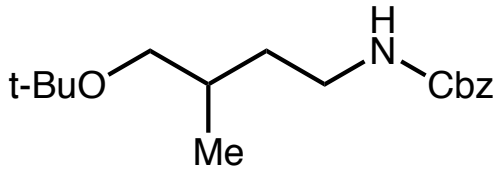
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) to provide the title compound as a pale yellow oil (123.7 mg, 79% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.28 (m, 7H), 7.24 – 7.17 (m, 3H), 5.13 (s, 2H), 4.82 (t, *J* = 6.1 Hz, 1H), 3.32 – 3.12 (m, 2H), 2.74 – 2.64 (m, 1H), 2.64 – 2.54 (m, 1H), 1.72 – 1.46 (m, 4H), 1.43 – 1.34 (m, 1H), 1.00 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.42, 142.67, 136.73, 128.55, 128.38 (2C), 128.15, 128.12, 125.73, 66.59, 39.12, 38.77, 36.92, 33.33, 30.10, 19.42.

IR (film) ν_{max} 3332, 3062, 3029, 2926, 2866, 1696, 1519, 1454, 1243, 1132, 1026, 739, 694, 577, 458 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{26}NO_2^+$ ([M+H]$^+$) 312.1958, found 312.1957.



(±)-benzyl (4-(*tert*-butoxy)-3-methylbutyl)carbamate (24): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), (±)-benzyl (4-(*tert*-butoxy)-3-methylbutyl)carbamate (66.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

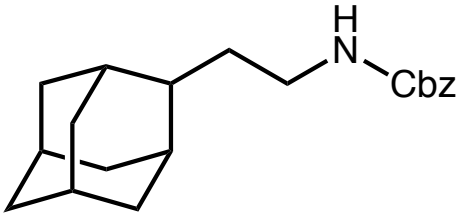
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–75% MeCN/H$_2$O with 0.1% NH$_4$OH) to provide the title compound as a clear colorless oil (107.5 mg, 73% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.27 (m, 5H), 5.31 (bs, 1H), 5.08 (s, 2H), 3.28 (h, *J* = 6.4 Hz, 1H), 3.24 – 3.15 (m, 2H), 3.12 (t, *J* = 7.9 Hz, 1H), 1.75 – 1.62 (m, *J* = 6.6 Hz, 1H), 1.57 (h, *J* = 6.8 Hz, 1H), 1.40 (h, *J* = 6.8 Hz, 1H), 1.16 (s, 9 H), 0.91 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.48, 136.89, 128.49, 128.05, 127.99, 72.70, 66.93, 66.43, 39.32, 34.38, 31.99, 27.53, 17.57.

IR (film) ν_{max} 3332, 3033, 2971, 2873, 1697, 1525, 1455, 1362, 1236, 1196, 1078, 1024, 882, 734, 695 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{27}NNaO_3^+$ ([M+Na]$^+$) 316.1883, found 316.1884.



benzyl (2-adamantan-2-yl)ethyl)carbamate (25): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), adamantan-2-ol (76.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

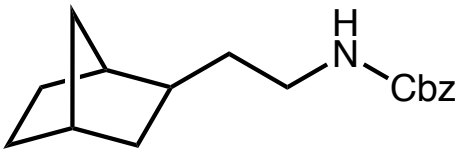
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 60–85% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (73.4 mg, 47% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 5.10 (s, 2H), 4.75 (bs, 1H), 3.20 (q, J = 6.7 Hz, 1H), 1.91 – 1.76 (m, 6H), 1.75 – 1.59 (m, 9H), 1.51 (d, J = 12.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.48, 136.78, 128.64, 128.25, 128.20, 66.68, 41.80, 39.66, 39.19, 38.40, 32.94, 31.84, 31.72, 28.26, 28.08.

IR (film) ν_{max} 3322, 3065, 3033, 2900, 2848, 1692, 1524, 1452, 1247, 1133, 1028, 1002, 912, 733, 695 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{28}NO_2^+$ ($[M+H]^+$) 314.2115, found 314.2117.



(±)-*exo*-benzyl (2-(bicyclo[2.2.1]heptan-2-yl)ethyl)carbamate (26): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), (±)-*exo*-norborneol (56.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

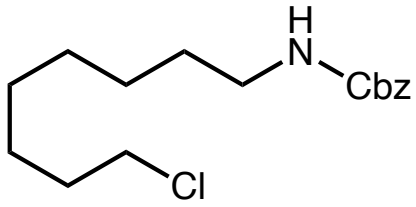
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (108.0 mg, 79% yield, >20:1 dr). The stereochemistry of the isolated product was assigned as *exo* by comparison to the NMR spectra of analogous compounds.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 5H), 5.09 (s, 2H), 4.85 (bs, 1H), 3.20 – 3.06 (m, 2H), 2.19 (bs, 1H), 1.95 (bs, 1H), 1.52 – 1.35 (m, 5H), 1.30 – 1.23 (m, 2H), 1.16 – 1.07 (m, 3H),

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.44, 137.74, 128.54, 128.15, 128.10, 66.56, 41.08, 39.70, 39.47, 38.03, 36.96, 36.57, 35.38, 30.09, 28.75.

IR (film) ν_{max} 3449, 3350, 3067, 3034, 2948, 2869, 1701, 1514, 1455, 1241, 1130, 905, 725, 696, 647 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{24}NO_2^+$ ($[M+H]^+$) 274.1802, found 274.1803.



benzyl (8-chlorooctyl)carbamate (27): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), 6-chlorohexan-1-ol (66.7 μL, 68.3 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

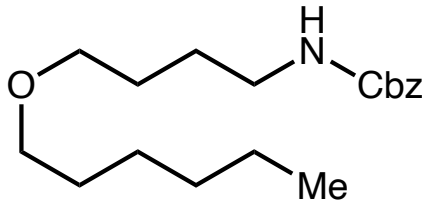
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 60–75% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (74.9 mg, 50% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 5.09 (s, 2H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.18 (q, *J* = 6.7 Hz, 2H), 1.75 (p, *J* = 6.9 Hz, 2H), 1.45 (dp, *J* = 37.9, 6.8 Hz, 4H), 1.34 – 1.24 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.47, 136.72, 128.57, 128.17, 128.14, 66.62, 45.20, 41.11, 32.62, 29.98, 29.14, 28.83, 26.83, 26.66.

IR (film) ν_{max} 3333, 2929, 2856, 1697, 1521, 1455, 1241, 1133, 1022, 734, 698, 648 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{25}ClNO_2^+$ ([M+H]$^+$) 298.1568, found 298.1568.



benzyl (4-(hexyloxy)butyl)carbamate (28): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), ethylene glycol monohexyl ether (73.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

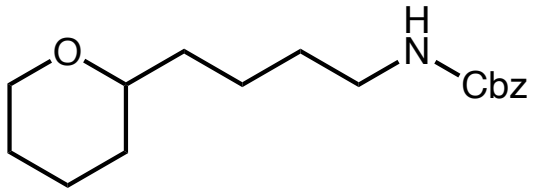
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, 1,3,5-trimethoxybenzene (28.5 mg, 0.339 equiv) was added as an internal standard, and the yield was determined via ^{1}H NMR spectroscopy (62% yield). The crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 60–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil, which was used for HRMS analysis and to confirm peak assignments for the reported ^{1}H NMR yield (as indicated in the spectral data).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 5.08 (s, 2H), 3.39 (p, *J* = 6.5 Hz, 4H), 3.21 (q, *J* = 6.3 Hz, 2H), 1.63 – 1.51 (m, 6H), 1.35 – 1.22 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.52, 136.78, 128.56, 128.15, 128.10, 71.18, 70.43, 66.58, 40.95, 31.77, 29.75, 27.11, 26.96, 25.93, 22.70, 14.14.

IR (film) ν_{max} 3331, 2930, 2858, 1700, 1527, 1455, 1370, 1245, 1109, 1022, 736, 696, 608, 460 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{29}NNaO_3^+$ ($[M+Na]^+$) 330.2040, found 330.2040.



(±)-benzyl (4-(tetrahydro-2*H*-pyran-2-yl)butyl)carbamate (29): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), 2-(tetrahydro-2*H*-pyran-2-yl)ethanol (65.1 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

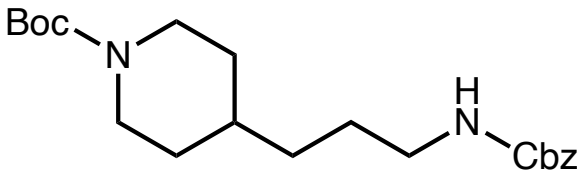
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, 1,3,5-trimethoxybenzene (31.2 mg, 0.371 equiv) was added as an internal standard, and the yield was determined via ^{1}H NMR spectroscopy (52% yield). The crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–70% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil, which was used for HRMS analysis and to confirm peak assignments for the reported ^{1}H NMR yield (as indicated in the spectral data).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 5.08 (s, 2H), 4.84 (bs, 1H), 3.94 (ddt, *J* = 11.3, 4.0, 1.9 Hz, 1H), 3.38 (td, *J* = 11.5, 2.6 Hz, 1H), 3.24 – 3.14 (m, 3H), 1.83 – 1.76 (m, 1H), 1.60 – 1.29 (m, 10H), 1.22 (qd, *J* = 12.4, 3.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.47, 136.76, 128.58, 128.18, 128.14, 77.69, 68.57, 66.62, 41.11, 36.26, 32.02, 30.06, 26.26, 23.64, 22.81.

IR (film) ν_{max} 3326, 2931, 2851, 1699, 1527, 1454, 1243, 1133, 1086, 1045, 1019, 736, 696, 607, 459 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{25}NNaO_3^+$ ([M+Na]$^+$) 314.1727, found 314.1728.



***tert*-butyl 4-(3-((benzyloxycarbonyl)amino)propyl)piperidine-1-carboxylate (30):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *tert*-butyl 4-(hydroxymethyl)piperidine-1-carboxylate (107.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

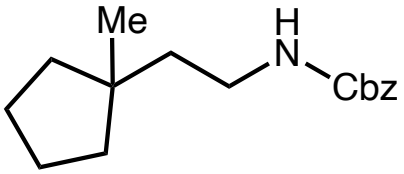
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 20–60% ethyl acetate/hexanes gradient) to provide the title compound as a yellow oil (140.3 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 5.08 (s, 2H), 4.90 (t, J = 6.0 Hz, 1H), 4.09 – 4.00 (m, 2H), 3.16 (q, J = 6.8 Hz, 2H), 2.63 (t, J = 12.0 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.54 – 1.46 (m, 2H), 1.44 (s, 9H), 1.38 – 1.30 (m, 1H), 1.27 – 1.19 (m, 2H), 1.10 – 0.97 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.50, 154.93, 136.72, 128.57, 128.24, 128.15, 79.27, 66.63, 44.01, 41.27, 35.75, 33.54, 32.16, 28.54, 27.19.

IR (film) ν_{max} 3330, 2927, 2855, 1675, 1529, 1422, 1365, 1241, 1163, 1144, 1034, 864, 734, 696, 459 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{32}N_2NaO_4^+$ ($[M+Na]^+$) 399.2254, found 399.2254.



benzyl (2-(1-methylcyclopentyl)ethyl)carbamate (31): The title compound was prepared according to the general procedure for tertiary alcohols using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), $Ni(TMHD)_2$ (42.5 mg, 100 μmol, 0.20 equiv), 1-methylcyclopentan-1-ol (55.4 μL, 50.1 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

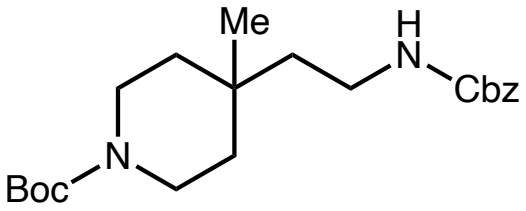
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (97.7 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 5.09 (s, 2H), 4.70 (bs, 1H), 3.25 – 3.16 (m, 2H), 3.25 – 3.12 (m, 2H), 1.67 – 1.56 (m, 4H), 1.52 (t, *J* = 8.5 Hz, 2H), 1.43 – 1.30 (m, 4H), 0.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.44, 136.78, 128.62, 128.23, 128.18, 66.66, 42.32, 41.18, 39.61, 38.49, 25.74, 24.36.

IR (film) ν_{max} 3333, 2948, 2867, 1699, 1530, 1455, 1374, 1249, 1130, 1025, 740, 697 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{24}NO_2^+$ ($[M+H]^+$) 262.1802, found 262.1803.



***tert*-butyl 4-(2-((benzyloxycarbonyl)amino)ethyl)-4-piperidine-1-carboxylate (32):** The title compound was prepared according to the general procedure for tertiary alcohols using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), $Ni(TMHD)_2$ (42.5 mg, 100 μmol, 0.20 equiv), *tert*-butyl 4-hydroxy-4-methylpiperidine-1-carboxylate (107.6 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

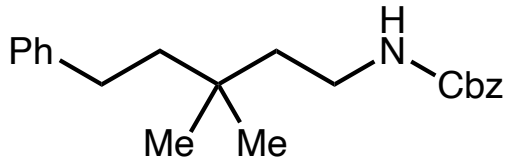
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 20–60% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (132.5 mg, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 5H), 5.08 (s, 2H), 4.83 (t, J = 5.8 Hz, 1H), 3.58 – 3.38 (m, 2H), 3.19 (tt, J = 9.4, 4.2 Hz, 4H), 1.52 – 1.20 (m, 6H), 1.44 (s, 9H), 0.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.50, 154.93, 136.72, 128.57, 128.15, 79.27, 66.63, 44.01, 41.27, 35.75, 33.54, 32.16, 28.54, 27.19.

IR (film) ν_{max} 3330, 2926, 2875, 1676, 1530, 1424, 1365, 1248, 1159, 1015, 911, 861, 744, 699 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{32}N_2NaO_4^+$ ($[M+Na]^+$) 399.2254, found 399.2256.



benzyl (3,3-dimethyl-5-phenylpentyl)carbamate (33): The title compound was prepared according to the general procedure for tertiary alcohols using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), $Ni(TMHD)_2$ (42.5 mg, 100 μmol, 0.20 equiv), 2-methyl-4-phenylbutan-2-ol (85.0 μL, 82.1 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

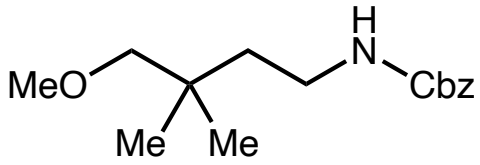
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (107.9 mg, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 7H), 7.24 – 7.14 (m, 3H), 5.14 (s, 2H), 4.81 (t, *J* = 5.8 Hz, 1H), 3.26 (dt, *J* = 8.4 Hz, 5.8 Hz, 2H), 2.63 – 2.56 (m, 2H), 1.63 – 1.47 (m, 4H), 1.01 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.43, 143.12, 136.70, 128.57, 128.42, 128.37, 128.17, 128.14, 125.70, 66.63, 44.44, 41.50, 37.39, 32.50, 30.69, 27.18.

IR (film) ν_{max} 3333, 3062, 3029, 2951, 2866, 1697, 1521, 1456, 1239, 1128, 1023, 738, 696, 614, 514 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{28}NO_2^+$ ($[M+H]^+$) 326.2115, found 326.2115.



benzyl (4-methoxy-3,3-dimethylbutyl)carbamate (34): The title compound was prepared according to the general procedure for tertiary alcohols using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), $Ni(TMHD)_2$ (42.5 mg, 100 μmol, 0.20 equiv), 1-methoxy-2-methylpropan-2-ol (58.4 μL, 52.1 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

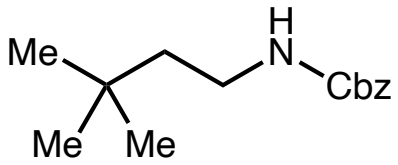
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 45–70% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (76.0 mg, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 5.09 (s, 2H), 5.03 (bs, 1H), 3.31 (s, 3H), 3.20 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 2H), 1.48 (dd, *J* = 9.0, 6.6 Hz, 2H), 0.90 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.42, 136.86, 128.53, 128.07, 128.05, 81.63, 66.48, 59.19, 39.04, 37.33, 33.99, 24.95.

IR (film) ν_{max} 3335, 2953, 2871, 1700, 1527, 1456, 1367, 1244, 1110, 1020, 741, 698, 616, 458 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{24}NO_3^+$ ($[M+H]^+$) 266.1751, found 266.1751.



benzyl (3,3-dimethylbutyl)carbamate (35): The title compound was prepared according to the general procedure for tertiary alcohols using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), Ni(TMHD)$_2$ (42.5 mg, 100 μmol, 0.20 equiv), *tert*-butanol (47.5 μL, 37.1 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

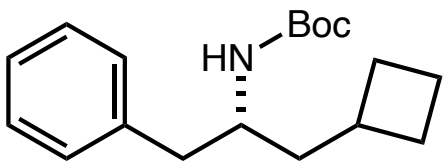
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–20% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (86.5 mg, 74% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 5.09 (s, 2H), 4.67 (bs, 1H), 3.25 – 3.12 (m, 2H), 1.44 – 1.37 (m, 2H), 0.92 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.44, 136.79, 128.63, 128.25, 128.20, 66.67, 43.77, 37.87, 29.94, 29.52.

IR (film) ν_{max} 3333, 2952, 2870, 1695, 1525, 1461, 1365, 1315, 1240, 1129, 1021, 738, 696, 612, 455 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{22}NO_2^+$ ([M+H]$^+$) 236.1645, found 236.1643.



***tert*-butyl (*R*)-(1-cyclobutyl-3-phenylpropan-2-yl)carbamate (37):** The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene dicyclobutanecarboxylate (444.3 mg, 1.00 mmol, 2.0 equiv).

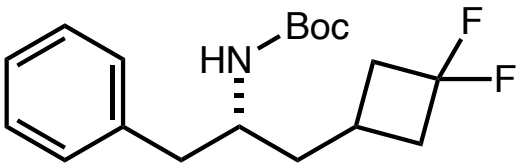
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 50–100% dichloromethane/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 60–85% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (82.7 mg, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 4.27 (d, J = 9.0 Hz, 1H) [4.08], 3.81 – 3.70 (m, 1H) [3.64], 2.73 (d, J = 6.4 Hz, 2H), 2.38 (hept, J = 8.0 Hz, 1H), 2.08 – 1.99 (m, 2H), 1.84 (h, J = 9.3 Hz, 1H), 1.75 (q, J = 9.3 Hz, 1H), 1.67 – 1.50 (m, 2H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.42, 138.45, 129.61, 128.35, 126.29, 78.99, 50.38, 41.62, 41.46, 33.38, 28.81, 28.75, 28.52, 18.81.

IR (film) ν_{max} 3367, 3064, 3027, 2968, 2863, 1686, 1523, 1445, 1365, 1249, 1171, 1062, 743, 700, 631 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{20}NO_2^+$ ([M+H–isobutene]$^+$) 234.1489, found 234.1490.



***tert*-butyl (*R*)-(1-(3,3-difluorocyclobutyl)-3-phenylpropan-2-yl)carbamate (38):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3,3-difluorocyclobutane-1-carboxylate) (516.3 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–30% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 55–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white crystalline solid (85.1 mg, 52% yield).

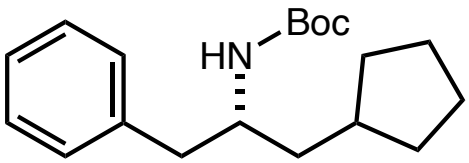
^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 – 7.13 (m, 2H), 4.27 (d, *J* = 9.3 Hz, 1H) [4.11], 3.85 – 3.74 (m, 1H) [3.66], 2.81 – 2.70 (m, 2H), 2.70 – 2.58 (m, 2H), 2.25 – 2.02 (m, 3H), 1.64 (ddd, *J* = 18.2, 7.8, 3.8 Hz, 1H), 1.53 (ddd, *J* = 14.0, 9.3, 5.1 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45, 137.85, 129.50, 128.58, 126.63, 120.36 (dd, *J* = 284.6, 273.6 Hz), 79.43, 50.50, 41.80, 40.97 (t, *J* = 21.9 Hz), 40.87 (t, *J* = 21.9 Hz), 40.75, 28.48, 20.82 (dd, *J* = 13.3, 5.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ -96.32 (dp, *J* = 192.9, 15.5 Hz) [-95.94 (d, *J* = 192.9 Hz)], -81.92 (d, *J* = 192.9 Hz) [-82.18 (d, *J* = 192.4 Hz)].

IR (film) ν_{max} 3341, 2975, 2927, 2854, 1681, 1527, 1447, 1364, 1285, 1223, 1169, 1051, 897, 748, 701, 644 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{18}F_2NO_2^+$ ([M+H–isobutene]$^+$) 270.1300, found 270.1302.



***tert*-butyl (*R*)-(1-cyclopentyl-3-phenylpropan-2-yl)carbamate (39):** The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene dicyclopentanecarboxylate (472.4 mg, 1.00 mmol, 2.0 equiv).

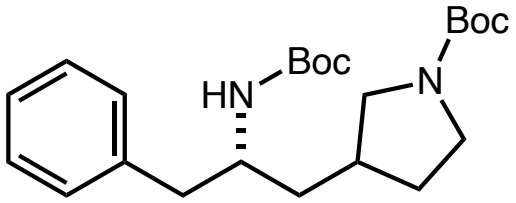
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 50–100% dichloromethane/hexanes gradient) to provide the title compound as a white solid (101.2 mg, 67% yield).

^{1}H NMR (500 MHz, CDCl$_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.32 (d, *J* = 9.1 Hz, 1H) [4.18], 3.91 – 3.81 (m, 1H) [3.73], 2.78 (d, *J* = 6.4 Hz, 2H), 1.96 – 1.70 (m, 3H), 1.64 – 1.46 (m, 4H), 1.41 (s, 9H), 1.13 – 0.96 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 155.47, 138.42, 129.66, 128.31, 126.24, 78.95, 51.02, 41.77, 40.66, 37.06, 33.05, 32.64, 28.50, 25.23, 25.07.

IR (film) ν_{max} 3339, 2950, 2914, 2866, 1699, 1682, 1527, 1451, 1363, 1266, 1170, 1041, 743, 698, 648 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{22}NO_2^+$ ([M+H–isobutene]$^+$) 248.1645, found 248.1646.



***tert*-butyl 3-((*R*)-2-((*tert*-butoxycarbonyl)amino)-3-phenylpropyl)pyrrolidine-1-carboxylate (40):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(*N*-Boc-pyrrolidine-3-carboxylate) (674.6 mg, 1.00 mmol, 2.0 equiv).

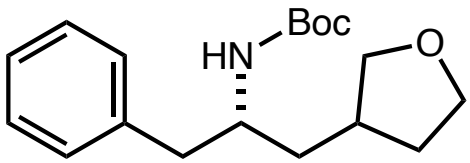
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–50% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (84.5 mg, 42% yield). Quantitative NMR and UHPLC analysis of the isolated material indicated that the product was formed in a 1.1:1 diastereomer ratio.

^{1}H NMR (500 MHz, $CDCl_3$) rotameric and diastereomeric mixture (resonances for minor rotamer are enclosed in square brackets, diastereomer in curly braces): δ 7.31 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 4.30 (t, *J* = 8.4 Hz, 3H) [4.11], 3.88 (m, 1H) {3.80} [3.70], 3.55 (dd, *J* = 10.6, 7.3 Hz, 1H) {3.49 (dd, *J* = 10.6, 7.5 Hz)}, 3.45 – 3.34 (m, 1H), 3.20 (p, *J* = 9.9 Hz, 1H), 2.86 – 2.64 (m, 3H), 2.20 (m, 1H), 2.08 – 1.89 (m, 1H), 1.52 – 1.43 (m, 3H), 1.44 (s, 9H) {1.43}, 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) rotameric and diastereomeric mixture: δ 155.53, 155.43, 154.67, 154.63, 137.94, 137.90, 129.58, 128.52, 126.55, 79.37, 79.16, 79.10, 51.68, 51.48, 50.82, 50.55, 45.68, 45.54, 42.17, 41.72, 37.93, 35.94, 31.87, 31.42, 28.66, 28.49.

IR (film) ν_{max} 3333, 2974, 2933, 2872, 1683, 1520, 1407, 1366, 1248, 1169, 1123, 879, 733, 701 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{23}H_{36}N_2NaO_4^+$ ($[M+Na]^+$) 427.2567, found 427.2567.



***tert*-butyl ((2*R*)-1-phenyl-3-(tetrahydrofuran-3-yl)propan-2-yl)carbamate (41):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(tetrahydrofuran-3-carboxylate) (476.3 mg, 1.00 mmol, 2.0 equiv).

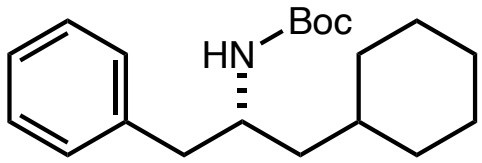
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 55–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a pale yellow oil (76.0 mg, 50% yield). Quantitative NMR and UHPLC analysis of the isolated material indicated that the product was formed in a 1:1 diastereomer ratio.

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 4.36 (t, *J* = 8.9 Hz, 1H) [4.23], 3.94 – 3.75 (m, 3H), 3.70 (p, *J* = 7.8 Hz, 1H), 3.72 (q, *J* = 7.3 Hz, 1H), 2.86 – 2.64 (m, 2H), 2.32 – 2.21 (m, *J* = 7.7 Hz, 1H), 2.13 – 1.97 (m, 1H), 1.54 – 1.41 (m, 3H), 1.39 (s, 9H).

quantitative ^{13}C NMR (126 MHz, $CDCl_3$) diastereomeric mixture (resonances for minor diastereomer are enclosed in curly braces): δ 155.51 {155.45}, 138.01 {137.93}, 129.54, 128.48, 126.49, 79.27, 73.49 {73.29}, 67.97 {67.89}, 50.92, 42.22 {41.86}, 37.95 {38.17}, 36.37 {36.68}, 32.80 {32.49}, 28.48.

IR (film) ν_{max} 3322, 2969, 2931, 2860, 1692, 1521, 1449, 1365, 1248, 1167, 1048, 1016, 904, 747, 701 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{13}H_{20}NO^+$ ($[M+H–Boc]^+$) 206.1539, found 206.1539.



***tert*-butyl (*R*)-(1-cyclohexyl-3-phenylpropan-2-yl)carbamate (42):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene dicyclohexanecarboxylate (364.2 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 50–100% dichloromethane/hexanes gradient) to provide the title compound as a white solid (103.4 mg, 65% yield).

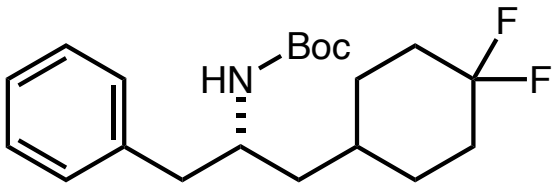
^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 4.25 (bs, 1H) [4.07], 3.94 (bs, 1H) [3.82], 2.84 – 2.63 (m, 2H), 1.79 (d, J = 12.7 Hz, 1H), 1.70 – 1.57 (m, 4H), 1.41 (s, 9H), 1.31 – 1.05 (m, 6H), 0.83 (dq, J = 75.5, 12.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.49, 138.41, 129.71, 128.32, 126.26, 79.02, 48.91, 42.18, 41.90, 34.39, 34.03, 32.75, 28.52, 26.65, 26.48, 26.27.

IR (film) ν_{max} 3368, 2971, 2923, 2839, 1688, 1518, 1449, 1364, 1237, 1167, 1042, 1011, 742, 700 614 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{31}NNaO_2^+$ ($[M+Na]^+$) 340.2247, found 340.2249.

Chiral HPLC: OD-H, 0.25% isopropanol/hexanes, 1.0 mL/min, >99% ee. t_R = 18.3 min (major (R)-enantiomer), t_s = 15.0 min (minor (S)-enantiomer).



***tert*-butyl (*R*)-(1-(4,4-difluorocyclohexyl)-3-phenylpropan-2-yl)carbamate (43):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(4,4-difluorocyclohexane-1-carboxylate) (572.4 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 50–100% dichloromethane/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 60–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (121.9 mg, 69% yield).

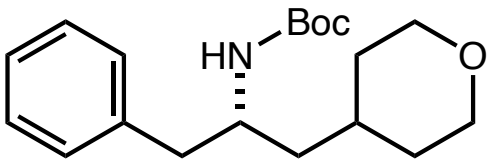
^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.32 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 4.29 (d, *J* = 9.4 Hz, 1H) [4.19], 3.99 – 3.88 (m, 1H) [3.79], 2.75 (ddd, *J* = 22.8, 13.5, 6.6 Hz, 2H), 2.09 – 1.97 (m, 2H), 1.95 – 1.81 (m, 1H), 1.76 – 1.55 (m, 3H), 1.41 (s, 9H), 1.38 – 1.23 (m, 4H), 1.11 (q, *J* = 12.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.54, 138.02, 129.55, 128.45, 126.46, 123.76 (t, *J* = 240.6 Hz), 79.27, 49.22, 42.20, 40.73, 33.62 (t, *J* = 25.9 Hz), 33.44 (t, *J* = 25.9 Hz), 32.61, 29.81 (d, *J* = 9.4 Hz), 28.46, 28.20 (d, *J* = 9.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.53 (d, *J* = 234.6 Hz, 1F), -102.0 (d, *J* = 234.6 Hz, 1F).

IR (film) ν_{max} 3362, 2959, 2928, 2863, 1686, 1524, 1450, 1364, 1240, 1171, 1115, 1012, 743, 700, 625 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{22}F_2NO_2^+$ ([M+H–isobutene]$^+$) 298.1613, found 298.1615.



***tert*-butyl (*R*)-(1-phenyl-3-(tetrahydro-2H-pyran-4-yl)propan-2-yl)carbamate (44):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(tetrahydro-2*H*-pyran-4-carboxylate) (504.4 mg, 1.00 mmol, 2.0 equiv).

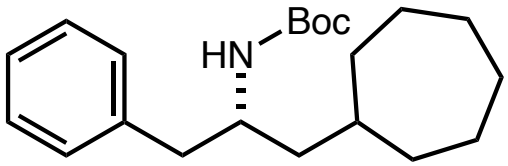
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–40% ethyl acetate/hexanes gradient) to provide the title compound as a white crystalline solid (105.6 mg, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets):δ 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.13 (m, 2H), 4.36 (d, *J* = 9.5 Hz, 1H) [4.31], 4.03 – 3.95 (m, 1H), 3.92 (dd, *J* = 10.7, 3.3 Hz, 2H) [3.82], 3.35 (qd, *J* = 12.0, 2.3 Hz, 2H), 2.83 – 2.63 (m, 2H), 1.75 (d, *J* = 13.5 Hz, 1H), 1.50 (d, *J* = 13.7 Hz, 1H), 1.42 (s, 9H), 1.38 – 1.24 (m, 4H), 1.15 (qd, *J* = 12.2, 4.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.49, 138.07, 129.59, 128.38, 126.38, 79.15, 68.07, 68.03, 48.43, 42.08, 41.82, 33.67, 32.51, 31.86, 28.46.

IR (film) ν_{max} 3328, 2922, 2843, 1692, 1517, 1447, 1364, 1244, 1165, 1090, 1012, 848, 735, 700, 647, 476 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_2NO^+$ ($[M+H–Boc]^+$) 220.1696, found 220.1696.



***tert*-butyl (*R*)-(1-cycloheptyl-3-phenylpropan-2-yl)carbamate (45):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene dicycloheptanecarboxylate (528.5 mg, 1.00 mmol, 2.0 equiv).

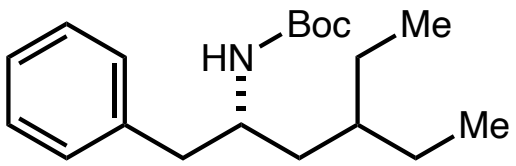
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) to provide the title compound as a white crystalline solid (110.1 mg, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 4.26 (d, *J* = 8.6 Hz, 1H), 3.91 (bs, 1H), 2.75 (d, *J* = 5.8 Hz, 2H), 1.75 – 1.69 (m, 1H), 1.65 – 1.50 (m, 6H), 1.48 – 1.29 (m, 4H), 1.41 (s, 9H), 1.28 – 1.11 (m, 3H), 1.10 – 1.01 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.50, 138.42, 129.70, 128.32, 126.26, 79.02, 49.44, 42.82, 41.90, 35.77, 35.56, 33.67, 28.62, 28.52, 28.43, 26.61, 26.35.

IR (film) ν_{max} 3360, 2962, 2918, 2851, 1700, 1685, 1523, 1455, 1363, 1248, 1171, 1044, 744, 701, 621 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{26}NO_2^+$ ($[M+H–isobutene]^+$) 276.1958, found 276.1957.



***tert*-butyl (*R*)-(4-ethyl-1-phenylhexan-2-yl)carbamate (46):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-ethylbutanoate) (476.4 mg, 1.00 mmol, 2.0 equiv).

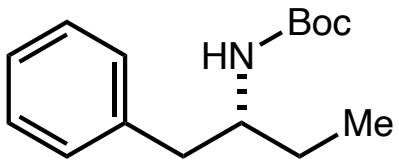
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 50–100% dichloromethane/hexanes gradient) to provide the title compound as a pale yellow solid (98.2 mg, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.28 (d, J = 9.2 Hz, 1H) [4.14], 3.95 – 3.84 (m, 1H) [3.78], 2.84 – 2.63 (m, 2H), 1.45 – 1.28 (m, 3H), 1.41 (s, 9H), 1.27 – 1.18 (m, 4H), 0.79 (dt, J = 37.6, 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.48, 138.47, 129.66, 128.31, 126.26, 78.98, 49.55, 42.03, 37.94, 36.83, 28.50, 25.79, 24.70, 11.04, 10.19.

IR (film) ν_{max} 3352, 3028, 2961, 2926, 2874, 1700, 1496, 1454, 1381, 1365, 1246, 1169, 1012, 745, 699 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{24}NO_2^+$ ([M+H–isobutene]$^+$) 250.1802, found 250.1803.



***tert*-butyl (*R*)-(1-phenylbutan-2-yl)carbamate (47):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene diacetate (364.2 mg, 1.00 mmol, 2.0 equiv).

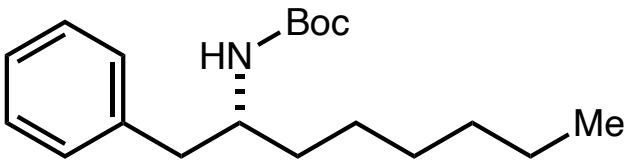
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, 1,3,5-trimethoxybenzene (30.2 mg, 0.359 equiv) was added as an internal standard, and the yield was determined via ^{1}H NMR spectroscopy (47% yield). The crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–100% ethyl acetate/hexanes gradient), followed by preparative HPLC (XBridge BEH C18 OBD column, 60–75% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid, which was used for HRMS analysis and to confirm peak assignments for the reported ^{1}H NMR yield (as indicated in the spectral data).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 4.31 (bs, 1H) [4.07], 3.74 (bs, 1H) [3.61], 2.84 – 2.65 (m, 2H), 1.53 (hept, J = 6.8 Hz, 1H) , 1.41 (s, 9H), 1.30 (hept, J = 7.4 Hz, 1H), 0.93 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.69, 138.47, 129.64, 128.41, 126.35, 79.11, 53.10, 41.09, 28.53, 27.08, 10.57.

IR (film) ν_{max} 3344, 3064, 3030, 2961, 2930, 2871, 1685, 1525, 1364, 1279, 1244, 1171, 1071, 982, 739 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{23}NNaO_2^+$ ($[M+Na]^+$) 272.1621, found 272.1623.



***tert*-butyl (*R*)-(1-phenyloctan-2-yl)carbamate (48):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene dihexanoate (476.4 mg, 1.00 mmol, 2.0 equiv).

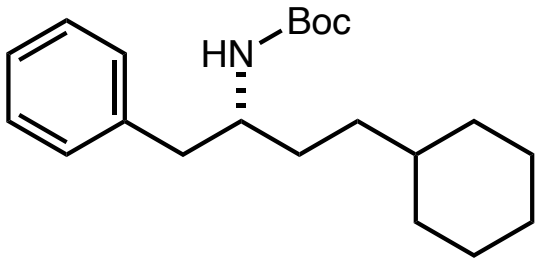
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, 1,3,5-trimethoxybenzene (31.1 mg, 0.370 equiv) was added as an internal standard, and the yield was determined via ^{1}H NMR spectroscopy (57% yield). The crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 65–85% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid, which was used for HRMS analysis and to confirm peak assignments for the reported ^{1}H NMR yield (as indicated in the spectral data).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 4.31 (d, J = 9.1 Hz, 1H) [4.09], 3.82 (p, J = 6.9 Hz, 1H) [3.68], 2.81 – 2.65 (m, 2H), 1.49 – 1.33 (m, 2H), 1.41 (s, 9H), 1.31 – 1.18 (m, 8H), 0.87 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.59, 138.47, 129.66, 128.37, 126.30, 79.05, 51.65, 41.47, 34.29, 31.89, 29.25, 28.52, 26.08, 22.70, 14.19.

IR (film) ν_{max} 3345, 2926, 2857, 1692, 1500, 1454, 1365, 1246, 1168, 1024, 857, 744, 700, 552, 493 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{24}NO_2^+$ ([M+H–isobutene]$^+$) 250.1802, found 250.1803.



***tert*-butyl (*R*)-(4-cyclohexyl-1-phenylbutan-2-yl)carbamate (49):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-cyclohexylacetate) (528.5 mg, 1.00 mmol, 2.0 equiv).

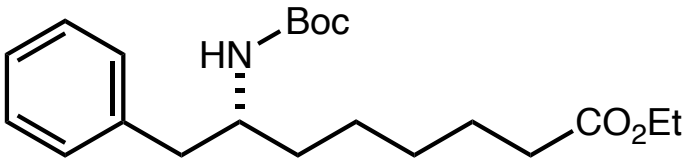
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 75–90% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (86.5 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 4.32 (d, J = 9.0 Hz, 1H) [4.14], 3.77 (p, J = 7.6 Hz, 1H) [3.64], 2.76 (d, J = 6.5 Hz, 2H), 1.70 – 1.59 (m, 4H), 1.55 – 1.45 (m, 1H), 1.41 (s, 9H), 1.31 – 1.06 (m, 8H), 0.84 (pd, J = 13.4, 3.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.59, 138.47, 129.66, 128.37, 126.30, 79.05, 51.65, 41.47, 34.29, 31.89, 29.25, 28.52, 26.08, 22.70, 14.19.

IR (film) ν_{max} 3372, 2976, 2919, 2849, 1683, 1519, 1449, 1363, 1249, 1170, 1049, 1021, 743, 701, 622 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{26}NO_2^+$ ($[M+H–isobutene]^+$) 276.1958, found 276.1958.



ethyl (*R*)-7-((*tert*-butoxycarbonyl)amino)-8-phenyloctanoate (50): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(6-ethoxy-6-oxohexanoate) (592.5 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, 1,3,5-trimethoxybenzene (29.8 mg, 0.354 equiv) was added as an internal standard, and the yield was determined via ^{1}H NMR spectroscopy (67% yield). The crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–30% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 65–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid, which was used for HRMS analysis and to confirm peak assignments for the reported ^{1}H NMR yield (as indicated in the spectral data).

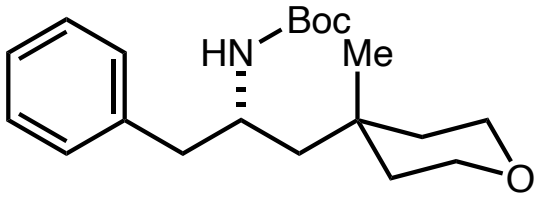
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 4.31 (d, J = 9.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.85 – 3.74 (m, 1H), 2.81 – 2.66 (m, 2H), 2.27 (t, J = 7.6 Hz, 2H), 1.59 (p, J = 7.4 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.40 (s, 9H), 1.36 – 1.27 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.90, 155.59, 138.35, 129.62, 128.40, 126.35, 79.12, 60.31, 51.58, 41.53, 34.36, 34.14, 29.07, 28.51, 25.81, 24.95, 14.37.

IR (film) ν_{max} 3362, 2974, 2933, 2861, 1696, 1508, 1452, 1365, 1245, 1165, 1066, 1027, 859, 742, 701 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{33}NNaO_4^+$ ([M+Na]$^+$) 386.2302, found 386.2304.

Chiral HPLC: OD-H, 1.0% isopropanol/hexanes, 1.0 mL/min, >99% ee. t_R = 18.2 min (major (R)-enantiomer), t_s = 19.9 min (minor (S)-enantiomer).



***tert*-butyl (*R*)-(1-(4-methyltetrahydro-2*H*-pyran-4-yl)-3-phenylpropan-2-yl)carbamate (51):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(4-methyltetrahydro-2*H*-pyran-4-carboxylate) (399.3 mg, 0.75 mmol, 1.5 equiv).

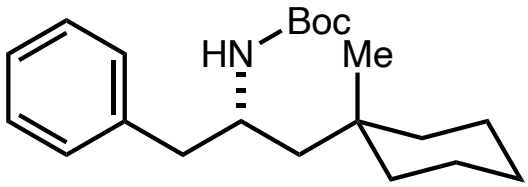
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–30% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 55–75% MeCN/H_2O gradient with 0.1% NH_4OH) to provide the title compound as a waxy solid (101.9 mg, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.43 (d, J = 9.4 Hz, 1H) [4.28], 3.98 (p, J = 8.5 Hz, 1H) [3.85], 3.66 – 3.46 (m, 4H), 2.85 (dd, J = 13.3, 5.7 Hz, 1H), [2.73 (m)], 2.64 (dd, J = 13.3, 7.8 Hz, 1H), 1.54 – 1.43 (m, 2H), 1.41 (s, 9H), 1.36 – 1.24 (m, 4H), 0.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.95, 138.34, 129.65, 128.39, 126.40, 79.16, 63.80 (2C), 48.09, 46.60, 44.01, 38.20, 37.85, 30.67, 28.51, 23.65.

IR (film) ν_{max} 3331, 2961, 2923, 2856, 1694, 1517, 1364, 1246, 1165, 1105, 1016, 840, 736, 699, 491 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{24}NO^+$ ($[M+H–Boc]^+$) 234.1852, found 234.1853.



***tert*-butyl (*R*)-(1-(1-methylcyclohexyl)-3-phenylpropan-2-yl)carbamate (52):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(1-methylcyclohexane-1-carboxylate) (528.5 mg, 1.00 mmol, 2.0 equiv).

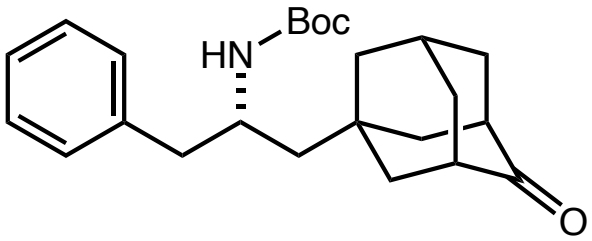
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 75–85% $MeCN/H_2O$ gradient with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (77.7 mg, 47% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 4.34 (d, J = 9.2 Hz, 1H) [4.16], 3.95 (p, J = 8.2 Hz, 1H) [3.84], 2.82 (dd, J = 13.3, 5.6 Hz, 1H), 2.65 (dd, J = 13.2, 7.7 Hz, 1H), 1.47 – 1.33 (m, 4H), 1.41 (s, 9H), 1.29 – 1.12 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 154.99, 138.66, 129.78, 128.29, 126.25, 78.99 [79.53], 48.32 [50.20], 46.26 [47.21], 44.08 [45.09], 38.32, 37.99, 32.84, 28.57 [28.40], 26.44, 25.16, 22.11, 21.96.

IR (film) ν_{max} 3354, 2968, 2922, 2855, 1694, 1502, 1451, 1365, 1246, 1168, 1021, 746, 700, 527, 483 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{26}NO_2^+$ ($[M+H–isobutene]^+$) 276.1958, found 276.1959.



tert-butyl ((*R*)-1-(4-oxoadamantan-1-yl)-3-phenylpropan-2-yl)carbamate (53): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(4-oxoadamantane-1-carboxylate) (474.4 mg, 0.75 mmol, 1.5 equiv).

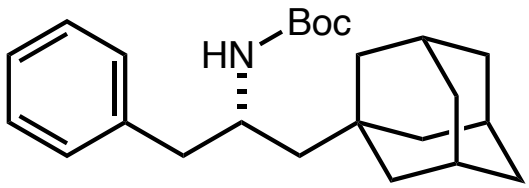
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–15% ethyl acetate/hexanes gradient) to provide the title compound as a white solid (126.9 mg, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 4.34 (d, J = 9.4 Hz, 1H) [4.39], 3.97 (t, J = 7.7 Hz, 1H) [3.83], 2.82 (dd, J = 13.4, 5.6 Hz, 1H), 2.64 (dd, J = 13.3, 7.6 Hz, 1H), 2.49 (bs, 2H), 2.11 – 2.05 (bs, 1H), 1.98 – 1.89 (m, 4H), 1.82 – 1.72 (m, 4H), 1.66 (dd, J = 31.8, 12.9 Hz, 2H), 1.41 (s, 9H), 1.36 (dd, J = 14.7, 2.1 Hz, 1H), 1.16 (dd, J = 14.7, 9.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 218.51, 154.96, 138.18, 129.64, 128.43, 126.47, 79.37, 47.75, 46.57, 46.49, 44.05, 43.79, 43.57, 38.76, 38.71, 28.53, 27.86.

IR (film) ν_{max} 3346, 2969, 2919, 2855, 1701, 1518, 1450, 1365, 1247, 1169, 1061, 1024, 915, 735, 702 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{26}NO_3^+$ ($[M+H–isobutene]^+$) 328.1907, found 328.1906.



tert-butyl ((*R*)-1-(adamantan-1-yl)-3-phenylpropan-2-yl)carbamate (54): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(adamantane-1-carboxylate) (604.6 mg, 1.00 mmol, 2.0 equiv).

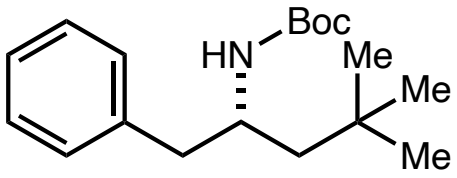
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 75–95% MeCN/H_2O gradient with 0.1% NH_4OH) to provide the title compound as a white crystalline solid (99.4 mg, 54% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.32 (d, *J* = 9.0 Hz, 1H) [4.11], 3.98 (p, *J* = 8.1 Hz, 1H) [3.88], 2.80 (dd, *J* = 13.4, 5.5 Hz, 1H), 2.64 (dd, *J* = 13.3 Hz, 7.5 Hz, 1H), 1.91 (bs, 3H), 1.70 – 1.63 (m, 3H), 1.61 – 1.56 (m, 3H), 1.54 – 1.45 (m, 3H), 1.42 (s, 9H), 1.40 – 1.34 (m, 3H), 1.26 (dd, *J* = 14.6, 2.3 Hz, 1H), 1.04 (dd, *J* = 14.7, 9.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.91, 138.63, 129.74, 128.24, 126.19, 78.95, 48.88, 47.39, 43.79, 42.64, 37.04, 32.37, 28.69, 28.56.

IR (film) ν_{max} 3352, 2972, 2899, 2846, 1695, 1502, 1449, 1365, 1246, 1170, 1050, 1021, 739, 700, 517 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{28}NO_2^+$ ([M+H–isobutene]$^+$) 314.2115, found 314.2117.



***tert*-butyl (*R*)-(4,4-dimethyl-1-phenylpentan-2-yl)carbamate (55):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2,2-dimethylpropanoate) (336.3 mg, 0.75 mmol, 1.5 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–20% ethyl acetate/hexanes gradient) to provide the title compound as a white powdered solid (84.4 mg, 58% yield).

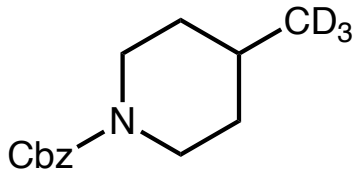
^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 4.29 (d, J = 9.2 Hz, 1H) [4.06], 3.97 – 3.88 (m, 1H) [3.82], 2.79 (dd, J = 13.3, 5.6 Hz, 1H), 2.66 (dd, J = 13.0 Hz, 7.3 Hz, 2H), 1.40 (s, 9H), 1.15 (dd, J = 14.5, 9.7 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.06, 138.58, 129.78, 128.30, 126.27, 79.02, 49.06, 47.89, 43.90, 30.51 29.90, 28.58.

IR (film) ν_{max} 3354, 2953, 2870, 1693, 1502, 1364, 1244, 1166, 1050, 1001, 870, 745, 699, 549, 480 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{22}NO_2^+$ ($[M+H–isobutene]^+$) 236.1645, found 236.1645.

Chiral HPLC: OD-H, 1.0% isopropanol/hexanes, 1.0 mL/min, >99% ee. t_R = 7.3 min (major (R)-enantiomer), t_s = 6.3 min (minor (S)-enantiomer).



benzyl 4-(methyl-*d*$_3$)piperidine-1-carboxylate (56): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(acetate-*d*$_3$) (370.2 mg, 1.00 mmol, 2.0 equiv).

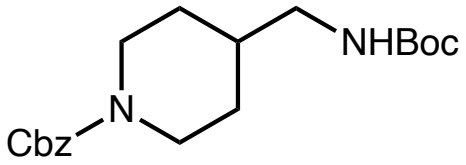
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) to provide the title compound as a pale yellow oil (92.1 mg, 78% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.28 (m, 5H), 5.13 (s, 2H), 4.14 (bs, 2H), 2.77 (t, *J* = 12.8 Hz, 2H), 1.61 (d, *J* = 13.2 Hz, 2H), 1.55 – 1.46 (m, 1H), 1.11 (qd, *J* = 12.1, 4.1 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 155.40, 137.13, 128.52, 127.95, 127.87, 66.96, 44.34, 33.95, 30.72.

IR (film) ν_{max} 2922, 2854, 1699, 1429, 1363, 1297, 1226, 1141, 1082, 1025, 945, 760, 698 cm^{-1}

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{17}D_3NO_2^+$ ([M+H]$^+$) 237.1677, found 237.1677.



benzyl 4-((*tert*-butoxycarbonyl)aminomethyl)piperidine-1-carboxylate (57): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-((*tert*-butoxycarbonyl)amino)acetate) (594.4 mg, 1.00 mmol, 2.0 equiv).

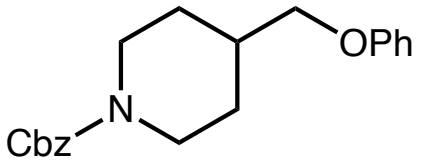
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 10–40% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 40-65% $MeCN/H_2O$ with 0.1% NH_4OH) to provide the title compound as a white solid (90.7 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.35 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.10 (s, 2H), 4.74 (t, J = 6.3 Hz, 1H) [4.56], 4.25 – 4.08 (m, 2H), 3.06 – 2.89 (m, 2H), 2.81 – 2.64 (m, 2H), 1.71 – 1.55 (m, 3H), 1.42 (s, 9H), 1.11 (qd, J = 12.2, 4.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.12, 155.28, 136.91, 128.52, 127.99, 127.87, 79.26, 67.03, 46.00, 43.87, 36.71, 29.61, 28.45.

IR (film) ν_{max} 3349, 2973, 2926, 2860, 1684, 1521, 1435, 1364, 1249, 1219, 1169, 1085, 1013, 760, 698 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{19}H_{28}N_2NaO_4^+$ ($[M+Na]^+$) 371.1941, found 371.1943.



benzyl 4-(phenoxymethyl)piperidine-1-carboxylate (58): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-phenoxyacetate) (548.4 mg, 1.00 mmol, 2.0 equiv).

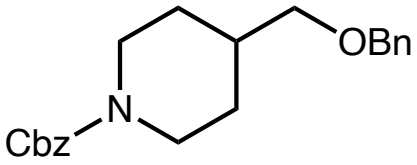
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–80% MeCN/H_2O gradient with 0.1% NH_4OH) to provide the title compound as a white solid (103.3 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 7H), 6.96 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.92 – 6.88 (m, 2H), 5.16 (s, 2H), 4.27 (bs, 2H), 3.82 (d, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 12.8 Hz, 2H), 2.06 – 1.92 (m, 1H), 1.86 (d, *J* = 13.2 Hz, 2H), 1.40 – 1.24 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.02, 155.37, 137.01, 129.54, 128.56, 128.03, 127.94, 120.81, 114.53, 72.16, 67.10, 43.92, 36.22, 28.92.

IR (film) ν_{max} 3062, 3033, 2923, 2859, 1695, 1596, 1430, 1242, 1217, 1145, 1084, 1035, 754, 695 cm^{-1}

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{24}NO_3^+$ ([M+H]$^+$) 326.1751, found 326.1752.



benzyl 4-(benzyloxymethyl)piperidine-1-carboxylate (59): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-benzyloxyacetate) (432.3 mg, 0.75 mmol, 1.5 equiv).

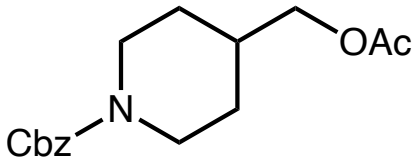
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–30% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (118.8 mg, 70% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.29 (m, 10H), 5.14 (s, 2H), 4.51 (s, 2H), 4.21 (bs, 2H), 3.33 (d, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 12.9 Hz, 2H), 1.87 – 1.79 (m, 1H), (d, *J* = 12.9 Hz, 2H), 1.20 (q, *J* = 13.1 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 155.35, 138.50, 137.01, 128.47, 127.99, 127.91, 127.66, 127.62, 74.98, 73.16, 67.03, 43.96, 36.58, 29.11.

IR (film) ν_{max} 3031, 2923, 2855, 1697, 1431, 1363, 1277, 1219, 1147, 1099, 1019, 740, 698 cm^{-1}.

HRMS (ESI-TOF) *m/z* calcd. for $C_{21}H_{26}NO_3^+$ ([M+H]$^+$) 340.1907, found 340.1907.



benzyl 4-(acetoxymethyl)piperidine-1-carboxylate (60): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-acetoxyacetate) (480.3 mg, 1.00 mmol, 2.0 equiv).

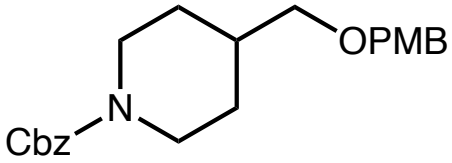
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–25% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 40-55% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (84.2 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 5.11 (s, 2H), 4.31 – 4.07 (m, 2H), 3.91 (d, J = 6.6 Hz, 2H), 2.84 – 2.68 (m, 2H),z 2.04 (s, 3H), 1.85 – 1.75 (m, 1H), 1.74 – 1.62 (m, 2H), 1.20 (q, J = 12.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.11, 155.26, 136.88, 128.53, 128.02, 127.91, 68.39, 67.08, 43.71, 35.47, 28.66, 20.93.

IR (film) ν_{max} 3031, 2942, 2859, 1737, 1697, 1432, 1365, 1280, 1222, 1149, 1087, 1035, 759, 700, 603 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{21}NNaO_4^+$ ($[M+Na]^+$) 314.1363, found 314.1365.



benzyl 4-(((4-methoxybenzyl)oxy)methyl)piperidine-1-carboxylate (61): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (117.6 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(2-((4-methoxybenzyl)oxy)acetate) (594.4 mg, 1.00 mmol, 2.0 equiv).

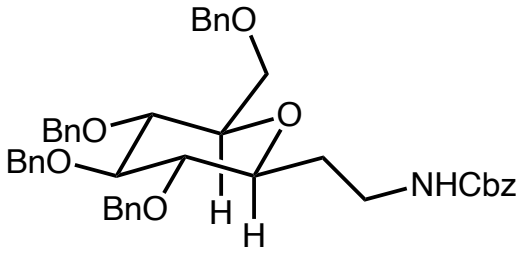
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 10–30% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 50–80% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a clear colorless oil (108.5 mg, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 7.22 (dt, *J* = 8.5, 2.6 Hz, 2H), 6.85 (dt, *J* = 8.5, 2.6 Hz, 2H), 5.10 (s, 2H), 4.40 (s, 2H), 4.25 – 4.07 (m, 2H), 3.77 (s, 3H), 3.25 (d, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 13.0 Hz, 2H), 1.81 – 1.74 (m, 1H), 1.74 – 1.68 (m, 2H), 1.14 (q, *J* = 12.3 Hz, 2H).

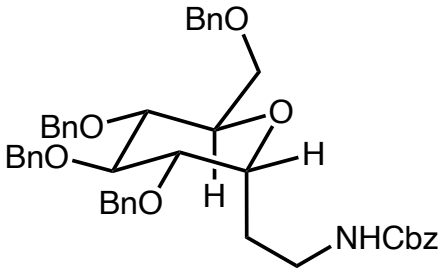
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.19, 155.31, 136.98, 130.51, 129.21, 128.50, 127.95, 127.87, 113.80, 74.63, 72.79, 66.98, 55.29, 43.93, 36.52, 29.07.

IR (film) ν_{max} 3002, 2929, 2854, 1696, 1512, 1433, 1362, 1246, 1220, 1148, 1092, 1032, 821, 757, 699 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{22}H_{27}NNaO_4^+$ ($[M+Na]^+$) 392.1832, found 392.1833.



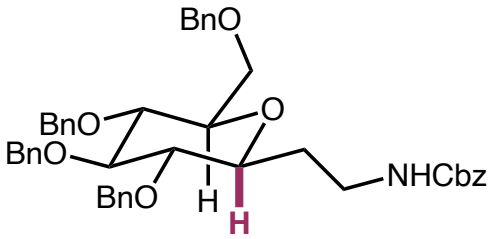
major diastereomer (62a)



minor diastereomer (62b)

benzyl (2-((3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)ethyl)carbamate (62): The title compound was prepared according to the general procedure using Ir[(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), Ni(TMHD)$_2$ (21.3 mg, 50 μmol, 0.10 equiv), 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (270.3 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–40% ethyl acetate/hexanes gradient) to provide the title compound as a white solid (153.9 mg, 44% yield), isolated as a mixture of C2 diastereomers (3:1). Separation of diastereomers by preparative HPLC (XBridge BEH C18 OBD column, 70–100% MeCN/H$_2$O with 0.1% NH$_4$OH) provided analytical quantities of each **62a** and **62b**, which were assigned on the basis of the anomeric proton shift (red) and comparison to the spectra of analogous compounds.[8]



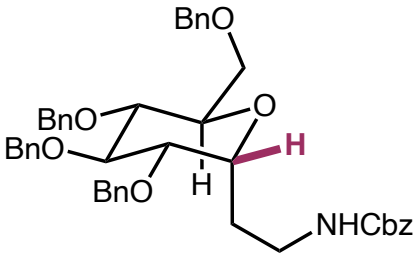
Major diastereomer – **62a**

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.26 (m, 23H), 7.17 – 7.14 (m, 2H), 5.51 (t, *J* = 5.5 Hz, 1H), 5.07 (s, 2H), 4.93 – 4.86 (m, 3H), 4.80 (d, *J* = 10.7 Hz, 1H), 4.63 (d, *J* = 10.9 Hz, 1H), 4.55 – 4.45 (m, 3H), 3.70 – 3.62 (m, 2H), 3.58 – 3.47 (m, 2H), 3.43 – 3.39 (m, 1H), **3.35** (td, *J* = 9.3 2.5 Hz, 1H), 3.31 – 3.21 (m, 2H), 2.09 – 2.01 (m, 1H), 1.66 – 1.58 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.53, 138.60, 138.10, 137.97, 136.97, 128.65, 128.61, 128.57, 128.50, 128.25, 128.23, 128.10, 128.09, 127.96, 127.93, 127.86, 127.83, 127.76, 82.74, 81.83, 79.19, 78.72, 78.70, 75.75, 75.47, 75.16, 73.66, 69.25, 66.57, 39.18, 31.20.

IR (film) ν_{max} 3350, 3061, 3032, 2868, 1711, 1515, 1452, 1361, 1242, 1069, 908, 728, 695, 460 cm^{-1}.

HRMS (ESI-TOF) *m/z* calcd. for $C_{44}H_{48}NO_7^+$ ($[M+H]^+$) 702.3425, found 702.3426.



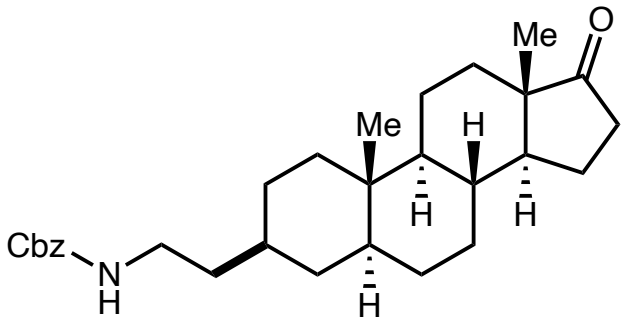
Minor diastereomer – **62b**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 23H), 7.15 – 7.11 (m, 2H), 5.49 (t, *J* = 6.0 Hz, 1H), 5.10 (s, 2H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.80 (apparent dd, *J* = 10.9, 5.3 Hz, 2H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 2H), **4.07** (dt, *J* = 10.5, 4.9 Hz, 1H), 3.78 – 3.68 (m, 3H), 3.64 – 3.44 (m, 4H), 3.28 – 3.20 (m, 1H), 2.00 – 1.88 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.65, 138.68, 138.18, 138.11, 137.91, 136.89, 128.58, 128.55, 128.52, 128.50, 128.45, 128.18, 128.08, 128.04, 128.02, 128.01, 127.99, 127.87, 127.77, 82.28, 79.78, 78.22, 75.54, 75.07, 73.98, 73.47, 73.40, 71.52, 68.97, 66.58, 39.16, 24.84.

IR (film) ν_{max} 3356, 3062, 3031, 2865, 1717, 1509, 1453, 1359, 1248, 1091, 1066, 740, 698, 462 cm^{-1}.

HRMS (ESI-TOF) *m/z* calcd. for $C_{44}H_{48}NO_7^+$ ($[M+H]^+$) 702.3425, found 704.3423.



benzyl (2-((3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)ethyl)carbamate (63): The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *trans*-androsterone (145.2 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (256.9 mg, 0.65 mmol, 1.3 equiv), pyridine (50.6 μL, 49.4 mg, 0.625 mmol, 1.25 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (690.5 mg, 1.00 mmol, 2.0 equiv).

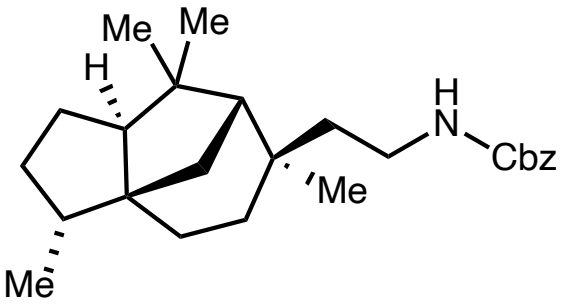
Addition of the acid coupling partner stock solution was performed with 1.0 equiv added in one portion prior to irradiation, and the remaining 1.0 equiv added uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–40% ethyl acetate/hexanes gradient) to provide the title compound as a clear colorless oil (180.6 mg, 80% yield). The diastereomer ratio of the isolated material was assigned as 4.3:1 by quantitative ^{13}C NMR analysis and further supported via comparison to the spectral data of analogous compounds.[9]

^{1}H NMR (500 MHz, $CDCl_3$) diastereomeric and rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.36 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 5.07 (s, 2H) [5.13], 4.83 (t, *J* = 6.1 Hz, 1H) [4.63], 3.17 (q, *J* = 7.0 Hz, 2H), 2.41 (dd, *J* = 19.7, 8.4 Hz, 1H), 2.04 (dt, *J* = 19.3, 9.0 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.81 – 1.70 (m, 3H), 1.69 – 1.42 (m, 7H), 1.42 – 1.33 (m, 2H), 1.33 – 1.15 (m, 6H), 1.13 – 1.00 (m, 2H), 1.00 – 0.89 (m, 1H), 0.83 (s, 3H), 0.79 (s, 3H) [0.75], 0.74 – 0.64 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) diastereomeric and rotameric mixture: δ 221.61, 156.46, 136.72, 128.56, 128.16, 128.13, 66.59, 54.83, 54.74, 51.59, 51.54, 47.89, 46.55, 40.52, 39.92, 38.93, 38.45, 37.36, 36.64, 36.26, 35.91, 35.50, 35.42, 35.12, 35.08, 33.25, 32.70, 32.11, 31.63, 30.99, 30.95, 30.32, 28.72, 28.66, 28.61, 25.40, 21.82, 21.79, 20.31, 20.08, 13.89, 12.35, 11.81.

IR (film) ν_{max} 3344, 2919, 2855, 1708, 1521, 1451, 1373, 1244, 1129, 1009, 909, 726, 646, 462 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{29}H_{42}NO_3^+$ ($[M+H]^+$) 452.3159, found 452.3160.



benzyl (2-((3*R*,3a*S*,6*R*,7*S*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl)ethyl)carbamate (64): The title compound was prepared according to the general procedure for tertiary alcohols using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (10.1 mg, 10.0 μmol, 0.02 equiv), $Ni(TMHD)_2$ (42.5 mg, 100 μmol, 0.20 equiv), (+)-cedrol (111.2 mg, 0.50 mmol, 1.0 equiv), **NHC-2** (254.8 mg, 0.55 mmol, 1.10 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(3-((benzyloxycarbonyl)amino)propanoate) (517.9 mg, 0.75 mmol, 1.5 equiv).

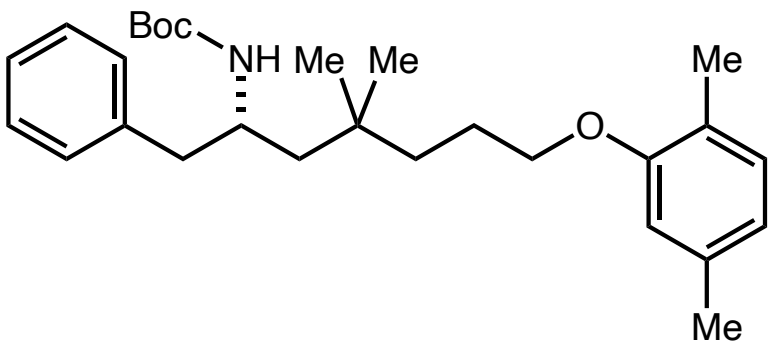
Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 0–30% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 65–90% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (65.0 mg, 34% yield, >20:1 dr). The stereochemistry of the isolated material was assigned as shown via comparison to the spectral data of analogous compounds, and via NOESY analysis (see spectral data).[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 5.09 (s, 2H), 4.65 (t, *J* = 5.8 Hz, 1H), 3.22 – 3.05 (m, 2H), 2.01 (td, *J* = 12.5, 5.7 Hz, 1H), 1.86 (h, *J* = 6.0 Hz, 1H), 1.72 (t, *J* = 8.2 Hz, 1H), 1.67 – 1.57 (m, 2H), 1.56 – 1.45 (m, 4H), 1.45 – 1.22 (m, 5H), 1.20 (s, 3H), 1.10 (s, 3H), 1.08 – 1.02 (m, 1H), 0.98 (s, 3H), 0.83 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.45, 136.80, 128.62, 128.22, 128.18, 66.64, 57.60, 56.53, 53.82, 44.39, 42.71, 41.96, 40.01, 37.06, 36.94, 34.46, 30.40, 29.98, 29.34, 27.41, 25.54, 15.61.

IR (film) ν_{max} 3333, 2938, 2871, 1699, 1525, 1458, 1378, 1307, 1250, 1132, 1027, 772, 698, 617, 470 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{25}H_{38}NO_2^+$ ($[M+H]^+$) 384.2897, found 384.2895.



***tert*-butyl (*R*)-(7-(2,5-dimethylphenoxy)-4,4-dimethyl-1-phenylheptan-2-yl)carbamate (65):** The title compound was prepared according to the general procedure using $Ir[(dF(Me)ppy)_2(dtbbpy)]PF_6$ (5.1 mg, 5.0 μmol, 0.01 equiv), $Ni(TMHD)_2$ (21.3 mg, 50 μmol, 0.10 equiv), *N*-Boc-L-phenylalaninol (125.7 mg, 0.50 mmol, 1.0 equiv), **NHC-1** (217.4 mg, 0.55 mmol, 1.1 equiv), pyridine (42.5 μL, 41.5 mg, 0.525 mmol, 1.05 equiv), and iodomesitylene bis(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate) (558.6 mg, 0.75 mmol, 1.5 equiv).

Addition of the acid coupling partner stock solution was performed uniformly over the first 5 minutes of irradiation. After irradiation for 1 hour, solvents were removed under reduced pressure, and the resulting crude residue was purified by automated flash chromatography (25 g high performance silica column, 5–20% ethyl acetate/hexanes gradient) followed by preparative HPLC (XBridge BEH C18 OBD column, 70–100% MeCN/H_2O with 0.1% NH_4OH) to provide the title compound as a white solid (103.3 mg, 47% yield).

^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture (resonances for minor rotamer are enclosed in square brackets): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 7.03 (d, J = 7.5 Hz, 1H), 6.68 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 4.36 (d, J = 9.3 Hz, 1H) [4.15], 3.96 (p, J = 8.3 Hz, 1H), 3.85 (t, J = 7.2 Hz, 2H), 2.84 (dd, J = 13.3, 5.6 Hz, 1H), 2.67 (dd, J = 13.2, 7.6 Hz, 1H), 2.33 (s, 3H), 2.20 (s, 3H), 1.71 – 1.61 (m, 1H), 1.60 – 1.52 (m, 1H), 1.50 – 1.45 (m, 1H), 1.42 (s, 9H), 1.36 – 1.31 (m, 2H), 1.23 (dd, J = 14.6, 9.6 Hz, 1H), 0.90 (d, J = 4.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.13, 155.01, 138.52, 136.49, 130.34, 129.74, 128.34, 126.33, 123.62, 120.66, 112.06, 79.06, 68.58, 48.79, 45.57, 44.05, 38.39, 32.76, 28.53, 27.49, 27.45, 24.25, 21.52, 15.94.

IR (film) ν_{max} 3363, 3025, 2952, 2869, 1698, 1504, 1365, 1256, 1164, 1128, 1045, 1020, 803, 744, 700 cm^{-1}.

HRMS (ESI-TOF) *m*/*z* calcd. for $C_{28}H_{41}NNaO_3^+$ ($[M+Na]^+$) 462.2979, found 462.2980.

7) UV-visible absorption spectra of reaction components

Samples were prepared in a volumetric flask at the indicated concentration in DMSO/MTBE (1:1). For each measurement, a 3 mL aliquot was added to a screw-top 10.0 mm optical glass cuvette, and absorption spectra were recorded on a Cary 60 UV-Vis spectrometer. Molar absorptivity ε was calculated using Beer's law $A = \varepsilon cl$, and is plotted as a function of wavelength below. At the wavelength of excitation in the PennPhD photoreactor with the m1 450 nm LED plate (**Figure S1**), the iridium photocatalyst is known to absorb substantially more strongly[2] than the nickel catalyst (**Figure S2**, $\varepsilon = 7.2 \times 10^1$), iodomesitylene diacetate (**Figure S3**, $\varepsilon = 3.2 \times 10^1$), and the alcohol–NHC adducts (**Figure S4**, $\varepsilon \leq 8.1 \times 10^1$) do not.

Figure S1. LED emission profile for PennPhD Photoreactor m1 450 nm LED plate measured by UPRtek MK350N LED Meter.

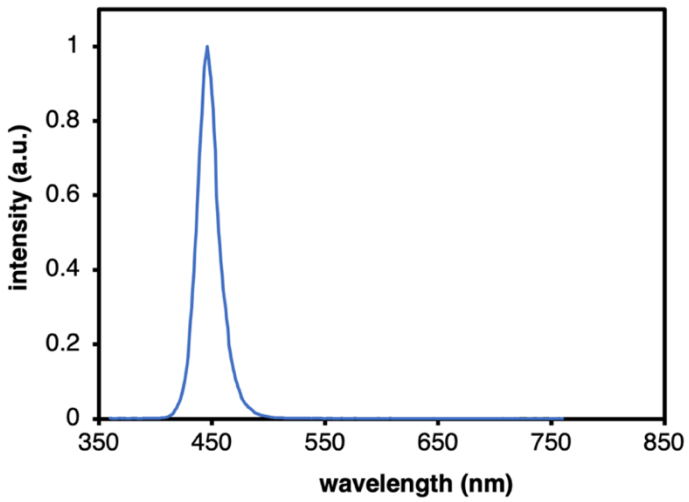


Figure S2. Absorption spectrum for $Ni(TMHD)_2$ at 1.0 mM in DMSO/MTBE (1:1).

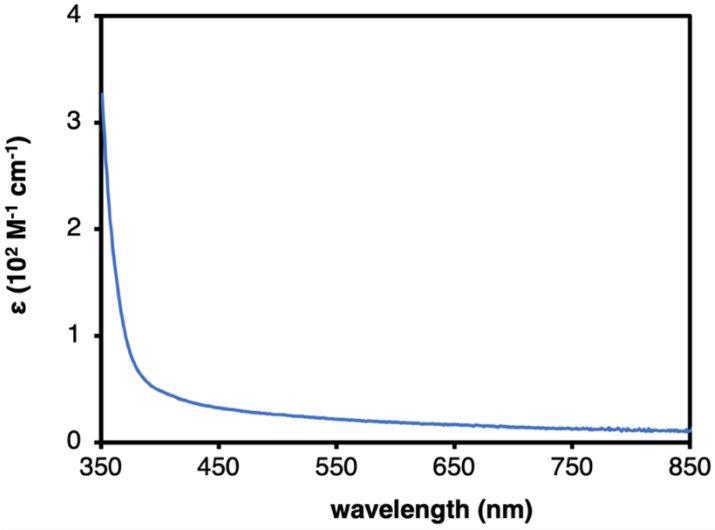


Figure S3. Absorption spectrum for $MesI(OAc)_2$ at 1.0 mM in DMSO/MTBE (1:1).

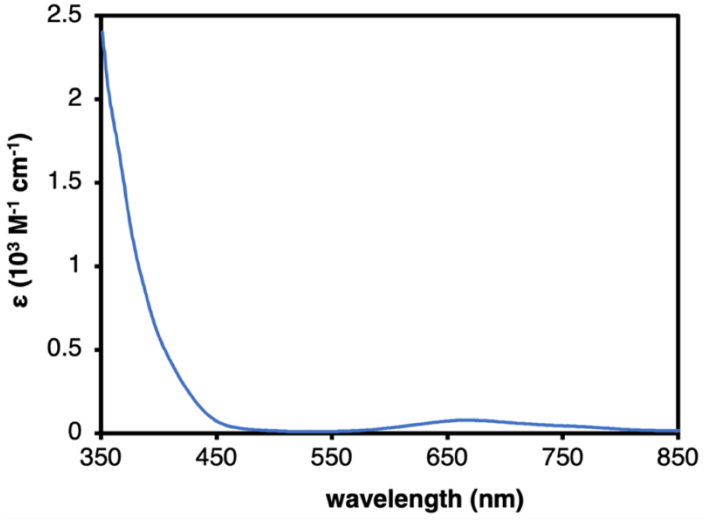
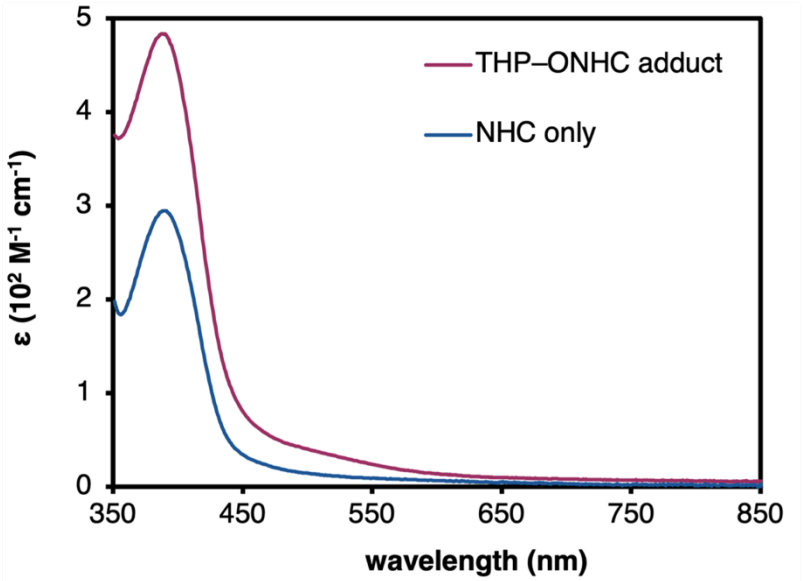
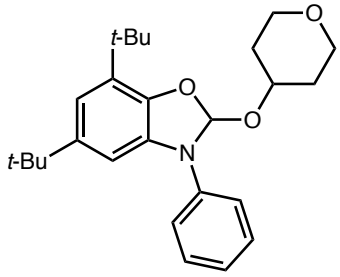
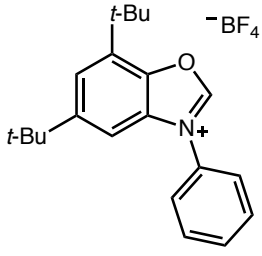


Figure S4. Absorption spectrum for **NHC-1** and 2º NHC–alcohol adduct at 2.5 mM in DMSO/MTBE (1:1).





THP–ONHC adduct



NHC only

8) Stern-Volmer quenching experiments

Steady-state emission quenching studies were performed using an Agilent Cary Eclipse Fluorescence Spectrophotometer. In each experiment, the photocatalyst and varying amount of quencher(s) were dispensed in the glovebox and combined in DMSO/MTBE (1:1) in screw-top 10.0 mm optical glass cuvettes. Both DMSO and MTBE solvents were degassed separately outside the glovebox by vigorously sparging with nitrogen for 30 minutes.

For emission quenching of the $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ photocatalyst, a 10 μM stock solution was prepared with the desired quencher concentration, the solution was irradiated at λ_{ex} = 400 nm, and the emission intensity was observed at λ_{em} = 520 nm. For quenching by iodonium dicarboxylate reagents, sample absorbance at the wavelength of photoexcitation and emission measurement was never above 0.1 OD to avoid inner filter effects (IFEs) and ensure single photon emission behavior.[11] For quenching by alcohol–NHC adducts with optical densities exceeding 0.1 OD at either 400 or 520 nm, IFEs were accounted for by measuring linear absorbance at the excitation (OD_{400}) and emission (OD_{520}) wavelengths, and adjusting emission intensities according to the following equation[12]:

$$I_{\text{corrected}} = I_{\text{raw}} 10^{0.5(OD_{400}+OD_{520})}$$

Linear least squares regression analysis was performed and the data were modeled according to the Stern–Volmer equation:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q]$$

where I_0 is the emission intensity without quencher present, I is the emission intensity with a quenching concentration $[Q]$, τ_0 is the excited state lifetime of $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ in DMSO/MTBE (1:1), and k_q is the rate constant for excited state quenching. While the excited state lifetime τ_0 is not reported in the literature for the solvent mixture used in this experiment, calculation of the Stern-Volmer quenching constant $K_{SV} = k_q \tau_0$ permits the determination of relative rates of quenching by two different species.

Comparing the relative slopes of the Stern-Volmer quenching plots for the iodonium dicarboxylates (**Figure S8**) and the alcohol–NHC adducts (**Figure S15**), we observe that the excited state of the iridium photocatalyst is quenched 50 to 100 times more rapidly by the latter than the former.

Figure S5. Emission spectra for $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ with varying $[MesI(OAc)_2]$

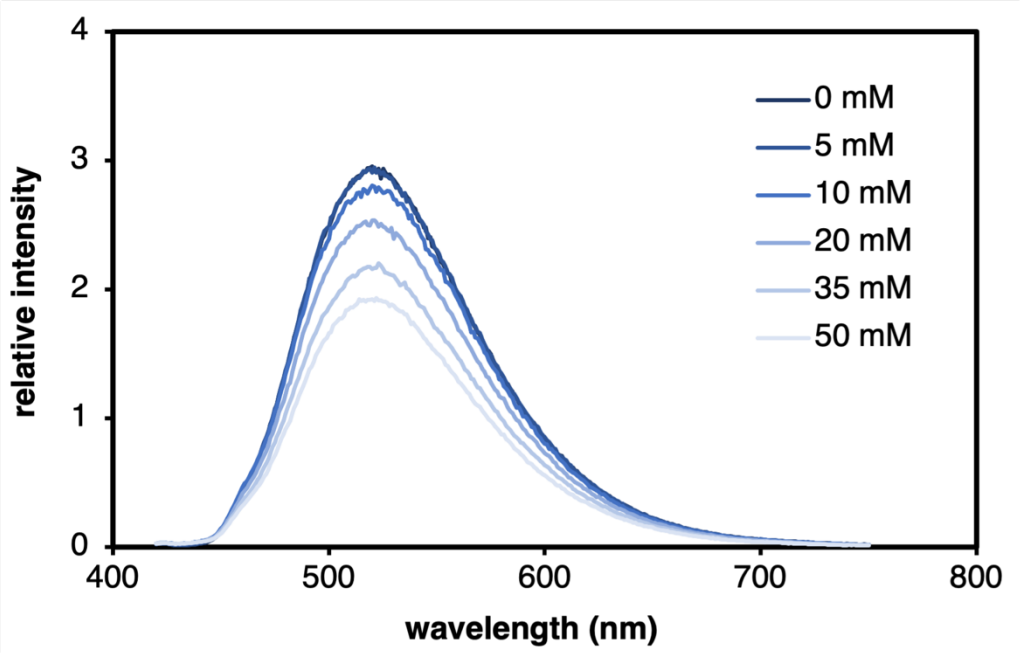


Figure S6. Emission spectra for $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ with varying $[MesI(O_2CCy)_2]$

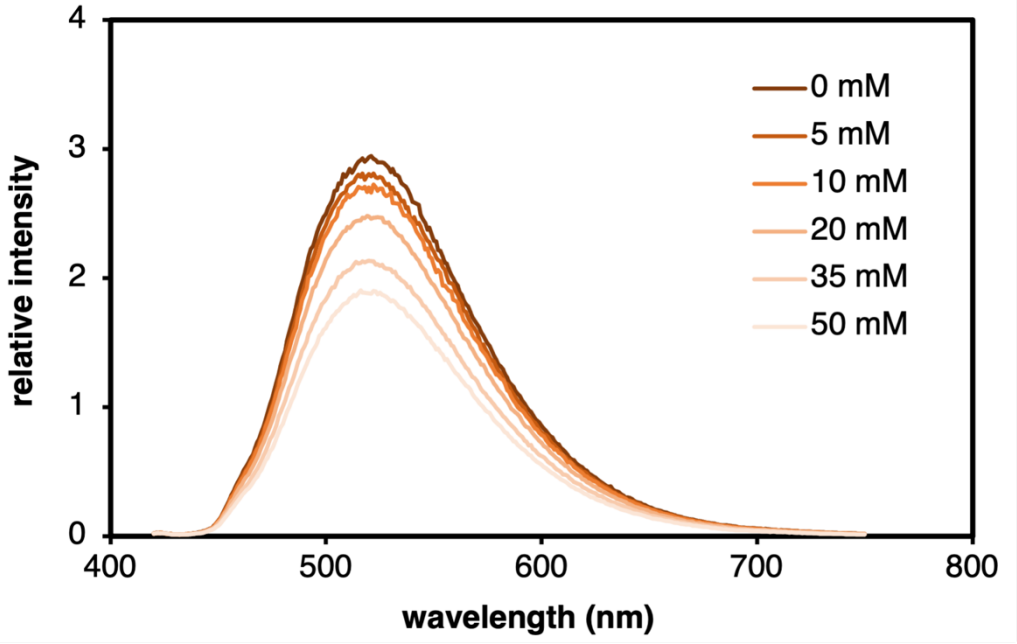


Figure S7. Emission spectra for $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ with varying $[MesI(OPiv)_2]$

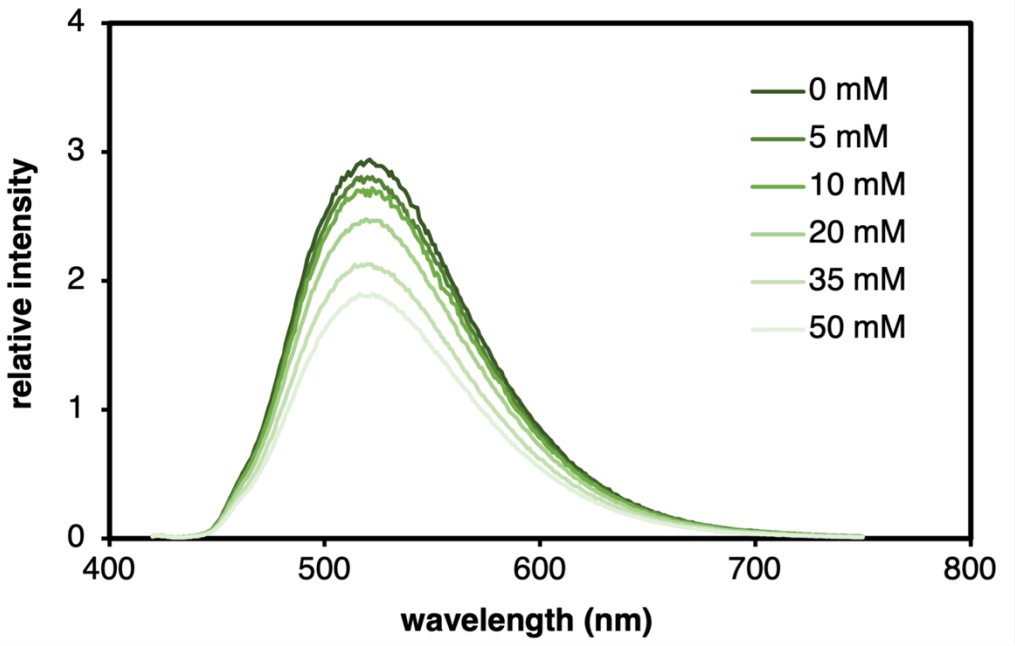


Table S15. Emission quenching of $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ by iodonium dicarboxylates ignoring inner filter effects (OD < 0.1 at λ_{ex} and λ_{em}).

	Me		**Cy**		**Piv**	
[Q] (mM)	**I**	**I_0/I**	**I**	**I_0/I**	**I**	**I_0/I**
0	295.34	1.00	293.38	1.00	286.97	1.00
5	290.54	1.02	280.55	1.05	268.81	1.07
10	280.60	1.05	270.30	1.09	264.12	1.09
20	253.31	1.17	247.45	1.19	249.51	1.15
35	215.66	1.37	213.38	1.37	205.21	1.40
50	192.13	1.54	188.10	1.56	196.34	1.46

Figure S8. Emission quenching of $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ by iodonium dicarboxylates.

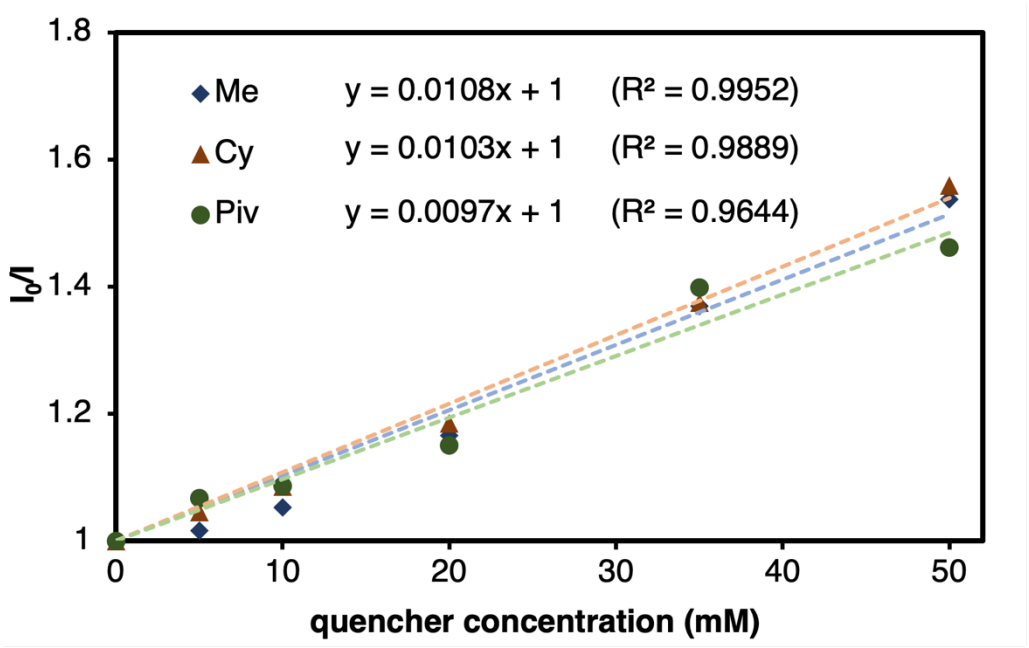
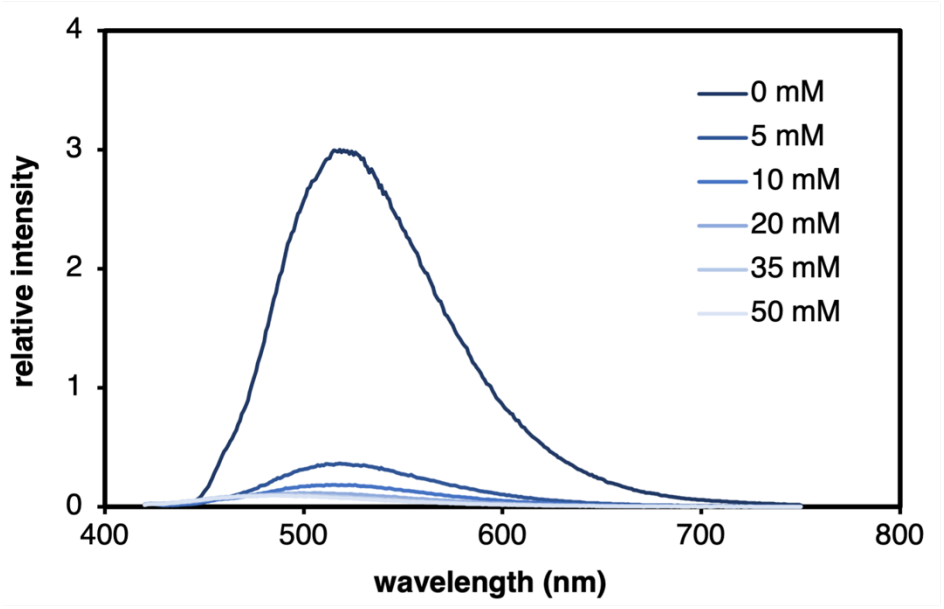
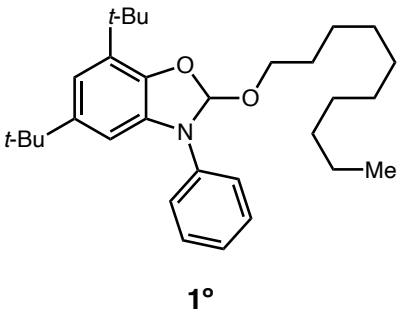


Figure S9. Emission spectra for $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ with varying [**1°**].





1°

Figure S10. Emission spectra for [Ir(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ with varying [**2°**].

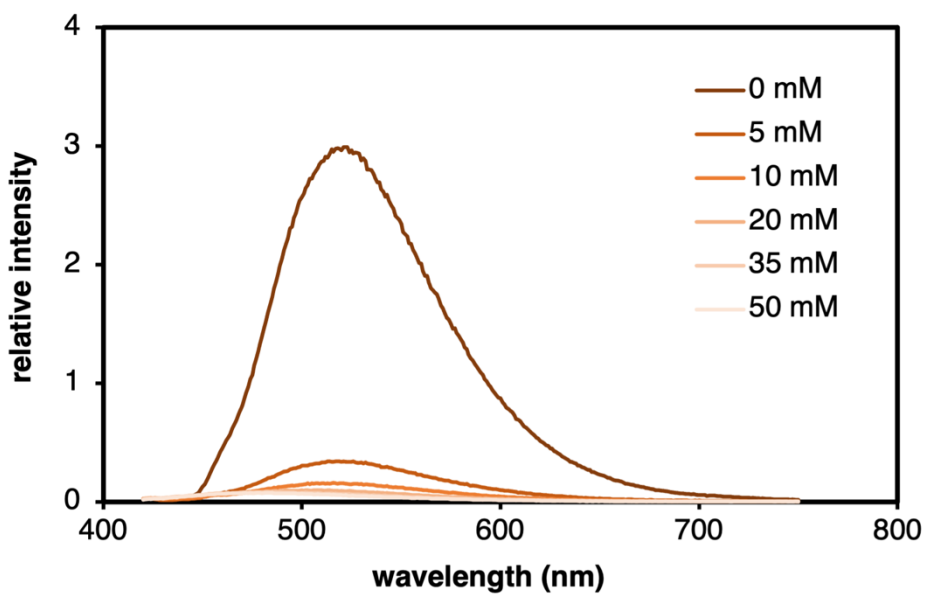


Figure S11. Emission spectra for [Ir(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ with varying [**3°**].

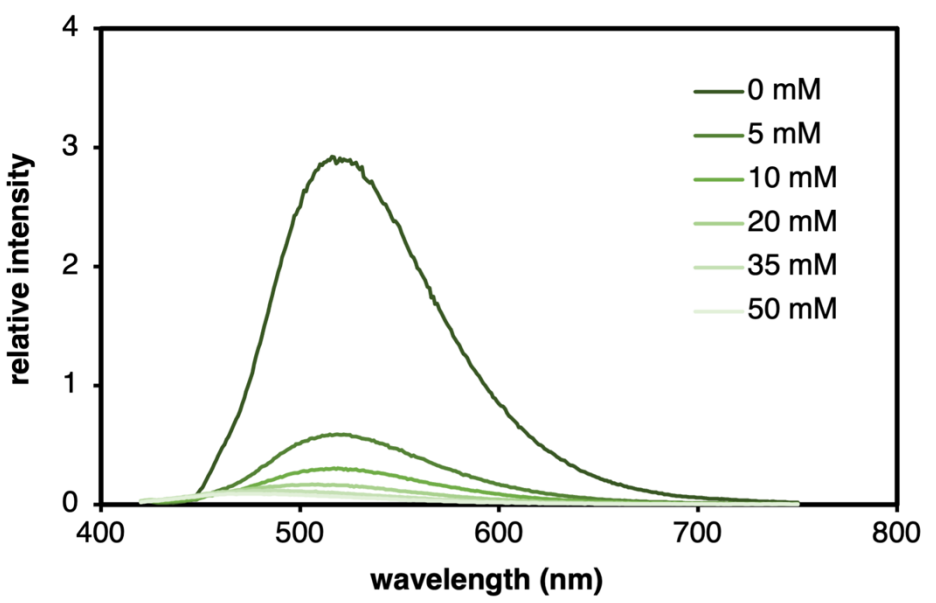


Figure S12. Absorbance spectra for varying [**1°**]. Values at 400 and 520 nm were used to correct for the inner-filter effect (see below).

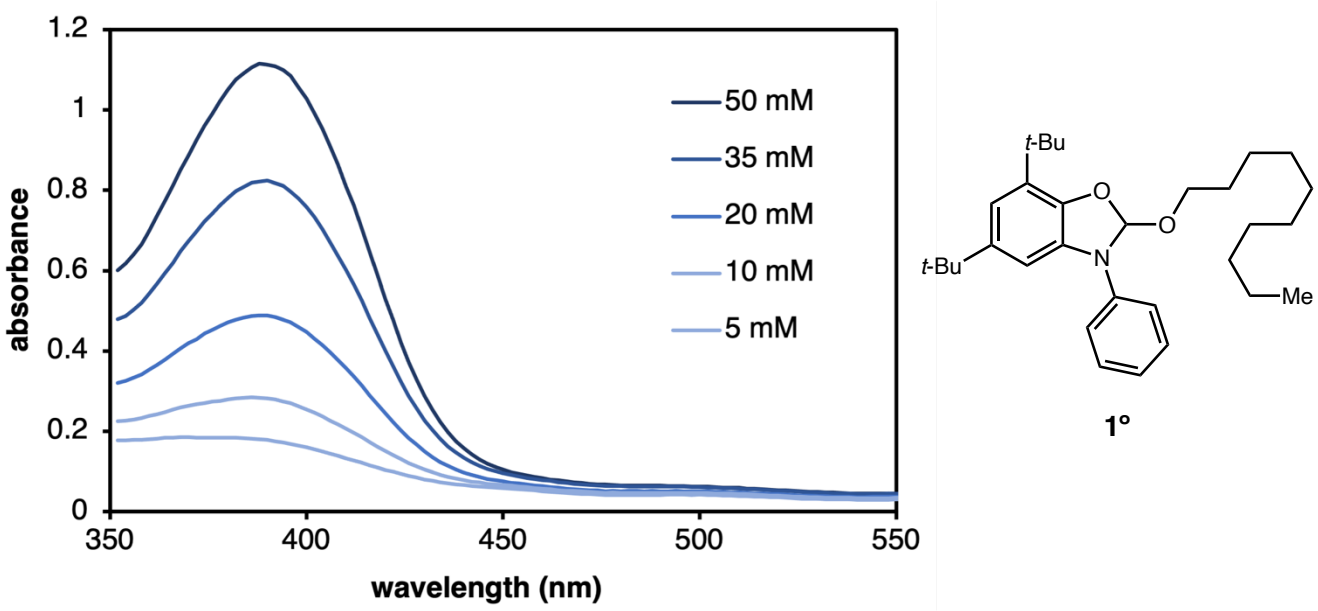


Figure S13. Absorbance spectra for varying [**2°**]. Values at 400 and 520 nm were used to correct for the inner-filter effect (see below).

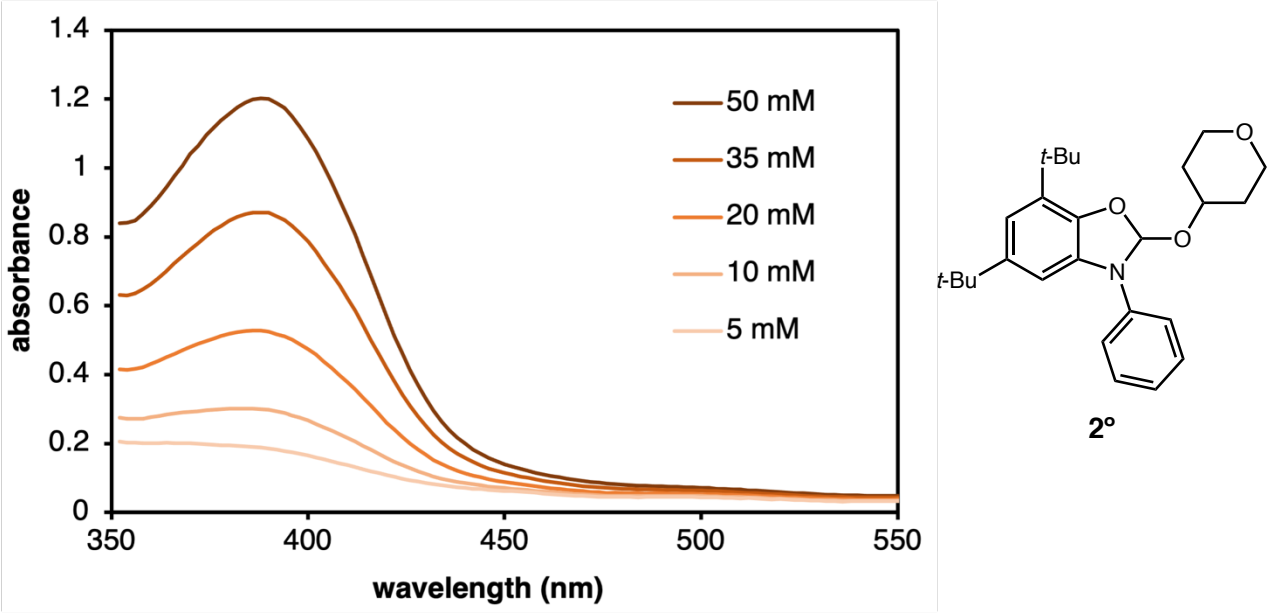


Figure S14. Absorbance spectra for varying [**3º**]. Values at 400 and 520 nm were used to correct for the inner-filter effect (see below).

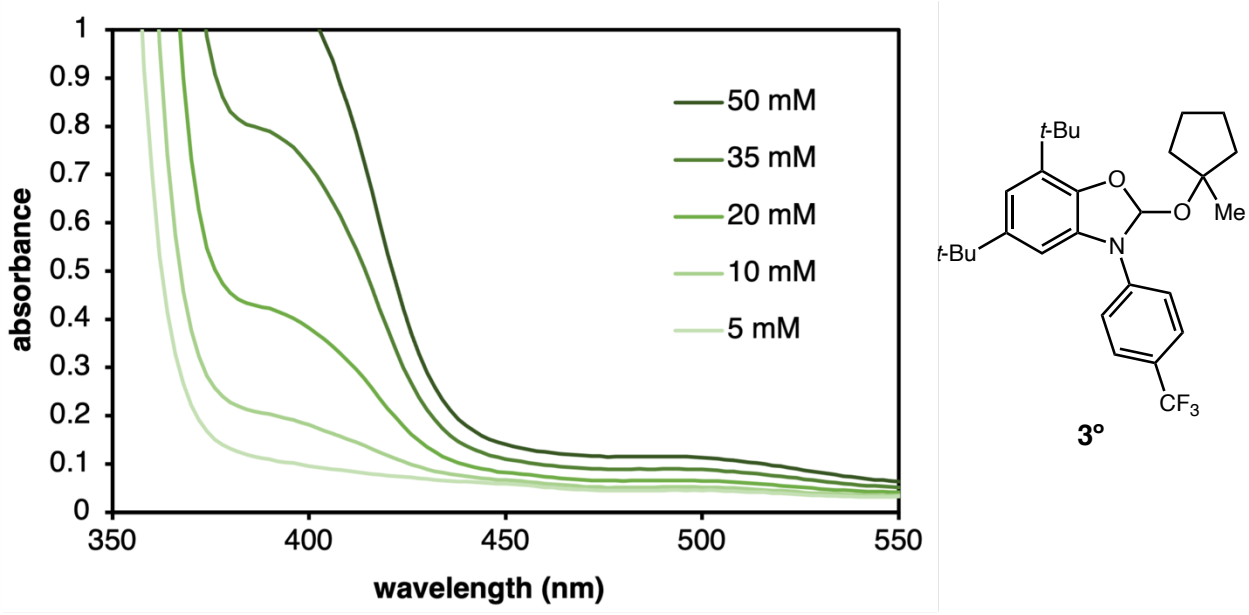


Figure S15. Emission quenching of $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ by alcohol–NHC adducts. Data corresponding to [quencher] = 35 mM and 50 mM were excluded for this analysis as the emission intensity approaches zero and error becomes significant.

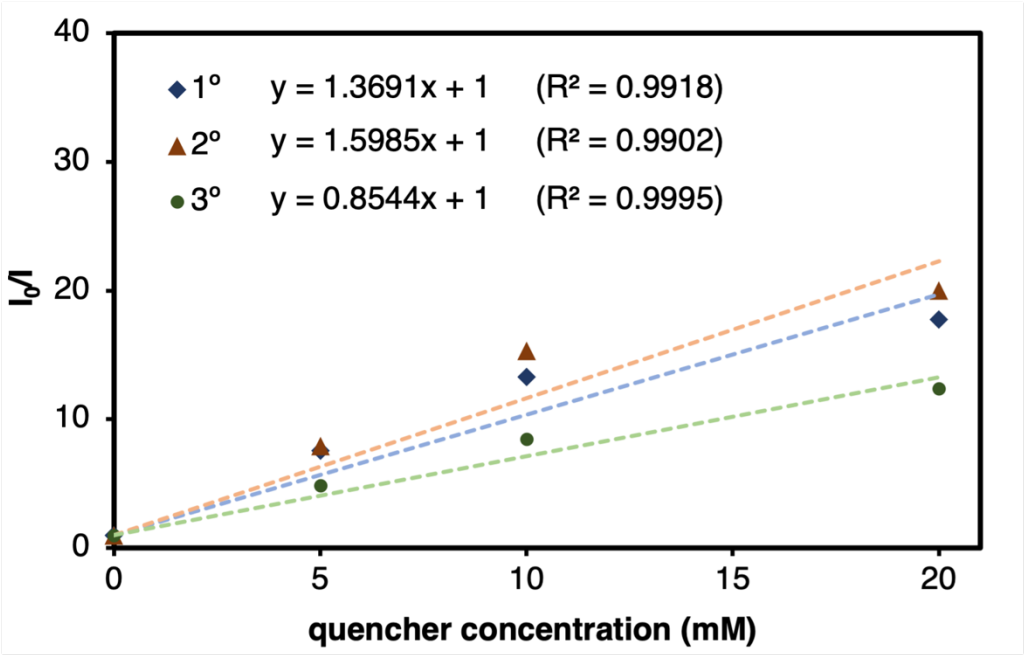
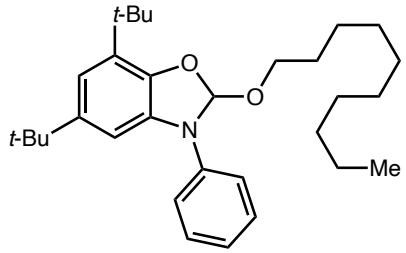


Table S16. Emission quenching of $[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$ by NHC–alcohol adducts **1°, 2°**, and **3°** with inner-filter effect corrections.

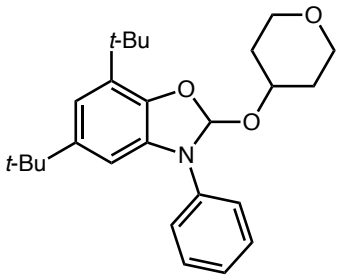
1°	**0 mM**	**5 mM**	**10 mM**	**20 mM**
I_{raw}	299.7901	36.0683784	18.2988644	10.9333601
OD_{400}	0.07788785	0.16022705	0.25493267	0.44746301
OD_{520}	0.03613333	0.03589712	0.04047477	0.043774
$I_{corrected}$	341.843934	45.2052317	25.7115263	19.2474036
$I_0/I_{corrected}$	1	7.56204364	13.2953575	17.7605219

2°	**0 mM**	**5 mM**	**10 mM**	**20 mM**
I_{raw}	296.302643	33.798893	15.4742928	9.27540684
OD_{400}	0.07788785	0.16506569	0.26695654	0.47403944
OD_{520}	0.03613333	0.03830069	0.04067036	0.04569636
$I_{corrected}$	337.867265	42.7155169	22.0507953	16.8733325
$I_0/I_{corrected}$	1	7.90970798	15.3222258	20.0237425

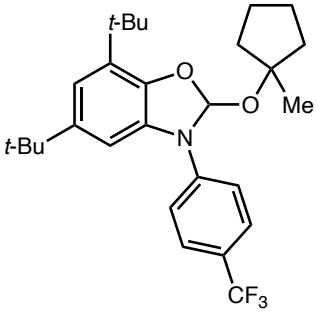
3°	**0 mM**	**5 mM**	**10 mM**	**20 mM**
I_{raw}	290.871399	58.2410583	30.0646477	16.0767078
OD_{400}	0.0742695	0.09587357	0.18100141	0.38232884
OD_{520}	0.03401531	0.03913675	0.04452013	0.05490271
$I_{corrected}$	329.490902	68.0353179	38.9777611	26.5957899
$I_0/I_{corrected}$	1	4.84293911	8.45330498	12.3888369



1°



2°



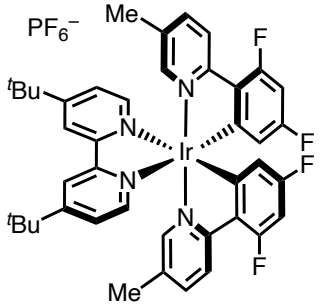
3°

9) Cyclic voltammetry data

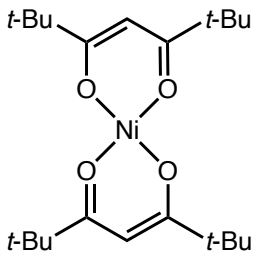
Cyclic voltammetry (CV) was performed using a CHI (model 600E) electrochemical analyzer/workstation. A three-electrode setup was used, consisting of a glassy carbon working electrode, platinum wire counter electrode, and a saturated calomel (SCE, CH Instruments) reference electrode. Samples were prepared with 1 mM analyte and 100 mM $TBAPF_6$ electrolyte solution in 1:1 DMSO/MTBE, and degassed by sparging with nitrogen for at least 5 minutes before performing measurements with a scan rate of 100 mV/s unless denoted otherwise. All data are reported with reference to SCE. When possible, reduction potentials are reported based on the midpoint between the peak of the anodic and cathodic waves ($E_{1/2}$). For irreversible reduction or oxidation waves, the peak potentials (E_{pa} or E_{pc} for anodic and cathodic waves, respectively) are reported instead and noted accordingly.

As shown below, the standard iridium photocatalyst $[Ir(dF(Me)ppy)_2(dtbbpy)](PF_6)$ shows fully reversible behavior at $E_{1/2} = -1.25$ V (**Figure S16**), which is assigned to the Ir(II/III) couple based on literature values.[2] In contrast, application of positive potential only led to solvent oxidation and the Ir(III/IV) couple was not observed (**Figure S17**). Iodomesitylene diacetate undergoes irreversible reduction at $E_{p,c} = -0.84$ V, while representative secondary and tertiary α-substituted acid derivatives bearing electron-rich alkyl substituents are reduced at slightly more negative potentials in the region of $E_{p,c} = -1.0$ V (**Figure S20**).

With respect to oxidation of NHC–alcohol adducts, these species all undergo quasi-reversible oxidation in the vicinity of $E_{p,a} = +1.15$ V, including adducts derived from representative primary, secondary, and tertiary alcohols (**Figure S21**). Notably, the tertiary alcohol adduct with **NHC-2** is not substantially more challenging to oxidize, despite the electron-deficient *p*-CF_3-substituted aniline. Upon addition of sodium acetate to each solution, oxidation is rendered irreversible, presumably due to rapid deprotonation of the oxidized NHC amine radical cation (**Figure S22**). Under the standard reaction conditions, reduction of the iodomesitylene dicarboxylate reagent would generate this carboxylate base *in situ*.



$Ir(dF(Me)ppy)_2(dtbbpy)PF_6$



$Ni(TMHD)_2$

Figure S16. Reversible Ir(II/III) couple for [Ir(dF(Me)ppy)$_2$(dtbbpy)](PF$_6$) with $E_{1/2}$ = –1.25 V.

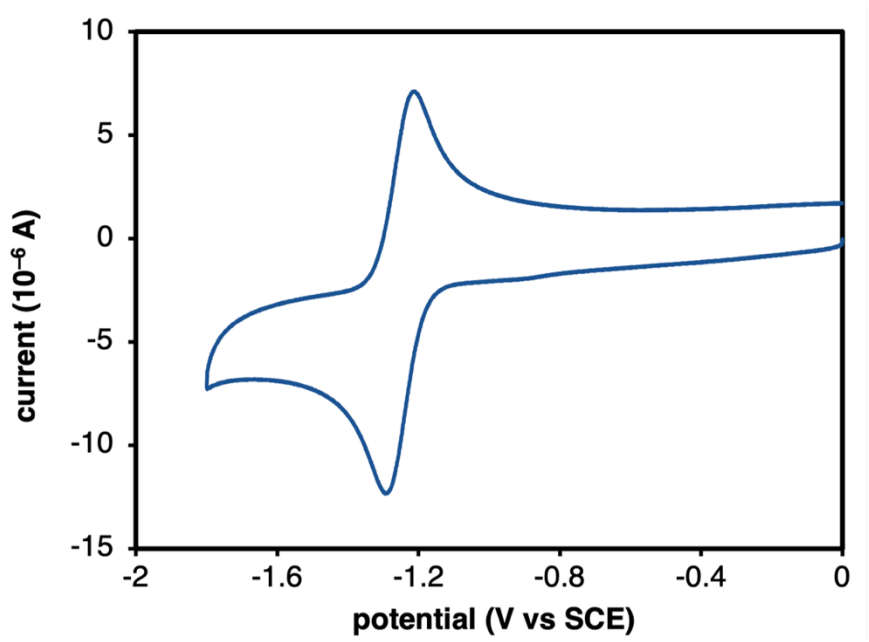


Figure S17. Solvent oxidation precedes Ir(III/IV) couple of [Ir(dF(Me)ppy)$_2$(dtbbpy)](PF$_6$)

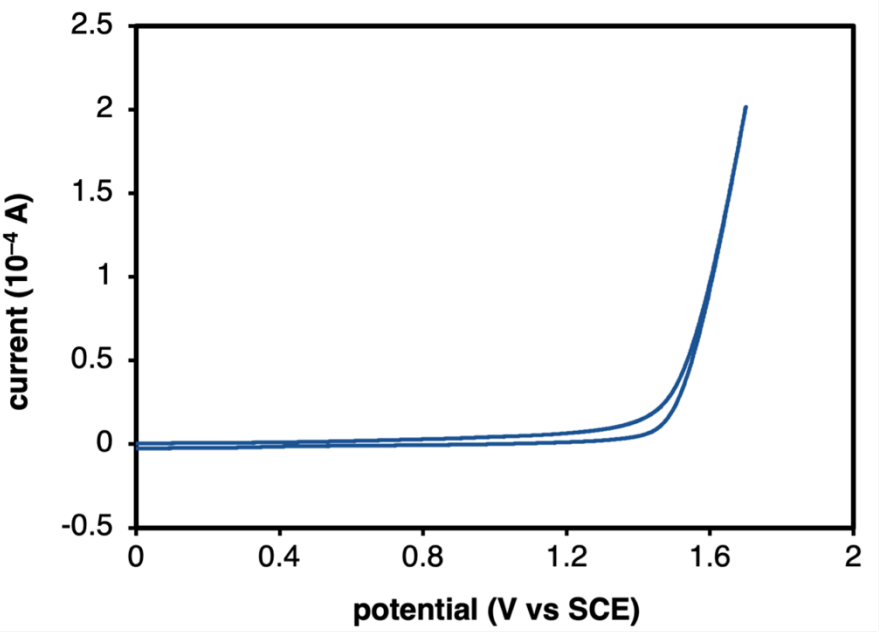


Figure S18. Oxidation of Ni(TMHD)$_2$ with $E_{p1,a}$ = +1.03 V and $E_{p2,a}$ = +1.39 V

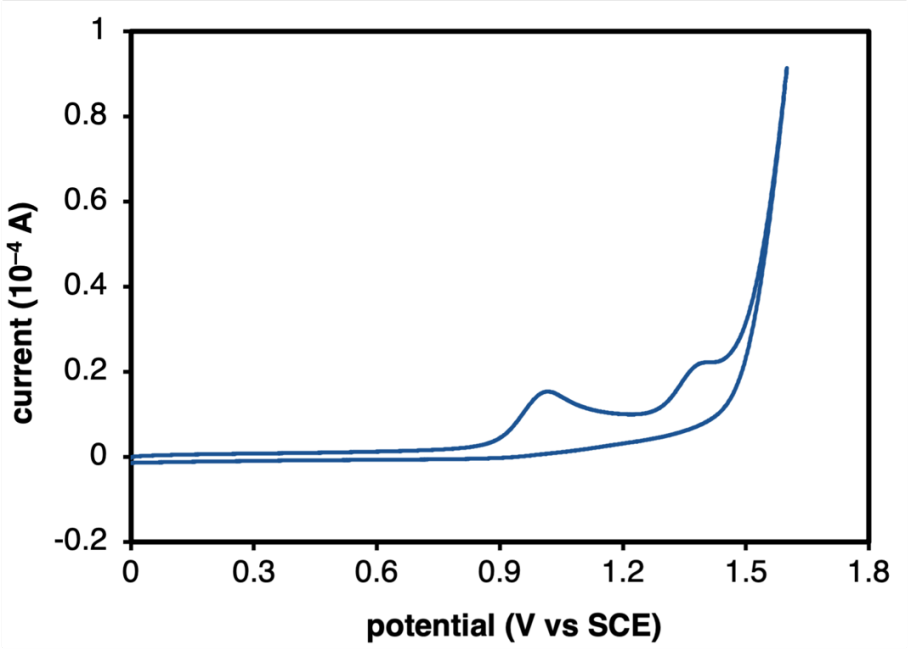


Figure S19. Reduction of Ni(TMHD)$_2$ with $E_{p,c}$ = –2.25 V.

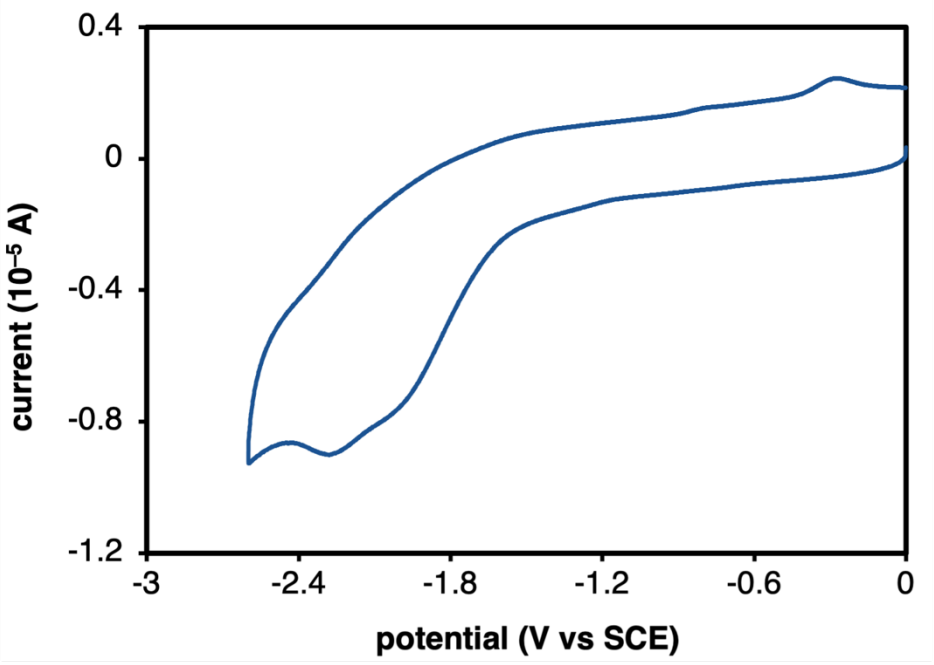
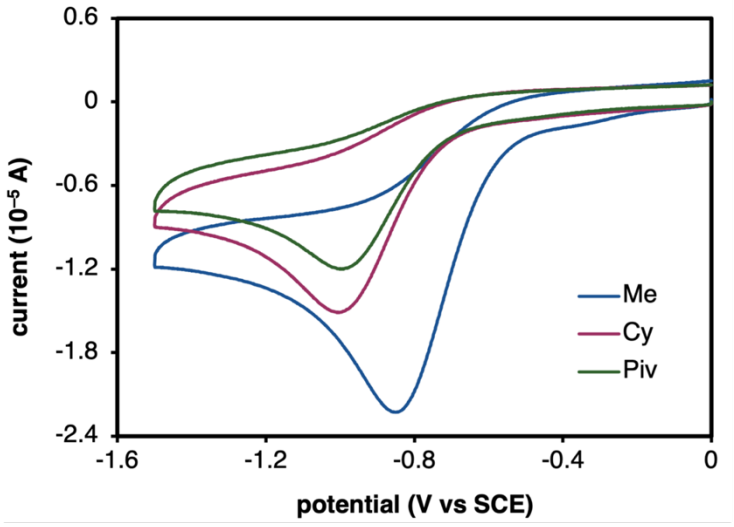
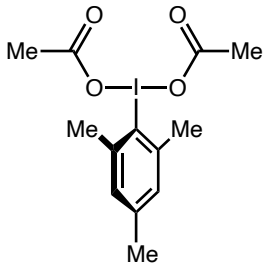
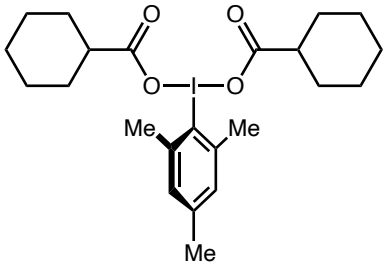


Figure S20. Reduction of iodomesitylene dicarboxylates derived from acetic acid (**Me**) with $E_{p,c}$ = –0.84 V, cyclohexane carboxylic acid (**Cy**) with $E_{p,c}$ = –1.02 V, and pivalic acid (**Piv**) with $E_{p,c}$ = –1.00 V.

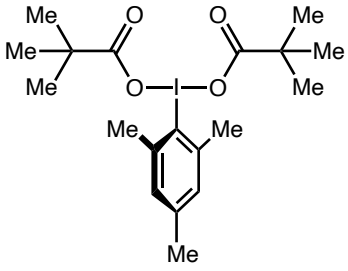




Me



Cy



Piv

Figure S21. Oxidation of alcohol–NHC adducts derived from *n*-decanol / **NHC-1** (**1°**) with $E_{p,a}$ = +1.14 V, 4-hydroxytetrahydropyran / **NHC-1** (**2°**) with $E_{p,a}$ = +1.12 V, and 1-methyl-cyclopentanol / **NHC-2** (**3°**) with $E_{p,a}$ = +1.17 V.

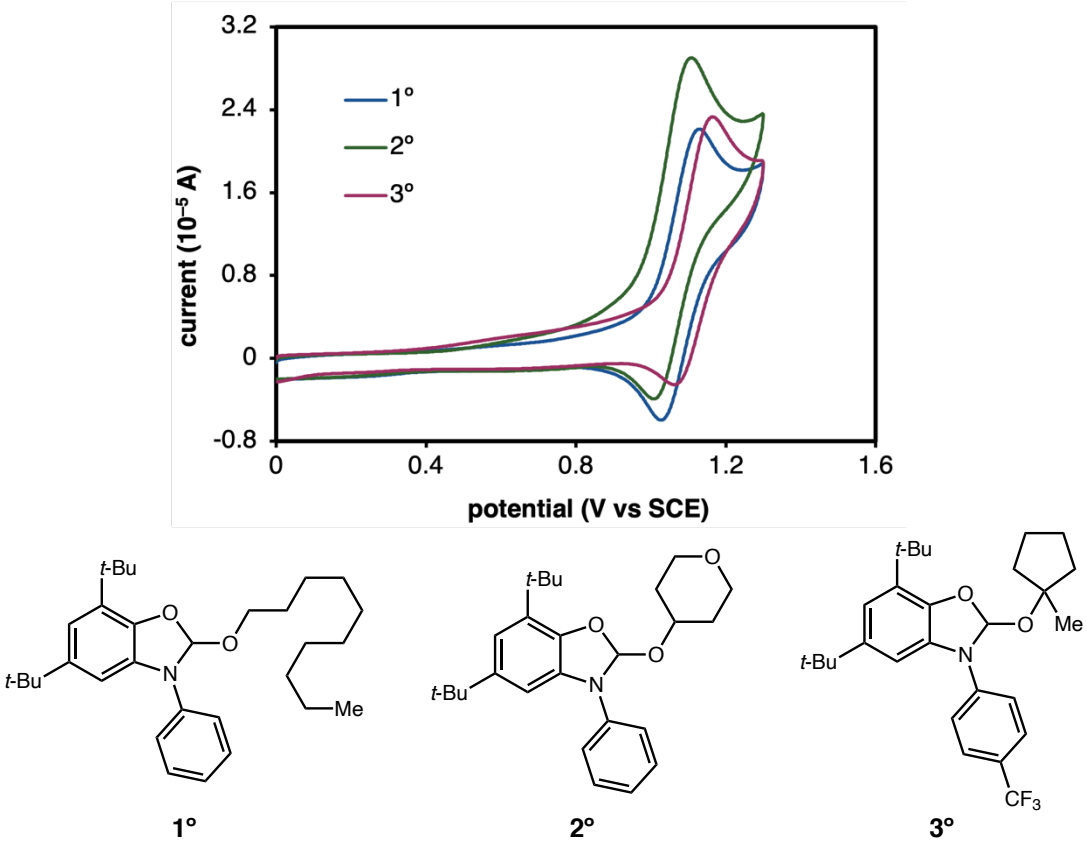
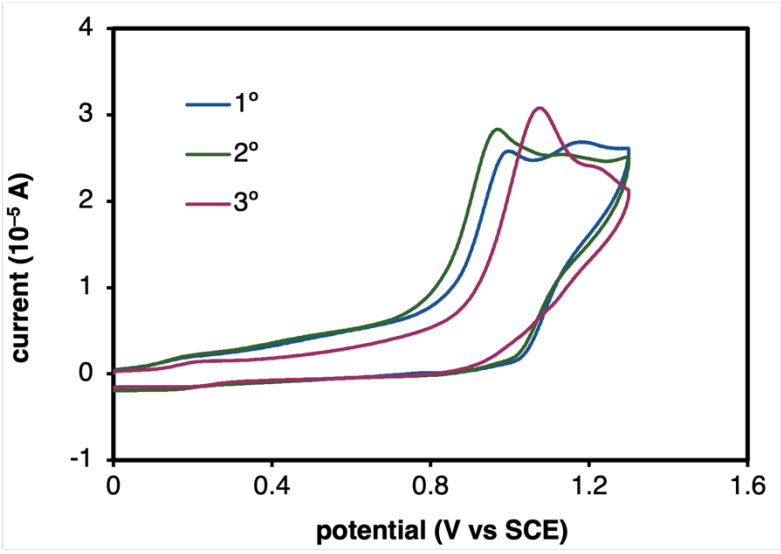


Figure S22. Oxidation of alcohol–NHC adducts as in **Figure S21** with excess (5 equiv) sodium acetate is shifted to $E_{p,a}$ = 1.02 V for **1°**, +0.97 V for **2°**, and +1.08 V for **3°**.

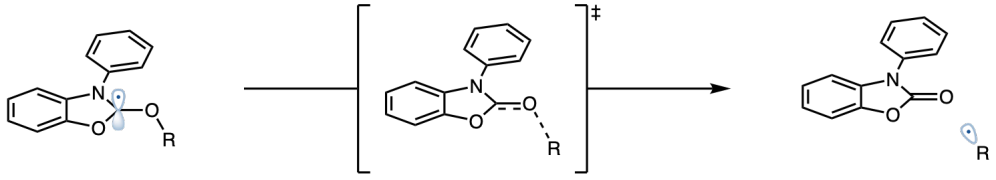


10) Computational Studies with Density Functional Theory

Rates and Driving Forces for Alcohol–NHC β-Scission

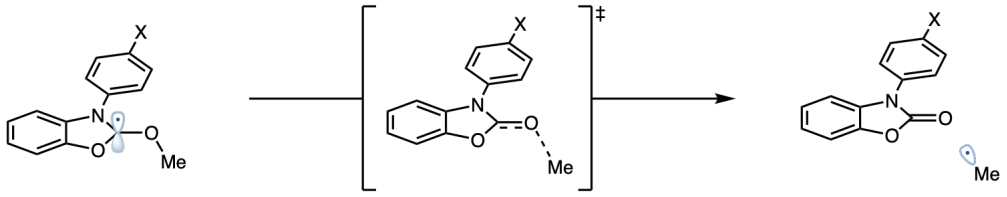
Quantum chemical calculations were performed using *Gaussian 16*.[13] Molecular geometries were optimized using the range-separated ωB97X-D functional[14] and the 6-31G(d) basis set. Solvation effects were included in the geometry optimizations using the SMD solvation model[15] with DMSO as the solvent. Single-point energy and frequency calculations were refined using the ωB97X-D functional and the 6-311++G(d,p) basis set, and stationary points were characterized as either minima (no imaginary frequencies) or saddle points (one imaginary frequency). Gibbs free energies at 298 K were corrected using Grimme's quasiharmonic entropy approximation[16] and Head-Gordon's quasiharmonic enthalpy correction,[17] as implemented in Paton's GoodVibes software package.[18] Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the transition state found connected the reactants and the products.

Table S17. Effect of alcohol substitution on rate and driving force of β-scission of alcohol–NHC adducts. Gibbs free energies of reaction (ΔG^{o}) and Gibbs free energies of activation ($\Delta G^{\ddagger}$) are given in kcal/mol at 298.15 K as a function of alkyl substituent, and rate constants are calculated according to the Eyring equation.



entry	R	ΔG^{o}	$\Delta G^{\ddagger}$	k_{298} (s^{-1})
A	Me	–27.6	11.9	1×10^{4}
B	Et	–28.6	11.0	5×10^{4}
C	i-Pr	–29.4	9.9	3×10^{5}
D	*t*-Bu	–32.3	5.8	4×10^{8}

Table S18. Effect of *para*-substitution of the *N*-aryl group on rate and driving force of *β*-scission of alcohol–NHC adducts. Gibbs free energies of reaction (ΔG°) and Gibbs free energies of activation (ΔG‡) are given in kcal/mol at 298.15 K as a function of substituent, and rate constants are calculated according to the Eyring equation.



INT 3 **TS 3** **INT 4**

entry	X	ΔG°	ΔG‡	k_{298} (s^{-1})
A	CN	–26.7	12.0	1.0×10^4
B	CF_3	–27.0	11.6	1.9×10^4
C	Cl	–27.5	11.7	1.7×10^4
D	OMe	–28.3	11.6	1.9×10^4
E	NMe_2	–28.5	11.4	2.6×10^4

Cartesian coordinates, energies, and vibrational frequencies. The following geometries were optimized at the ωB97X-D/6-311++G(d,p)/SMD(DMSO)//ωB97X-D/6-31G(d)/SMD(DMSO) level of theory, as described above. Electronic energy (*E*), zero-point energy correction (ZPE), standard thermal correction to free energy (Δ*G*), sum of electronic and thermal free energies (*G*), and the sum of electronic and quasi-harmonic thermal free energies (G_{qh}) are listed in hartrees. Imaginary frequencies are listed for transition states in wavenumbers (cm^{-1}).

Methyl radical (Me•)

C	0.00003400	0.00000200	-0.00005200
H	-0.54853500	0.93591600	0.00006200
H	-0.53652400	-0.94285600	0.00005800
H	1.08485700	0.00692900	0.00019200

E = –39.831832 hartree
ZPE = +0.029471 hartree
ΔG = +0.009679 hartree
G = –39.822154 hartree
G_{qh} = –39.822155 hartree

Ethyl radical (Et•)

C	-0.79309500	0.00000000	-0.02416500
C	0.69298500	0.00002600	-0.00114200
H	1.10701900	-0.88820700	-0.49303900
H	1.10696000	0.88978900	-0.49026400
H	1.08669400	-0.00165800	1.03037300
H	-1.34994100	-0.92969300	0.05237200
H	-1.35006800	0.92960900	0.05239600

E = –79.151038 hartree
ZPE = +0.059113 hartree
ΔG = +0.035184 hartree
G = –79.115854 hartree
G_{qh} = –79.115914 hartree

iso-Propyl radical (*i*-Pr•)

C	0.00000000	0.53874400	-0.05695500
C	1.29311500	-0.19915500	0.00391300
H	1.30007500	-1.05478800	-0.68609000
H	2.14561500	0.44408600	-0.23955600
H	1.47901500	-0.61606600	1.00994800
C	-1.29311600	-0.19915300	0.00391400
H	-2.14562900	0.44412600	-0.23940200
H	-1.30013700	-1.05469300	-0.68620500
H	-1.47893700	-0.61620400	1.00990500
H	0.00000300	1.61092700	0.12617100

E = –118.470210 hartree
ZPE = +0.087944 hartree
ΔG = +0.061269 hartree
G = –118.408941 hartree
G_{qh} = –118.409050 hartree

tert-Butyl radical (*t*-Bu•)

C	-0.00026200	-0.00019200	-0.17060900
C	1.00466500	-1.09106100	0.01701100
H	0.66399600	-2.03819600	-0.41973500
H	1.97303000	-0.83387500	-0.43037300
H	1.19500700	-1.28801500	1.08821200
C	-1.44756400	-0.32421200	0.01739200
H	-2.09692600	0.44074200	-0.42658800
H	-1.70807500	-1.29502800	-0.42255000
H	-1.71508200	-0.38156400	1.08868000
C	0.44290100	1.41527900	0.01692200
H	-0.26865600	2.12625400	-0.42135100
H	0.52906300	1.67505800	1.08818300
H	1.42920600	1.59573600	-0.42877300

E = –157.789022 hartree
ZPE = +0.116372 hartree
ΔG = +0.087458 hartree
G = –157.701563 hartree
G_{qh} = –157.701730 hartree

INT-1A (MeOH / NHC-1 adduct)

C	-2.19684500	0.39870600	-0.26295200
C	-1.14886700	-0.50733600	-0.07858500
C	-1.40942400	-1.85744100	0.10900700
C	-2.75129100	-2.25616400	0.12856000
C	-3.78797400	-1.34044300	-0.04143000
C	-3.52203900	0.01922000	-0.24958200
H	-0.61093900	-2.58048000	0.23103100
H	-2.98322200	-3.30641400	0.27681200
H	-4.81805700	-1.68203400	-0.02073100
H	-4.31559800	0.74372900	-0.39763600
O	-1.70408100	1.65462700	-0.47160300
N	0.02342700	0.23594400	-0.17678800
O	0.35332500	2.58164400	0.03721600
C	0.25399300	2.63673300	1.47324700

H	0.69972400	1.74472200	1.92647400
H	0.81008200	3.52231700	1.78302700
H	-0.79116100	2.72980500	1.78463500
C	1.35169000	-0.23461400	-0.14412900
C	2.28723100	0.26568900	-1.05415100
C	1.74024900	-1.17474200	0.81411400
C	3.60353800	-0.17936300	-1.00361200
H	1.97683200	0.99272700	-1.79793000
C	3.05597000	-1.62732100	0.84075000
H	1.02397300	-1.53430800	1.54580700
C	3.99276600	-1.13183800	-0.06334000
H	4.32579800	0.21376500	-1.71305400
H	3.35069200	-2.36069600	1.58545400
H	5.01996100	-1.48213900	-0.03321000
C	-0.31000000	1.56512100	-0.54424100

E = –745.794420 hartree
ZPE = +0.230132 hartree
ΔG = +0.188899 hartree
G = –745.605521 hartree
G_{qh} = –745.605868 hartree

INT-1B (EtOH / NHC-1 adduct)

C	-2.25286100	0.39804200	-0.35957300
C	-1.32897700	-0.60527900	-0.05386200
C	-1.76010000	-1.85532500	0.36740800
C	-3.14086300	-2.05091600	0.49191800
C	-4.05137200	-1.03757300	0.19859100
C	-3.61478600	0.21781100	-0.24463100
H	-1.06156700	-2.65461000	0.58740300
H	-3.50471200	-3.01889800	0.82270600
H	-5.11581100	-1.22136200	0.30589800
H	-4.30958600	1.01367900	-0.49065100
O	-1.60672700	1.52010500	-0.79098300
N	-0.07385400	-0.06305000	-0.31038500
O	0.58423000	2.21334300	-0.51067400
C	0.57493900	2.53818900	0.90292000
H	0.81021800	1.63423400	1.47683400
H	-0.42883100	2.87748600	1.18097900
C	1.18069600	-0.69606200	-0.21248800
C	2.14800900	-0.47538100	-1.19733100
C	1.47059100	-1.51574700	0.88186900
C	3.39590600	-1.07802700	-1.08448400
H	1.91493000	0.15914000	-2.04646900
C	2.71675600	-2.12836100	0.97277700
H	0.73416100	-1.65688100	1.66634700
C	3.68460800	-1.91173300	-0.00535800
H	4.14287300	-0.90243400	-1.85308800
H	2.93429800	-2.76637900	1.82425800
H	4.65816600	-2.38569700	0.07421900
C	-0.24218500	1.22305600	-0.88739100
C	1.60680300	3.61595600	1.13548900
H	1.37009600	4.51449200	0.55683400
H	1.62632600	3.88361900	2.19699100
H	2.60340900	3.26548100	0.84856200

E = –785.113258 hartree
ZPE = +0.258489 hartree
ΔG = +0.215289 hartree
G = –784.897969 hartree
G_{qh} = –784.898127 hartree

INT-1C (*i*-PrOH / NHC-1 adduct)

C	-2.30047600	0.18548500	-0.41279800
C	-1.36664600	-0.80111100	-0.08323900
C	-1.78188100	-2.02555400	0.42075500
C	-3.15774300	-2.21346200	0.60038100
C	-4.07822900	-1.21734100	0.28080000
C	-3.65758700	0.01218600	-0.24362600
H	-1.07443200	-2.81057000	0.66299100
H	-3.50978200	-3.16160400	0.99516500
H	-5.13848100	-1.39438400	0.43182800
H	-4.36103400	0.79413200	-0.50894300
O	-1.66949000	1.28271300	-0.92282700
N	-0.12150800	-0.27568800	-0.41022800
O	0.53862100	1.97960700	-0.76255100
C	0.63675300	2.39217800	0.64021500
H	0.15603400	1.61947800	1.25110600
C	1.14296800	-0.87750300	-0.26212700
C	2.10826200	-0.71509800	-1.26004500
C	1.44958300	-1.59359100	0.89795000
C	3.37273900	-1.26812100	-1.09216500
H	1.86311600	-0.15842700	-2.15881800
C	2.71244200	-2.15957400	1.04476500
H	0.71373100	-1.68782500	1.68990100
C	3.67975000	-1.99712100	0.05568900
H	4.11904100	-1.13552400	-1.86994600
H	2.94344800	-2.71611300	1.94828500
H	4.66671900	-2.43232300	0.17923200
C	-0.30545700	0.97912100	-1.04936700
C	2.11289000	2.46792800	0.98058200
H	2.61688800	3.19738100	0.33664800
H	2.24241900	2.78066200	2.02219300
H	2.59369600	1.49358300	0.84806300
C	-0.08865800	3.71445400	0.80924100
H	0.36695400	4.48420600	0.17640800
H	-1.14336800	3.61620300	0.53640600
H	-0.02969600	4.04513100	1.85204800

E = –824.431707 hartree
ZPE = +0.286265 hartree
ΔG = +0.241796 hartree
G = –824.189911 hartree
G_{qh} = –824.189977 hartree

INT-1D (*t*-BuOH / NHC-1 adduct)

C	-2.26539000	0.01105500	-0.47935500
C	-1.33930200	-0.97280600	-0.11906200
C	-1.77221700	-2.19305500	0.38186700
C	-3.15273400	-2.37743800	0.52741800
C	-4.06337400	-1.38210400	0.18014500
C	-3.62634700	-0.15717800	-0.34161300
H	-1.07563100	-2.98056800	0.64536500
H	-3.51564500	-3.32300300	0.91860900
H	-5.12741100	-1.55595300	0.30614300
H	-4.32042800	0.62469700	-0.63086500
O	-1.62388800	1.10310800	-0.98827700
N	-0.08604100	-0.44910000	-0.41434700
O	0.59215500	1.80616900	-0.82728500
C	0.57773400	2.58335500	0.43431800
C	1.17001300	-1.06188800	-0.26186000
C	2.15964600	-0.86957000	-1.23165100
C	1.44710500	-1.83076600	0.87276900
C	3.41152600	-1.45036800	-1.06507100
H	1.94127000	-0.27233600	-2.11081700
C	2.69876800	-2.42195600	1.01806900
H	0.69719000	-1.94784300	1.64802300
C	3.68644600	-2.23455900	0.05437100
H	4.17386100	-1.29630600	-1.82321100
H	2.90398800	-3.01948400	1.90146700
H	4.66389900	-2.69126800	0.17599500
C	-0.25845500	0.80443900	-1.06504300
C	0.18085000	1.73683700	1.63915500
H	0.85398300	0.88486200	1.77308700
H	0.24675600	2.36303100	2.53551000
H	-0.84896800	1.37284200	1.56957900
C	-0.37749900	3.75678500	0.24475400
H	-0.10603900	4.32836800	-0.64877800
H	-1.40891800	3.40974300	0.13709800
H	-0.32609800	4.42532100	1.11129400
C	2.01802200	3.06006500	0.56447700
H	2.31313200	3.63678100	-0.31822800
H	2.12621500	3.69925800	1.44692400
H	2.69625900	2.20625100	0.66560200

E = –863.746834 hartree
ZPE = +0.314052 hartree
ΔG = +0.269011 hartree
G = –863.477823 hartree
G_{qh} = –863.477972 hartree

TS-1A (MeOH / NHC-1 scission)

C	-2.22271200	0.44403800	-0.21154300
C	-1.19925600	-0.49518500	-0.07389900
C	-1.49061700	-1.83994600	0.09770800
C	-2.84251500	-2.19988500	0.14386700
C	-3.85612500	-1.25159200	0.01544500
C	-3.55766600	0.10400500	-0.17300200
H	-0.70799000	-2.58463100	0.19049300
H	-3.10177500	-3.24521200	0.28072100
H	-4.89465300	-1.56448300	0.05586300
H	-4.33369400	0.85329200	-0.28590300
O	-1.69255500	1.68908200	-0.40668900
N	-0.00769900	0.21805100	-0.19050600
O	0.44193400	2.53853500	-0.25404500
C	0.72962500	2.91714200	1.50790800
H	-0.25482900	3.17713500	1.88818000
H	1.15332200	1.99971100	1.90975100
H	1.42547100	3.74692700	1.42987000
C	1.31020600	-0.29070100	-0.14525400
C	2.25044200	0.12966100	-1.08861200
C	1.66950700	-1.20323300	0.84886300
C	3.54862500	-0.36498600	-1.03109700
H	1.96182500	0.83599800	-1.85979600
C	2.96674900	-1.70655500	0.88324900
H	0.94450900	-1.50540400	1.59789900
C	3.91083200	-1.28822700	-0.05145700
H	4.27753500	-0.03380800	-1.76480700
H	3.24089100	-2.41852100	1.65598500
H	4.92397600	-1.67691200	-0.01575000
C	-0.31305000	1.55689900	-0.46602600

E = –745.770733 hartree
ZPE = +0.225986 hartree
ΔG = +0.184282 hartree
G = –745.586451 hartree
G_{qh} = –745.586839 hartree

TS-1B (EtOH / NHC-1 scission**)**

C	-2.34031600	0.60220600	-0.23727000
C	-1.46556900	-0.47466500	-0.07765700
C	-1.94478200	-1.73620200	0.24044700
C	-3.32825400	-1.87135800	0.40790900
C	-4.19135300	-0.78787300	0.25481000
C	-3.70432400	0.48260400	-0.08048500
H	-1.27942800	-2.58504300	0.35290300
H	-3.73278600	-2.84674000	0.66036500
H	-5.25921700	-0.92641000	0.39154600
H	-4.36345700	1.33396300	-0.21219700
O	-1.64338800	1.72630800	-0.58049000
N	-0.19279400	0.02454400	-0.34109000
O	0.60729900	2.23100000	-0.62533300
C	1.14187300	2.66333000	1.08669400
H	0.47640800	2.06053000	1.70367200
H	0.89590100	3.72230100	1.09511600
C	1.03966400	-0.66031900	-0.27185900
C	1.99555300	-0.46941500	-1.27213200
C	1.31326300	-1.49611600	0.81286300
C	3.22516800	-1.11154100	-1.17833900
H	1.77388200	0.18116800	-2.11142300

C	2.54073800	-2.14815400	0.88574800
H	0.57936700	-1.61955900	1.60304800
C	3.50204400	-1.95557000	-0.10394300
H	3.96753900	-0.95709200	-1.95578500
H	2.74921400	-2.79772700	1.73065500
H	4.46190000	-2.45869800	-0.03806800
C	-0.30501900	1.37224100	-0.71489000
C	2.59379100	2.31776800	1.13817500
H	3.14026100	2.80053100	0.32035600
H	3.04042600	2.66420300	2.08161900
H	2.75339700	1.23668100	1.07197500

E = –785.091568 hartree
ZPE = +0.254540 hartree
ΔG = +0.211367 hartree
G = –784.880201 hartree
G_{qh} = –784.880540 hartree

TS-1C (*i*-PrOH / NHC-1 scission**)**

C	2.34442700	0.51113100	0.33543800
C	1.56167300	-0.61420700	0.06582700
C	2.14204000	-1.78928700	-0.38653700
C	3.53019500	-1.78767300	-0.57186800
C	4.30049500	-0.65709900	-0.30723800
C	3.71155600	0.52488600	0.16251300
H	1.54977700	-2.67528600	-0.58712500
H	4.01238600	-2.69290100	-0.92800900
H	5.37455900	-0.68865300	-0.46100000
H	4.29762000	1.41079100	0.38238600
O	1.56058000	1.52967700	0.79764300
N	0.25519900	-0.25662400	0.38558700
O	-0.72661300	1.83260100	0.89462500
C	-1.29785600	2.40951500	-0.78216800
H	-0.63644100	1.82730200	-1.42484200
C	-0.91585200	-1.03280100	0.25354400
C	-1.86834100	-1.02715900	1.27540400
C	-1.13769600	-1.77253000	-0.91005700
C	-3.04156500	-1.75780300	1.12544700
H	-1.68770700	-0.44960300	2.17575000
C	-2.30778400	-2.51502400	-1.04041500
H	-0.40979900	-1.75104400	-1.71512500
C	-3.26505900	-2.50761700	-0.02841400
H	-3.78119900	-1.74707500	1.92067800
H	-2.47567300	-3.08905700	-1.94688900
H	-4.18072900	-3.08054500	-0.13859100
C	0.25591300	1.05094200	0.90000300
C	-2.73250100	1.98652900	-0.81189100
H	-3.27812900	2.40726100	0.04113100
H	-3.22190500	2.35005200	-1.72784600
H	-2.83379100	0.89707400	-0.78706500
C	-1.00797600	3.87677500	-0.74757800
H	-1.55047400	4.36162600	0.07242100
H	0.06155600	4.07020800	-0.62036600
H	-1.32819600	4.35650600	-1.68481400

E = –824.411851 hartree
ZPE = +0.282662 hartree
ΔG = +0.237889 hartree
G = –824.173962 hartree
G_{qh} = –824.174168 hartree

TS-1D (*t*-BuOH / NHC-1 scission**)**

C	-2.35090700	0.53515100	-0.43349700
C	-1.64871300	-0.63560200	-0.13347100
C	-2.30932700	-1.74753500	0.36744900
C	-3.69057200	-1.63602800	0.57092800
C	-4.37859900	-0.46079700	0.27760500
C	-3.71019400	0.65675800	-0.24156900
H	-1.78280000	-2.66884300	0.59067800
H	-4.23259000	-2.49035400	0.96491800
H	-5.44938000	-0.40612400	0.44719500
H	-4.23234300	1.57611100	-0.48427800
O	-1.50442000	1.47647600	-0.94397600
N	-0.32538500	-0.38994300	-0.48345500
O	0.80427300	1.62580000	-1.03703400
C	1.47523400	2.31794300	0.54429000
C	0.79178500	-1.23007600	-0.30735000
C	1.76517400	-1.30463400	-1.30725700
C	0.94890300	-1.95010300	0.87956700
C	2.89162300	-2.09543000	-1.11296700
H	1.63719000	-0.74043100	-2.22482900
C	2.07307600	-2.75225000	1.05491700
H	0.20733100	-1.86789000	1.66794300
C	3.04950900	-2.82565400	0.06438200
H	3.64679800	-2.14731000	-1.89184000
H	2.18968300	-3.31003900	1.97940300
H	3.92912800	-3.44552900	0.20895000
C	-0.23099800	0.90882000	-1.02015100
C	0.51720700	1.93600900	1.63812100
H	0.48363000	0.85263400	1.79241700
H	0.84687100	2.39007100	2.58450000
H	-0.49555700	2.30104800	1.43837500
C	1.49763300	3.77924700	0.19844700
H	2.08165700	3.95964300	-0.71016100
H	0.48512200	4.16689500	0.04541300
H	1.96005700	4.35481800	1.01412400
C	2.82194100	1.65585900	0.61103300
H	3.37716400	1.80018900	-0.32195600
H	3.41689000	2.09491900	1.42587500
H	2.73336800	0.58150600	0.80267500

E = –863.733373 hartree
ZPE = +0.310407 hartree
ΔG = +0.264850 hartree
G = –863.468523 hartree
G_{qh} = –863.468783 hartree

INT-2 (NHC-1 byproduct**)**

C	2.19076100	0.58045800	-0.05843900
C	1.12362400	-0.30365600	0.05375600
C	1.33398500	-1.65852900	0.24999900
C	2.66347900	-2.08487800	0.31841400
C	3.72781500	-1.18907000	0.19841000
C	3.50735800	0.17898800	0.00794500
H	0.50852200	-2.35523500	0.34634400
H	2.86903100	-3.13993000	0.46957200
H	4.74724600	-1.55678800	0.25586200
H	4.32295000	0.88808900	-0.08101500
O	1.71012000	1.85531600	-0.22605000
N	-0.02797300	0.48190800	-0.04600600
C	-1.37591900	0.02777600	-0.01680000
C	-2.28435200	0.61742300	0.85984900
C	-1.76677300	-1.01018300	-0.86066600
C	-3.60010900	0.16552500	0.88197000
H	-1.96134000	1.41919400	1.51523500
C	-3.08063500	-1.46726100	-0.81641400
H	-1.04999900	-1.45029200	-1.54705600
C	-3.99918000	-0.87887700	0.05004800
H	-4.31204500	0.62522600	1.56064000
H	-3.38686100	-2.27889100	-1.46924100
H	-5.02503300	-1.23353800	0.07718800
C	0.33878400	1.80122900	-0.22189100
O	-0.35883000	2.77407800	-0.35927100

E = –705.982014 hartree
ZPE = +0.192411 hartree
ΔG = +0.154570 hartree
G = –705.827444 hartree
G_{qh} = –705.827748 hartree

INT-3A (*p*-CN NHC adduct**)**

C	-2.79804600	0.15885400	-0.24588100
C	-1.63603300	-0.59860300	-0.08453600
C	-1.71114200	-1.97461000	0.07992000
C	-2.98656500	-2.54952900	0.10982300
C	-4.13903800	-1.77877500	-0.03178100
C	-4.06075400	-0.39455300	-0.22356300
H	-0.82509400	-2.59159400	0.17218900
H	-3.07275300	-3.62350300	0.24233700
H	-5.11345300	-2.25601500	-0.00359000
H	-4.94537900	0.21933700	-0.35387800
O	-2.48623800	1.47237500	-0.44883200
N	-0.57420700	0.30257900	-0.19553500
O	-0.57223400	2.67107300	0.03624000
C	-0.67225200	2.71783900	1.47403600
H	-0.11639200	1.89017800	1.92730700
H	-0.23017700	3.66712500	1.77782500
H	-1.71975400	2.67998300	1.78788300
C	0.79801500	0.03974800	-0.15501700
C	1.66645900	0.77000500	-0.97822900
C	1.31118100	-0.92084800	0.72607000
C	3.02898300	0.53453700	-0.92896900
H	1.26813800	1.50916100	-1.66408300
C	2.67384800	-1.16569800	0.76573800
H	0.65277500	-1.45232100	1.40331400
C	3.53939400	-0.43963300	-0.06098500
H	3.69957500	1.09490300	-1.57175200
H	3.07037200	-1.90723100	1.45106200
C	-1.09940100	1.57860000	-0.54098300
C	4.94906400	-0.68838800	-0.01472500
N	6.09101300	-0.88990500	0.02219400

E = –838.029195 hartree
ZPE = +0.229081 hartree
ΔG = +0.185723 hartree
G = –837.843471 hartree
G_{qh} = –837.843860 Hartree

TS-3A (*p*-CN NHC scission**)**

C	-2.83111300	0.16268500	-0.18491700
C	-1.67081400	-0.60481100	-0.08457600
C	-1.74459100	-1.98267500	0.05357300
C	-3.02159000	-2.55096800	0.11518600
C	-4.17382800	-1.77083700	0.03038300
C	-4.09583600	-0.38296900	-0.13188000
H	-0.85692600	-2.60245000	0.10459900
H	-3.11034600	-3.62687100	0.22843300
H	-5.14922500	-2.24394000	0.08235000
H	-4.98120900	0.23785100	-0.21480900
O	-2.51168000	1.47942000	-0.36769000
N	-0.60714300	0.29480300	-0.21539300
O	-0.54148800	2.65885400	-0.25186900
C	-0.25559700	3.06367400	1.51395700
H	0.33705300	2.22978100	1.88217400
H	0.28028500	4.00298800	1.42019800
H	-1.25694000	3.14177700	1.92884500
C	0.76793500	0.02188800	-0.16378600
C	1.64530500	0.70347400	-1.01670100
C	1.26142000	-0.91883000	0.74768100
C	3.00327700	0.44283700	-0.96052100
H	1.26148800	1.42710400	-1.72576600
C	2.61933400	-1.18927400	0.79484600
H	0.59117100	-1.41826800	1.43789500
C	3.49613200	-0.50861400	-0.05784700
H	3.68352100	0.96546100	-1.62450700
H	3.00279800	-1.91515800	1.50387100
C	-1.13486700	1.57300200	-0.45597900
C	4.90132400	-0.78222300	-0.00436000
N	6.03924800	-1.00375000	0.03865500

E = –838.005138 hartree
ZPE = +0.224713 hartree
ΔG = +0.180805 hartree

G = –837.824333 hartree
G_{qh} = –837.824741 hartree

INT-4A (*p*-CN NHC byproduct)

C	-2.84546600	0.39599400	0.05904800
C	-1.68619300	-0.36139600	-0.05863300
C	-1.74504300	-1.73041900	-0.26221400
C	-3.01848700	-2.30298000	-0.32295400
C	-4.17593700	-1.53323200	-0.19267900
C	-4.10923000	-0.14981300	-0.00115400
H	-0.84973800	-2.33195300	-0.37194200
H	-3.10443200	-3.37378700	-0.47781000
H	-5.14777500	-2.01326000	-0.24450100
H	-4.99826000	0.46390900	0.09219700
O	-2.51421600	1.71900800	0.22141900
N	-0.63014300	0.55470700	0.03104100
C	0.75634300	0.26809400	0.01932800
C	1.61309300	1.03955000	-0.76649200
C	1.24611000	-0.78482400	0.79265400
C	2.97050700	0.75843000	-0.77682000
H	1.21899800	1.85020700	-1.36773100
C	2.60105700	-1.07902700	0.77105900
H	0.57529100	-1.36376400	1.41818200
C	3.46388800	-0.30497000	-0.01210500
H	3.64520800	1.35150800	-1.38451600
H	2.99060000	-1.89626400	1.36809600
C	-1.15010000	1.82628100	0.20776200
O	-0.56714900	2.87135700	0.34207000
C	4.86706100	-0.60388300	-0.03033700
N	6.00091500	-0.84561300	-0.04513700

E = –798.214623 hartree
ZPE = +0.190972 hartree
ΔG = +0.150819 hartree
G = –798.063804 hartree
G_{qh} = –798.064081 hartree

INT-3B (*p*-CF_3 NHC adduct)

C	-3.51151800	0.05846100	-0.26357100
C	-2.30523600	-0.62135700	-0.08027500
C	-2.29312900	-1.99729100	0.09926500
C	-3.52894300	-2.65401300	0.11709500
C	-4.72666800	-1.96126100	-0.04924300
C	-4.73556500	-0.57595700	-0.25282900
H	-1.36836700	-2.55057200	0.21509900
H	-3.54747100	-3.72990500	0.26075700
H	-5.66838100	-2.50062700	-0.03009600
H	-5.65646200	-0.02220200	-0.40049000
O	-3.28052400	1.38783400	-0.47137400
N	-1.30286900	0.34323400	-0.18124500
O	-1.45170600	2.70813900	0.03314800
C	-1.57149700	2.75306700	1.46883000
H	-0.97237700	1.96178200	1.93200000
H	-1.19100200	3.72812800	1.77475900
H	-2.61849600	2.65311700	1.77098700
C	0.08667700	0.15870800	-0.13585700
C	0.91192600	0.89860000	-0.99042700
C	0.65322300	-0.73282100	0.78072200
C	2.28763000	0.74032400	-0.93092800
H	0.47291600	1.58730200	-1.70396900
C	2.03062900	-0.89919800	0.82226500
H	0.02583700	-1.27387300	1.48011500
C	2.85085800	-0.16149200	-0.02832300
H	2.92015900	1.31621300	-1.59854900
H	2.46150500	-1.59241800	1.53674300
C	-1.89995100	1.58064500	-0.54551900
C	4.33497700	-0.37147200	-0.01499600
F	4.72435600	-1.29063100	-0.92438900
F	4.77918800	-0.80372300	1.17898700
F	5.00974500	0.75690700	-0.30349700

E = –1082.853882 hartree
ZPE = +0.234714 hartree
ΔG = +0.187643 hartree
G = –1082.666239 hartree
G_{qh} = –1082.666066 Hartree

TS-3B (*p*-CF_3 NHC scission)

C	-3.53945100	0.04577800	-0.20376600
C	-2.32876500	-0.63635200	-0.07985700
C	-2.30516900	-2.01390300	0.07588300
C	-3.53905000	-2.67220400	0.12550500
C	-4.74275900	-1.97797800	0.01413800
C	-4.76209700	-0.58913700	-0.16202500
H	-1.37426300	-2.56422800	0.15177500
H	-3.55236000	-3.75032500	0.25142300
H	-5.68238100	-2.51950600	0.05696000
H	-5.68861800	-0.03469300	-0.26385200
O	-3.31032500	1.38047200	-0.39309300
N	-1.33101100	0.33325800	-0.20216600
O	-1.42709200	2.69529600	-0.25502900
C	-1.20345600	3.12445100	1.51006400
H	-0.54470200	2.34652400	1.88856300
H	-0.75101600	4.10749600	1.42375000
H	-2.21248100	3.11483300	1.91366700
C	0.06290800	0.15044200	-0.14600800
C	0.89143400	0.84092600	-1.03616700
C	0.61794800	-0.70788800	0.80646900
C	2.26535800	0.66991500	-0.97053800
H	0.45941600	1.50393800	-1.77677800
C	1.99388900	-0.88811400	0.85472900
H	-0.01769300	-1.21513200	1.52386700
C	2.81941700	-0.19670900	-0.02822300
H	2.90391000	1.20725000	-1.66414300
H	2.41809600	-1.55547700	1.59708200

C	-1.94040800	1.56917400	-0.46382800
C	4.30232000	-0.41814500	-0.00858900
F	4.68623300	-1.34635300	-0.91068100
F	4.74014300	-0.84385400	1.18952200
F	4.98537800	0.70341000	-0.30427300

E = –1082.829931 hartree
ZPE = +0.230055 hartree
ΔG = +0.182117 hartree
G = –1082.647814 hartree
G_{qh} = –1082.647577 hartree

INT-4B (*p*-CF_3 NHC byproduct)

C	-3.60467700	0.32188500	0.04737600
C	-2.40485100	-0.37252300	-0.05208700
C	-2.38603800	-1.74389500	-0.24553000
C	-3.62560400	-2.38532400	-0.31978300
C	-4.82476000	-1.67863800	-0.21047100
C	-4.83592900	-0.29245600	-0.02596300
H	-1.45671200	-2.29508600	-0.33673900
H	-3.65140300	-3.46015600	-0.46851000
H	-5.76834900	-2.21100500	-0.27254600
H	-5.75825900	0.27221500	0.05256800
O	-3.34607500	1.66099700	0.20793800
N	-1.40114200	0.59766900	0.04694800
C	0.00065000	0.38205000	0.03740900
C	0.81287500	1.15748800	-0.78656000
C	0.54873600	-0.60845400	0.85196800
C	2.18533500	0.94278400	-0.79221400
H	0.37555300	1.92072600	-1.41983700
C	1.91842600	-0.83005600	0.83063900
H	-0.08880800	-1.19395900	1.50603600
C	2.73565400	-0.05140800	0.01249800
H	2.81841000	1.54713400	-1.43219800
H	2.34676700	-1.60110900	1.46258500
C	-1.98775400	1.83964200	0.21028000
O	-1.46292900	2.91536700	0.34459400
C	4.21015600	-0.33469300	-0.02562700
F	4.70533900	-0.58280500	1.20110100
F	4.91679400	0.68560400	-0.53928800
F	4.49003600	-1.41966300	-0.77646300

E = –1043.040050 hartree
ZPE = +0.196692 hartree
ΔG = +0.152792 hartree
G = –1042.887259 hartree
G_{qh} = –1042.886980 hartree

INT-3C (*p*-Cl NHC adduct)

C	-2.92514900	0.13122900	-0.26696000
C	-1.74849300	-0.59690000	-0.07378200
C	-1.79229800	-1.97063600	0.11614900
C	-3.05379600	-2.57718000	0.12837800
C	-4.22134500	-1.83781400	-0.05128500
C	-4.17347300	-0.45386100	-0.26153400
H	-0.89035400	-2.55805800	0.24499600
H	-3.11705400	-3.65054800	0.27853500
H	-5.18416300	-2.33874100	-0.03654500
H	-5.07096400	0.13494000	-0.41777500
O	-2.63739400	1.44934500	-0.47632000
N	-0.70782200	0.32431500	-0.16919300
O	-0.75646500	2.69310000	0.03901500
C	-0.87728900	2.74097700	1.47415700
H	-0.30366700	1.93133700	1.93797600
H	-0.46782500	3.70376500	1.78180500
H	-1.92733700	2.67301800	1.77499000
C	0.67525100	0.07410200	-0.13711200
C	1.52141500	0.73602400	-1.03122400
C	1.21180700	-0.80743900	0.80478600
C	2.89192900	0.51603900	-0.98911100
H	1.10591400	1.41726100	-1.76632800
C	2.58083600	-1.04629300	0.83678200
H	0.56859100	-1.29361200	1.53024900
C	3.40814700	-0.38006400	-0.05937000
H	3.54632800	1.02975600	-1.68510200
H	2.99504500	-1.73293000	1.56716100
C	-1.24794000	1.58364900	-0.54117600
Cl	5.13844200	-0.67040900	-0.01290400

E = –1205.402475 hartree
ZPE = +0.220601 hartree
ΔG = +0.177382 hartree
G = –1205.225094 hartree
G_{qh} = –1205.225380 Hartree

TS-3C (*p*-Cl NHC scission)

C	-2.95664000	0.13258600	-0.20602800
C	-1.78044900	-0.60721400	-0.07600300
C	-1.82305300	-1.98323200	0.08819700
C	-3.08746300	-2.58143100	0.13573800
C	-4.25596400	-1.83082700	0.01594200
C	-4.20824100	-0.44302200	-0.16592700
H	-0.91916500	-2.57605700	0.17208800
H	-3.15326600	-3.65704500	0.26700600
H	-5.22070900	-2.32638100	0.05742500
H	-5.10724500	0.15425300	-0.27268100
O	-2.66131200	1.45403900	-0.39729300
N	-0.73733600	0.31161700	-0.19423500
O	-0.71493300	2.67484000	-0.25203900
C	-0.48899600	3.09700100	1.51172600
H	0.10482500	2.27560900	1.90573300
H	0.03562300	4.04395500	1.43005600
H	-1.50210900	3.16369700	1.89951600
C	0.64815500	0.05562900	-0.14851000
C	1.50074000	0.66839000	-1.06968600

C	1.16879100	-0.79930500	0.82481100
C	2.86747100	0.42779800	-1.01932400
H	1.09662900	1.33003900	-1.82768300
C	2.53399900	-1.05838200	0.86633600
H	0.51559600	-1.25178300	1.56321900
C	3.36995900	-0.43930800	-0.05492000
H	3.52977000	0.90308800	-1.73486500
H	2.93784100	-1.72421000	1.62134100
C	-1.28247100	1.57459300	-0.46250600
Cl	5.09520600	-0.75454000	0.00200500

E = –1205.378706 hartree
ZPE = +0.216163 hartree
ΔG = +0.172185 hartree
G = –1205.206521 hartree
G_{qh} = –1205.206771 hartree

INT-4C (*p*-Cl NHC byproduct)

C	-2.98409600	0.38793400	0.04907500
C	-1.81481100	-0.35667500	-0.05351200
C	-1.85246900	-1.72764300	-0.24522700
C	-3.11785400	-2.31692300	-0.31840200
C	-4.28630400	-1.56050800	-0.20822500
C	-4.23985100	-0.17498200	-0.02272500
H	-0.94600300	-2.31606000	-0.33498300
H	-3.18911700	-3.38985800	-0.46629200
H	-5.25137100	-2.05301200	-0.26968100
H	-5.13830300	0.42678400	0.05782300
O	-2.66774400	1.71404300	0.21345600
N	-0.77105100	0.56834800	0.04888700
C	0.62100800	0.29076500	0.03043600
C	1.45387000	0.99056300	-0.83951600
C	1.13912700	-0.68502800	0.87906200
C	2.81692500	0.72017100	-0.85706300
H	1.04127600	1.74242000	-1.50301500
C	2.49889500	-0.97363600	0.85266100
H	0.48631000	-1.21552900	1.56477200
C	3.32219700	-0.26325100	-0.01347100
H	3.47191400	1.26275000	-1.52982100
H	2.90846500	-1.73378200	1.50871900
C	-1.30180100	1.83294500	0.21699900
O	-0.73036800	2.88437900	0.35577600
Cl	5.03941600	-0.61599500	-0.04377300

E = –1165.589621 hartree
ZPE = +0.182729 hartree
ΔG = +0.142815 hartree
G = –1165.446807 hartree
G_{qh} = –1165.447034 hartree

INT-3D (*p*-OMe NHC adduct)

C	-2.93066500	0.17178000	-0.33624000
C	-1.77789500	-0.57695700	-0.08232000
C	-1.85676800	-1.94530100	0.13352200
C	-3.12993300	-2.52722800	0.10291000
C	-4.27358600	-1.76901700	-0.14115000
C	-4.18925800	-0.38930100	-0.37319500
H	-0.97065400	-2.54328900	0.31612300
H	-3.22190900	-3.59602300	0.27084400
H	-5.24612500	-2.25084300	-0.15901800
H	-5.06812500	0.21323800	-0.57657600
O	-2.60396100	1.47968400	-0.55076900
N	-0.71681200	0.31751500	-0.14049400
O	-0.71798600	2.68887500	0.03335000
C	-0.88665900	2.74791400	1.46235400
H	-0.33506900	1.93754300	1.95107500
H	-0.48081200	3.70989300	1.77788400
H	-1.94667700	2.68966700	1.72915600
C	0.66200200	0.02176600	-0.05262100
C	1.55515700	0.55092800	-0.98027200
C	1.14463700	-0.78073800	0.98657200
C	2.91959400	0.28914300	-0.88147700
H	1.18400100	1.17248100	-1.78941600
C	2.49759600	-1.06437200	1.07469800
H	0.46107400	-1.17348900	1.73287700
C	3.39800700	-0.52946200	0.14488800
H	3.59020900	0.71860300	-1.61683100
H	2.87822200	-1.69039300	1.87559100
C	-1.20647200	1.58084000	-0.55542400
O	4.69934400	-0.85637800	0.32399800
C	5.64592000	-0.32947700	-0.59077300
H	5.65909900	0.76687800	-0.56742300
H	6.61723600	-0.70727000	-0.26811900
H	5.44797900	-0.67014900	-1.61419200

E = –860.316097 hartree
ZPE = +0.262712 hartree
ΔG = +0.218111 hartree
G = –860.097986 hartree
G_{qh} = –860.098250 hartree

TS-3D (*p*-OMe NHC scission)

C	-2.96351300	0.17037600	-0.28187800
C	-1.80948200	-0.59015200	-0.08346300
C	-1.88680200	-1.95980500	0.11659800
C	-3.16430800	-2.53241200	0.12207100
C	-4.31060800	-1.76287800	-0.07067600
C	-4.22672800	-0.38026300	-0.28370400
H	-0.99732100	-2.56324800	0.26155500
H	-3.25863200	-3.60261100	0.27887900
H	-5.28625700	-2.23846400	-0.06096500
H	-5.10854500	0.23072500	-0.44404200

O	-2.62916000	1.48063800	-0.48497200
N	-0.74436300	0.30064700	-0.16763900
O	-0.66271400	2.66119600	-0.26389700
C	-0.52020300	3.10482700	1.49666300
H	0.04350900	2.28300800	1.93215200
H	0.01923200	4.04492100	1.43188400
H	-1.54934700	3.18913700	1.83630300
C	0.63559400	0.00180900	-0.06320400
C	1.53138600	0.47381900	-1.01746500
C	1.10649500	-0.75984800	1.01035600
C	2.89209500	0.19898200	-0.90786700
H	1.16771500	1.06311400	-1.85316500
C	2.45580400	-1.05664200	1.11098500
H	0.41614300	-1.11362100	1.76996800
C	3.36115800	-0.57592300	0.15663500
H	3.56731800	0.58461000	-1.66294000
H	2.82978200	-1.65137700	1.93833300
C	-1.24313900	1.56823400	-0.48595300
O	4.65806700	-0.90941700	0.35021400
C	5.61113000	-0.43636800	-0.58743900
H	5.63703600	0.65962100	-0.61445000
H	6.57769900	-0.81032900	-0.24673600
H	5.40939200	-0.82187700	-1.59401700

E = –860.292663 hartree
ZPE = +0.258408 hartree
ΔG = +0.213205 hartree
G = –860.079458 hartree
G_{qh} = –860.079743 hartree

INT-4D (*p*-OMe NHC byproduct)

C	-2.99601800	0.43658600	-0.01323300
C	-1.84374700	-0.34003900	-0.06165900
C	-1.91012800	-1.71206200	-0.23715300
C	-3.18688400	-2.26893400	-0.35650100
C	-4.33819300	-1.48048700	-0.30357700
C	-4.26232100	-0.09425100	-0.13026900
H	-1.01537000	-2.32367400	-0.27906200
H	-3.28130500	-3.34149200	-0.49451100
H	-5.31290100	-1.94800900	-0.39962200
H	-5.14739900	0.53118800	-0.09149000
O	-2.64886100	1.75399700	0.15487300
N	-0.78018200	0.55325400	0.08060200
C	0.60504800	0.22885100	0.11391400
C	1.47992500	0.81180700	-0.79405800
C	1.07992600	-0.68489400	1.05663500
C	2.83650300	0.49886500	-0.76392300
H	1.10539000	1.51646100	-1.52948000
C	2.42411500	-1.01606100	1.07882500
H	0.39516600	-1.13295000	1.77041500
C	3.31381200	-0.42343100	0.17233400
H	3.50081300	0.97066200	-1.47837300
H	2.80717900	-1.72809300	1.80270600
C	-1.27871600	1.83170000	0.21831000
O	-0.68478600	2.86929600	0.37071700
O	4.60512000	-0.80497800	0.28054300
C	5.54647000	-0.23278900	-0.61428800
H	6.51063600	-0.67182100	-0.35428100
H	5.30758400	-0.47645200	-1.65619100
H	5.60095100	0.85572200	-0.49554400

E = –820.504730 hartree
ZPE = +0.224952 hartree
ΔG = +0.183641 hartree
G = –820.321089 hartree
G_{qh} = –820.321255 hartree

INT-3E (*p*-NMe_2 NHC adduct)

C	-3.25972300	0.04658800	-0.29475700
C	-2.04124100	-0.61476300	-0.11410900
C	-1.99886900	-1.99490800	0.02266100
C	-3.21921900	-2.68084600	-0.01196800
C	-4.42902100	-2.01032400	-0.18289300
C	-4.46727900	-0.61701700	-0.33418900
H	-1.06018700	-2.52308000	0.14983300
H	-3.21662600	-3.76143200	0.09471600
H	-5.35790000	-2.57159100	-0.20555800
H	-5.39926000	-0.08103700	-0.47913200
O	-3.04890100	1.38757000	-0.43741700
N	-1.06096500	0.36677400	-0.14075300
O	-1.25361100	2.71506400	0.17883400
C	-1.39040000	2.67426000	1.61138400
H	-0.76496000	1.88250500	2.03779300
H	-1.05344100	3.64473500	1.97813600
H	-2.43556600	2.51577800	1.89576900
C	0.34115100	0.18102500	-0.10451000
C	1.16335800	0.80523900	-1.04174300
C	0.92682400	-0.61431600	0.87959300
C	2.54041100	0.64558100	-0.99576700
H	0.71928400	1.41939200	-1.81984100
C	2.30211000	-0.79942700	0.91672500
H	0.30485100	-1.09438200	1.62961000
C	3.15222400	-0.16057900	-0.01116200
H	3.13828000	1.14697300	-1.74748300
H	2.71096200	-1.43758800	1.69104000
C	-1.66366900	1.60591200	-0.46655700
N	4.52503400	-0.30874100	0.04879000
C	5.32920200	0.15970100	-1.06391800
H	6.38175900	-0.02528800	-0.84412500
H	5.07849900	-0.34385900	-2.01030200
H	5.20914300	1.23888500	-1.20790400
C	5.07973200	-1.35262200	0.89019400
H	6.16625000	-1.34985600	0.79017400
H	4.84656400	-1.17478800	1.94594000
H	4.71040100	-2.35368400	0.61983900

E = –879.760195 hartree
ZPE = +0.302869 hartree

ΔG = +0.255907 hartree
G = –879.504288 hartree
G_{qh} = –879.504491 Hartree

TS-3E (*p*-NMe_2 NHC scission)

C	-3.29669300	0.08701200	-0.20895400
C	-2.09355300	-0.61559300	-0.11410600
C	-2.08383800	-1.99721100	-0.00054600
C	-3.32556300	-2.64370000	0.02314300
C	-4.52125200	-1.93258200	-0.06669500
C	-4.52553400	-0.53621900	-0.19051900
H	-1.15510100	-2.55348600	0.06656000
H	-3.35230500	-3.72543700	0.11280300
H	-5.46698600	-2.46488500	-0.04525100
H	-5.44705000	0.03056600	-0.26881100
O	-3.04482000	1.42489300	-0.33685200
N	-1.08510000	0.33774900	-0.18258700
O	-1.13708100	2.70026600	-0.11800900
C	-0.94034400	3.03136700	1.65910900
H	-0.31602600	2.21435200	2.01349800
H	-0.45365900	4.00188800	1.63970600
H	-1.95599500	3.03643300	2.04655300
C	0.31368200	0.10819800	-0.16181200
C	1.13645700	0.64456300	-1.15022900
C	0.88762200	-0.64573200	0.86004300
C	2.50714800	0.43522000	-1.11967300
H	0.70206100	1.24068800	-1.94711800
C	2.25521700	-0.88040100	0.88454900
H	0.26179300	-1.04836100	1.65146500
C	3.10560200	-0.35130800	-0.11050600
H	3.11108000	0.88411500	-1.89907300
H	2.65880300	-1.47128100	1.69792700
C	-1.66581700	1.59192500	-0.39110200
N	4.46390400	-0.59891100	-0.10089500
C	5.32337100	0.15922600	-0.99061100
H	6.35523300	-0.16767700	-0.85216100
H	5.06018900	-0.02009400	-2.03881200
H	5.27492400	1.24290700	-0.80386000
C	5.06178000	-1.17925000	1.08694000
H	6.13471500	-1.29296100	0.92538100
H	4.91040400	-0.55777400	1.98263600
H	4.65178600	-2.17524000	1.28764700

E = –879.736992 hartree
ZPE = +0.298481 hartree
ΔG = +0.250954 hartree
G = –879.486038 hartree
G_{qh} = –879.486282 hartree

INT-4E (*p*-NMe_2 NHC byproduct)

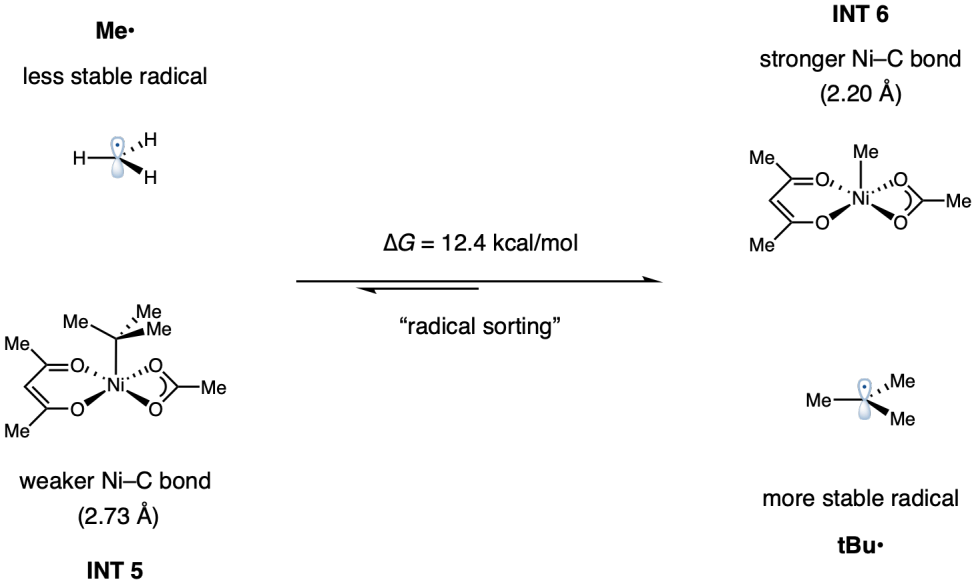
C	3.35098500	0.31193800	-0.03993600
C	2.14318900	-0.36661200	0.07898000
C	2.10581300	-1.72500000	0.34423800
C	3.33738900	-2.37223300	0.48212700
C	4.54532300	-1.68236600	0.35910800
C	4.57414200	-0.30882300	0.09327300
H	1.16614600	-2.25848100	0.43944000
H	3.35091700	-3.43757900	0.69014300
H	5.48244700	-2.21806900	0.47183100
H	5.50430600	0.24052100	-0.00176300
O	3.10251400	1.63788800	-0.29247700
N	1.14868300	0.59351900	-0.10943700
C	-0.25816500	0.37411800	-0.08673000
C	-1.05775800	1.02289800	0.84990400
C	-0.84213200	-0.51087600	-0.98893900
C	-2.42659400	0.80528900	0.87768800
H	-0.60620000	1.70314600	1.56568600
C	-2.20766200	-0.75109300	-0.95696300
H	-0.22332000	-1.02192700	-1.72125800
C	-3.04301200	-0.08660700	-0.03012600
H	-3.01507700	1.32855400	1.62161200
H	-2.62288500	-1.45564800	-1.66741500
C	1.73963300	1.81640300	-0.34137900
O	1.22469100	2.88536200	-0.55468500
N	-4.40206000	-0.29581400	-0.01459200
C	-5.19611600	0.25797800	1.06547400
H	-6.24303200	-0.00415900	0.90813800
H	-4.88844400	-0.12350300	2.05029300
H	-5.12827900	1.35172100	1.08524200
C	-4.96891600	-1.36047200	-0.82054200
H	-6.04875200	-1.38599900	-0.66843900
H	-4.78835000	-1.18867800	-1.88803300
H	-4.56020800	-2.34708200	-0.55703800

E = –839.949568 hartree
ZPE = +0.265445 hartree
ΔG = +0.221911 hartree
G = –839.727657 hartree
G_{qh} = –839.727824 hartree

Nickel-catalyzed radical sorting

Quantum chemical calculations were performed using *Gaussian 16.*[13] Molecular geometries were optimized using the dispersion-corrected spin-unrestricted UB3LYP[19]-D3[20] functional and the def2-SVP[21] basis set. Solvation effects were included in the geometry optimizations using the SMD solvation model[15] with DMSO as the solvent. Frequency calculations were also performed at the same level of theory to characterize stationary points as minima (no imaginary frequencies). Single point energies were refined using the larger def2TZVP basis set in implicit solvent. These methods have been previously used to model nickel complexes of the type Ni(acac)(X), where acac is used a model system for the THMD (2,2,6,6-tetramethylheptanedione) ligand.[22] Gibbs free energies at 298 K were corrected using Grimme's quasiharmonic entropy approximation[16] and Head-Gordon's quasiharmonic enthalpy correction,[17] as implemented in Paton's GoodVibes software package.[18]

Figure S23. Radical sorting by a nickel catalyst preferentially binds and stabilizes the less-substituted alkyl radical due to differences in Ni–C bond strengths and radical stabilities.



Cartesian coordinates, energies, and vibrational frequencies. The following geometries were optimized at the B3LYP-D3/def2TZVP/SMD(DMSO)//B3LYP-D3/defSVP/SMD(DMSO) level of theory, as described above. Electronic energy (*E*), zero-point energy correction (ZPE), standard thermal correction to free energy (Δ*G*), sum of electronic and thermal free energies (*G*), and the sum of electronic and quasi-harmonic thermal free energies (G_{qh}) are listed in hartrees. Imaginary frequencies are listed for transition states in wavenumbers (cm^{-1}).

Methyl radical (Me•)

C	0.00002900	0.00000000	0.00005200
H	-0.54028400	-0.95040900	-0.00006200
H	-0.55316800	0.94297300	-0.00005800
H	1.09327600	0.00743800	-0.00019300

E = –39.855366 hartree
ZPE = +0.029200 hartree
ΔG = +0.009359 hartree
G = –39.846007 hartree
G_{qh} = –39.846009 hartree

tert-Butyl radical (tBu•)

C	-0.00026000	-0.00017000	-0.17243900
C	0.97827500	-1.11574700	0.01591000
H	0.61562800	-2.06352800	-0.41840200
H	1.96199100	-0.88388300	-0.42810800
H	1.16266000	-1.31673200	1.09583000
C	-1.45578500	-0.28901900	0.01593800
H	-2.09474400	0.49574500	-0.42497300
H	-1.74604200	-1.26004300	-0.42148300
H	-1.72369800	-0.33996400	1.09587500
C	0.47748500	1.40476200	0.01588900
H	-0.21910700	2.14180700	-0.41997600
H	0.56908600	1.66142900	1.09586400
H	1.47593400	1.56621600	-0.42641300

E = –157.867194 hartree
ZPE = +0.115325 hartree
ΔG = +0.085940 hartree
G = –157.781254 hartree
G_{qh} = –157.781520 hartree

INT 5

Ni	0.28271600	-0.49971700	-0.41769500
O	1.84110200	-1.50487400	0.14900800
C	2.52846100	-0.85020900	-0.69915300
O	1.88441700	-0.01122800	-1.40824200
C	0.80292900	1.55258800	1.29996700
C	4.00545400	-1.02119600	-0.82417200
H	4.31077100	-2.01493700	-0.46972900
H	4.32259100	-0.86295600	-1.86441600
H	4.49698600	-0.25920600	-0.19595000
O	-0.95496700	-1.35567300	0.64661300
O	-0.93461200	0.53207100	-1.34342300
C	-2.21797500	-1.16425200	0.62851200
C	-2.20014000	0.53589600	-1.16551100
C	-2.87633400	-0.26358100	-0.22719100
H	-3.96053600	-0.18116000	-0.16005800
C	-2.96265400	1.49673700	-2.03708700
H	-2.66257700	1.35907400	-3.08801500
H	-4.05029600	1.37883400	-1.94393300
H	-2.68863600	2.52764000	-1.75503500
C	-2.99948700	-1.97832200	1.62393400
H	-2.69985800	-1.68040800	2.64290300
H	-4.08441200	-1.84858700	1.51652500
H	-2.74121700	-3.04353900	1.51089200
C	-0.47896300	1.48720700	2.07095500
H	-0.58094800	0.53567800	2.61671000
H	-0.52728800	2.30162000	2.82818800
H	-1.36006800	1.60570000	1.42045400
C	0.94264800	2.63137700	0.27105900
H	1.78532900	2.43156700	-0.40961600
H	0.03182700	2.72861800	-0.34001100
H	1.12911700	3.61898600	0.74933900
C	2.04450400	1.09864900	2.00391400
H	2.91330700	1.05616600	1.32739500
H	2.31337200	1.80224100	2.82327600
H	1.91830500	0.10500400	2.46351900

E = –2240.301333 hartree
ZPE = +0.282204 hartree
ΔG = +0.229940 hartree
G = –2240.071394 hartree
G_{qh} = –2240.071592 hartree

INT 6

Ni	-0.48606600	0.00027300	-0.04184100
O	-2.09744400	1.07970000	-0.21795800
C	-2.77396500	0.00233200	-0.27199000
O	-2.09916900	-1.07668600	-0.21791500
C	-0.44920100	0.00012800	2.15449400
H	0.61765800	0.00764200	2.41414900
H	-0.98107000	0.91569100	2.44352300
H	-0.96785500	-0.92320900	2.44276500
C	-4.25882600	0.00026500	-0.41029100
H	-4.67803100	0.96218800	-0.08624400
H	-4.51270900	-0.15789400	-1.47213100
H	-4.69117600	-0.82836700	0.16861400
O	0.74495800	1.37551800	-0.20467300
O	0.74410900	-1.37582700	-0.20450100
C	2.01451900	1.23536900	-0.17008900
C	2.01373900	-1.23626300	-0.17006700
C	2.68160800	-0.00063600	-0.10902200
H	3.77046600	-0.00098900	-0.08178000
C	2.79364700	-2.52187200	-0.21915700
H	2.54476800	-3.06043900	-1.14849800
H	3.87806400	-2.35781300	-0.17296900
H	2.48191600	-3.16555500	0.61961900
C	2.79498300	2.52061600	-0.21934800
H	2.48415500	3.16404200	0.61995300
H	3.87936000	2.35605800	-0.17400800
H	2.54562600	3.05972000	-1.14824700

E = –2122.307759 hartree
ZPE = +0.198601 hartree
ΔG = +0.151995 hartree
G = –2122.155764 hartree
G_{qh} = –2122.155795 hartree

11) Spectral data for new compounds

Figure S24. ^{1}H NMR spectrum of **SI-1**.

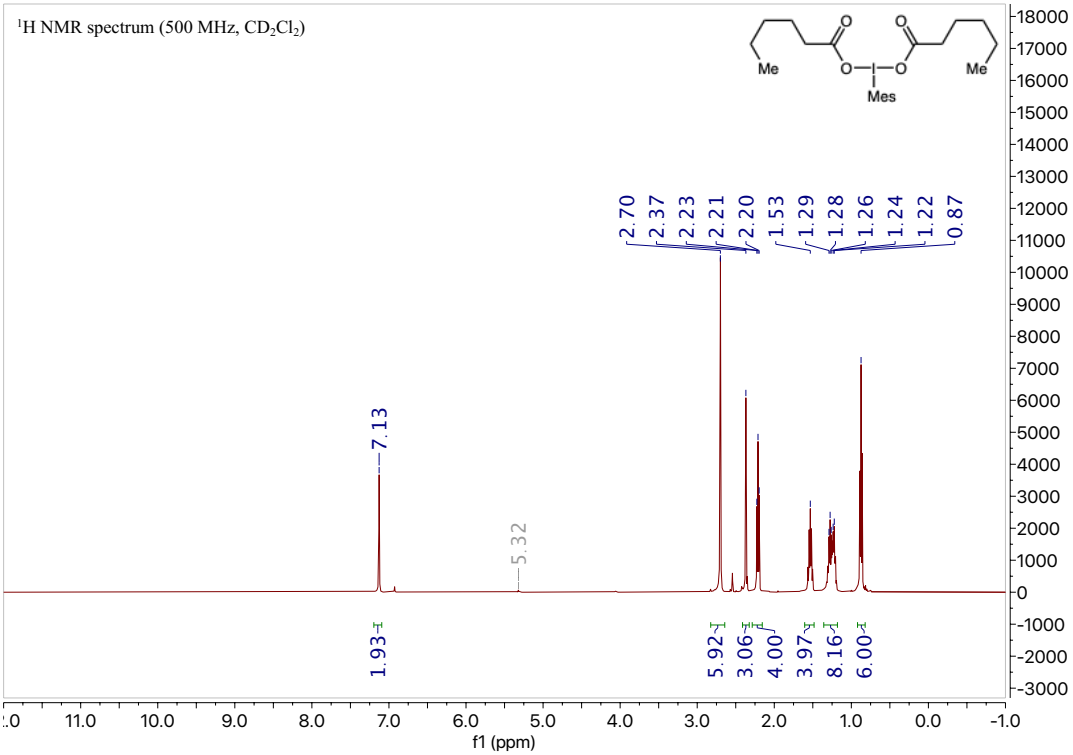


Figure S25. ^{13}C NMR spectrum of **SI-1**.

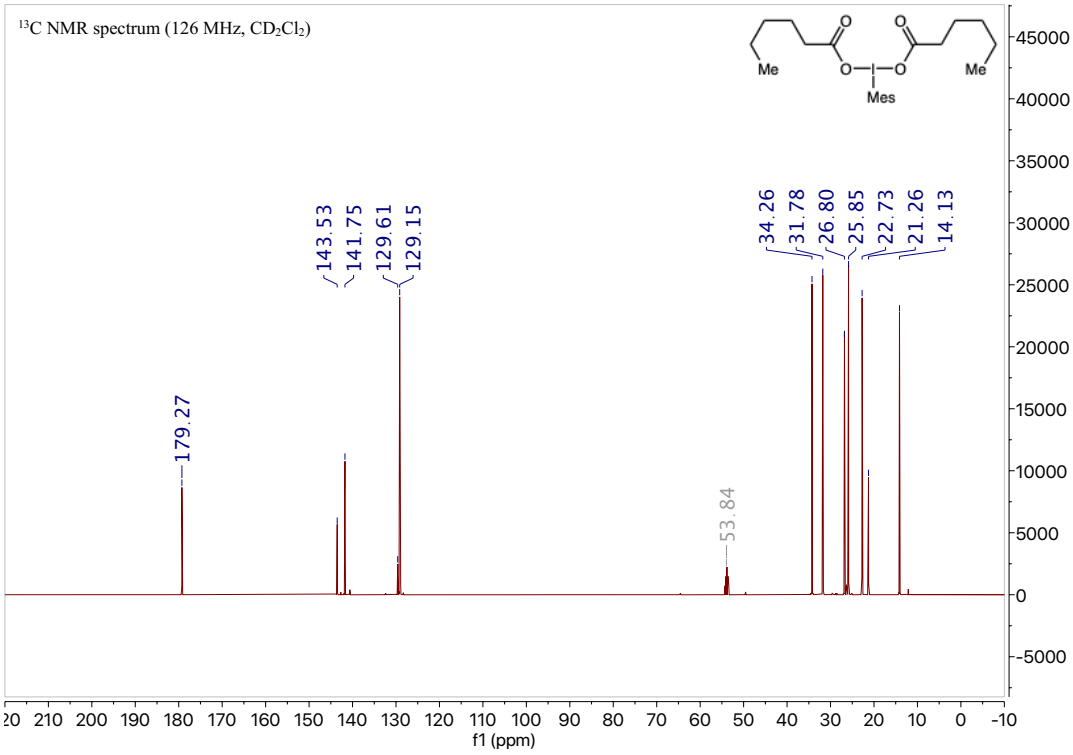


Figure S26. ^{1}H NMR spectrum of **SI-2**.

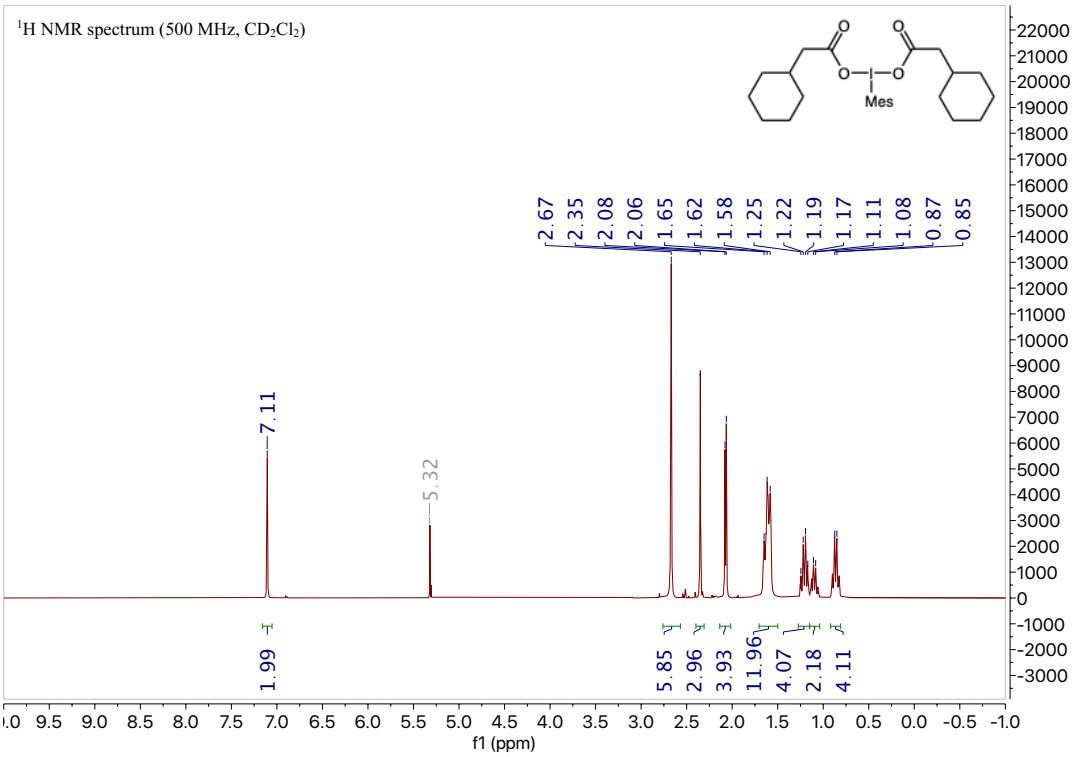


Figure S27. ^{13}C NMR spectrum of **SI-2**.

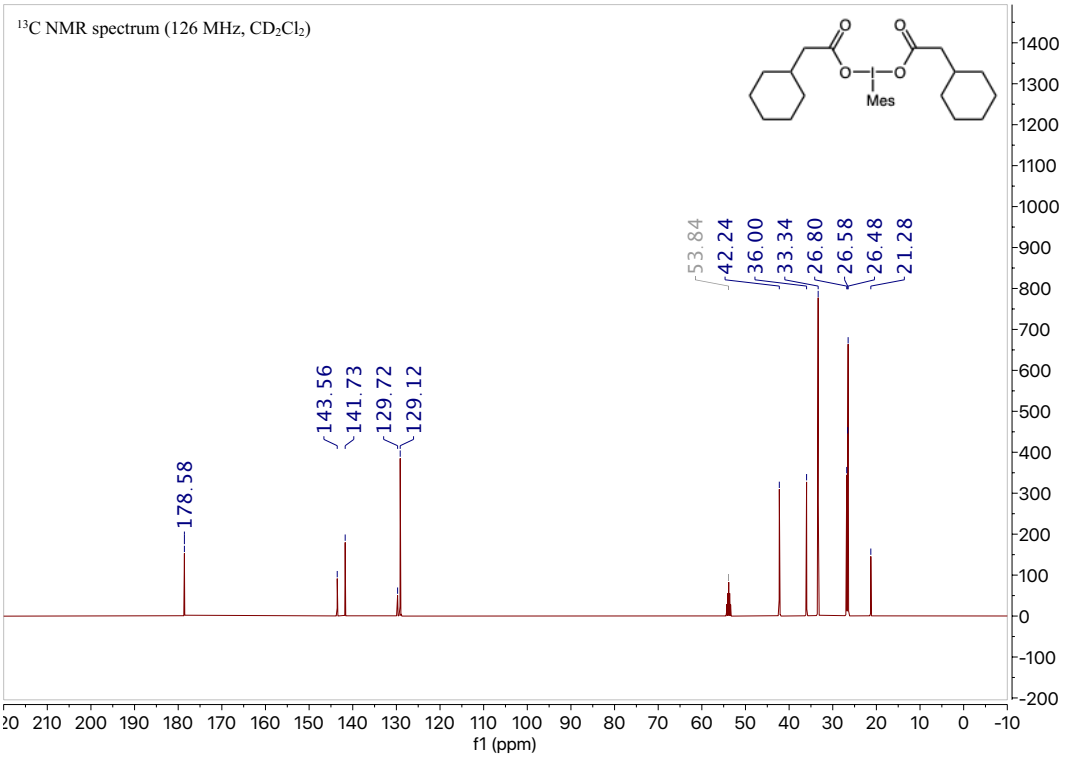


Figure S28. ^{1}H NMR spectrum of **SI-3**.

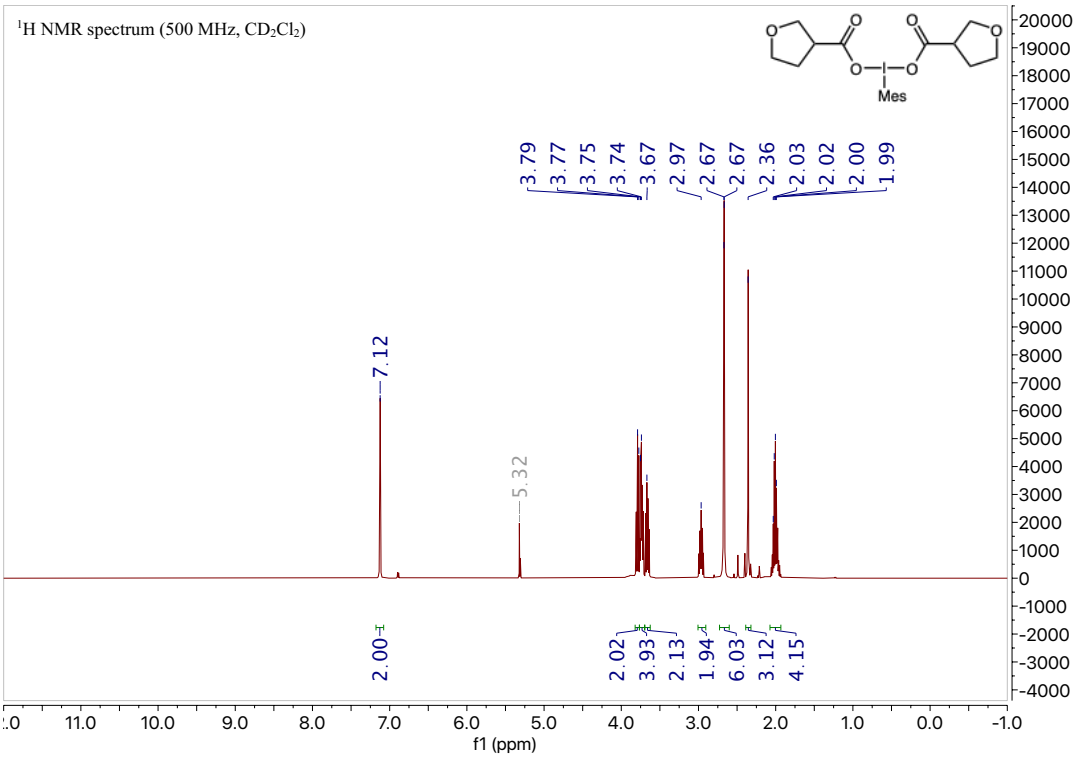


Figure S29. ^{13}C NMR spectrum of **SI-3**.

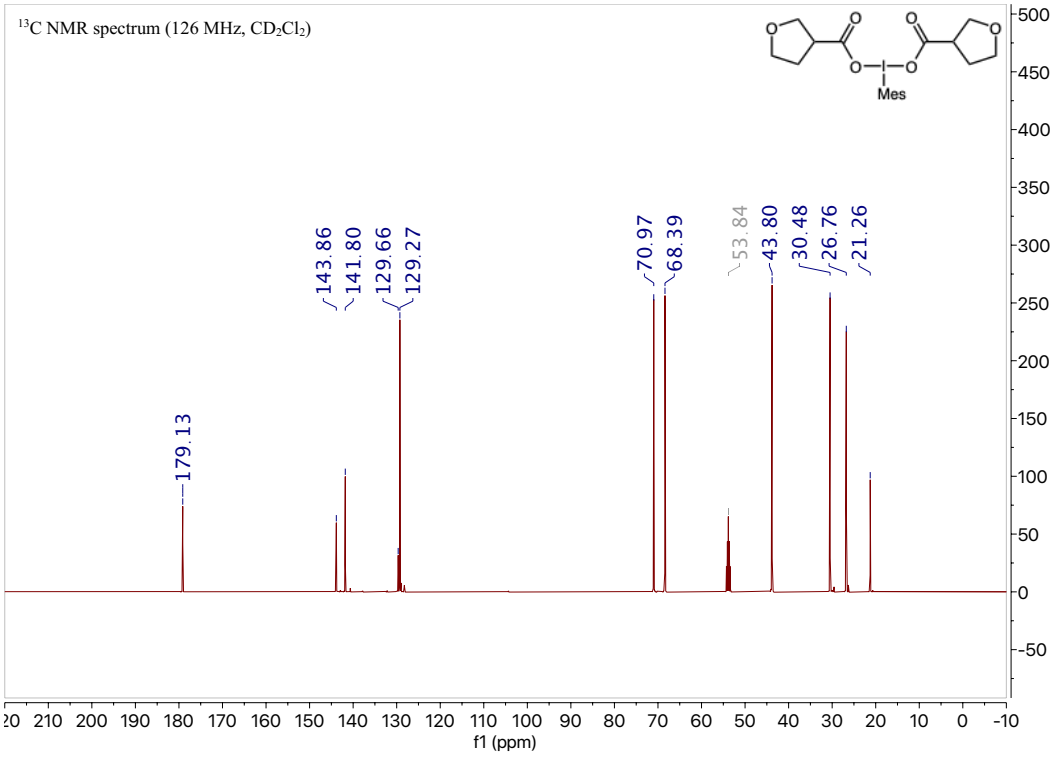


Figure S30. ^{1}H NMR spectrum of **SI-4**.

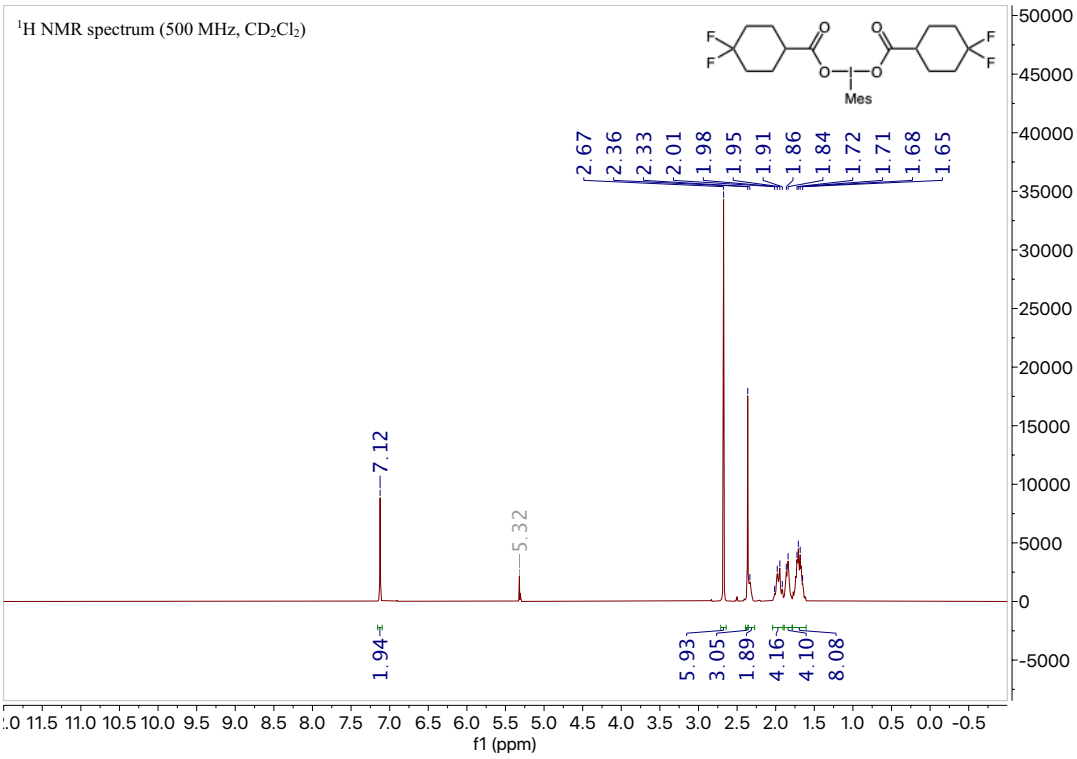


Figure S31. ^{13}C NMR spectrum of **SI-4**.

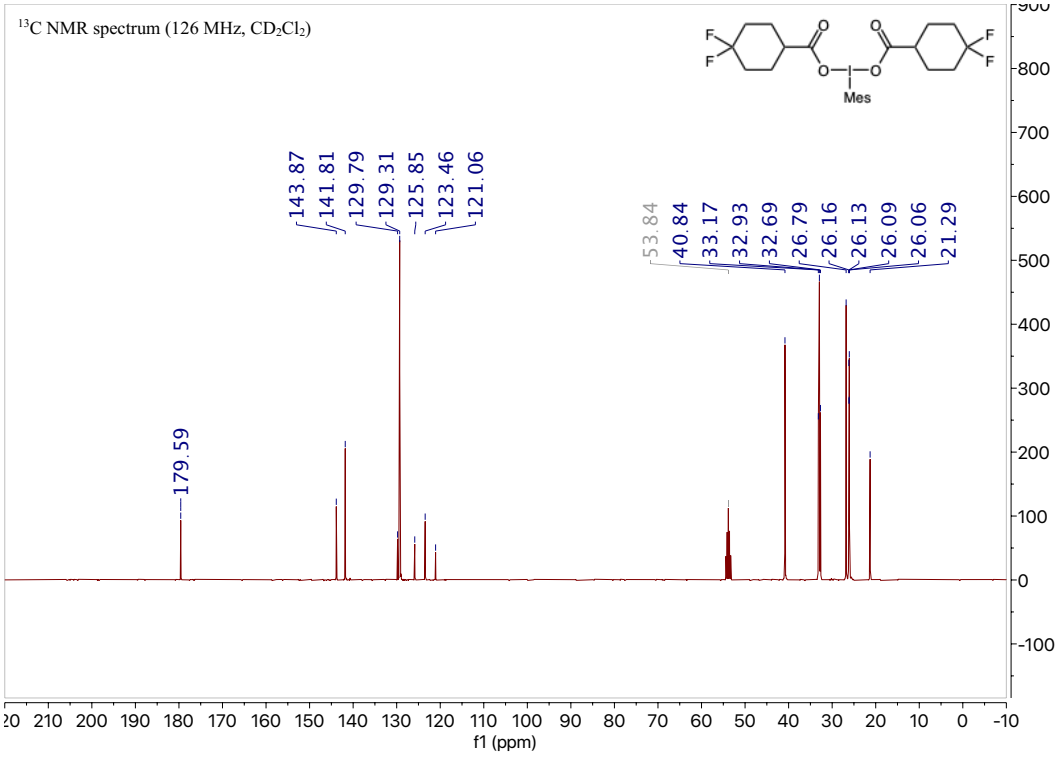


Figure S32. ^{19}F NMR spectrum of **SI-4**.

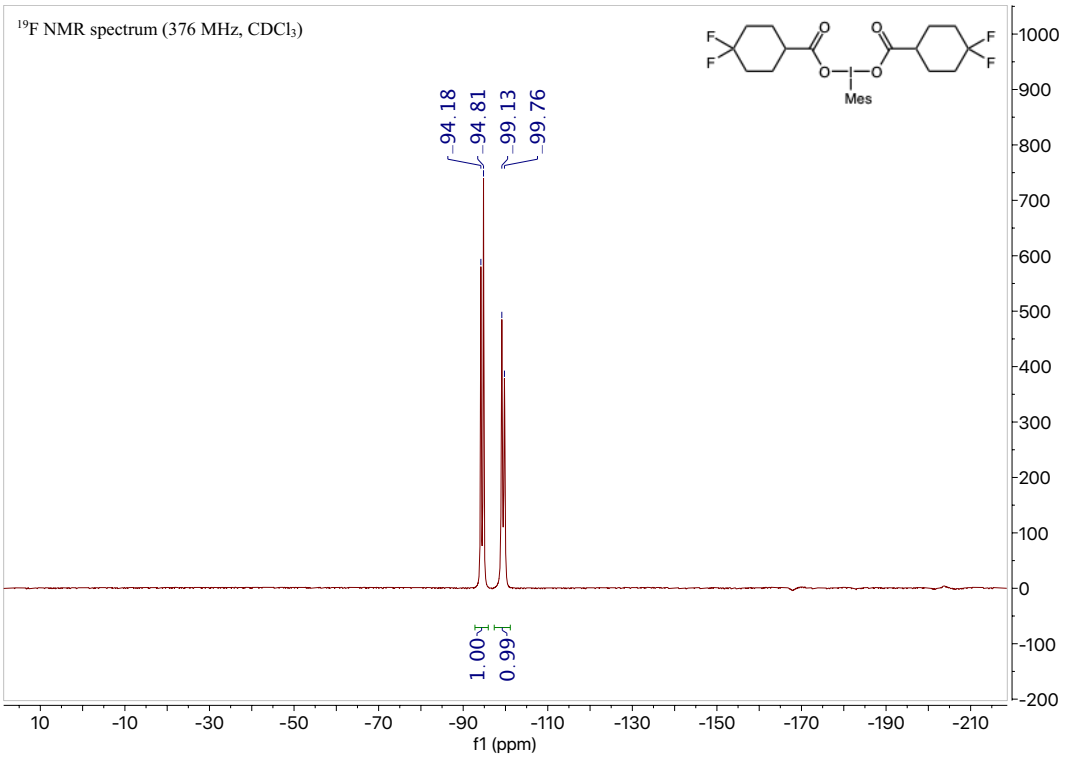


Figure S33. ^{1}H NMR spectrum of **SI-5**.

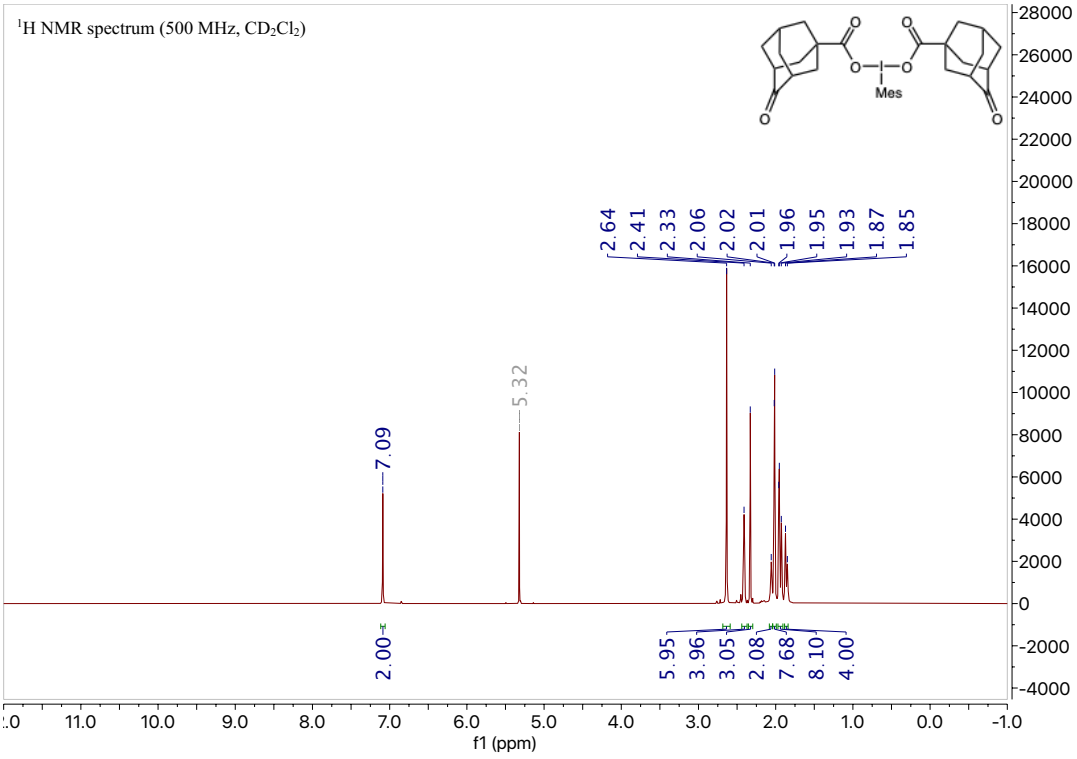


Figure S34. ^{13}C NMR spectrum of **SI-5**.

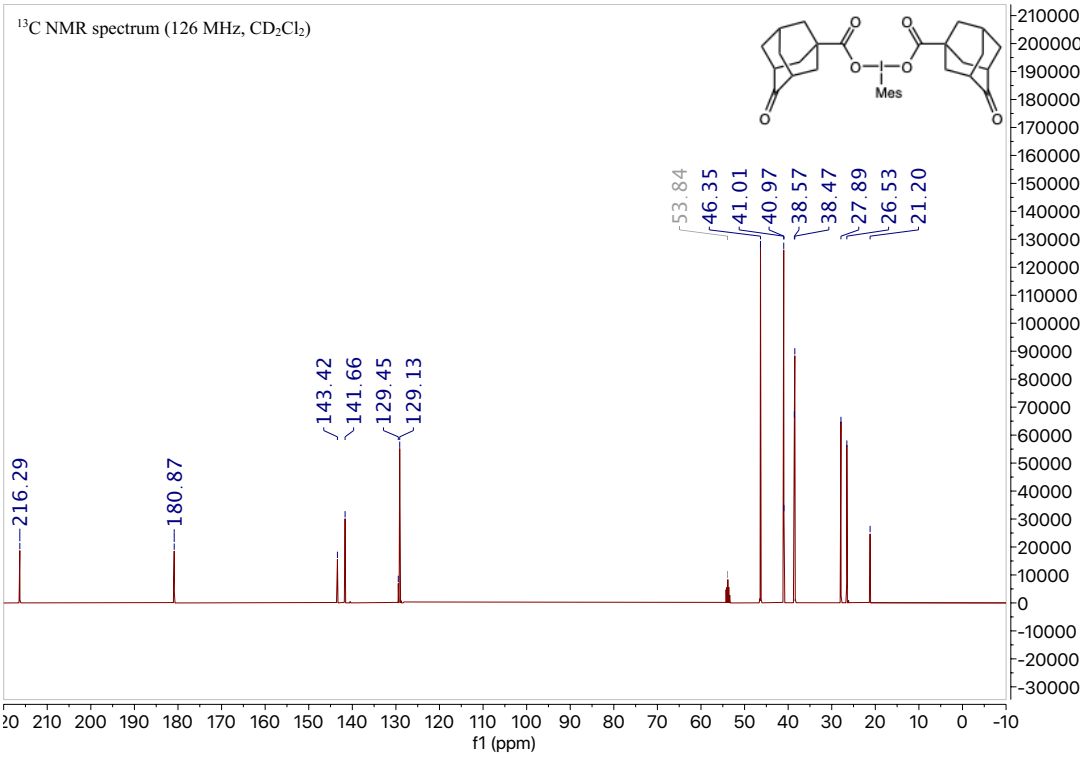


Figure S35. ^{1}H NMR spectrum of **SI-6**.

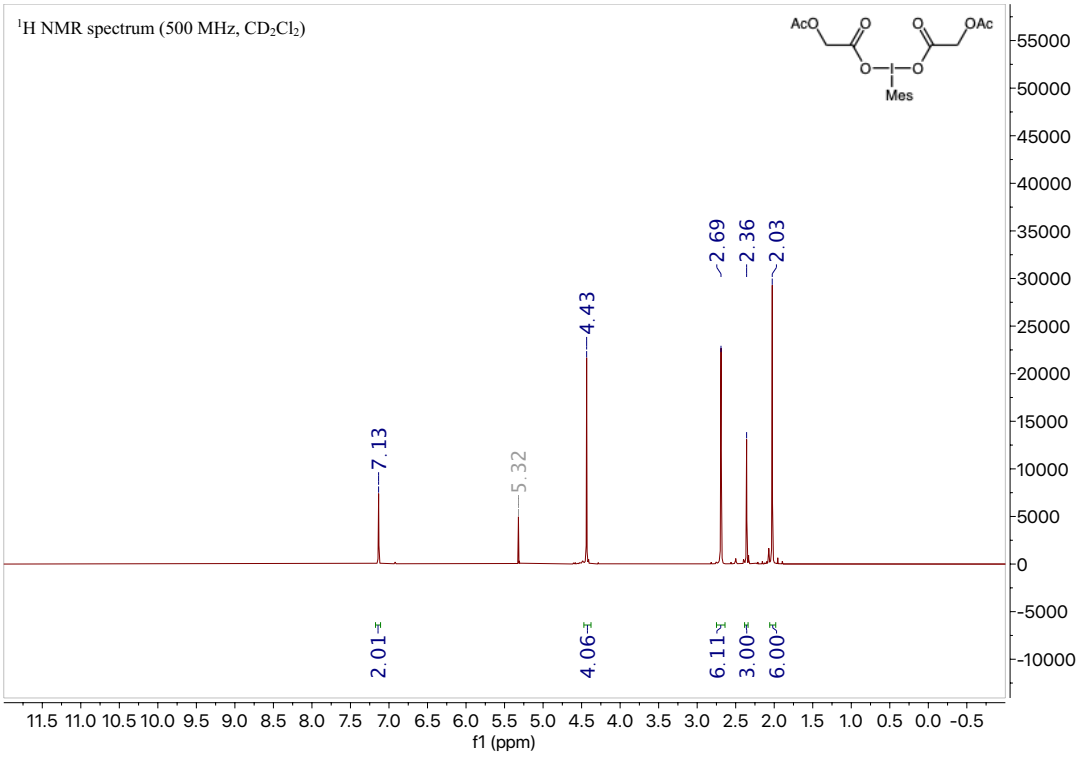


Figure S36. ^{13}C NMR spectrum of **SI-6**.

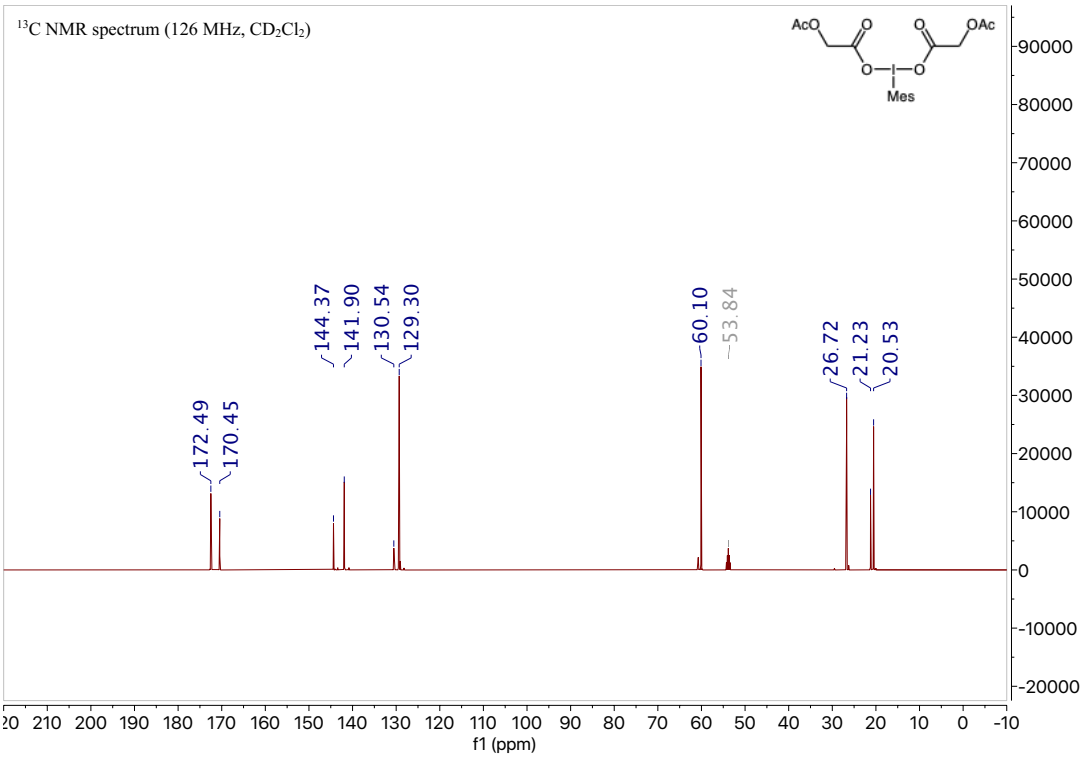


Figure S37. ^{1}H NMR spectrum of **SI-7**.

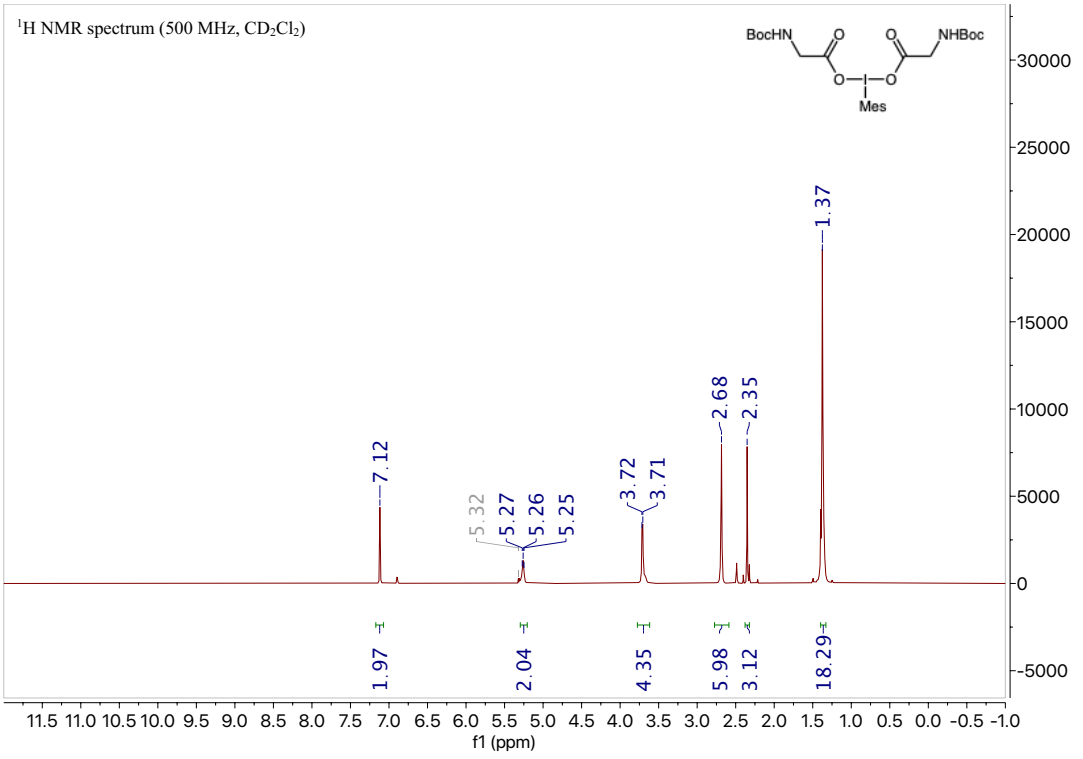


Figure S38. ^{13}C NMR spectrum of **SI-7**.

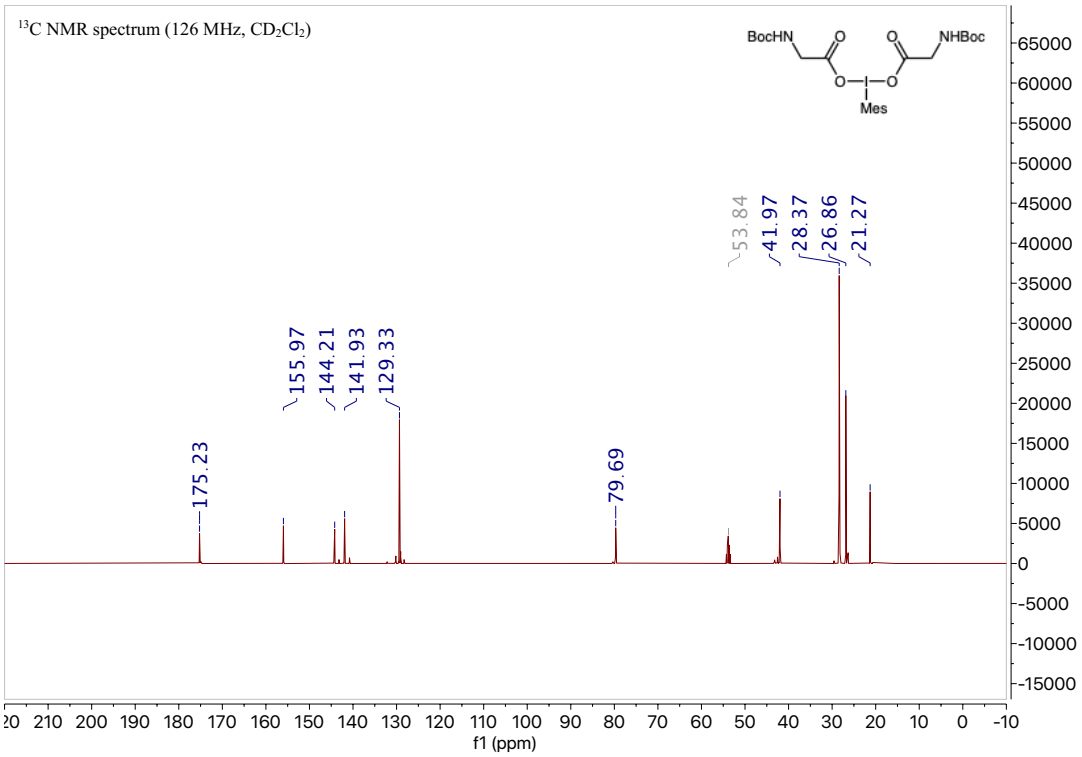


Figure S39. ^{1}H NMR spectrum of **SI-8**.

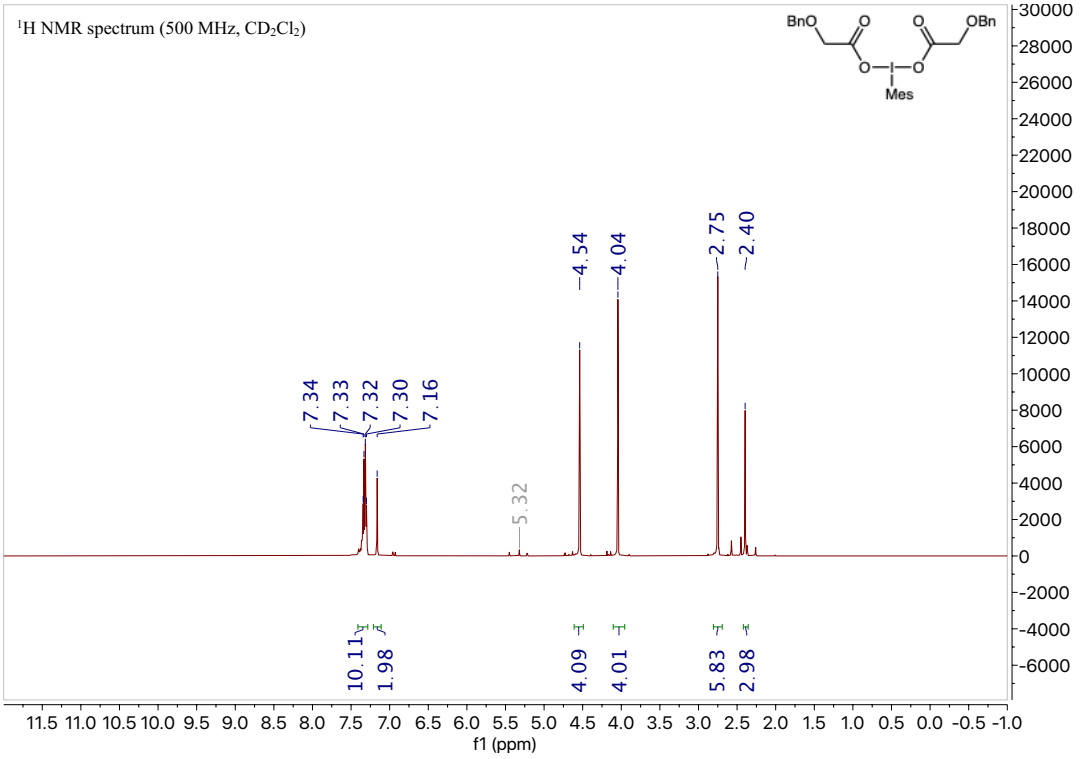


Figure S40. ^{13}C NMR spectrum of **SI-8**.

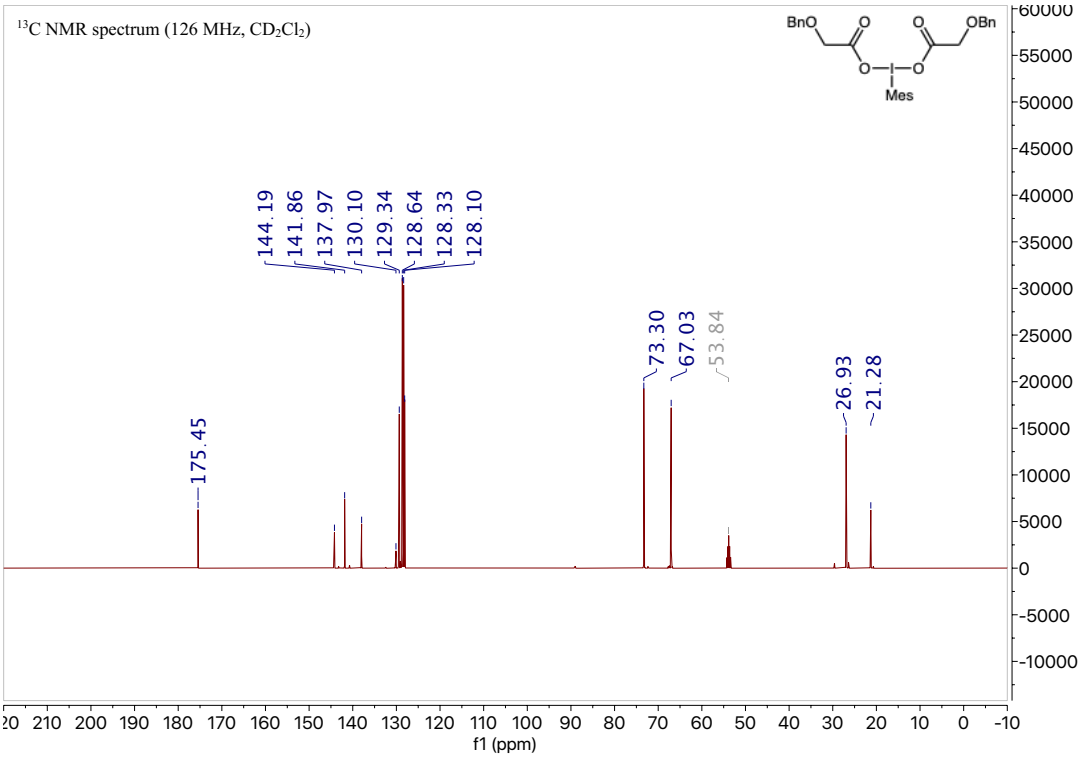


Figure S41. ^{1}H NMR spectrum of **SI-9**.

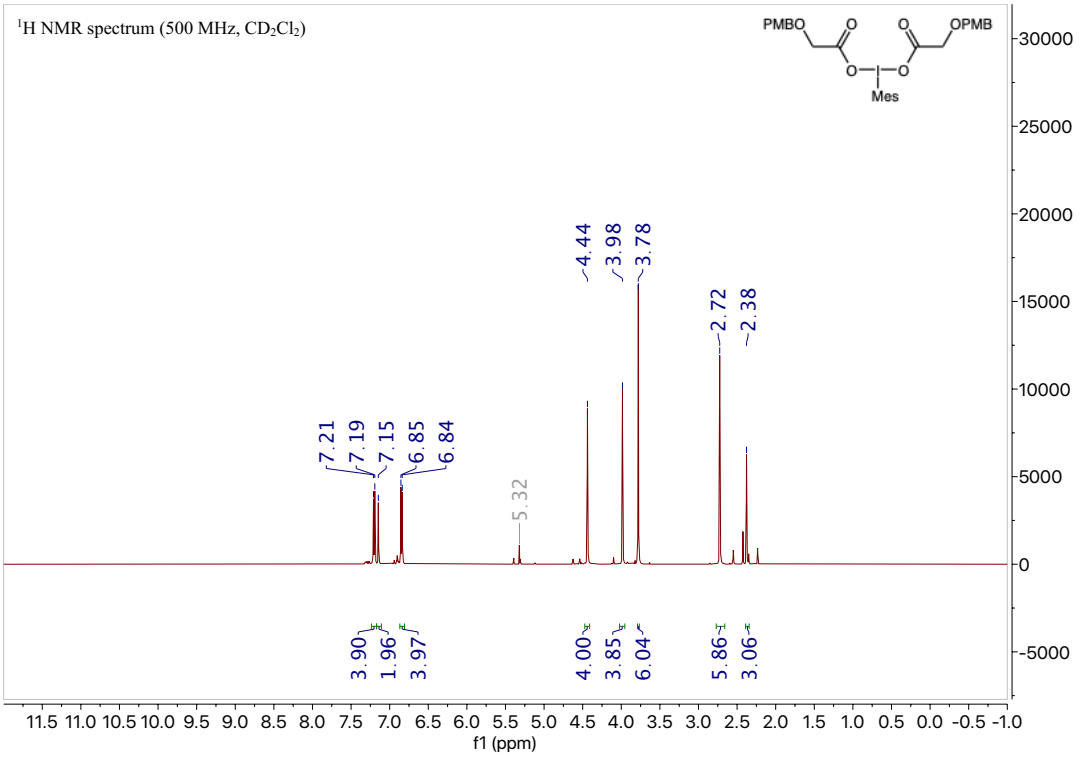


Figure S42. ^{13}C NMR spectrum of **SI-9**.

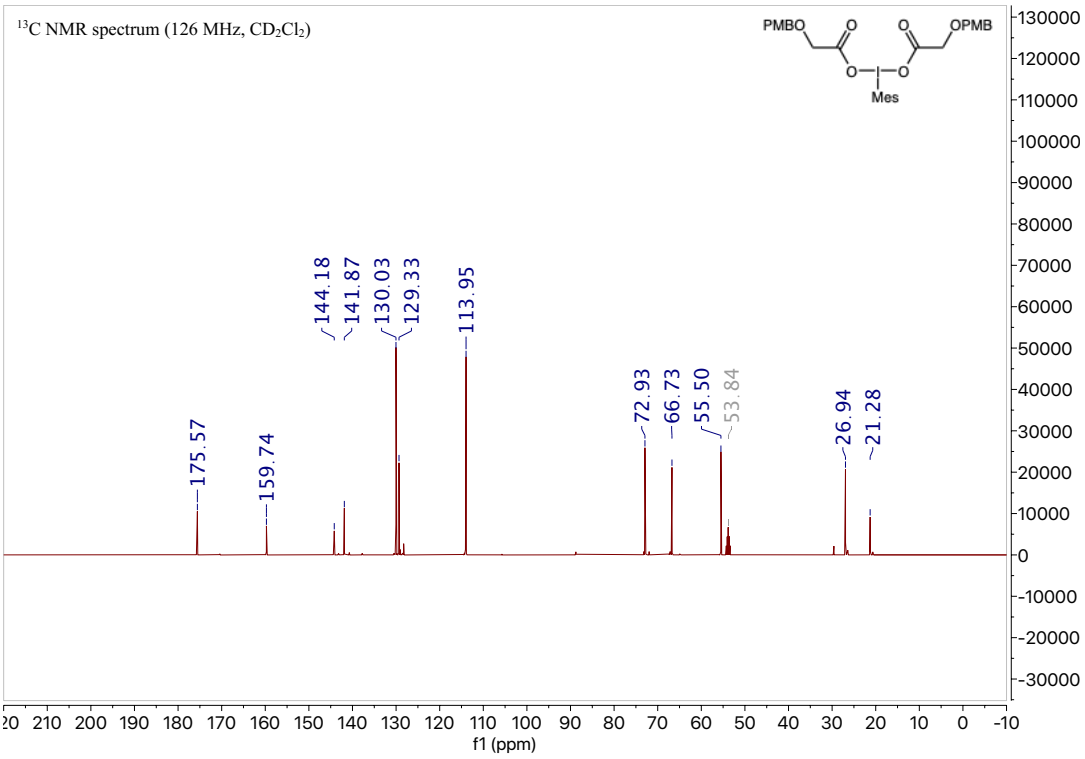


Figure S43. ^{1}H NMR spectrum of **SI-10**.

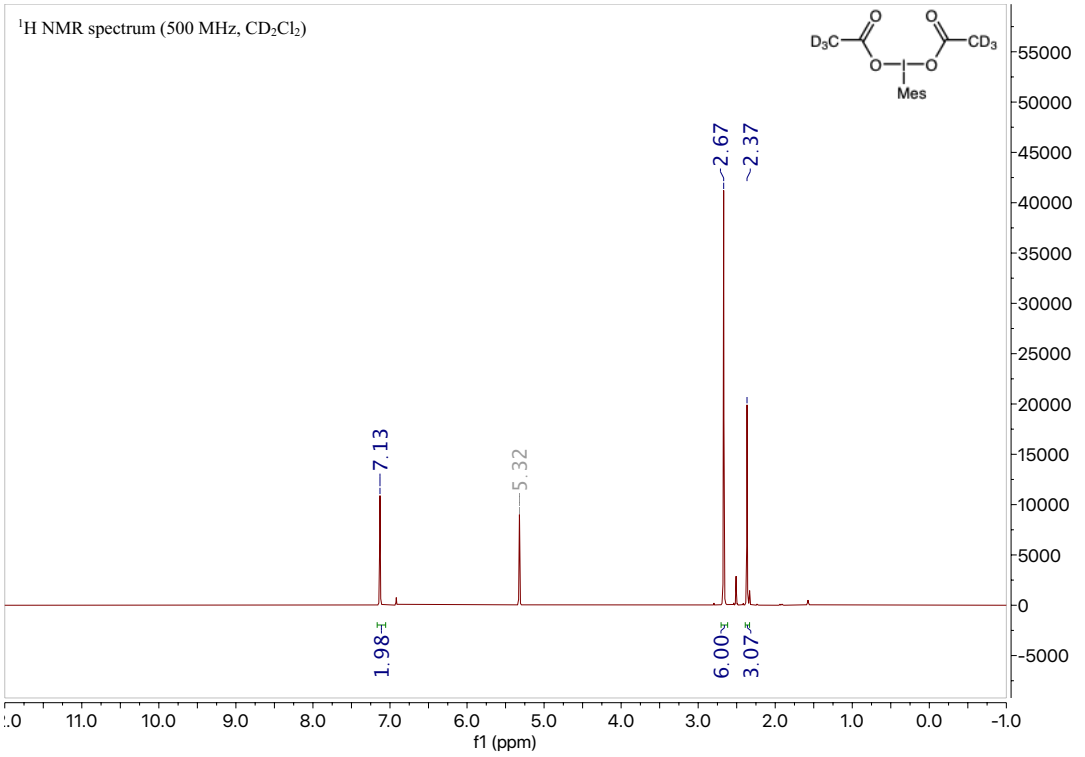


Figure S44. ^{13}C NMR spectrum of **SI-10**.

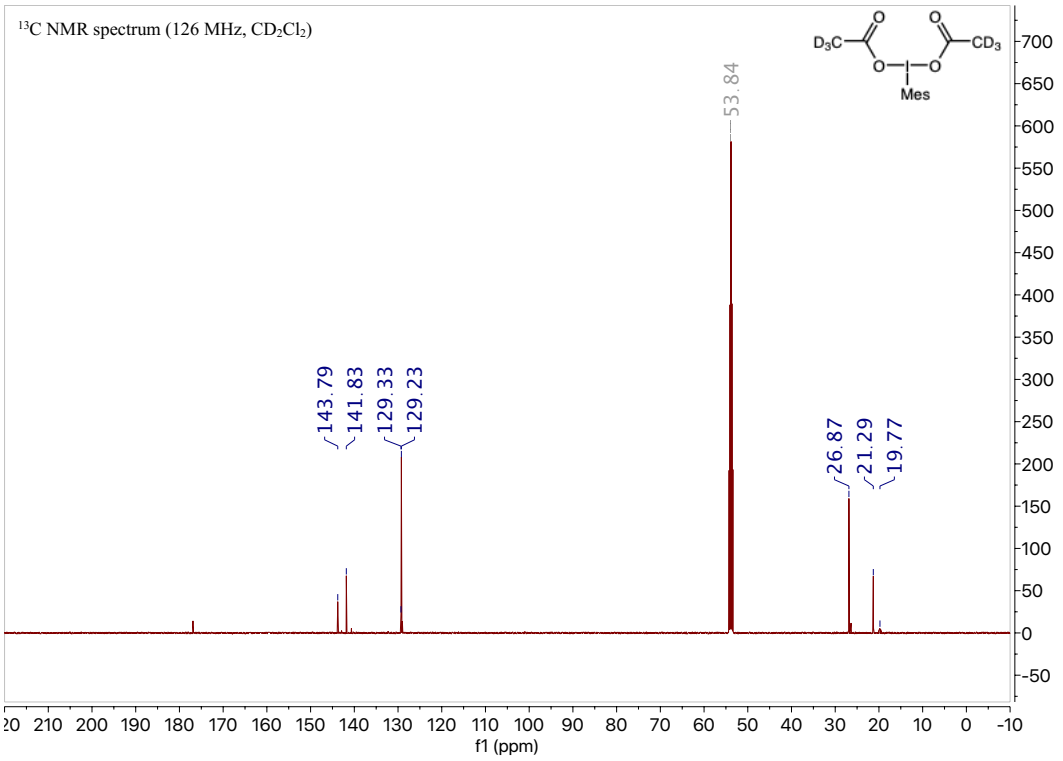


Figure S45. ^{1}H NMR spectrum of **SI-11**.

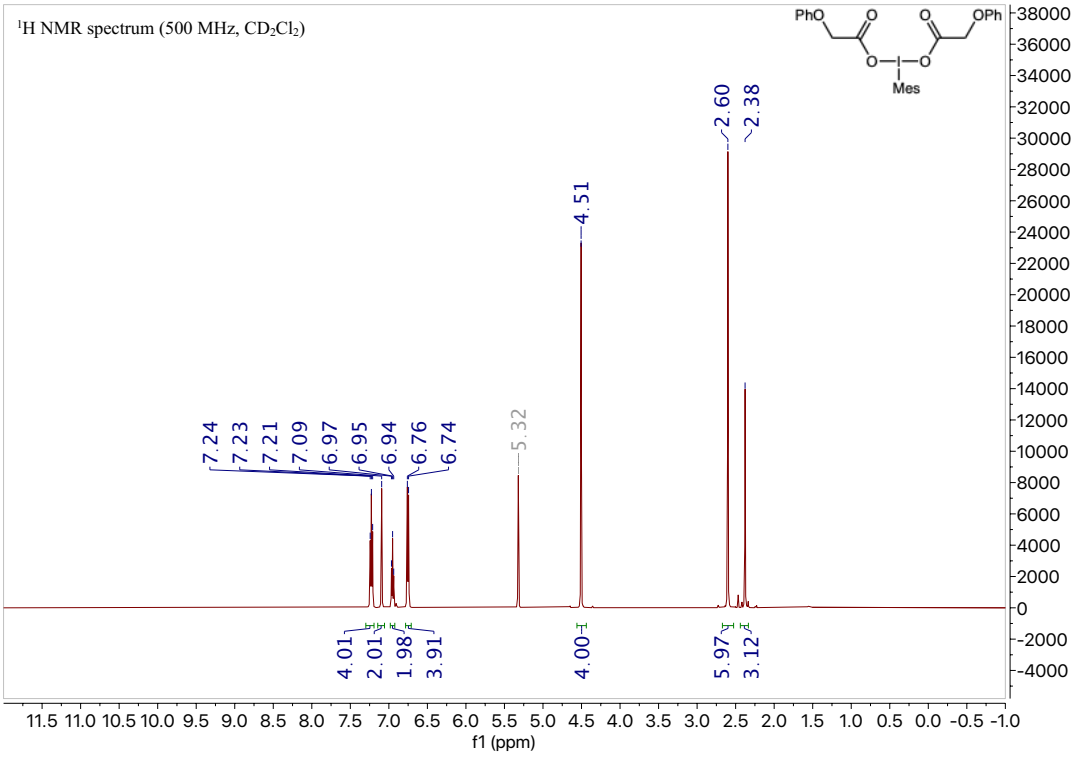


Figure S46. ^{13}C NMR spectrum of **SI-11**.

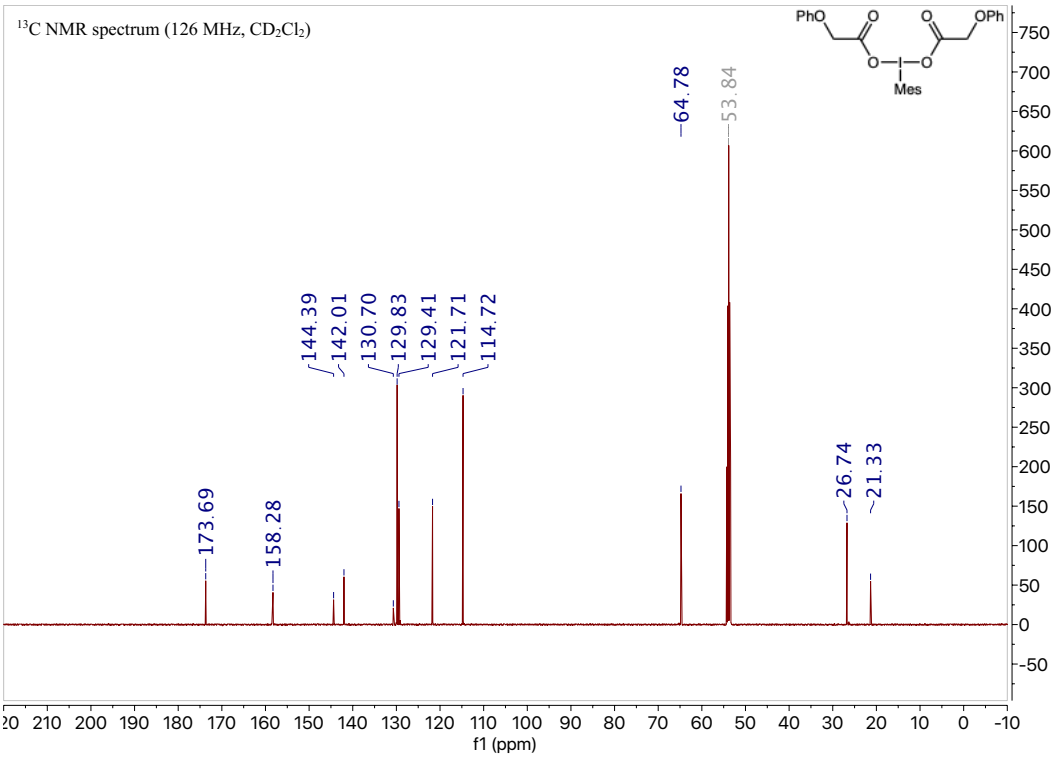


Figure S47. ^{1}H NMR spectrum of isolated mixture of **17a** and **17b**.

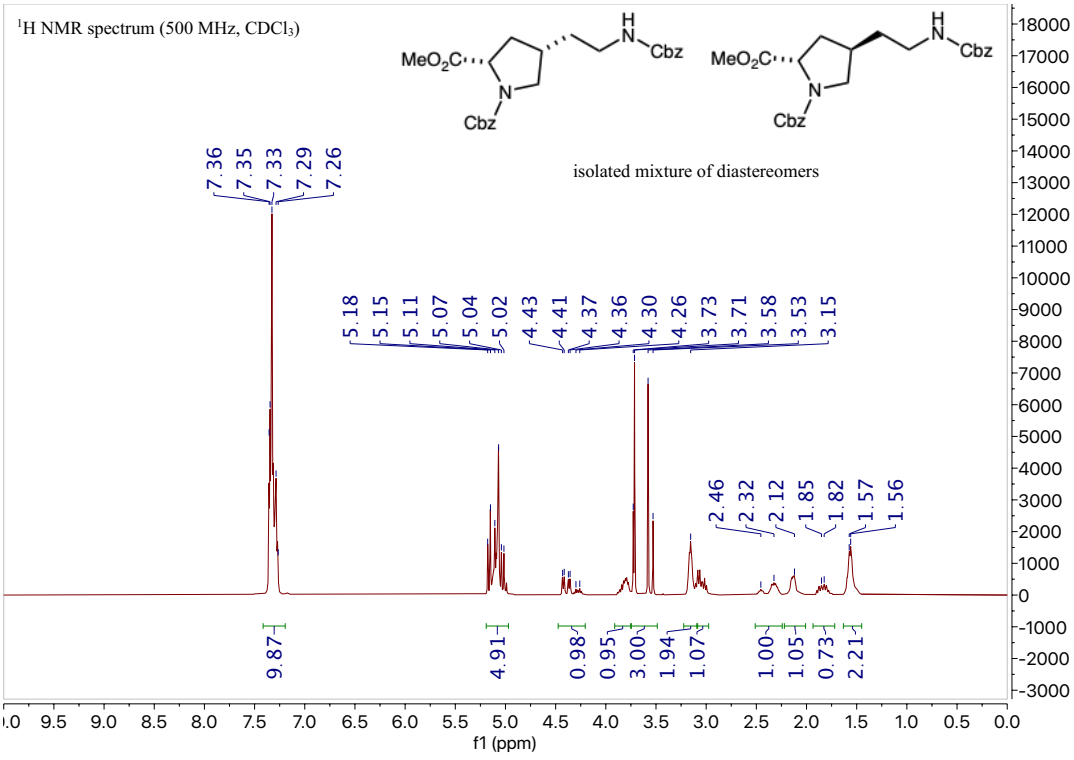


Figure S48. ^{13}C NMR spectrum of isolated mixture of **17a** and **17b**.

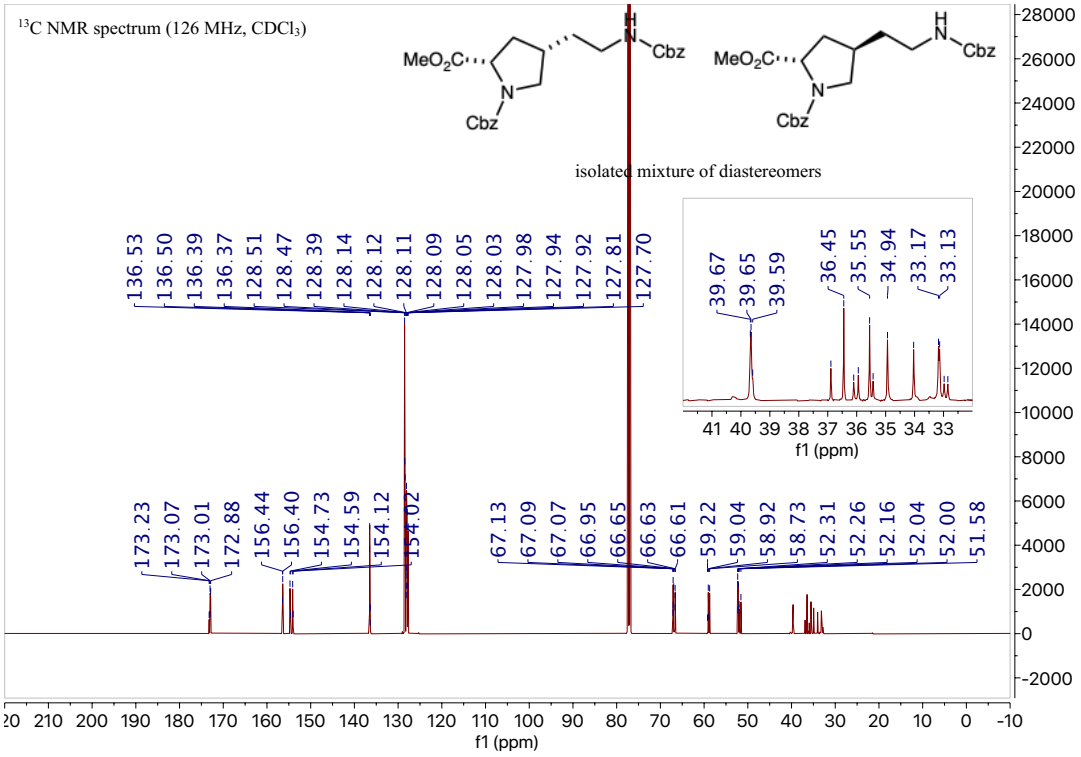


Figure S49. Diastereomeric analysis for **17** by ^{1}H NMR of the crude reaction mixture.

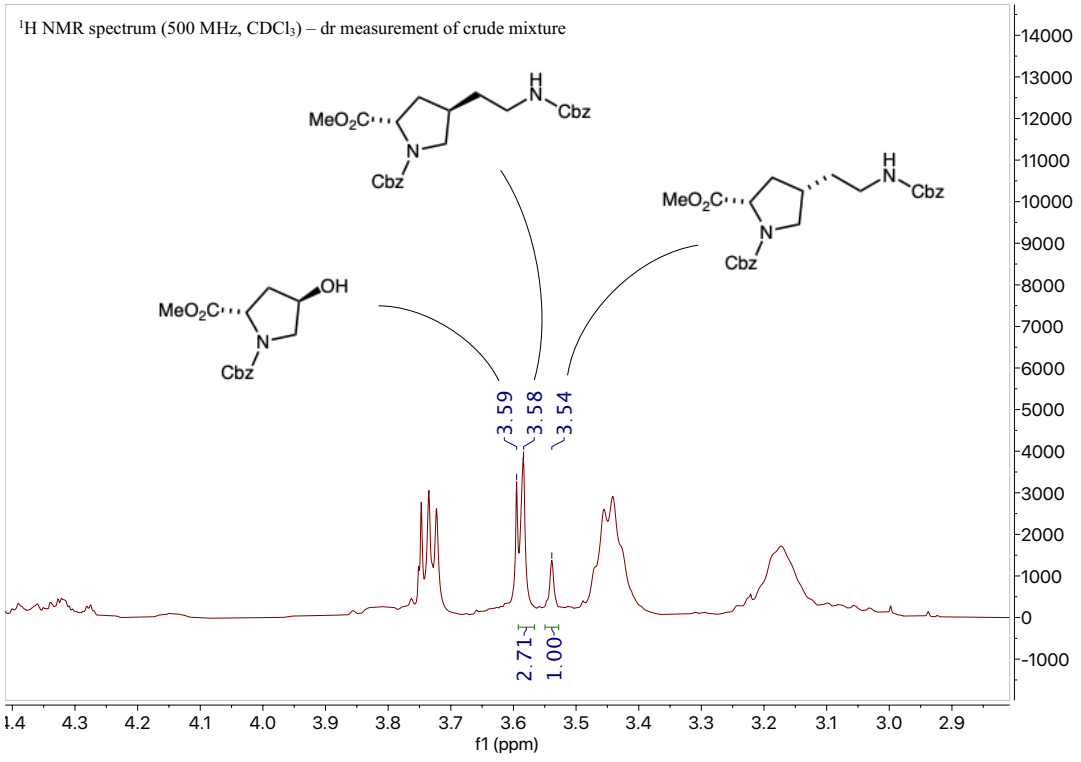


Figure S50. Diastereomeric analysis for **17** by uHPLC of the crude reaction mixture.

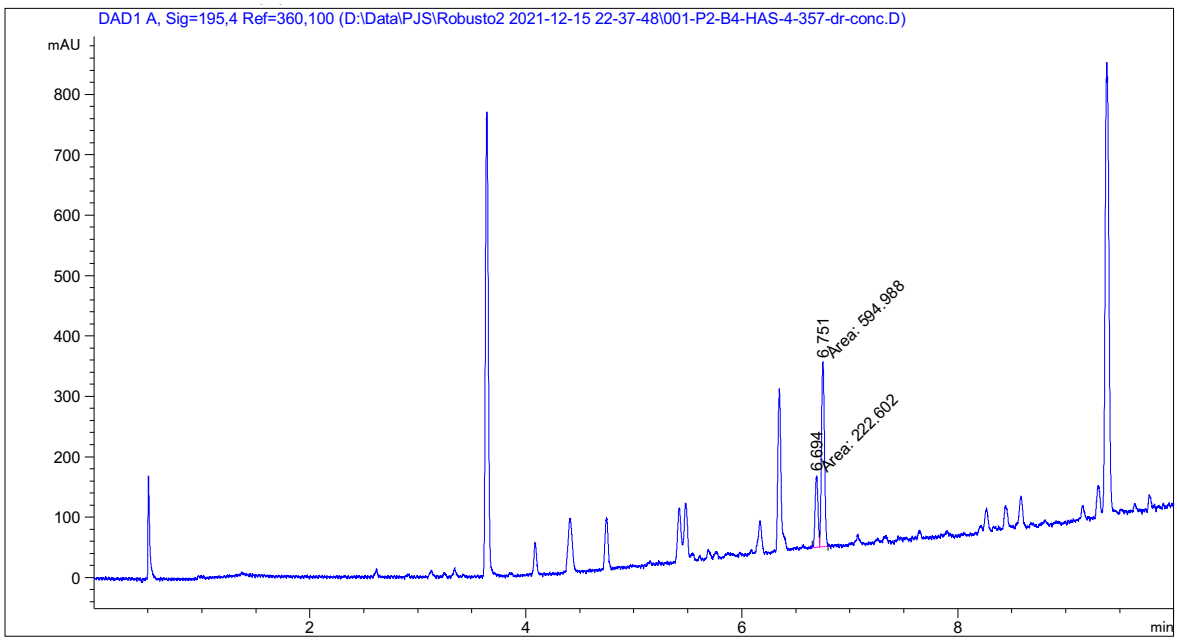


Figure S51. ^{1}H NMR spectrum of **17a**.

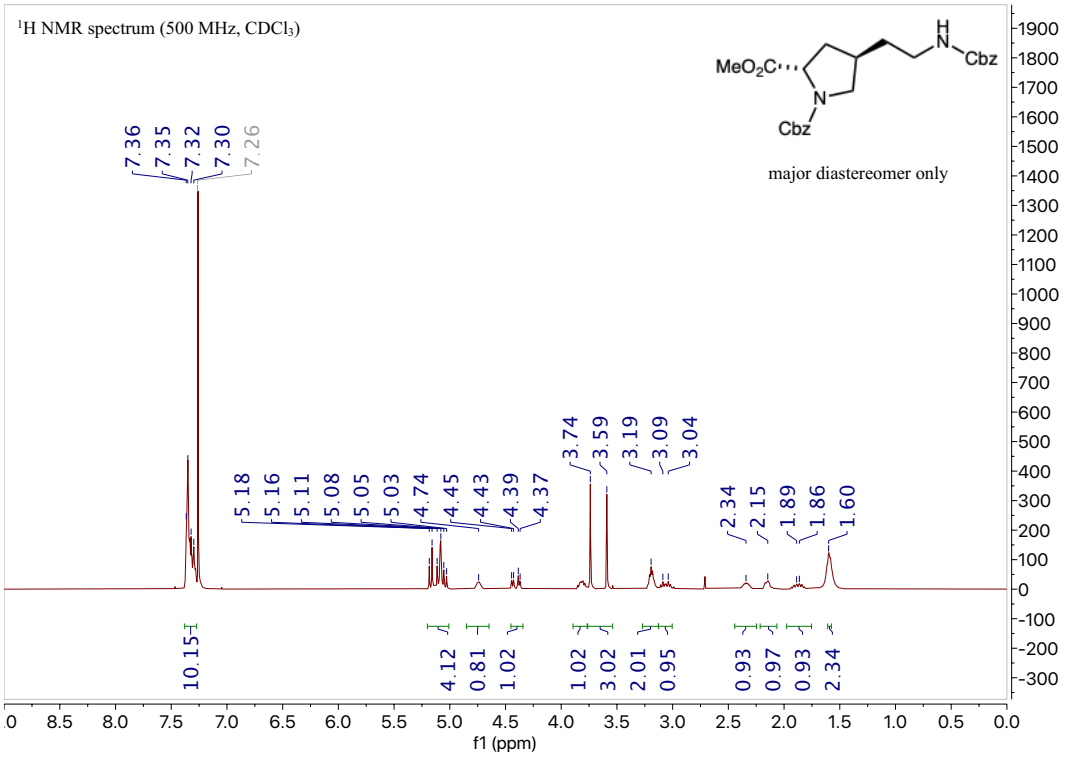


Figure S52. ^{13}C NMR spectrum of **17a**.

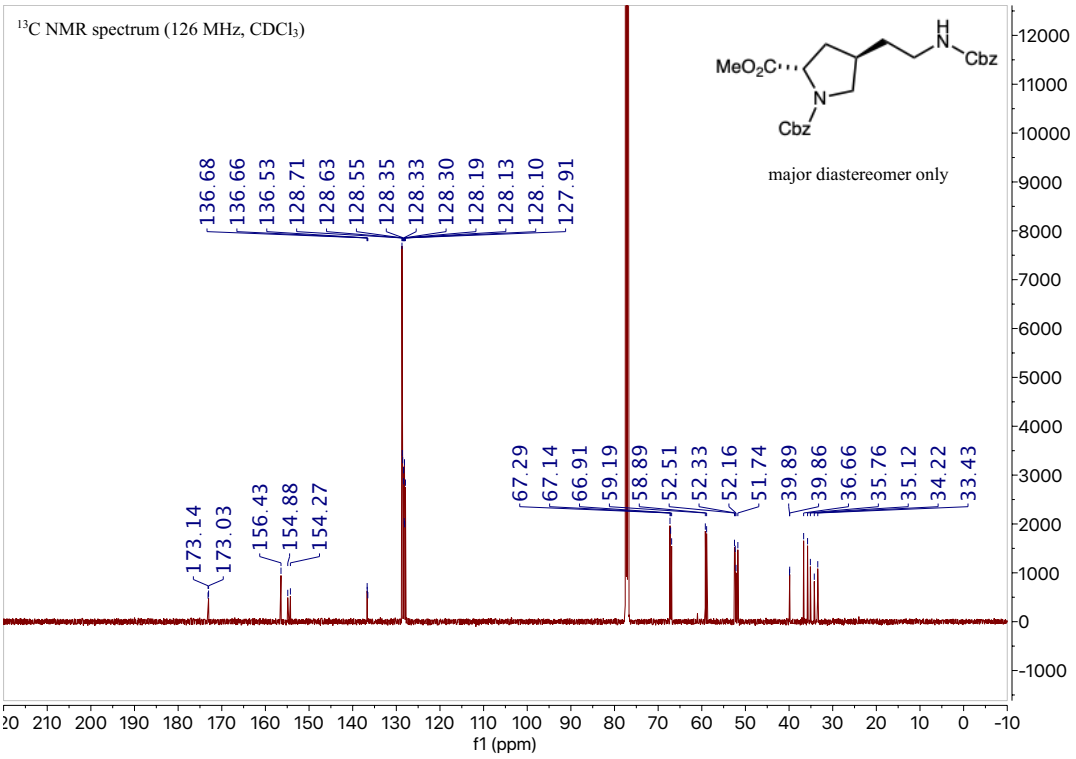


Figure S53. ^{1}H–^{1}H COSY NMR spectrum of **17a**.

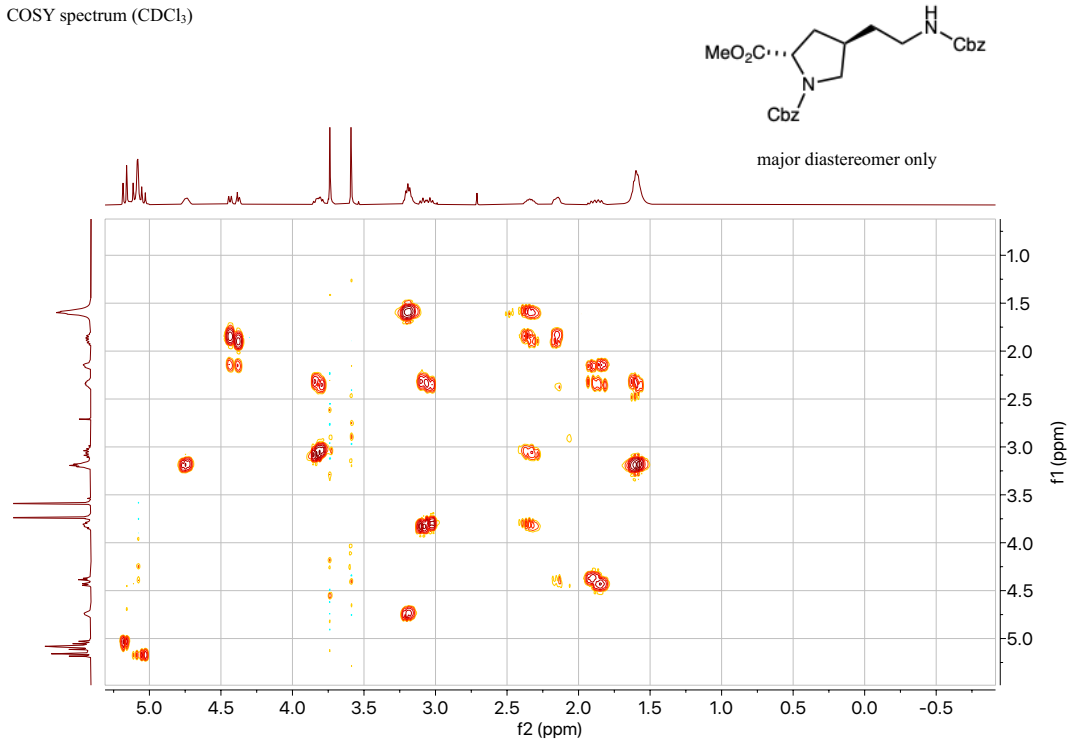


Figure S54. $^{1}H–^{13}C$ HSQC NMR spectrum of **17a**.

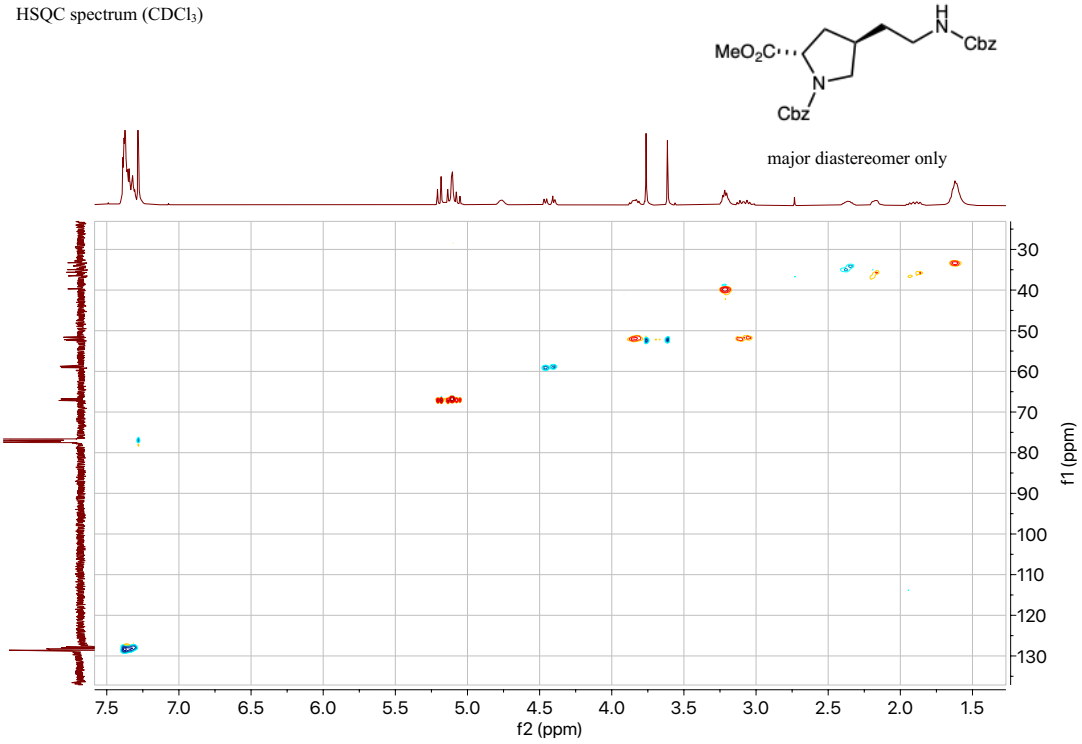


Figure S55. $^{1}H–^{1}H$ NOESY NMR spectrum of **17a**.

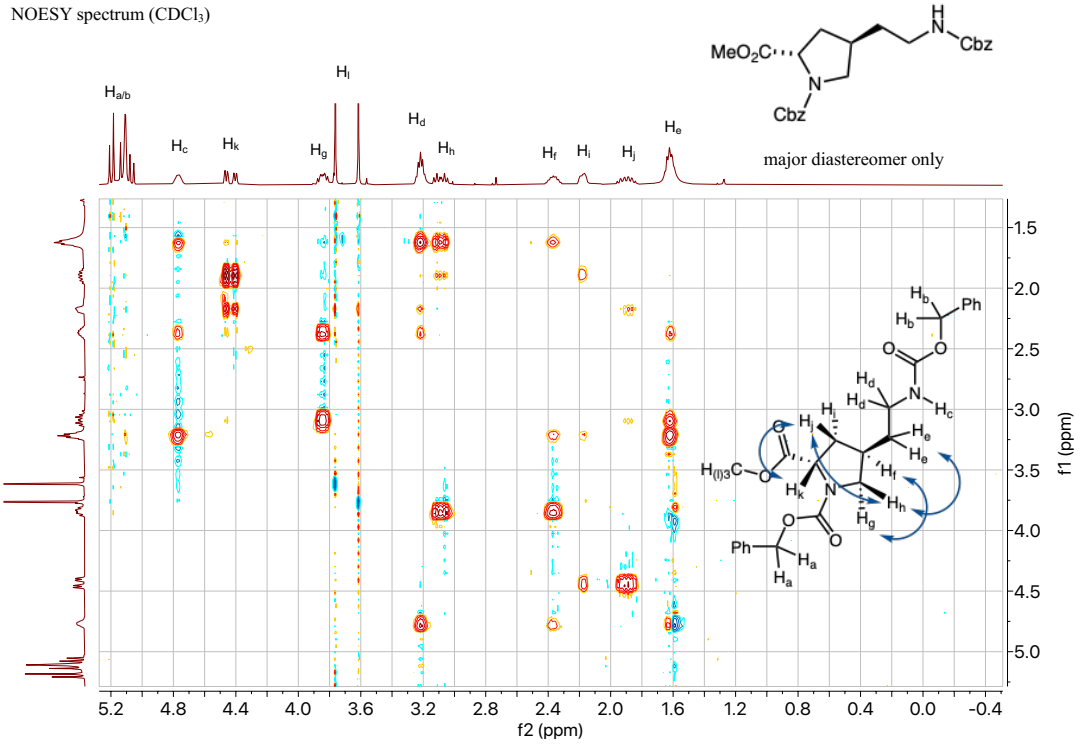


Figure S56. ^{1}H NMR spectrum of **18**.

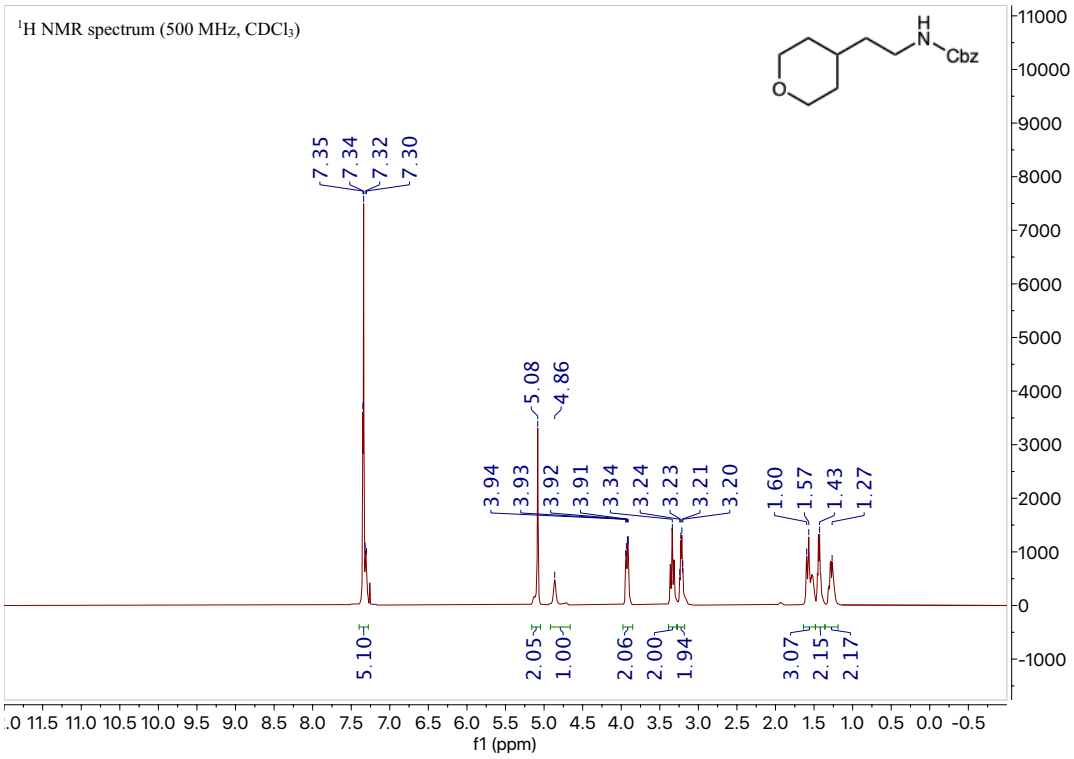


Figure S57. ^{13}C NMR spectrum of **18**.

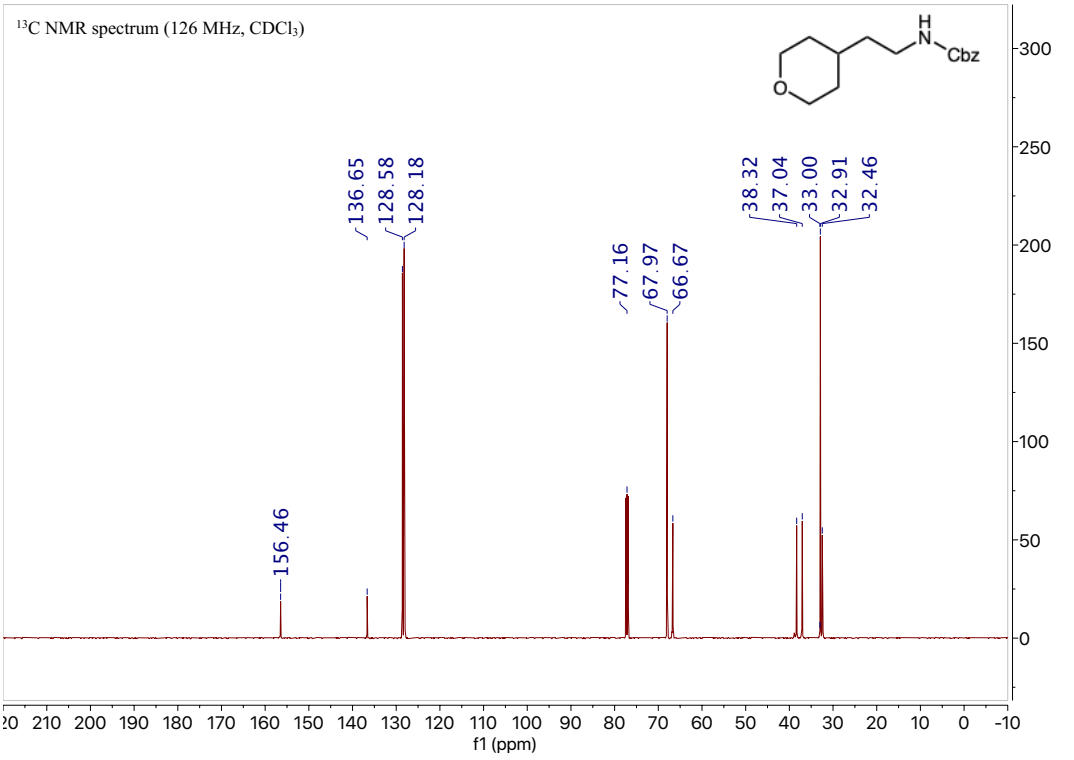


Figure S58. ^{1}H NMR spectrum of **19**.

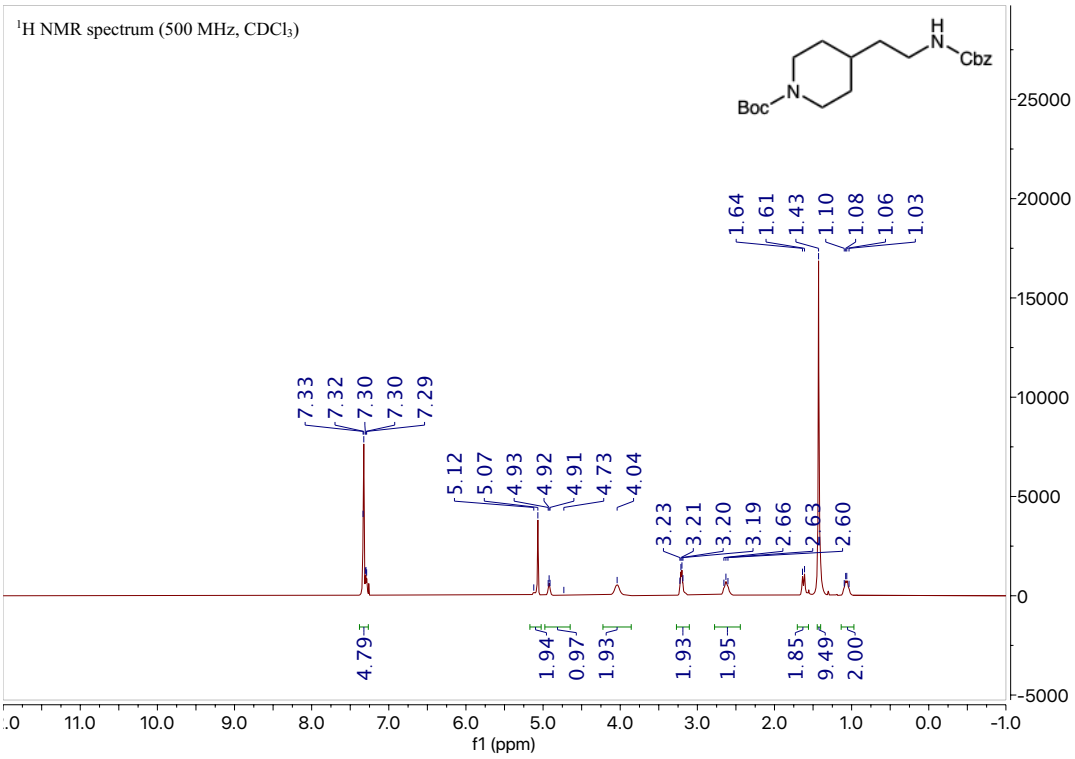


Figure S59. ^{13}C NMR spectrum of **19**.

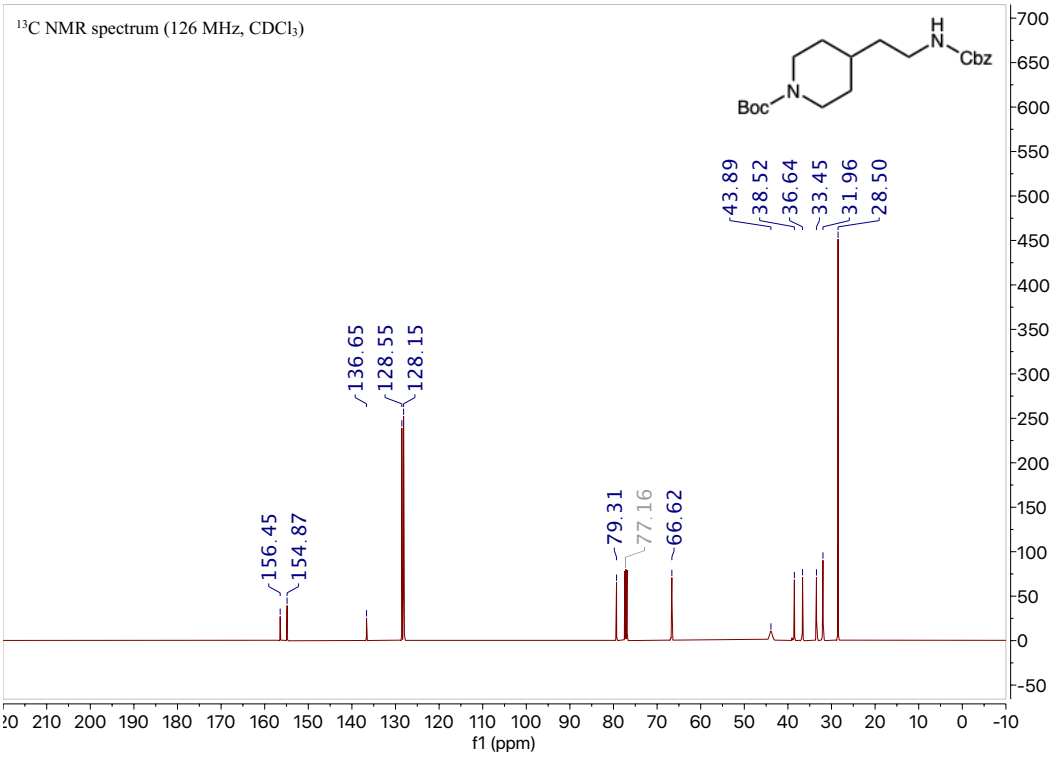


Figure S60. ^{1}H NMR spectrum of **(±)-20**.

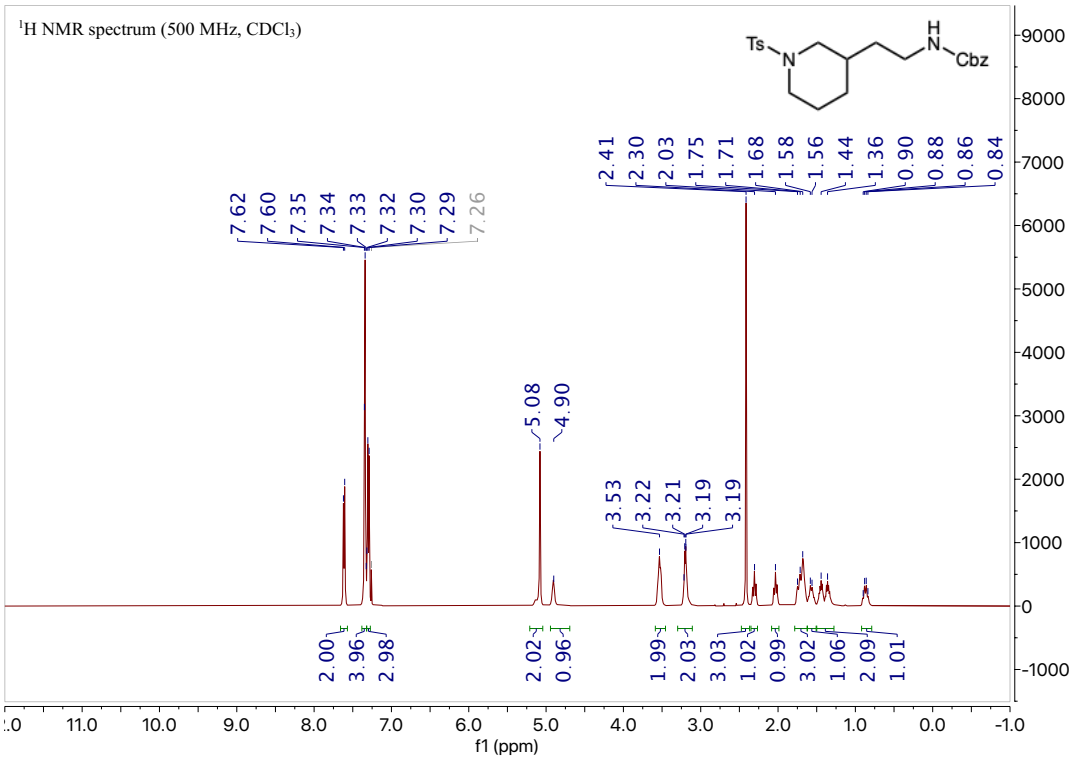


Figure S61. ^{13}C NMR spectrum of **(±)-20**.

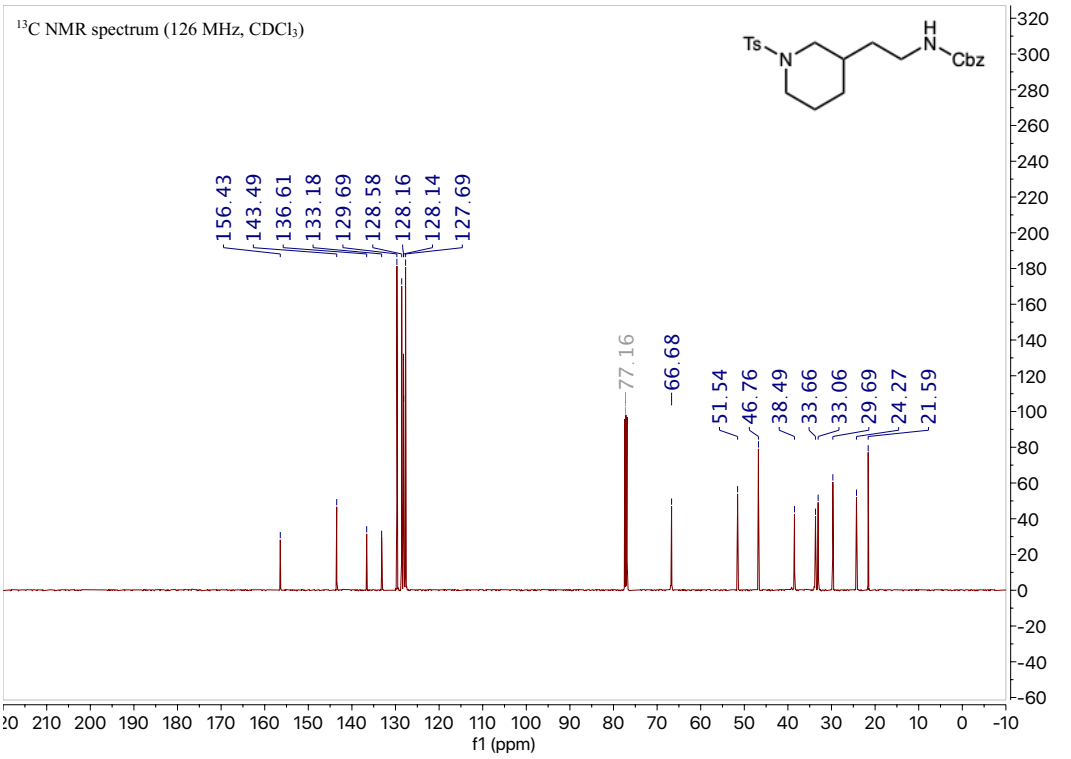


Figure S62. ^{1}H NMR spectrum of **21**

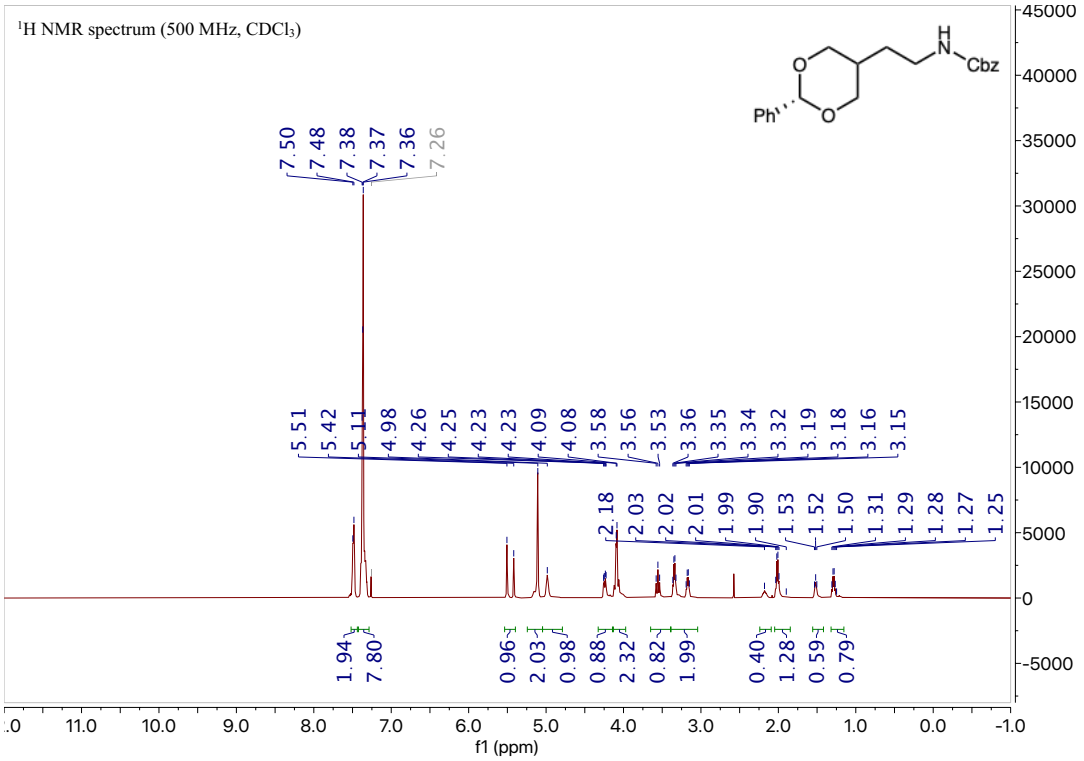


Figure S63. ^{13}C NMR spectrum of **21**

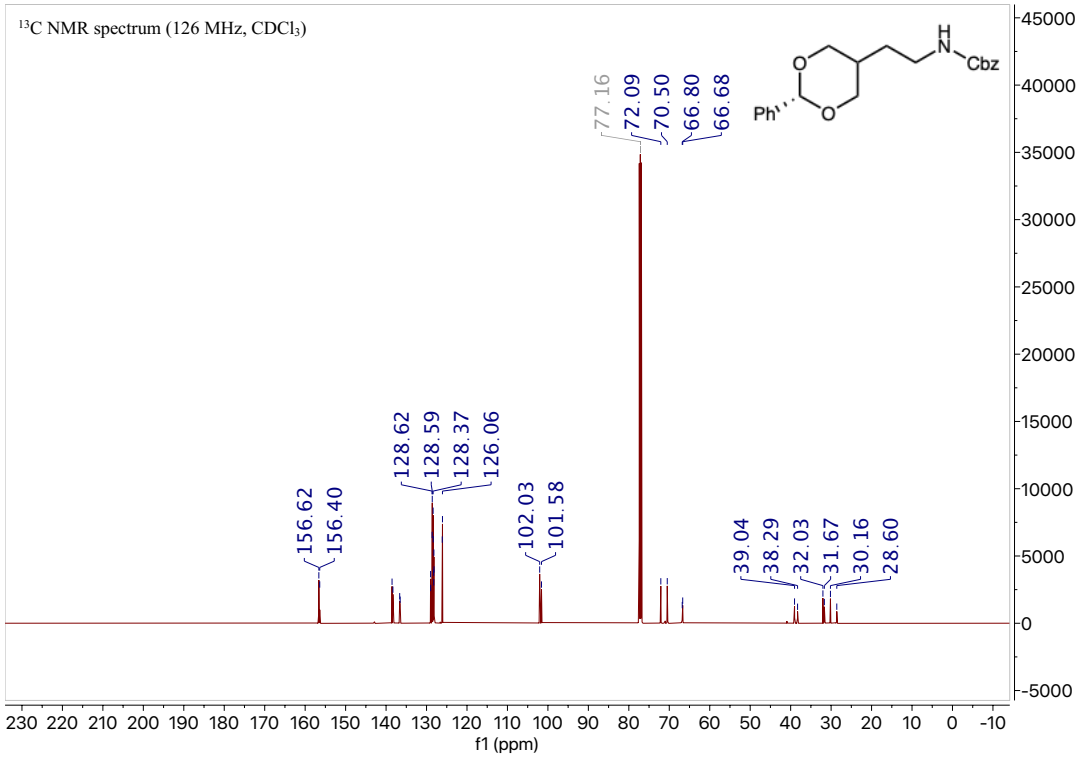


Figure S64. ^{1}H NMR spectrum of **(±)-22**

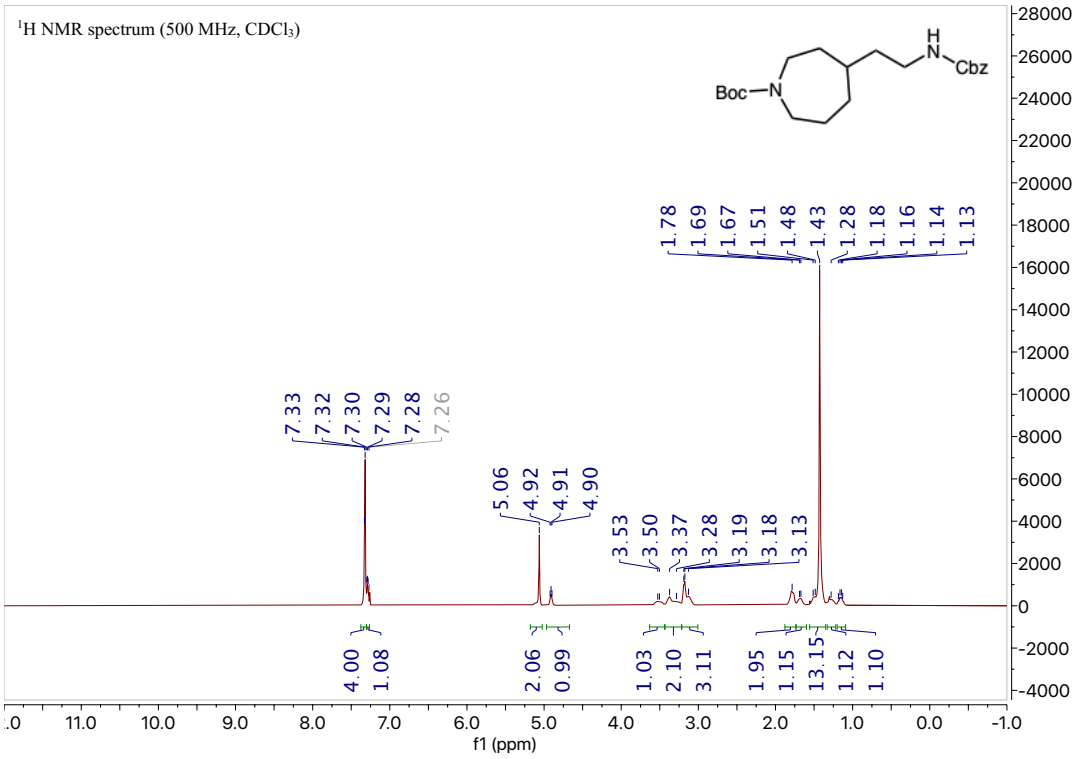


Figure S65. ^{13}C NMR spectrum of **(±)-22**

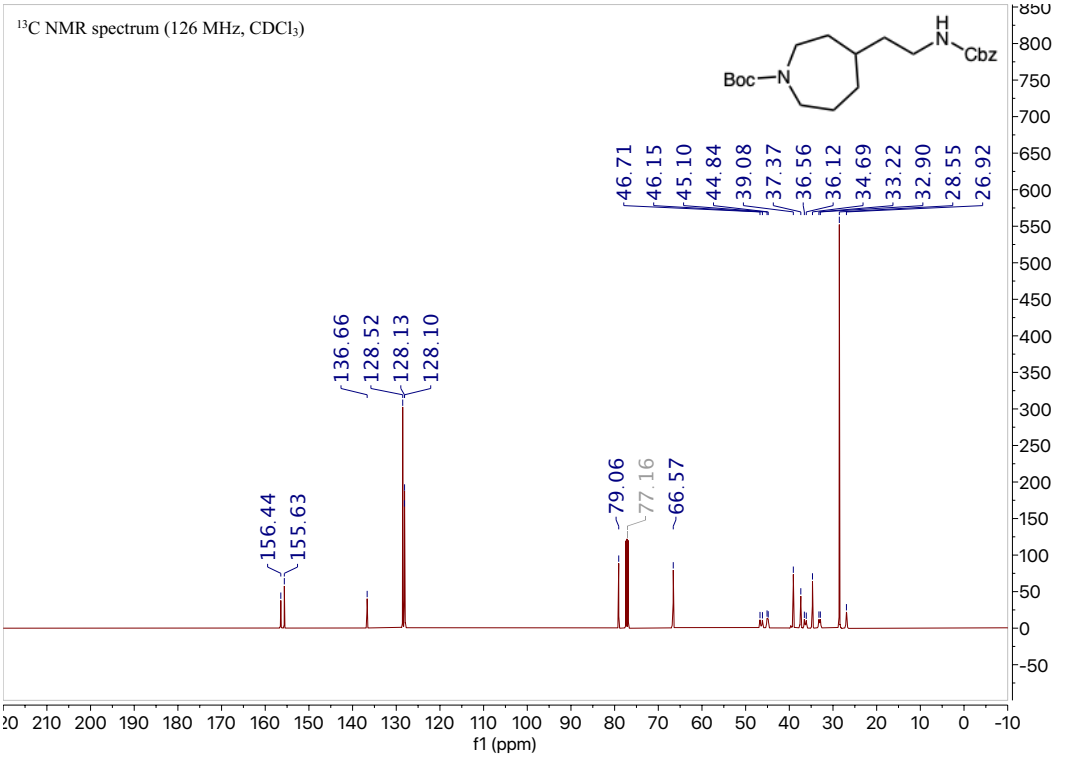


Figure S66. ^{1}H NMR spectrum of **(±)-23**

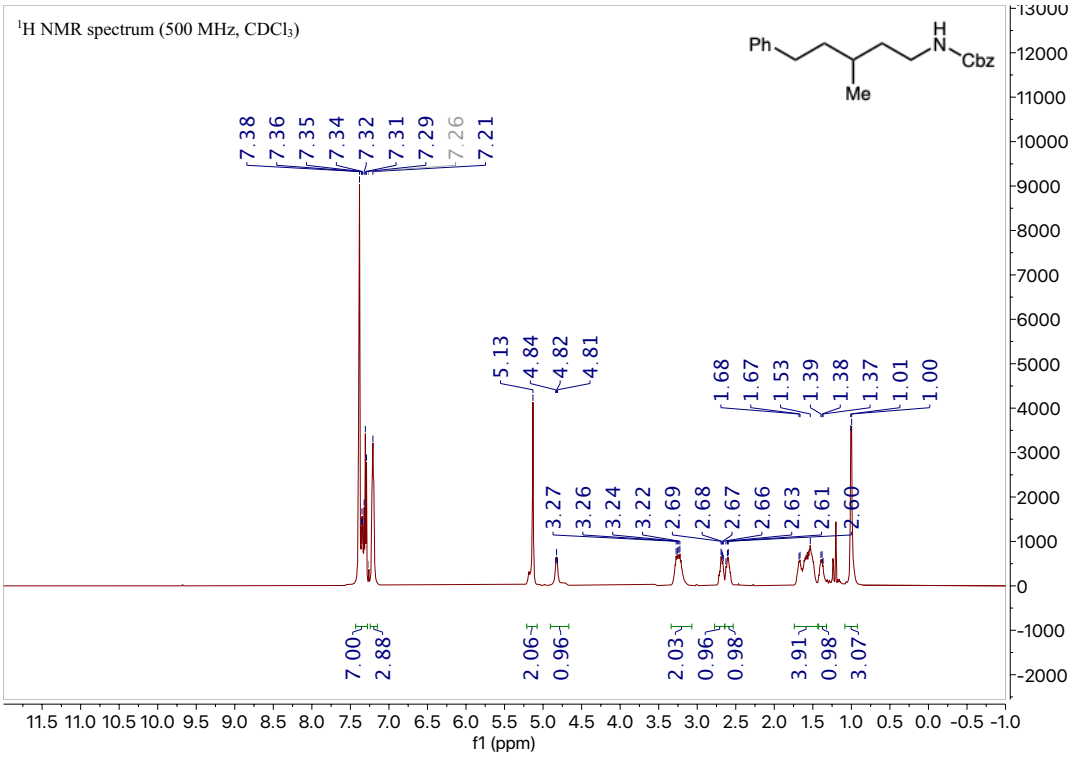


Figure S67. ^{13}C NMR spectrum of **(±)-23**

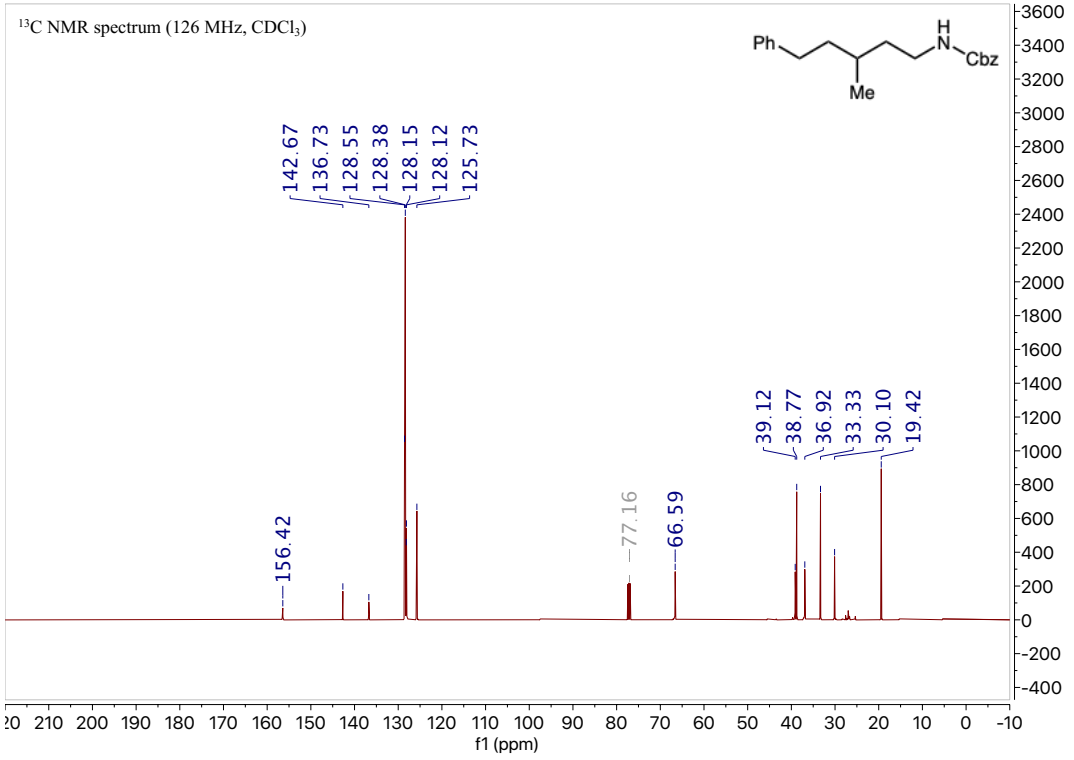


Figure S68. ^{1}H NMR spectrum of **(±)-24**

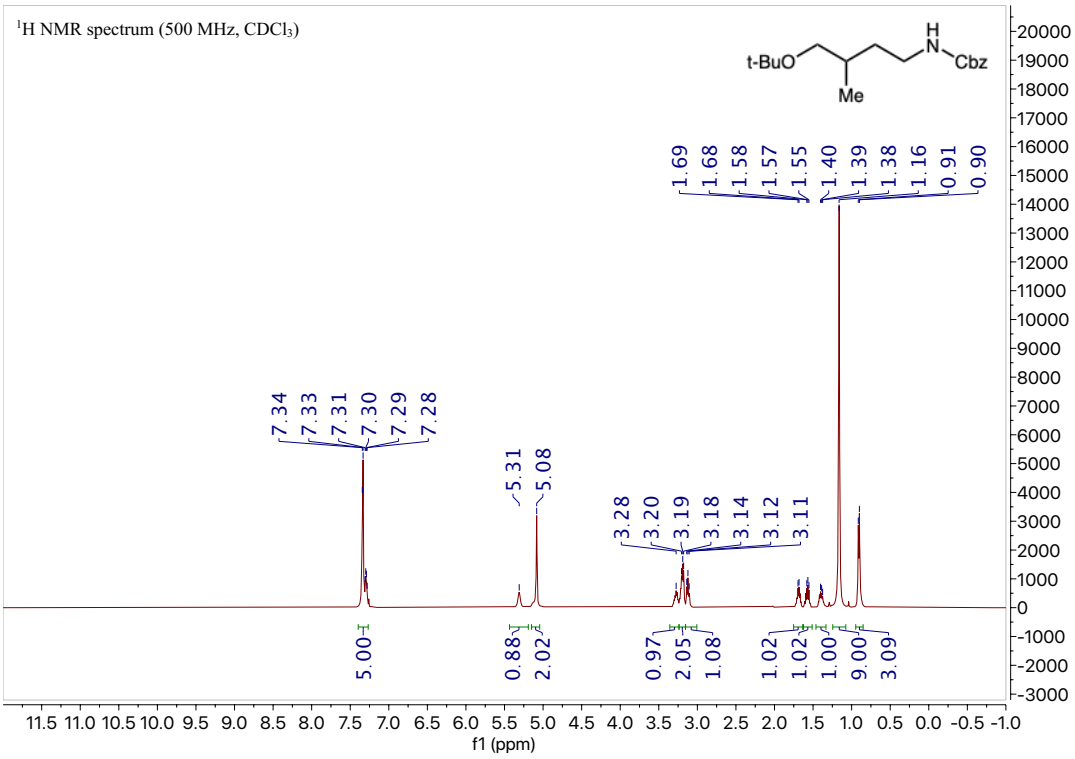


Figure S69. ^{13}C NMR spectrum of **(±)-24**

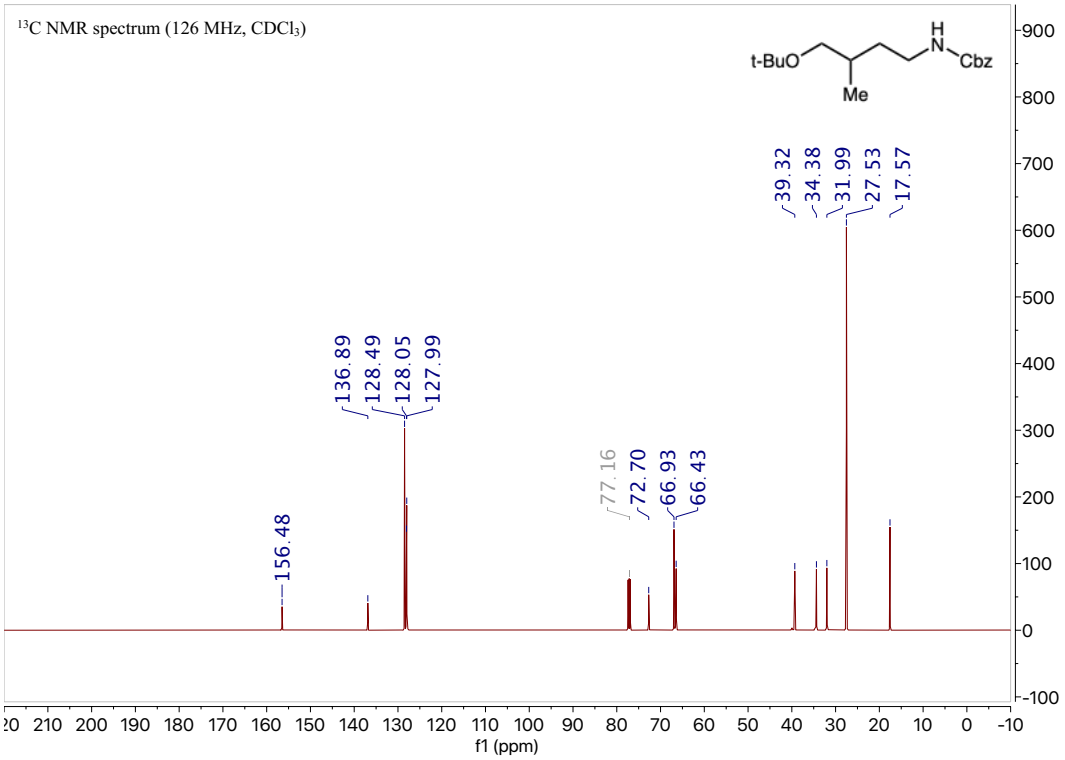


Figure S70. ^{1}H NMR spectrum of **25**

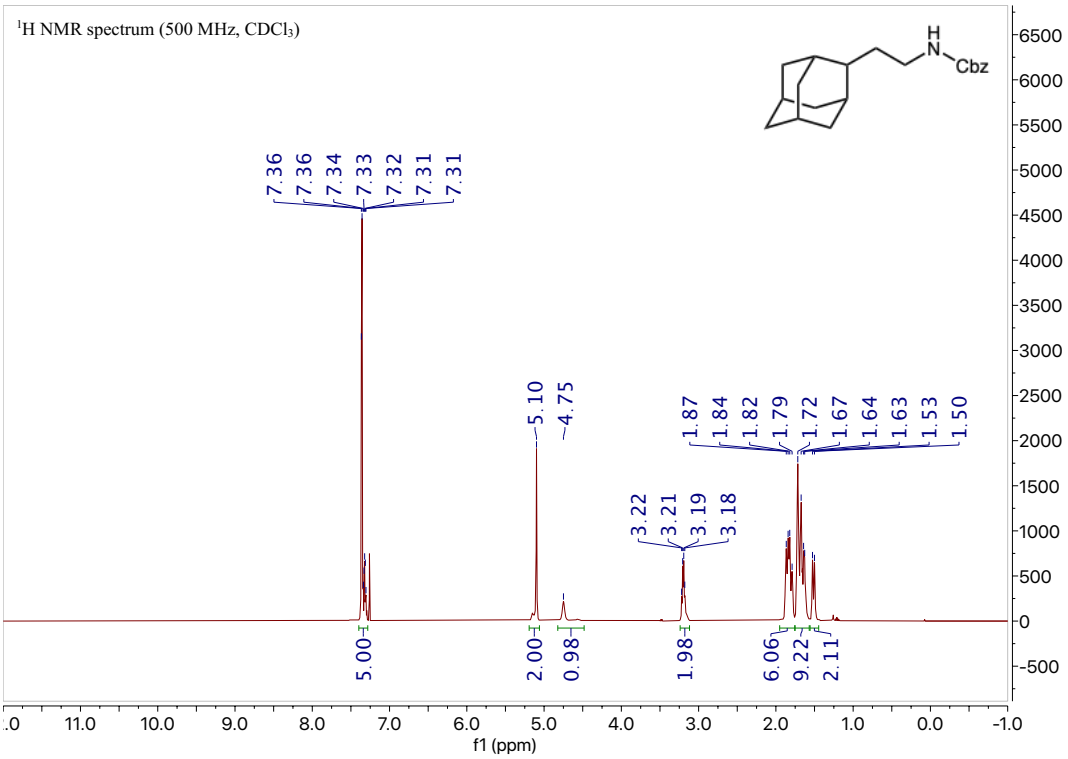


Figure S71. ^{13}C NMR spectrum of **25**

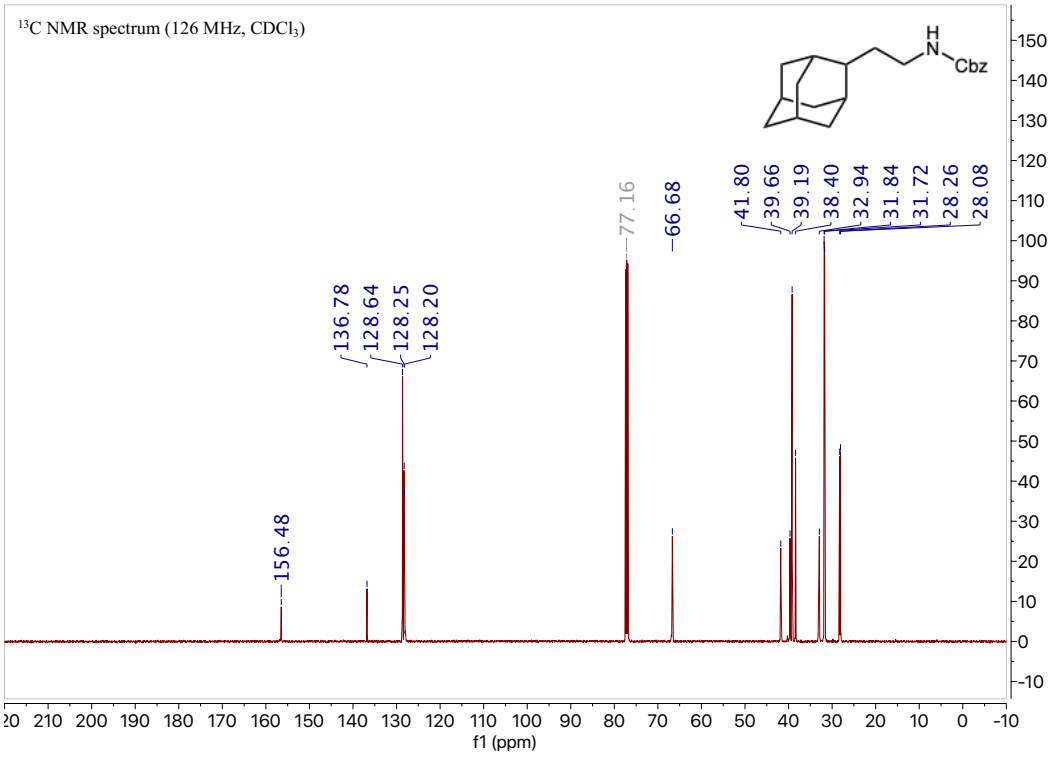


Figure S72. ^{1}H NMR spectrum of **(±)-26**

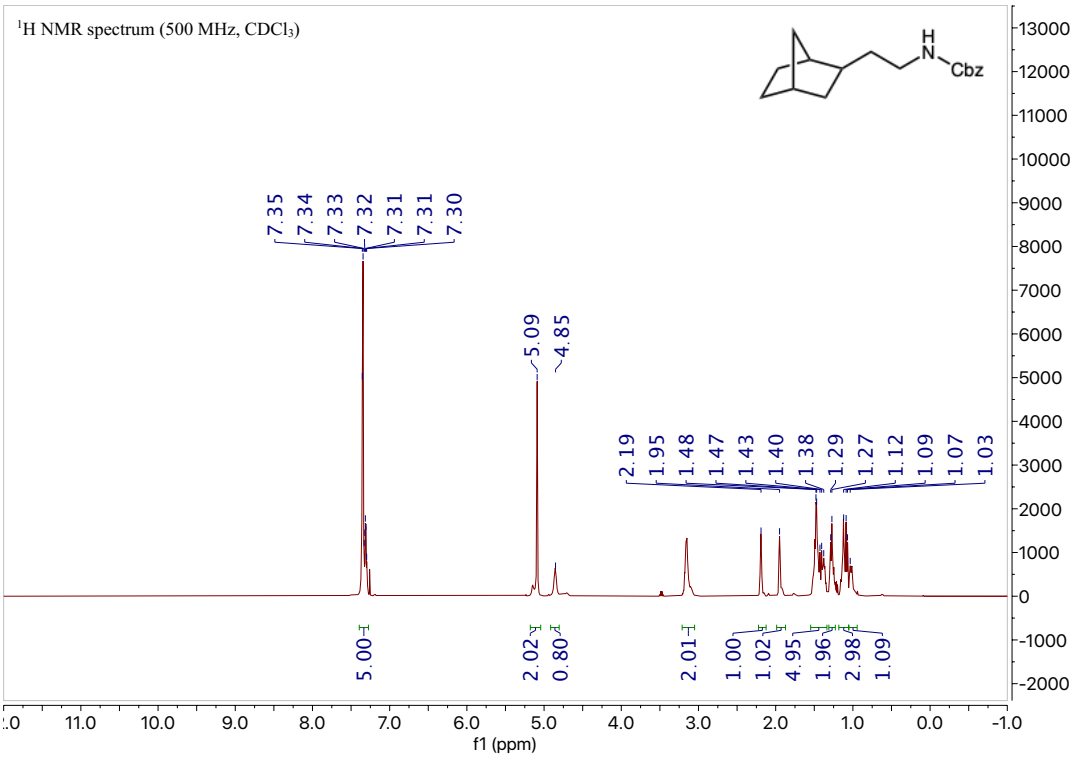


Figure S73. ^{13}C NMR spectrum of **(±)-26**

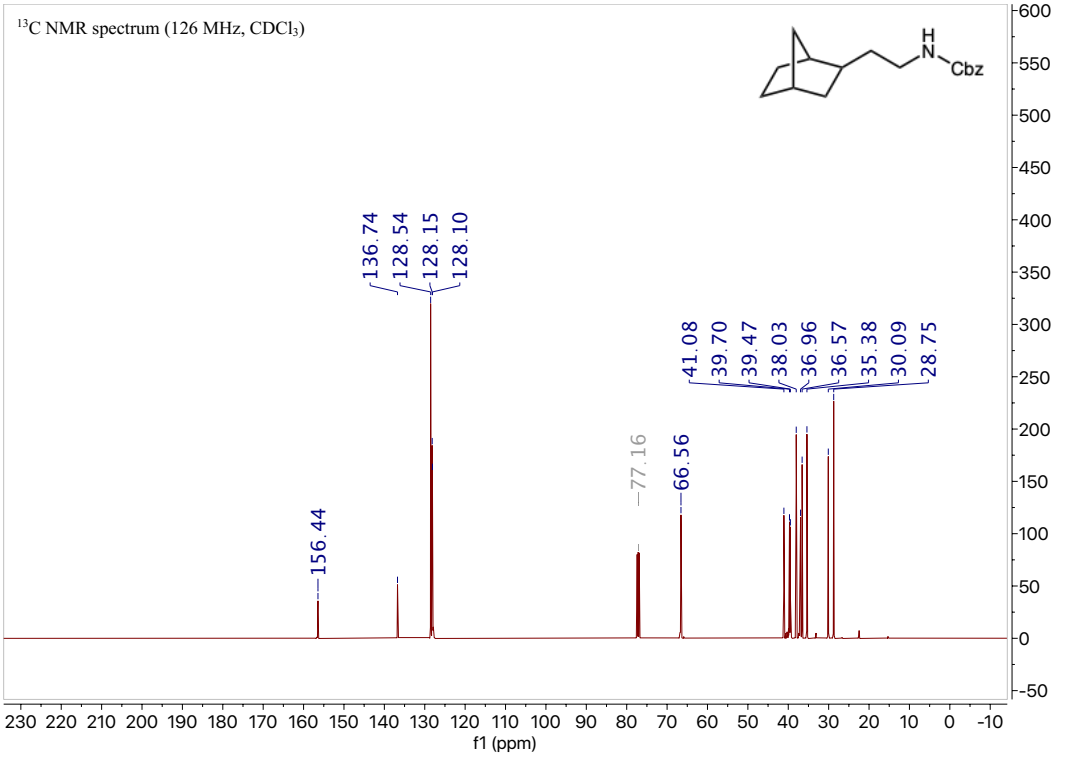


Figure S74. ^{1}H NMR spectrum of **27**

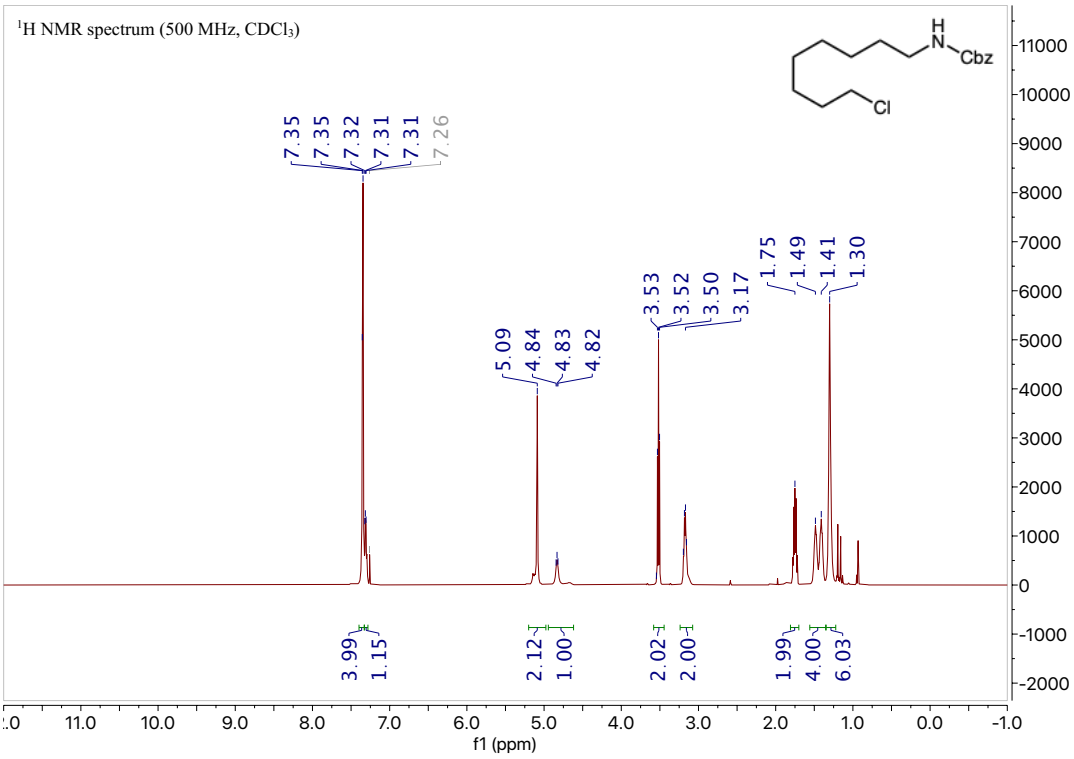


Figure S75. ^{13}C NMR spectrum of **27**

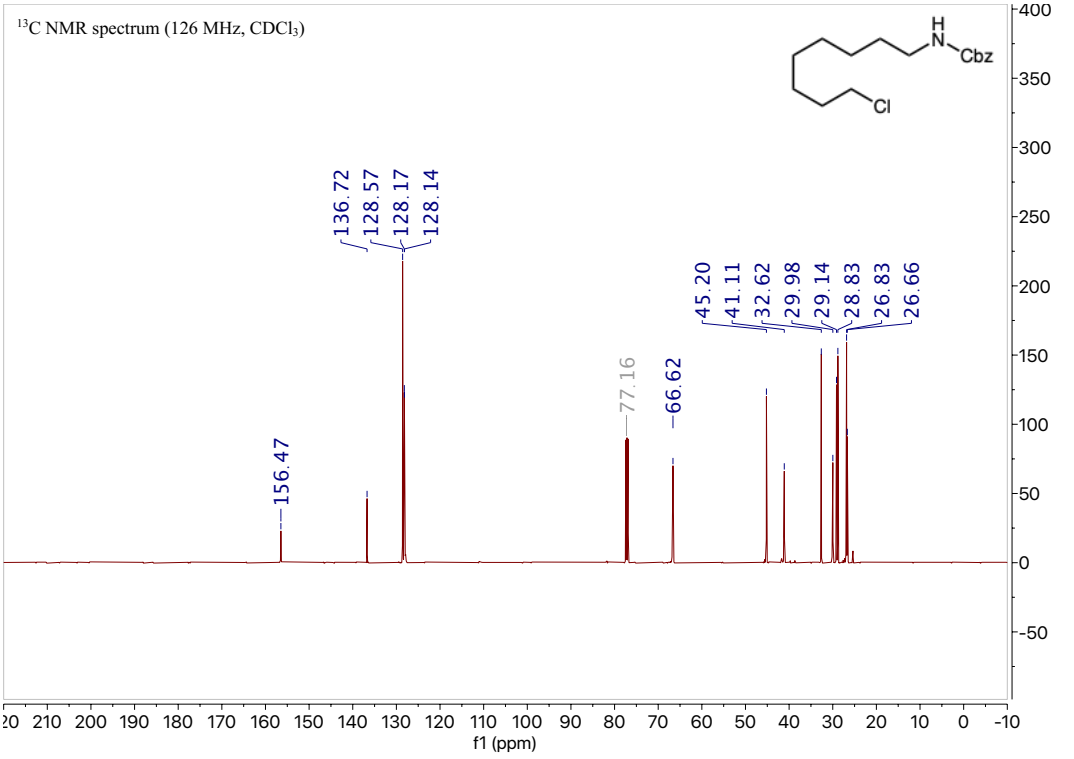


Figure S76. ^{1}H NMR spectrum of **28**

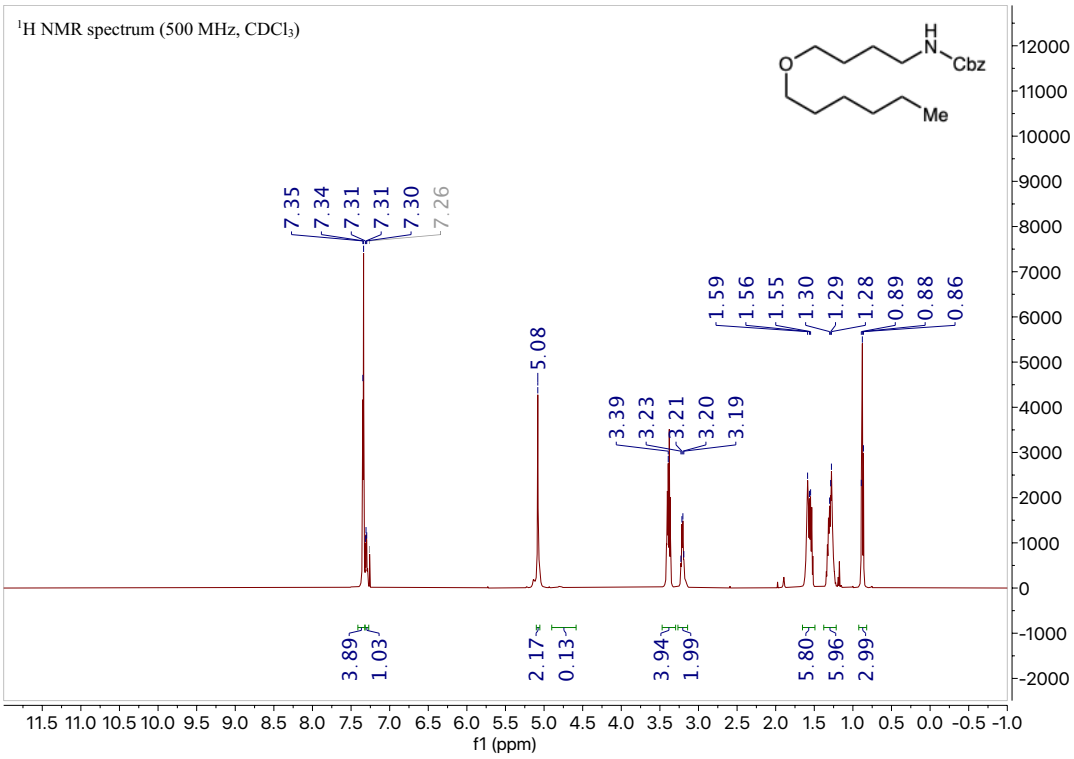


Figure S77. ^{13}C NMR spectrum of **28**

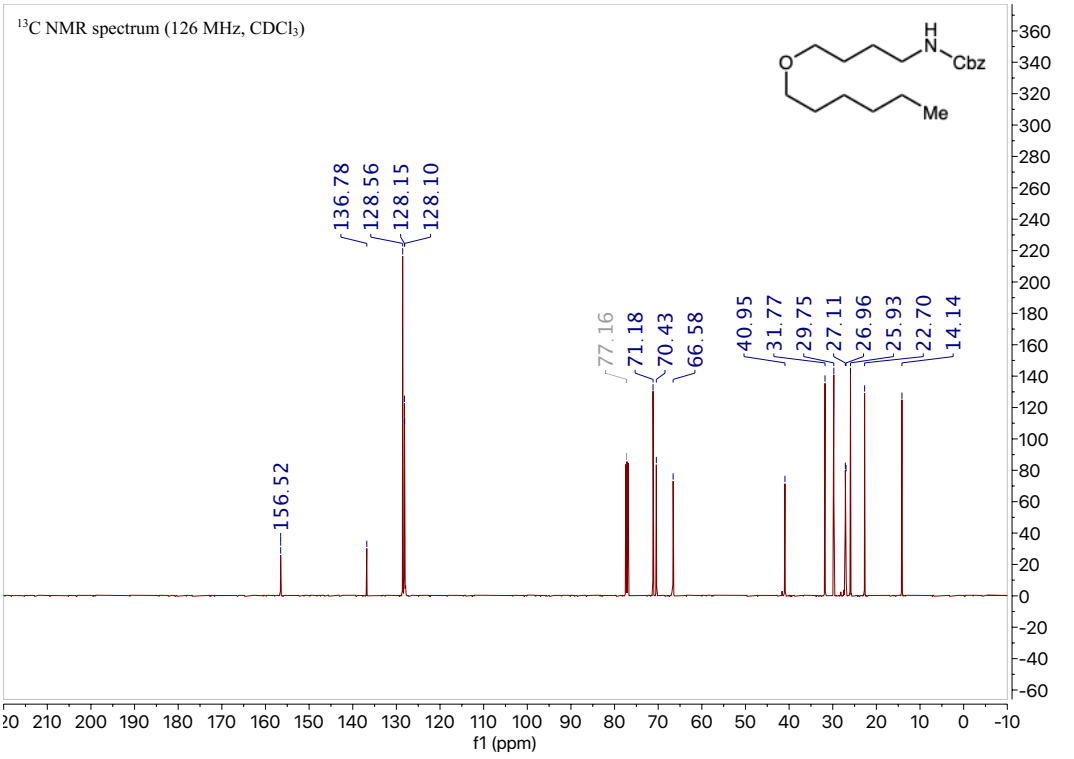


Figure S78. ^{1}H NMR assay of **28** with 1,3,5-trimethoxybenzene (0.339 equiv)

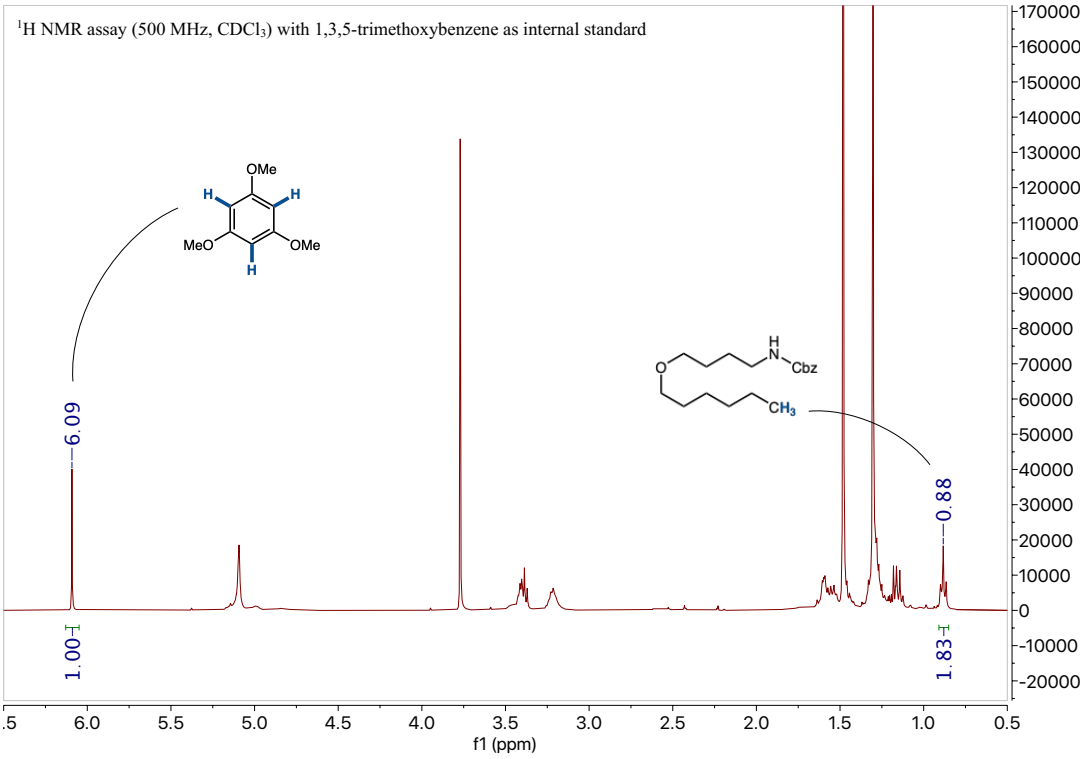


Figure S79. ^{1}H NMR spectrum of **(±)-29**

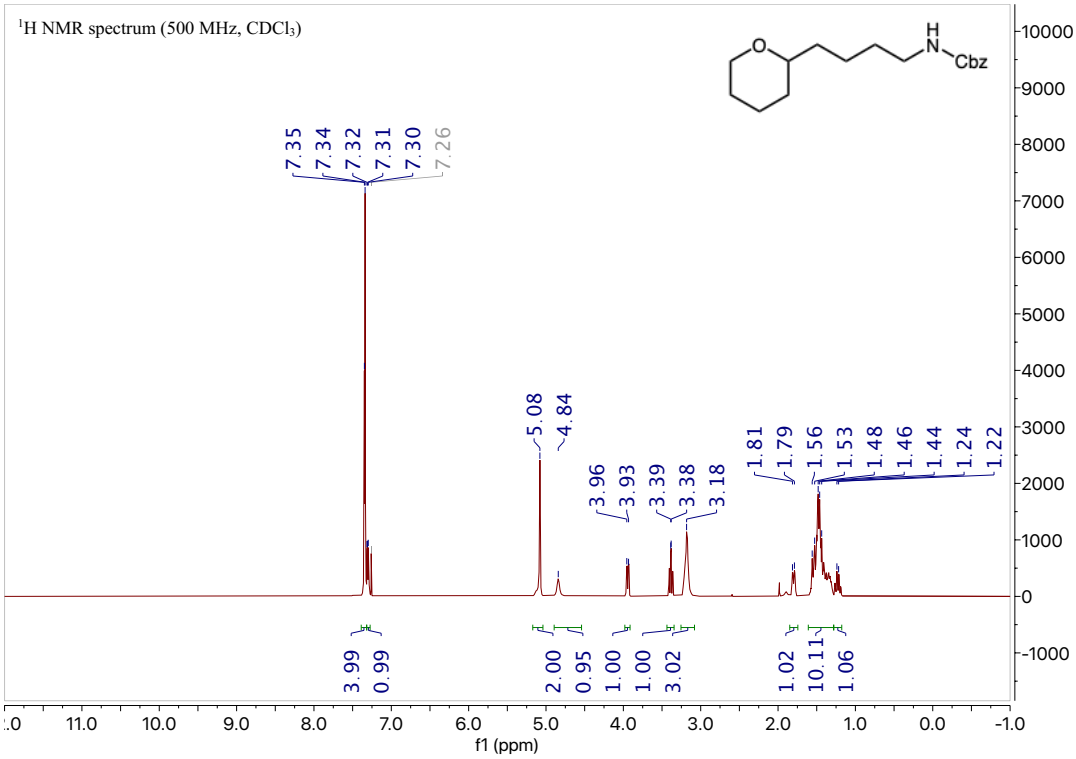


Figure S80. ^{13}C NMR spectrum of **(±)-29**

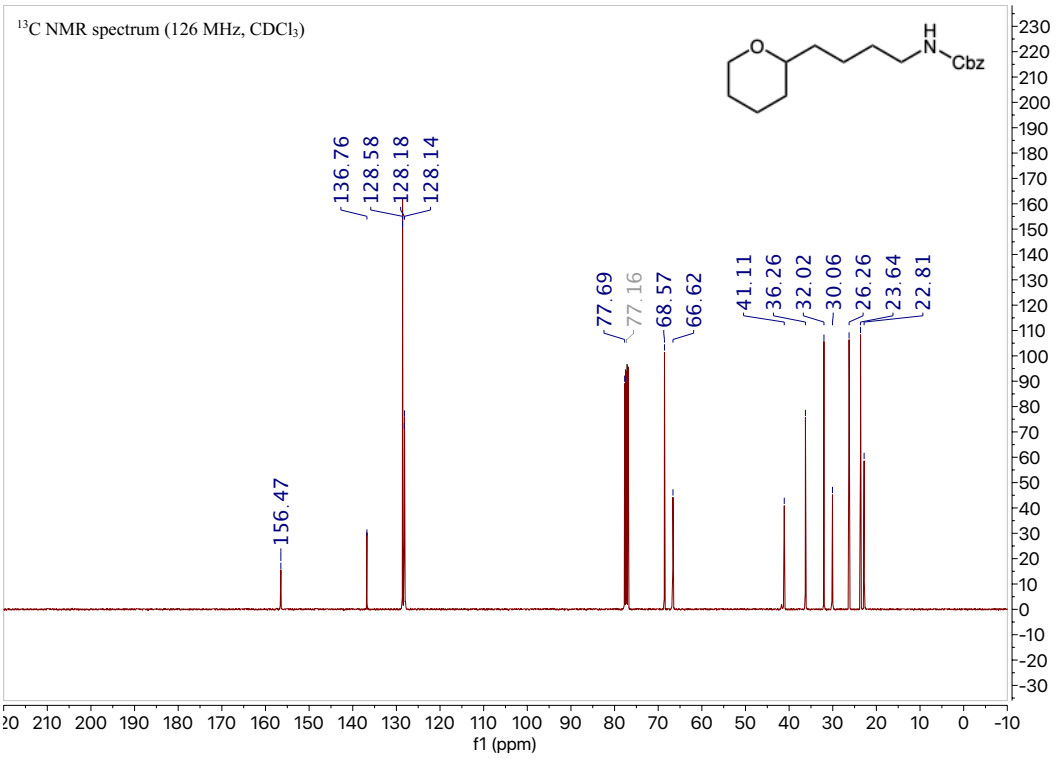


Figure S81. ^{1}H NMR assay of **(±)-29** with 1,3,5-trimethoxybenzene (0.371 equiv).

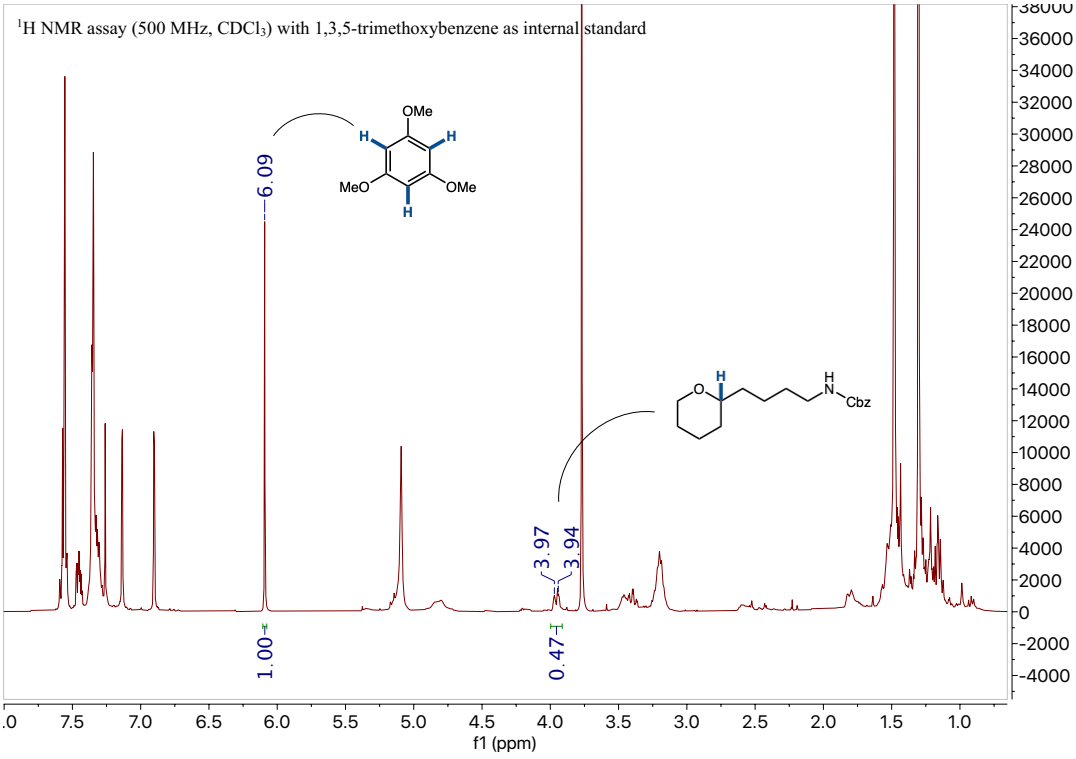


Figure S82. ^{1}H NMR spectrum of **30**

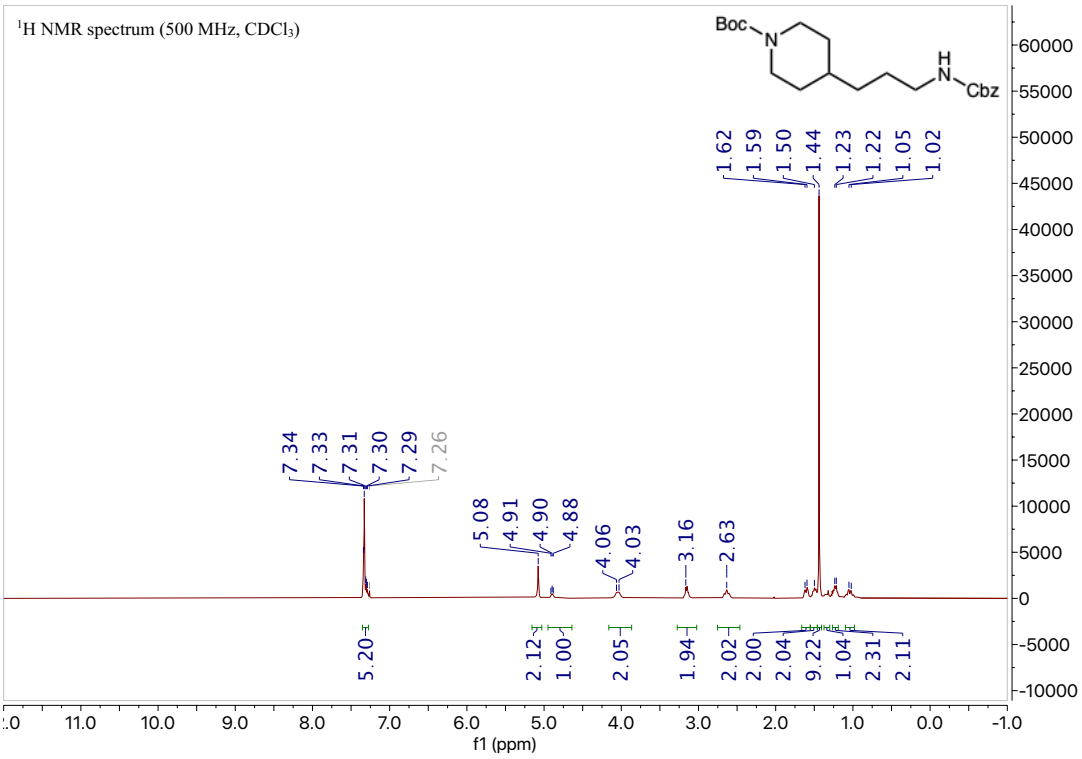


Figure S83. ^{13}C NMR spectrum of **30**

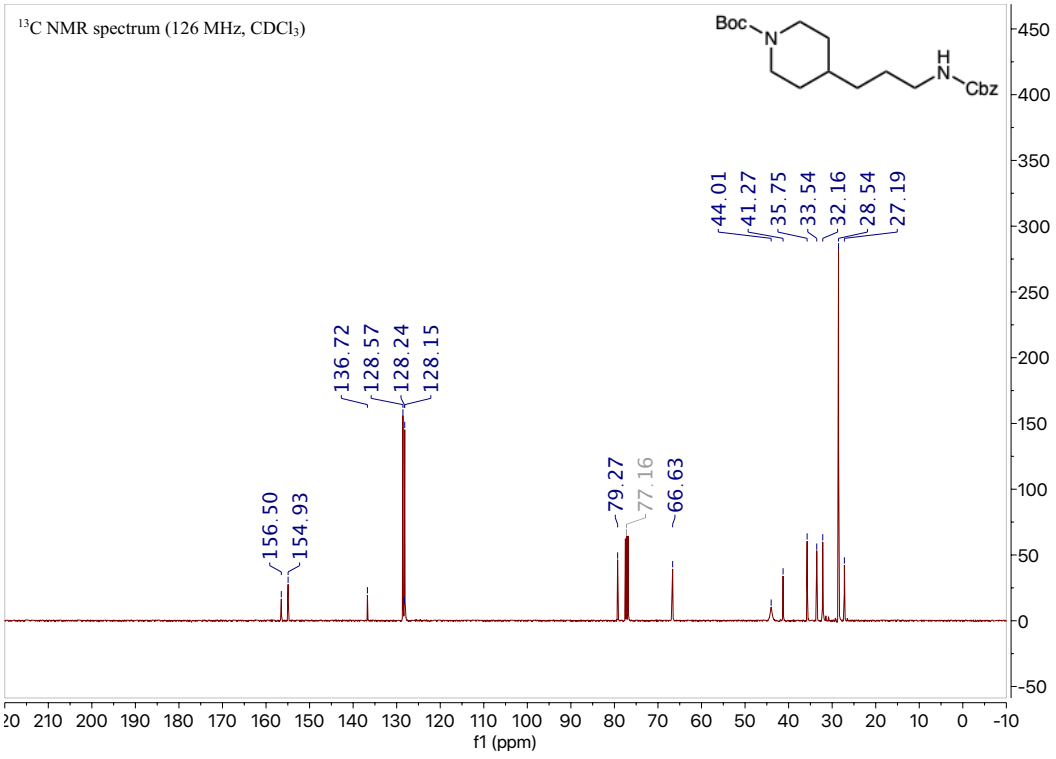


Figure S84. ^{1}H NMR spectrum of **31**

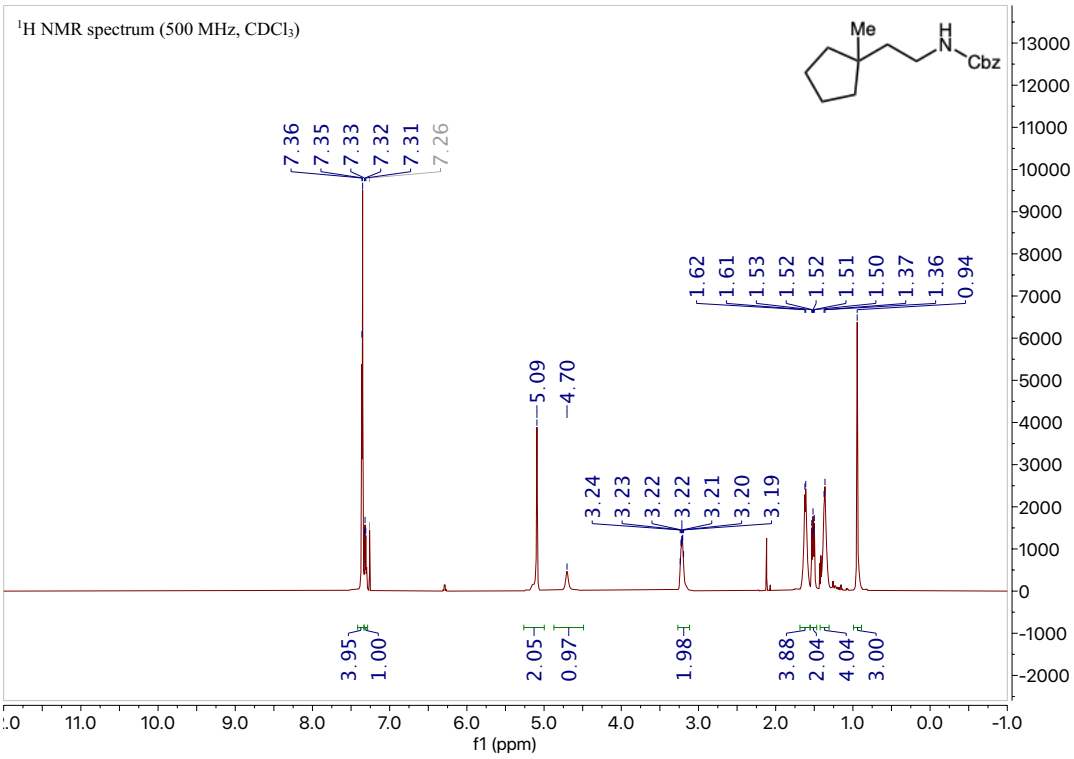


Figure S85. ^{13}C NMR spectrum of **31**

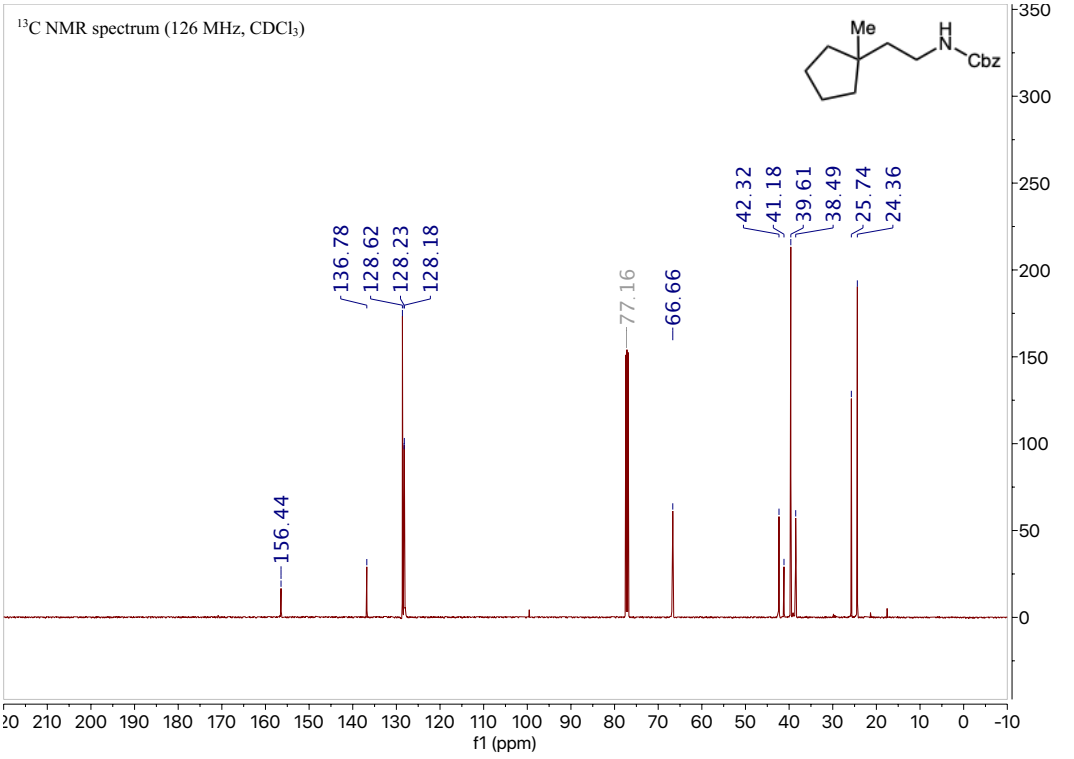


Figure S86. ^{1}H NMR spectrum of **32**

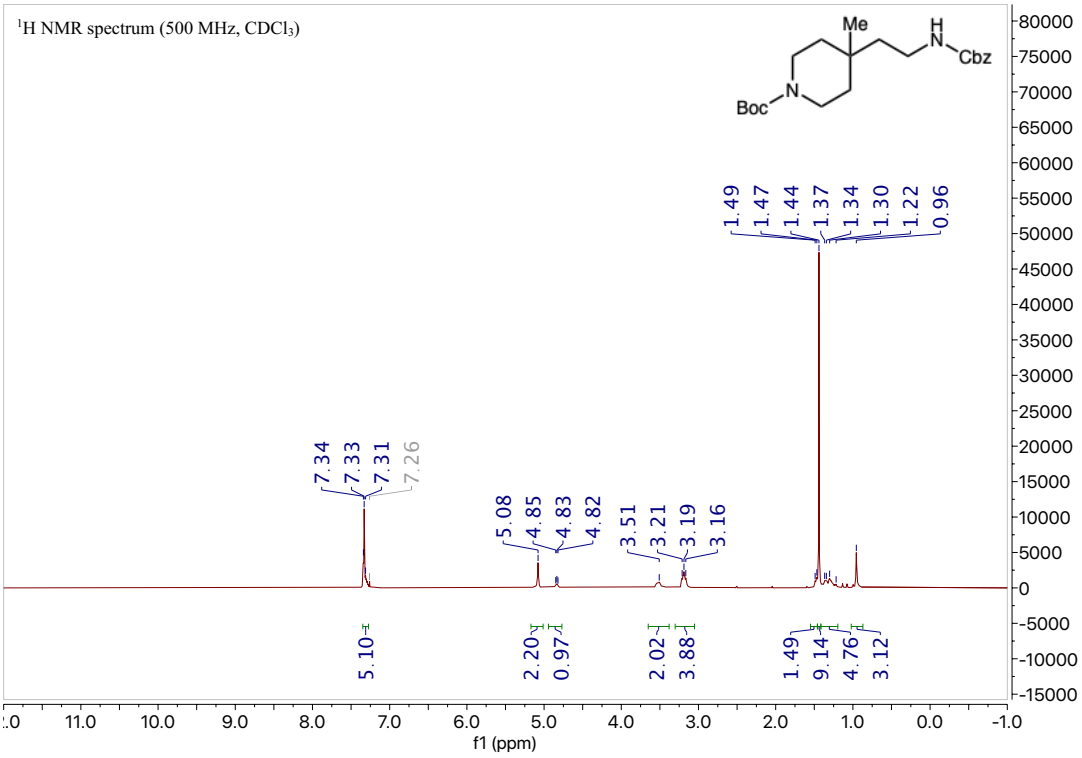


Figure S87. ^{13}C NMR spectrum of **32**

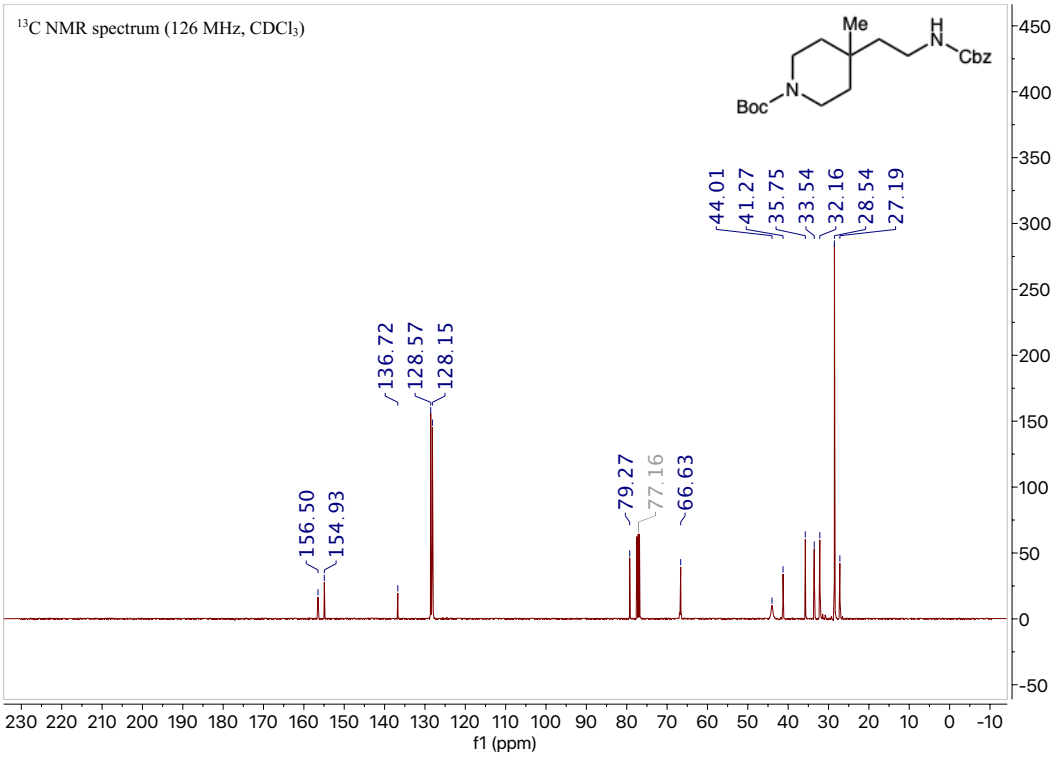


Figure S88. ^{1}H NMR spectrum of **33**

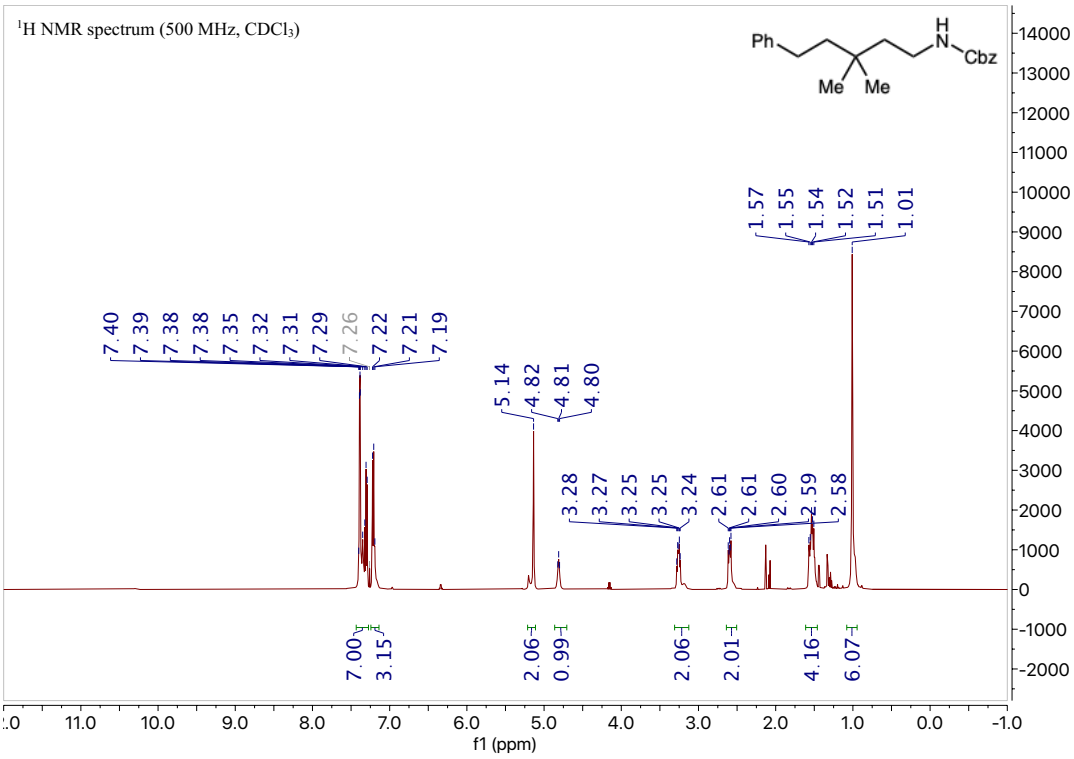


Figure S89. ^{13}C NMR spectrum of **33**

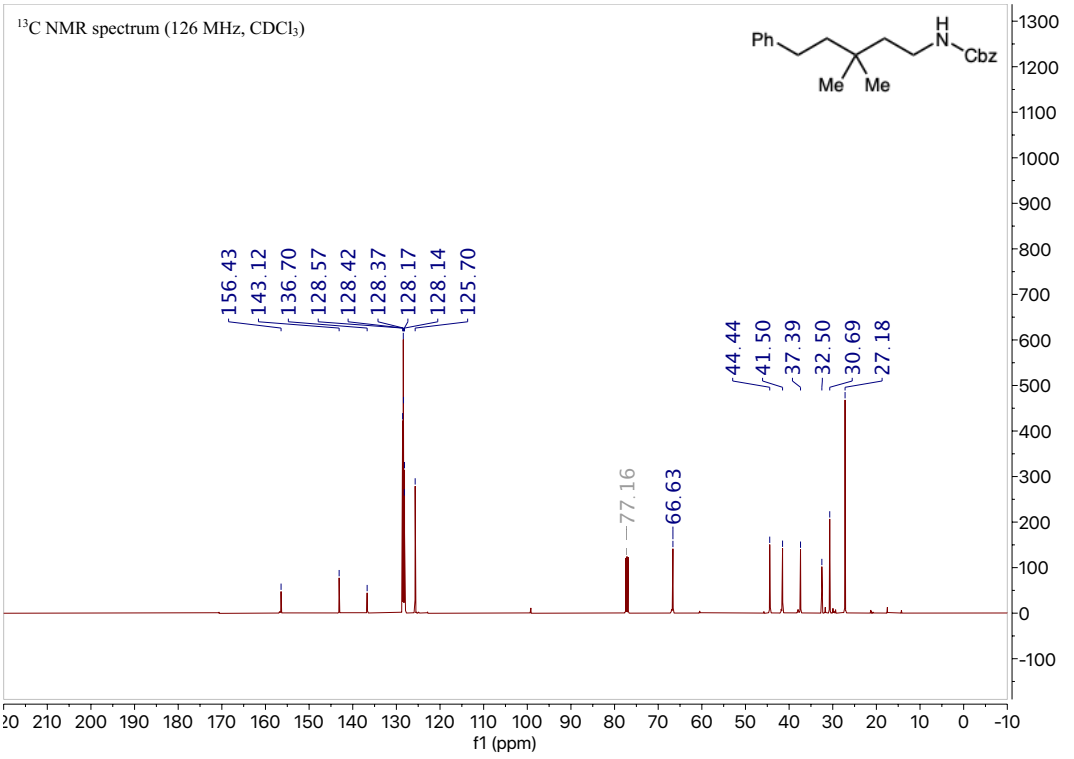


Figure S90. ^{1}H NMR spectrum of **34**

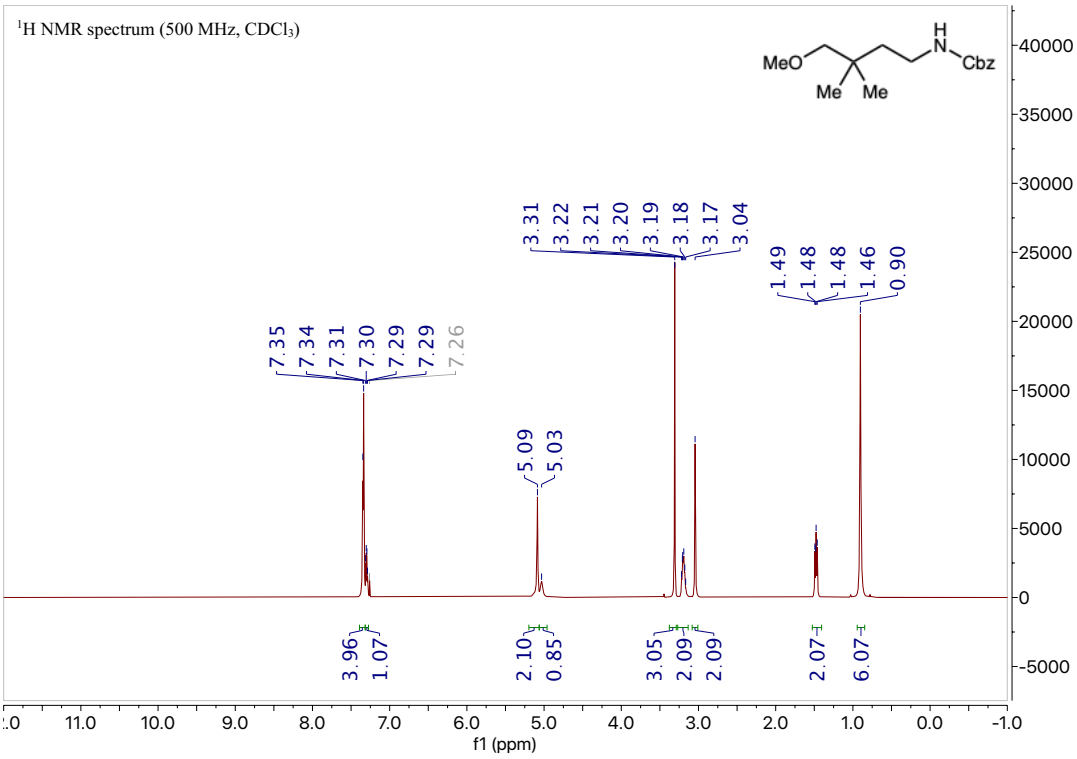


Figure S91. ^{13}C NMR spectrum of **34**

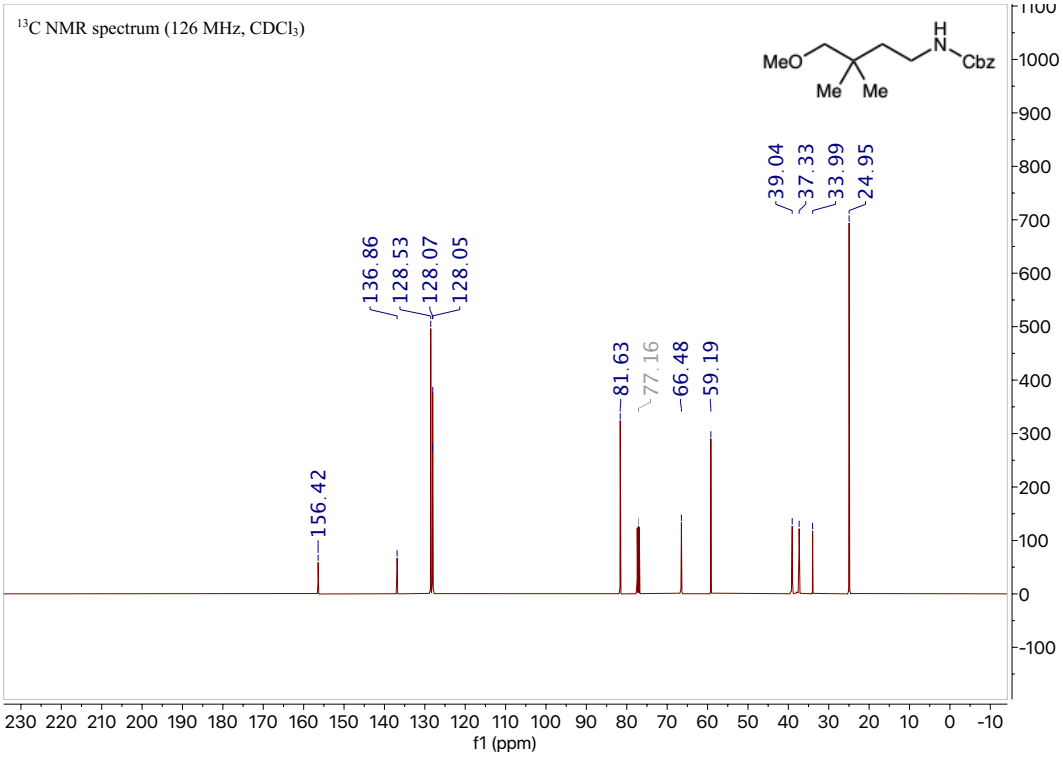


Figure S92. ^{1}H NMR spectrum of **35**

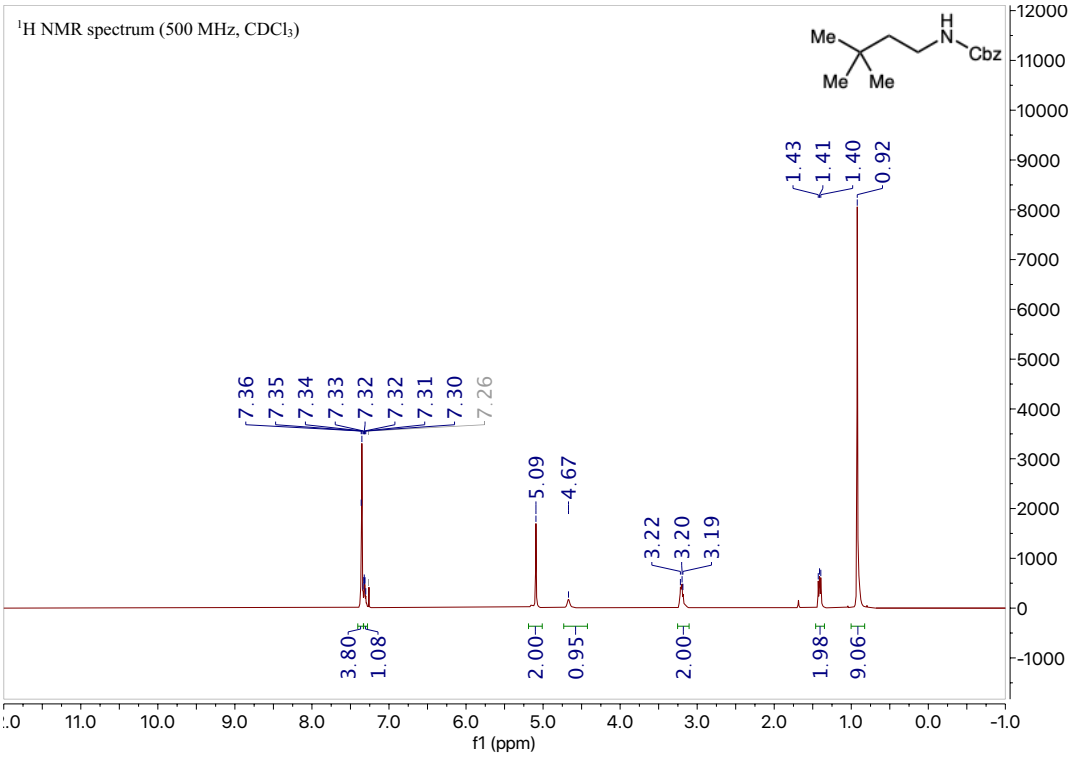


Figure S93. ^{13}C NMR spectrum of **35**

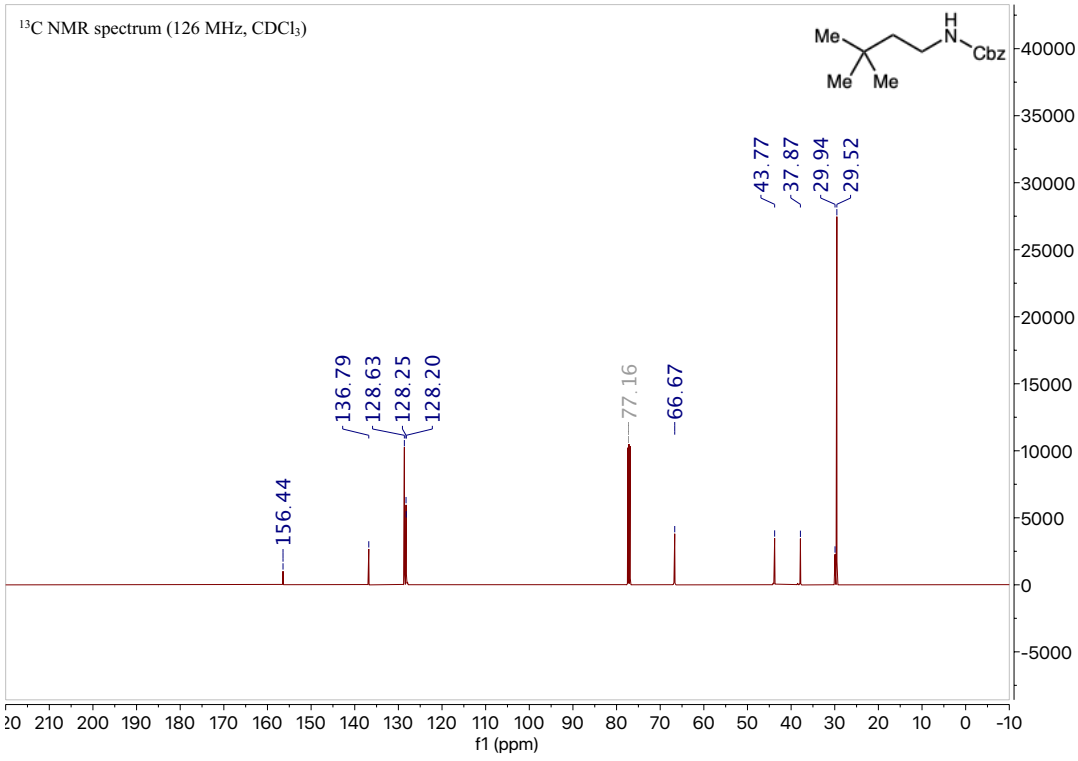


Figure S94. ^{1}H NMR spectrum of **37**

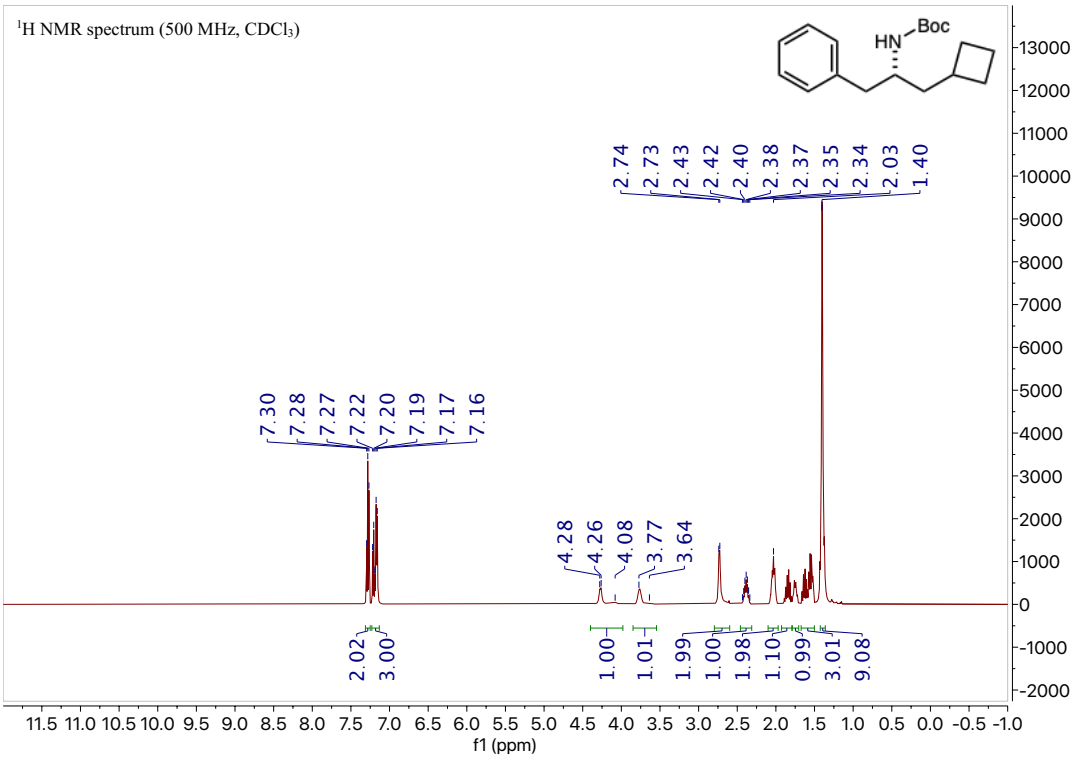


Figure S95. ^{13}C NMR spectrum of **37**

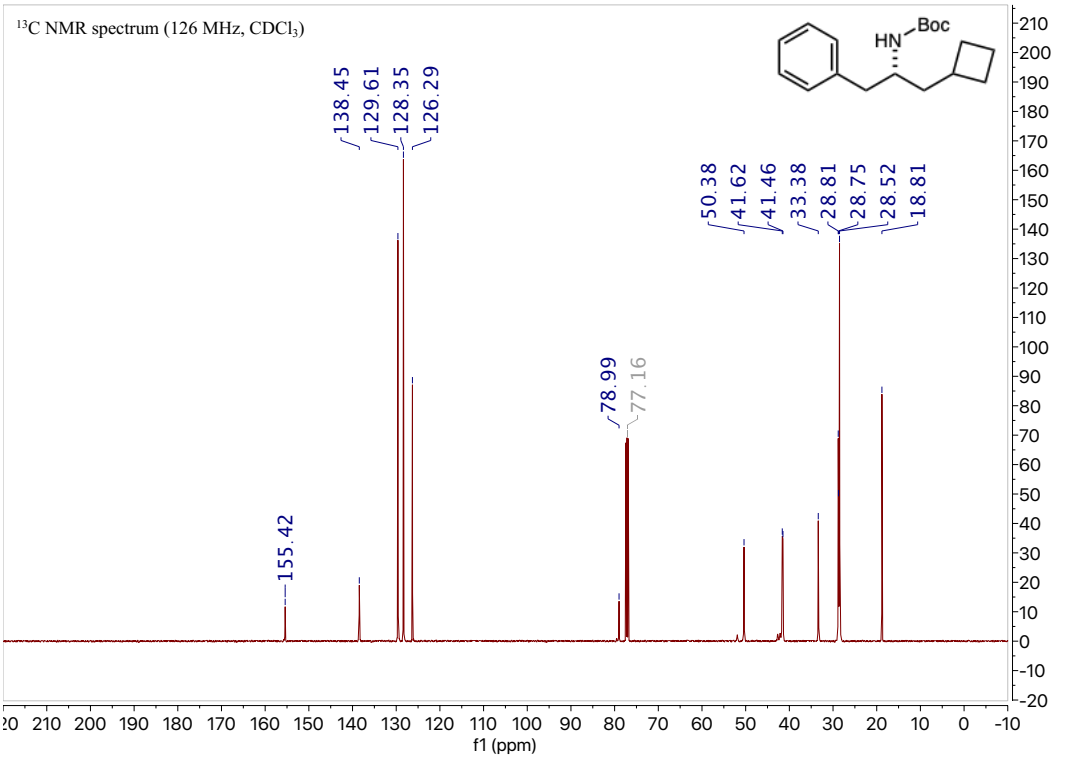


Figure S96. ^{1}H NMR spectrum of **38**

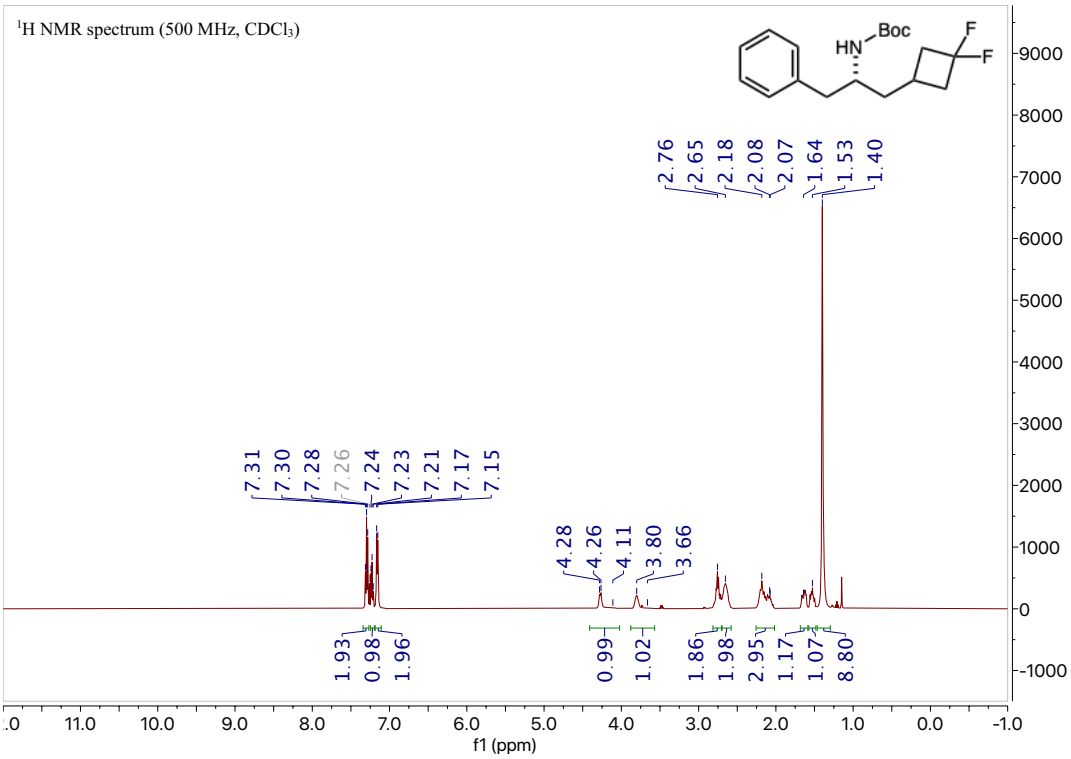


Figure S97. ^{13}C NMR spectrum of **38**

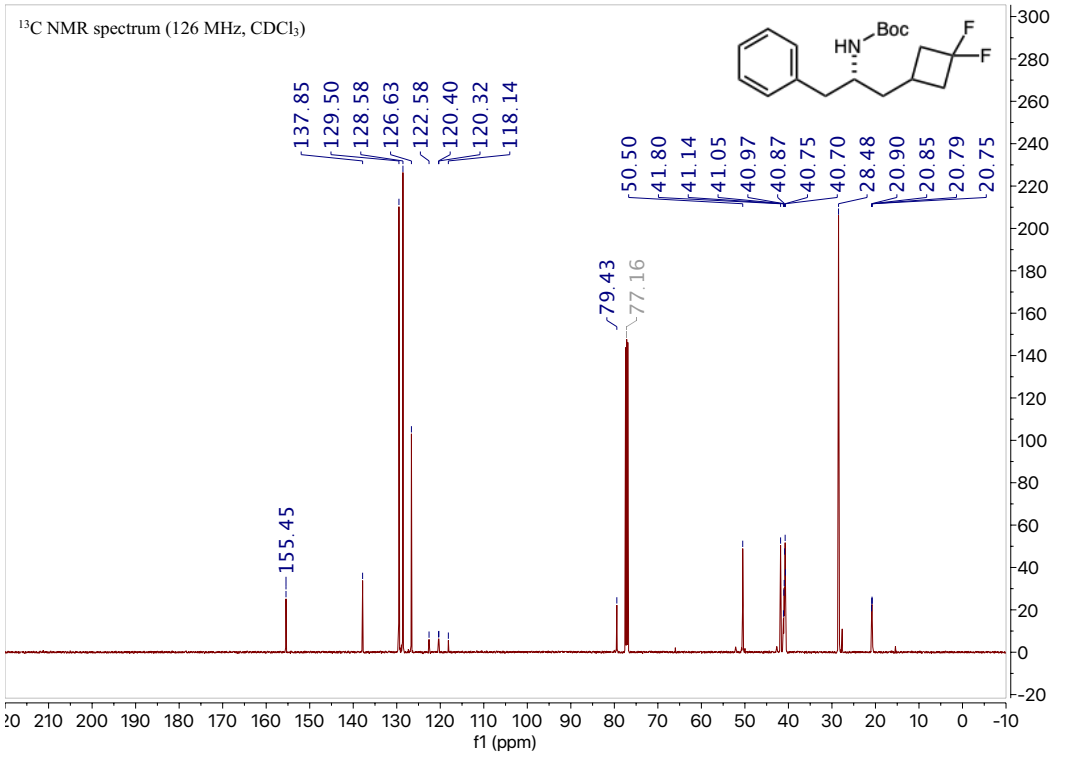


Figure S98. ^{19}F NMR spectrum of **38**

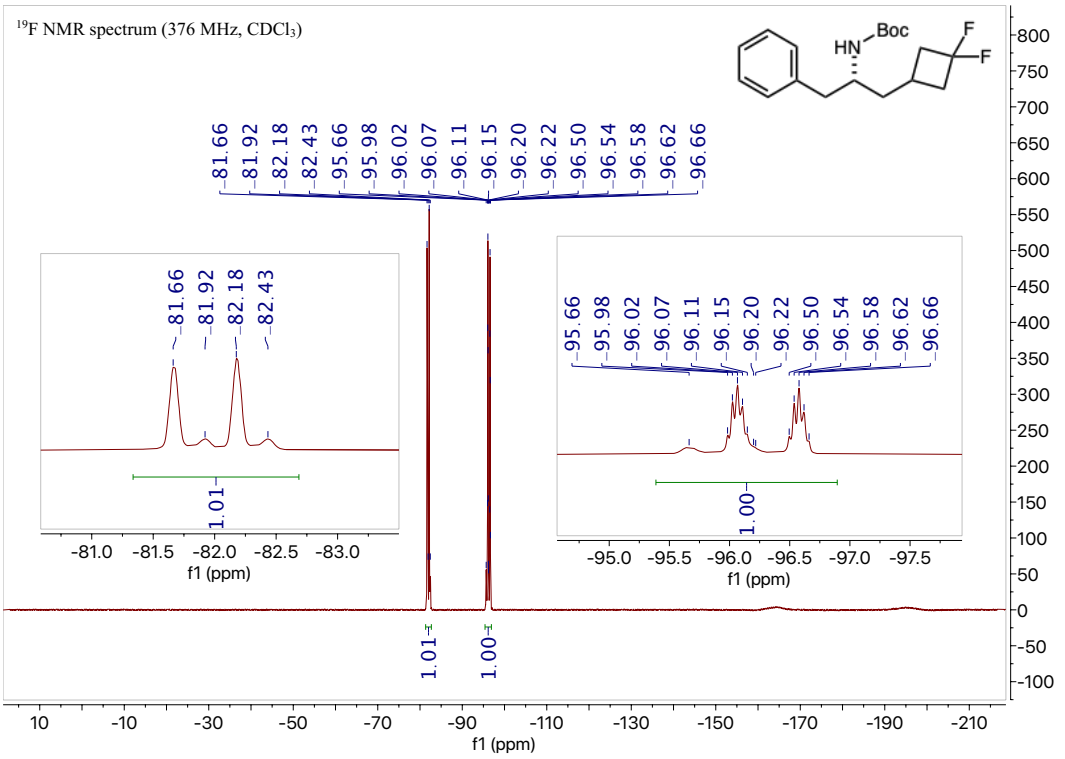


Figure S99. ^{1}H NMR spectrum of **39**

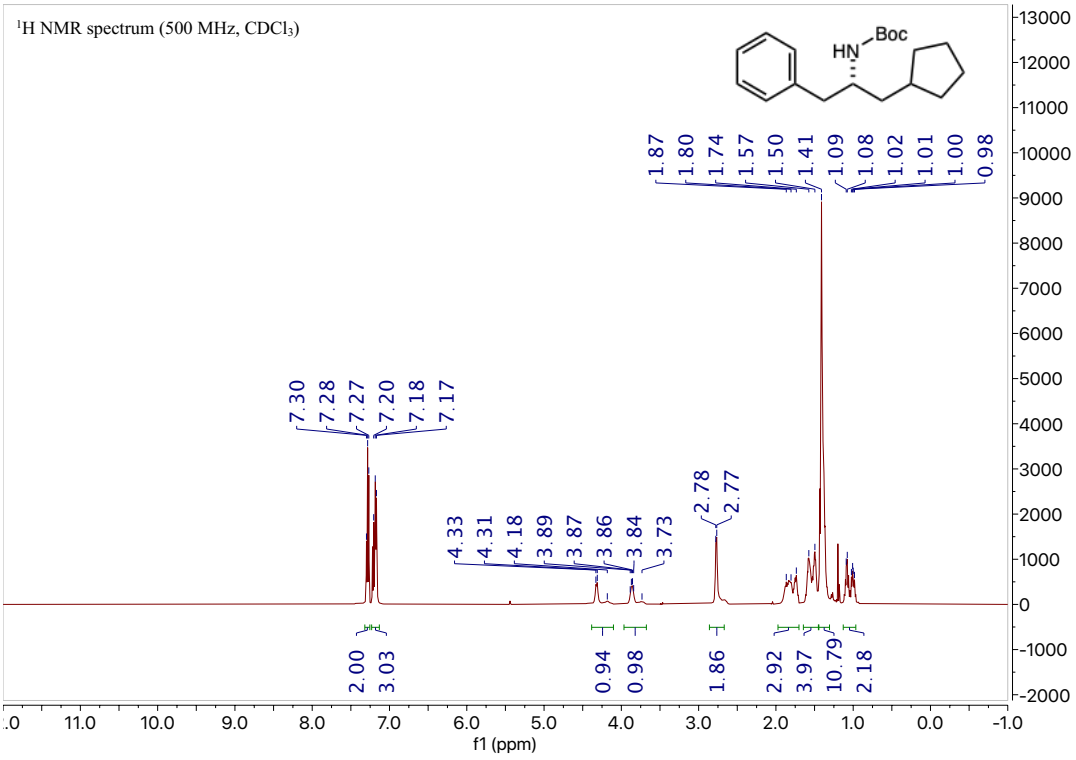


Figure S100. ^{13}C NMR spectrum of **39**

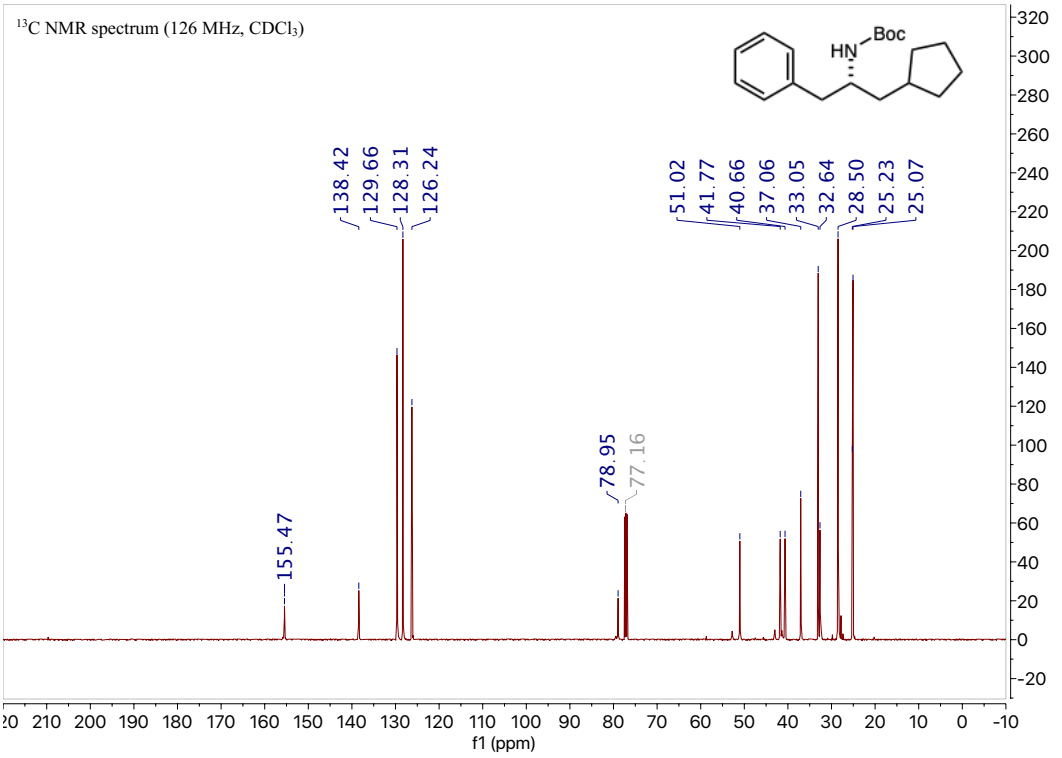


Figure S101. ^{1}H NMR spectrum of **40**

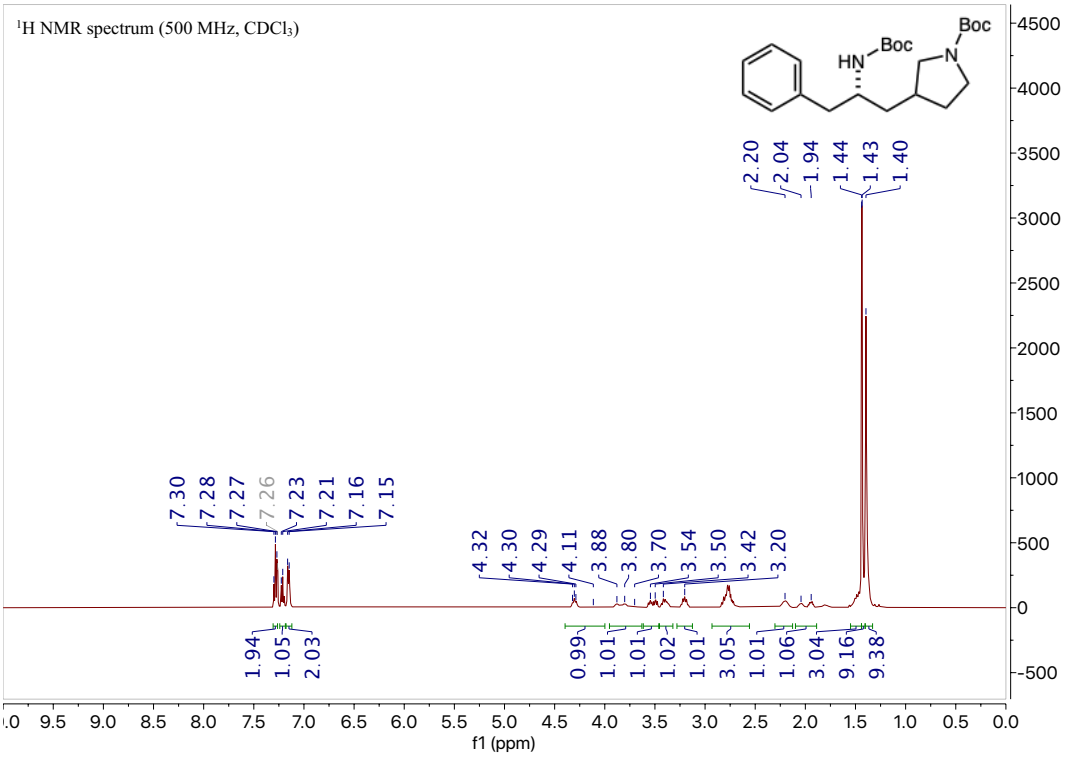


Figure S102. ^{13}C NMR spectrum of **40**

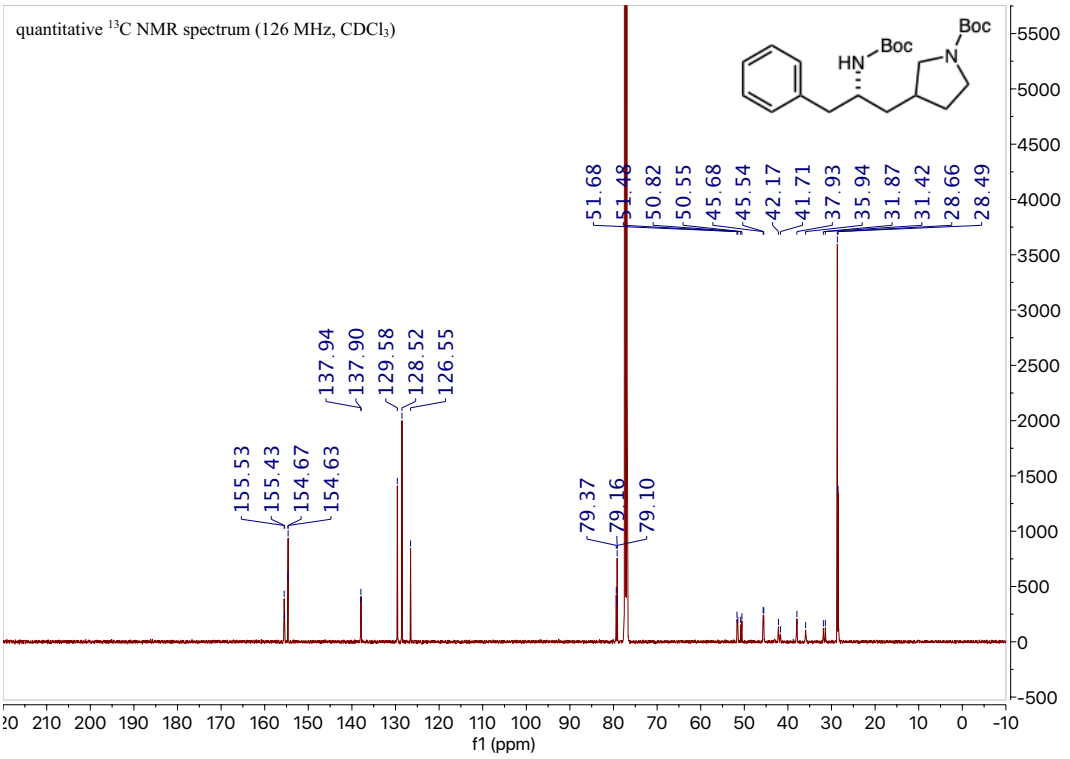


Figure S103. ^{1}H NMR spectrum of **41**

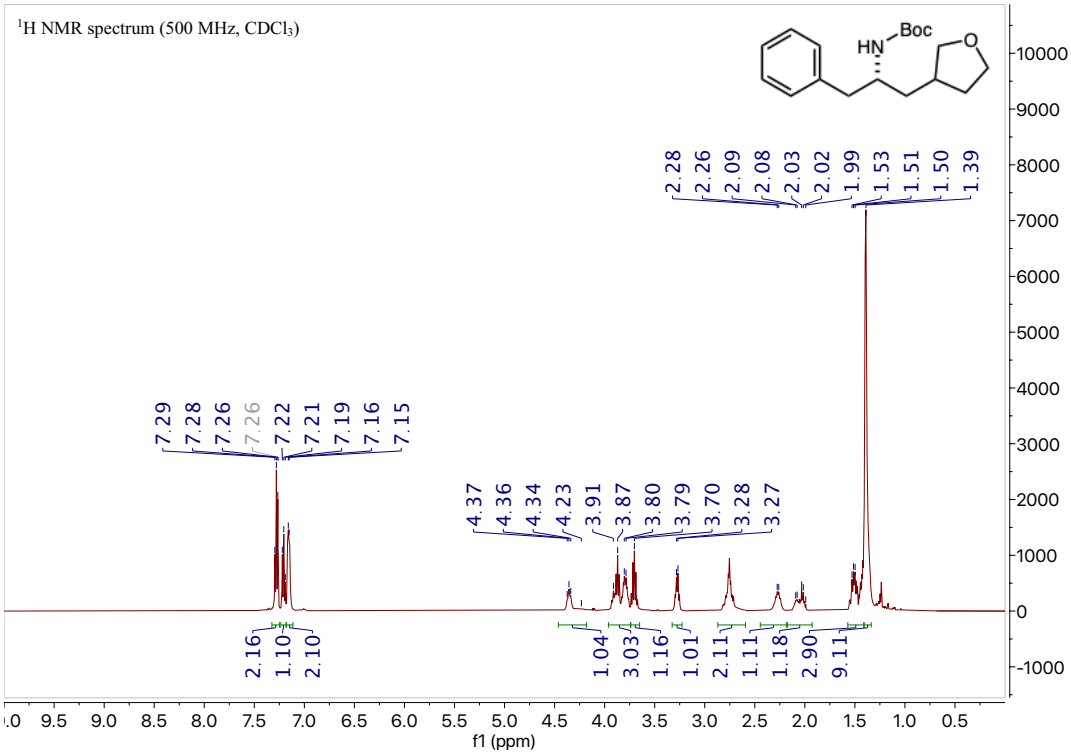


Figure S104. ^{13}C NMR spectrum of **41**

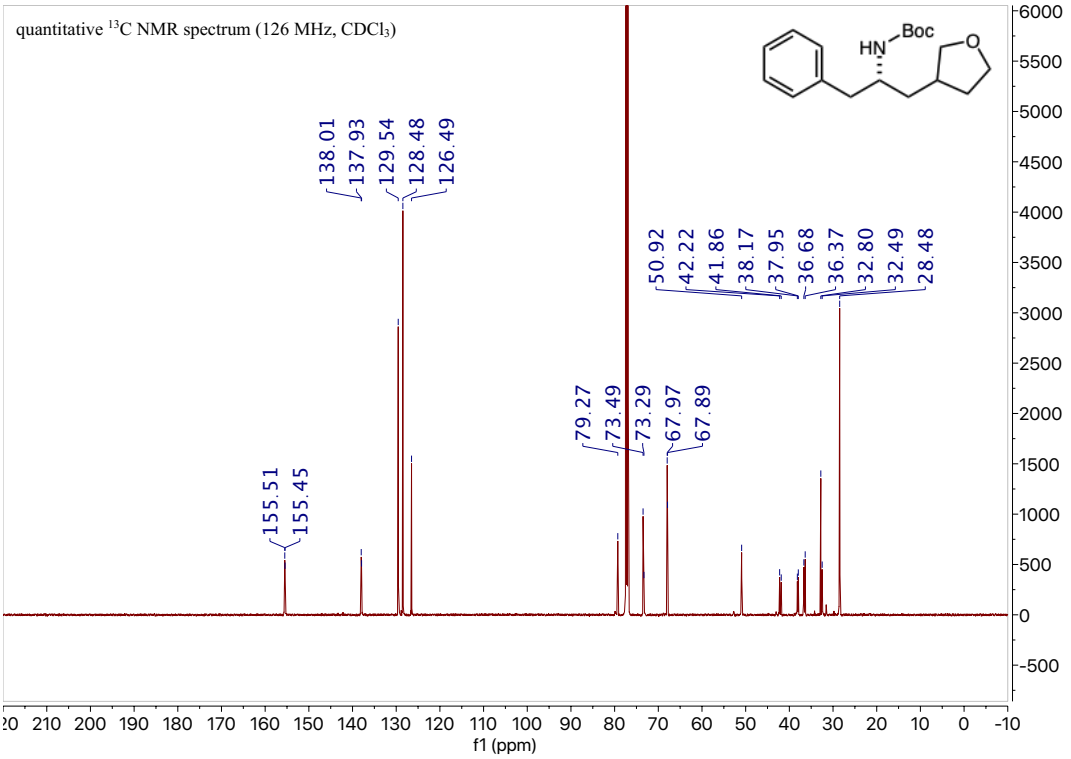


Figure S105. ^{1}H NMR spectrum of **42**

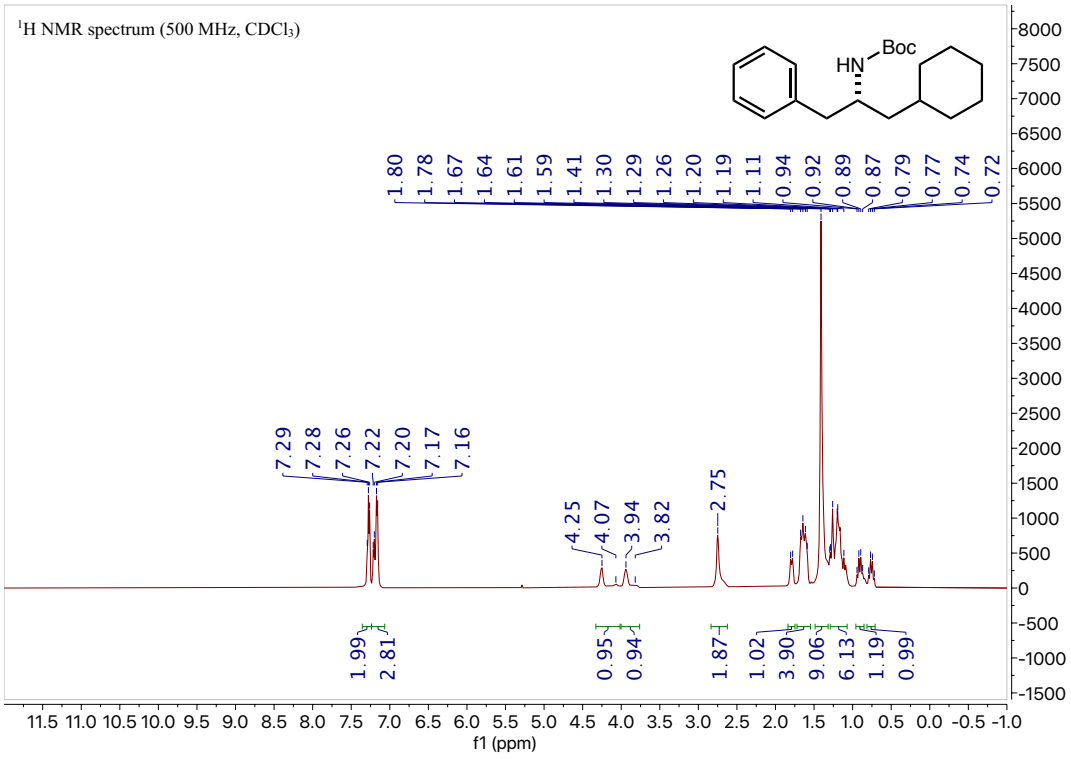


Figure S106. ^{13}C NMR spectrum of **42**

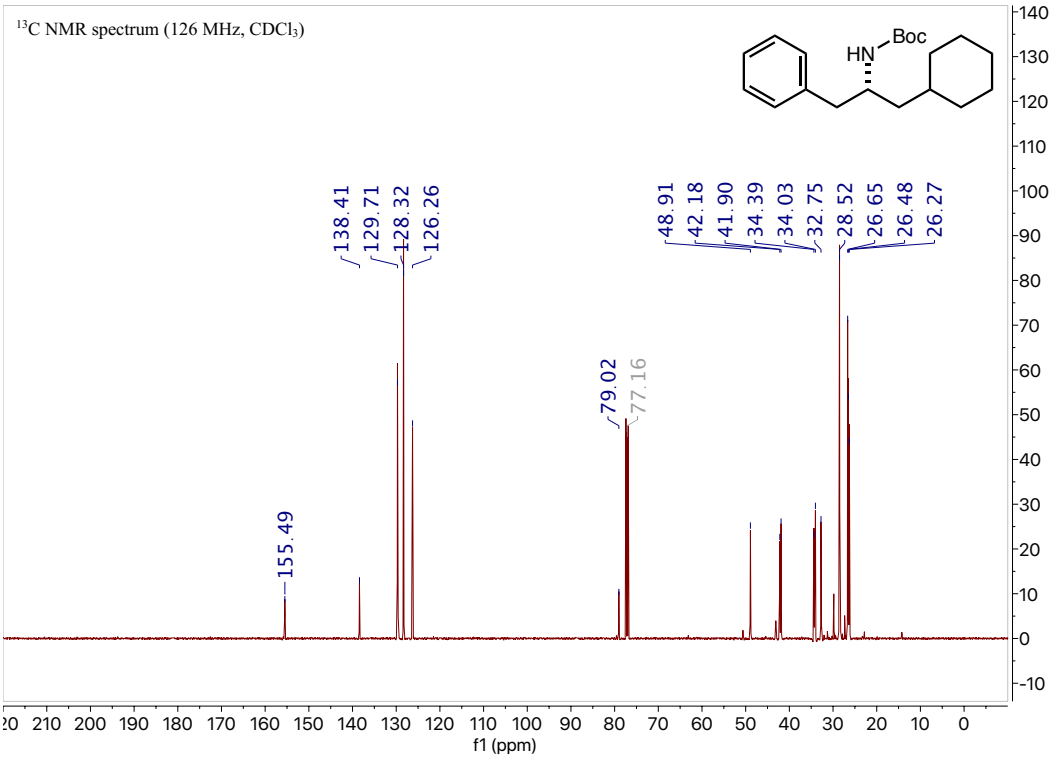


Figure S107. Chiral HPLC assay of **(±)-42**

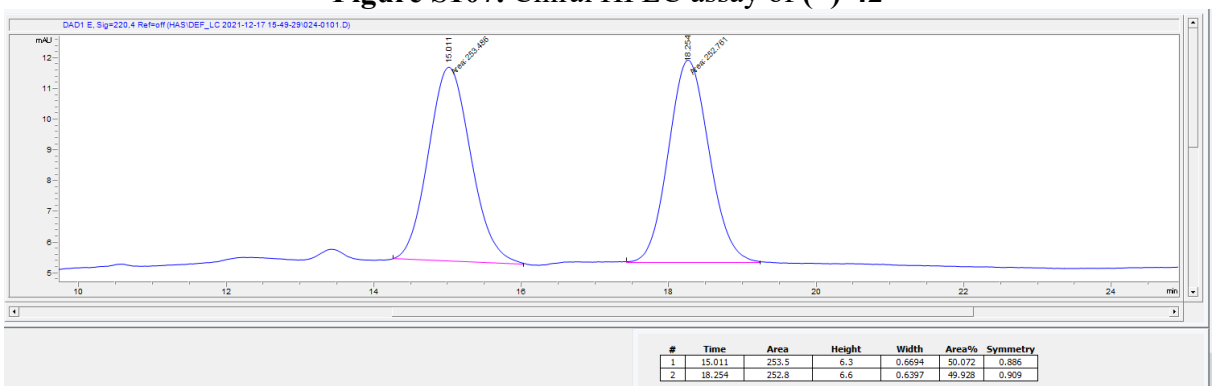


Figure S108. Chiral HPLC assay of isolated **42**

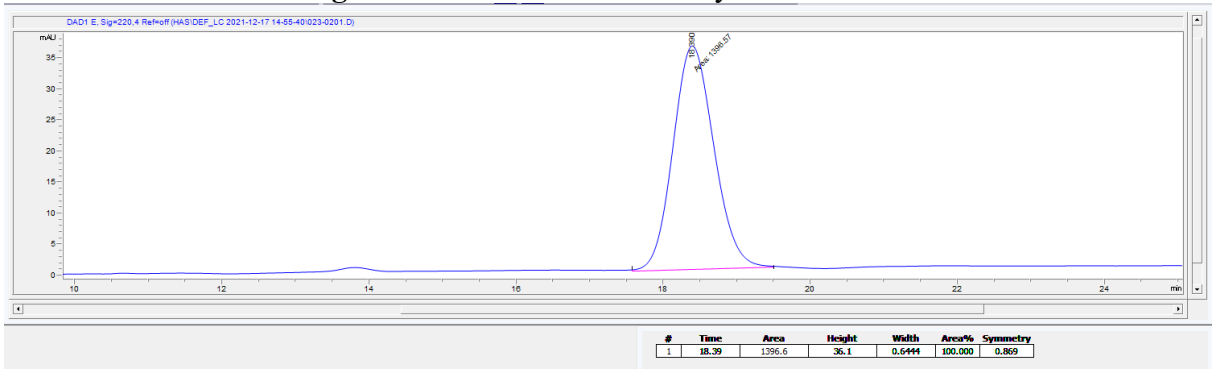


Figure S109. ^{1}H NMR spectrum of **43**

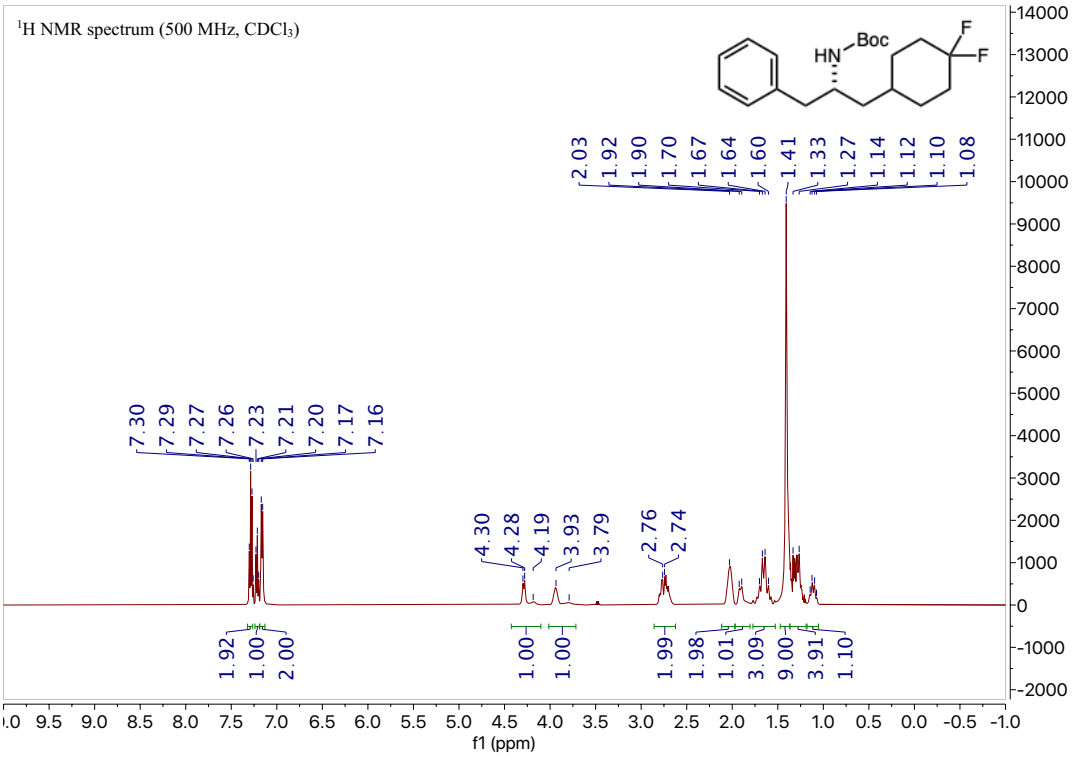


Figure S110. ^{13}C NMR spectrum of **43**

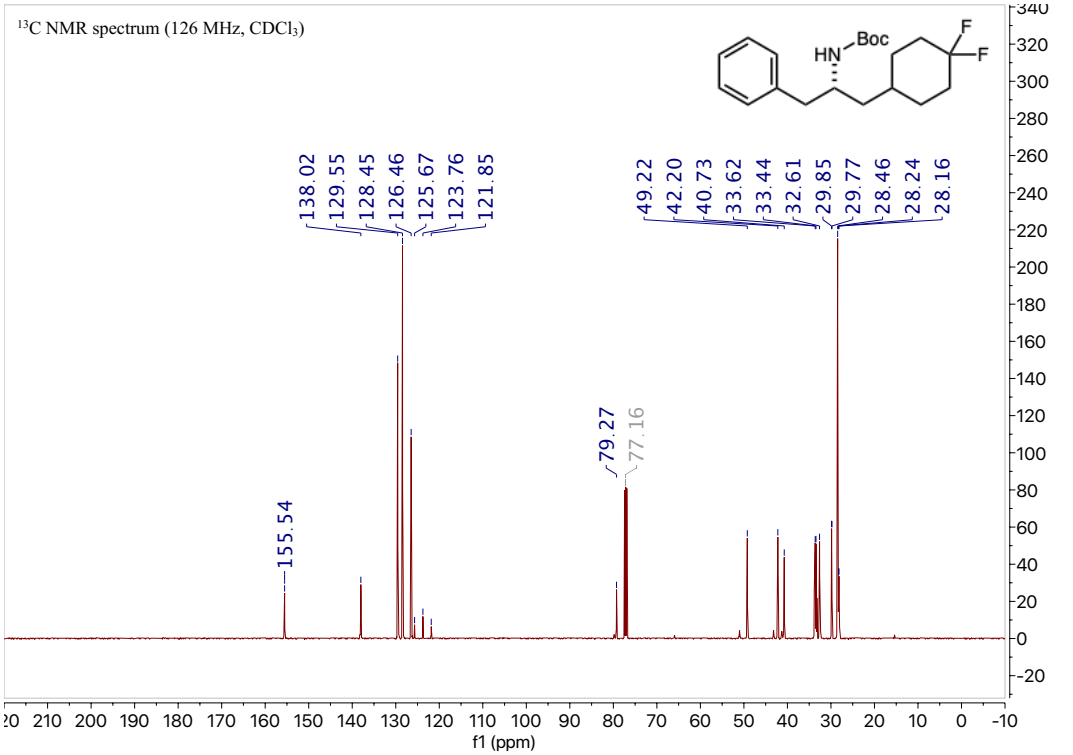


Figure S111. ^{19}F NMR spectrum of **43**

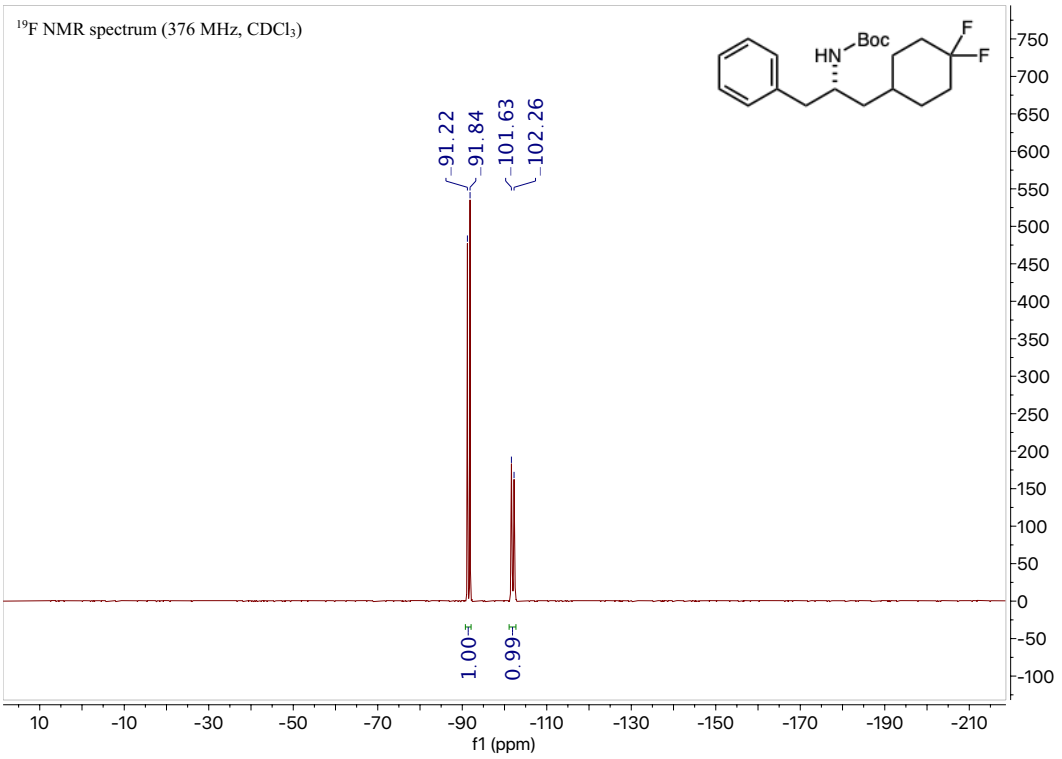


Figure S112. ^{1}H NMR spectrum of **44**

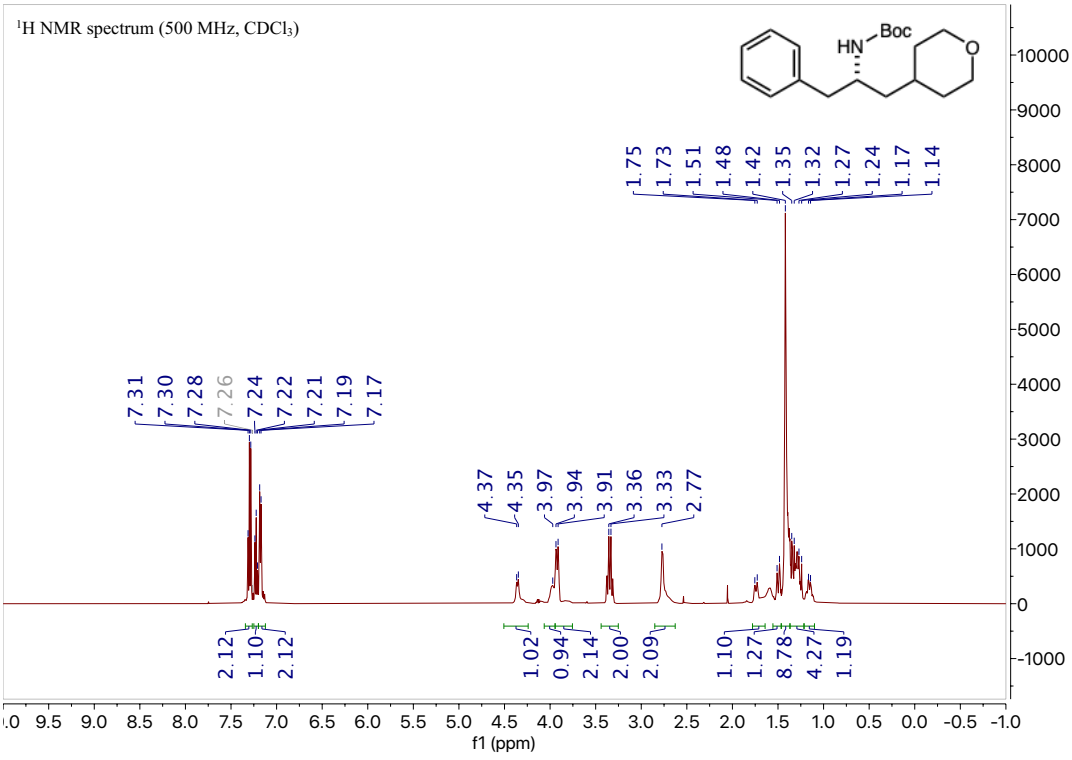


Figure S113. ^{13}C NMR spectrum of **44**

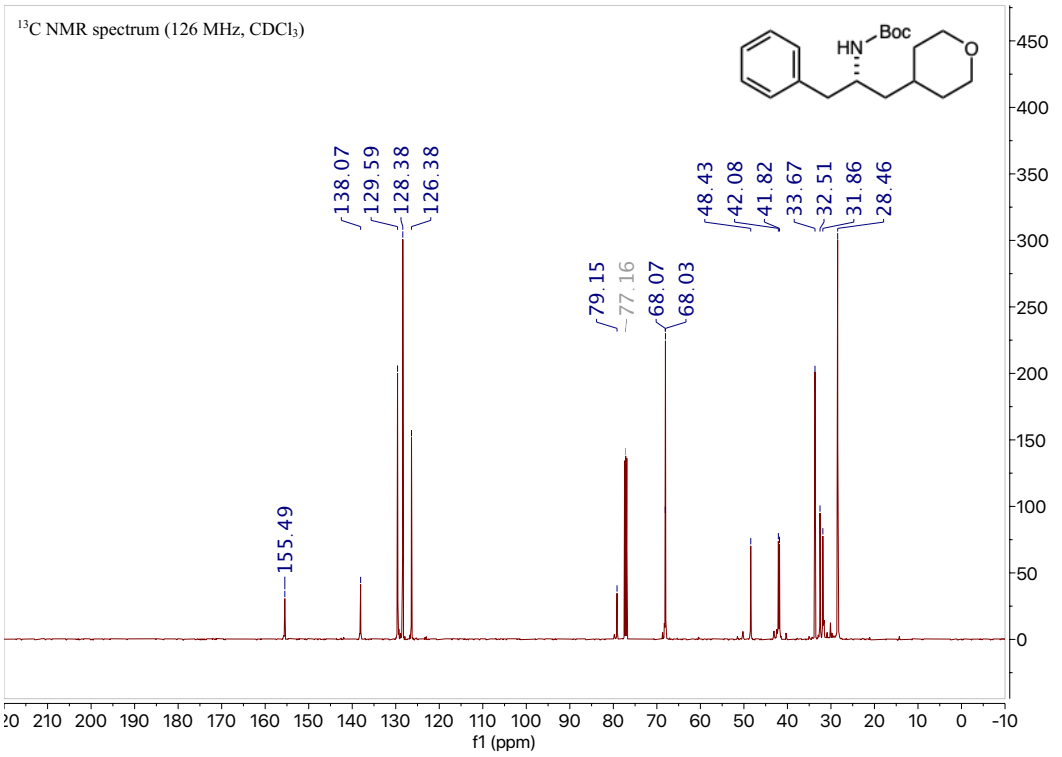


Figure S114. ^{1}H NMR spectrum of **45**

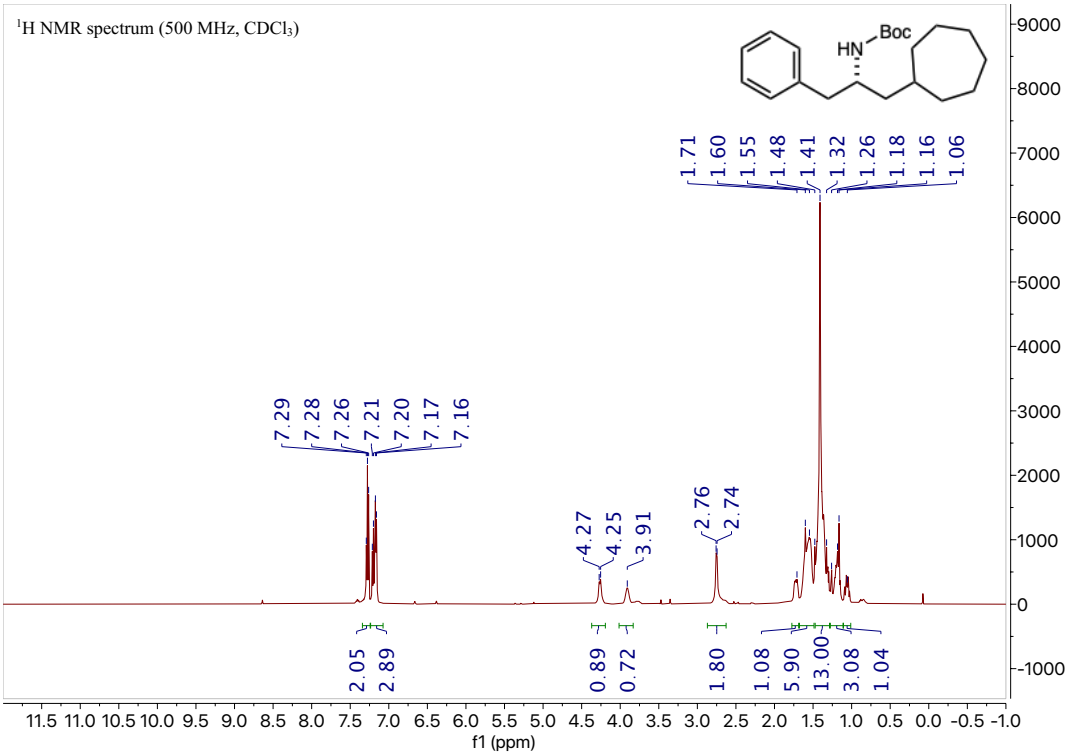


Figure S115. ^{13}C NMR spectrum of **45**

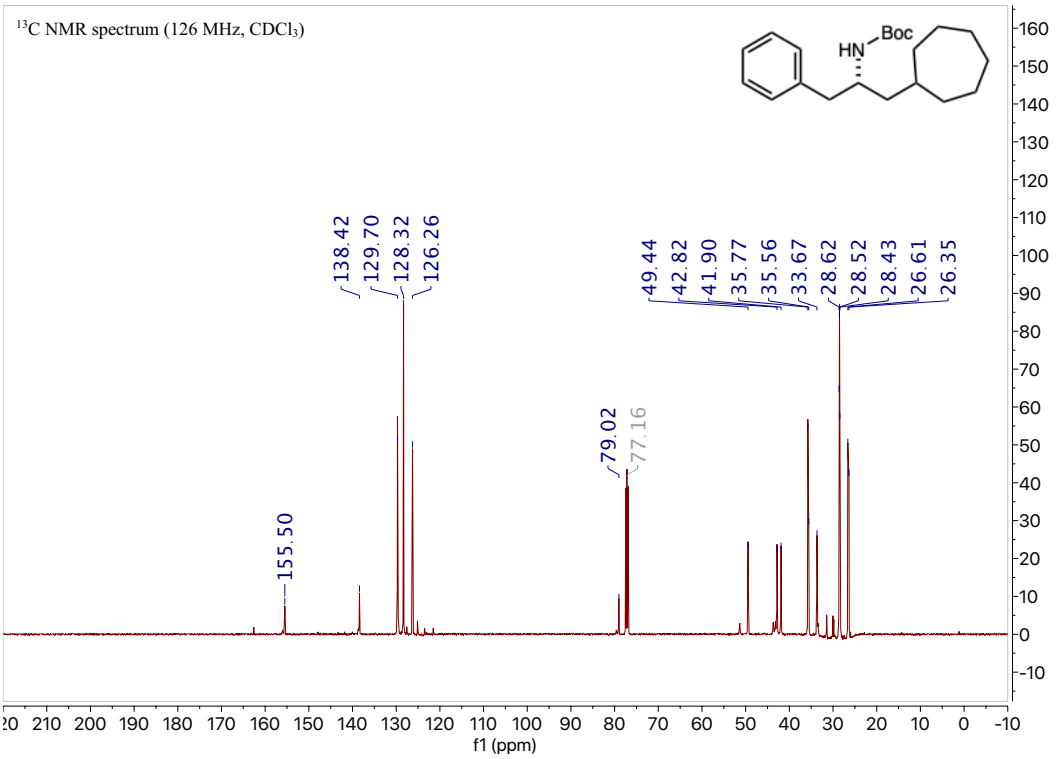


Figure S116. ^{1}H NMR spectrum of **46**

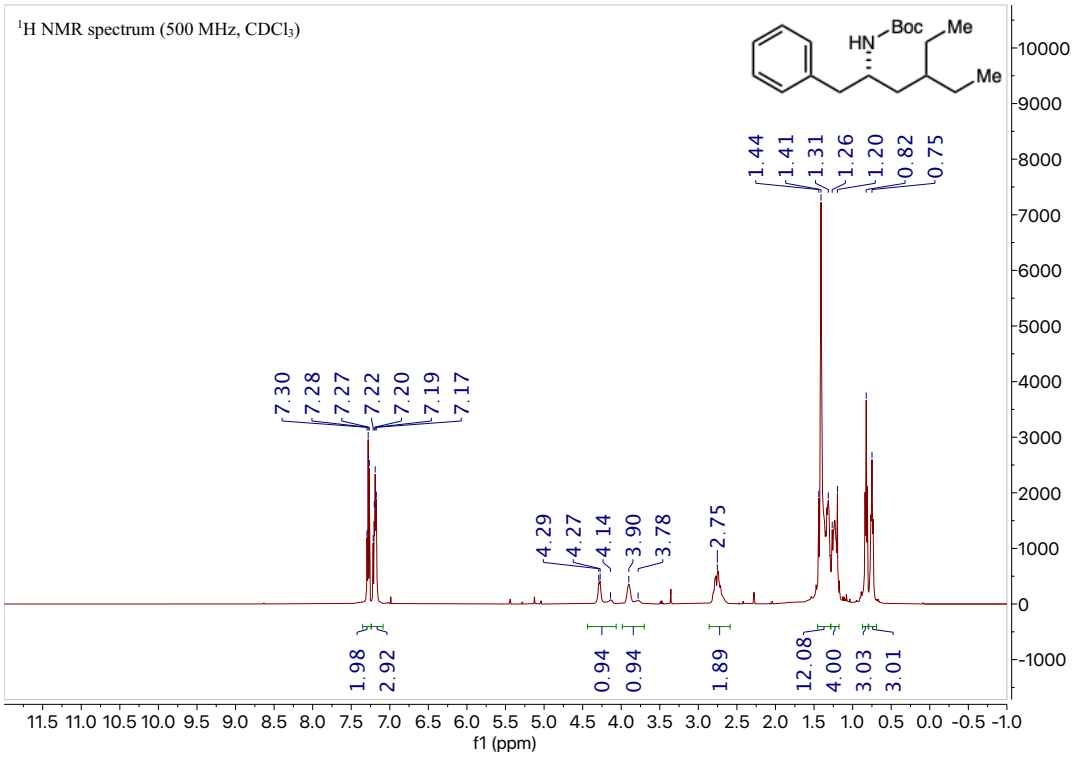


Figure S117. ^{13}C NMR spectrum of **46**

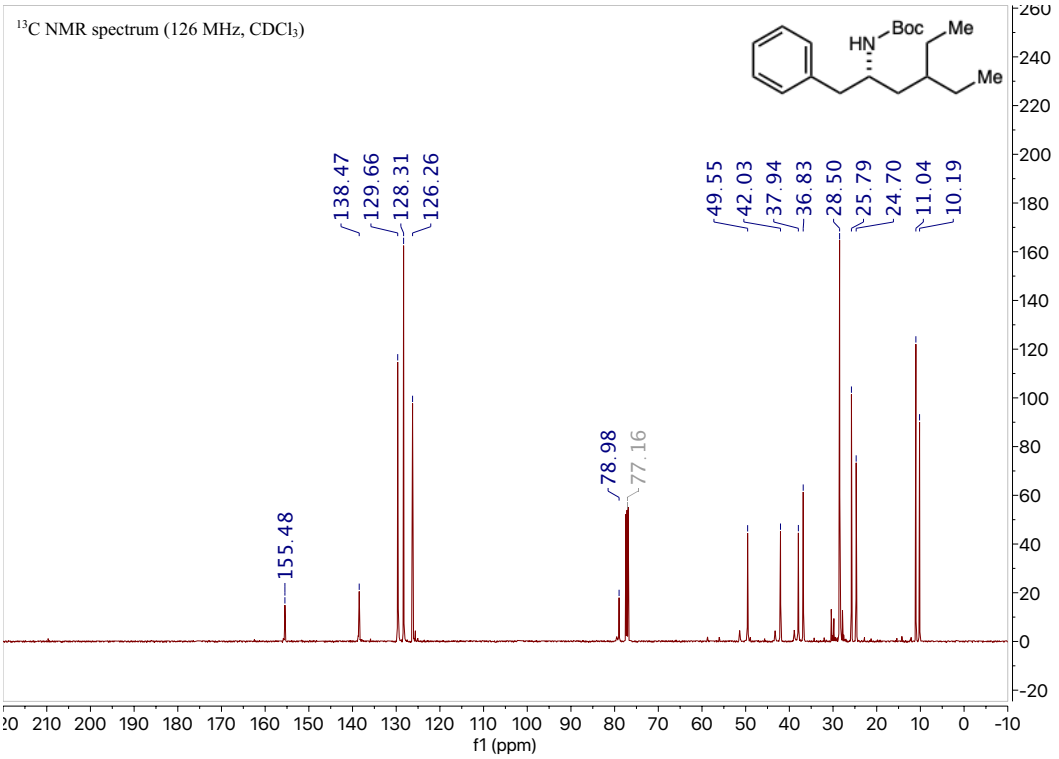


Figure S118. ^{1}H NMR spectrum of **47**

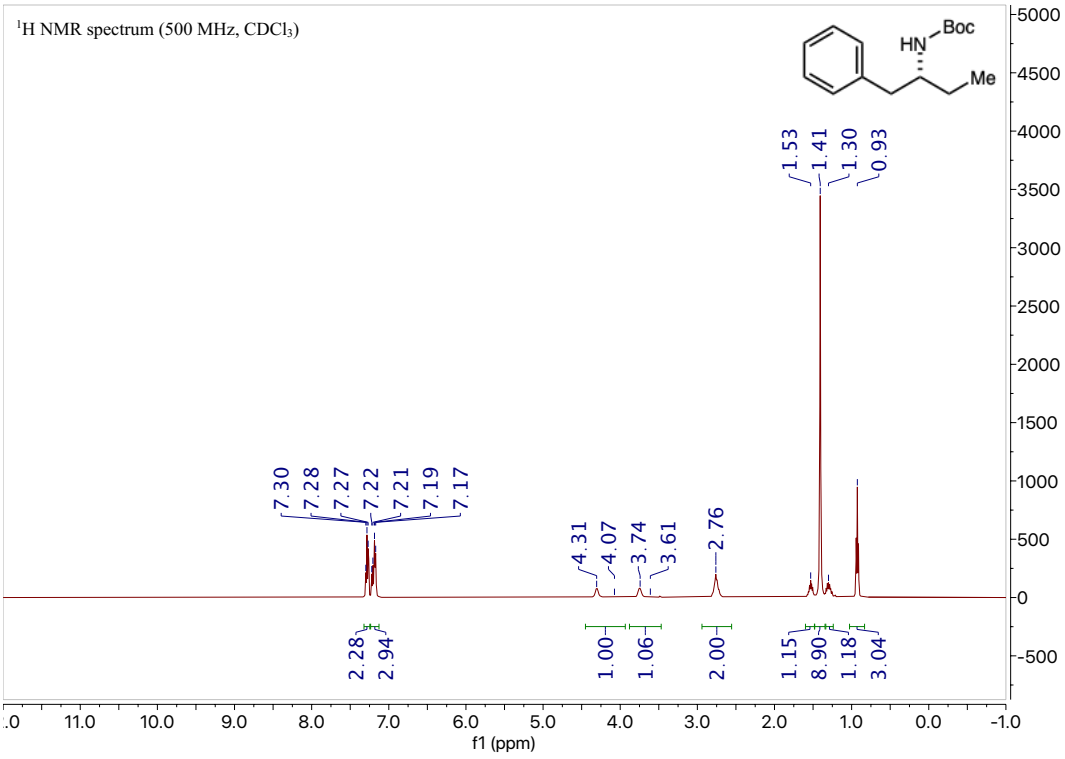


Figure S119. ^{13}C NMR spectrum of **47**

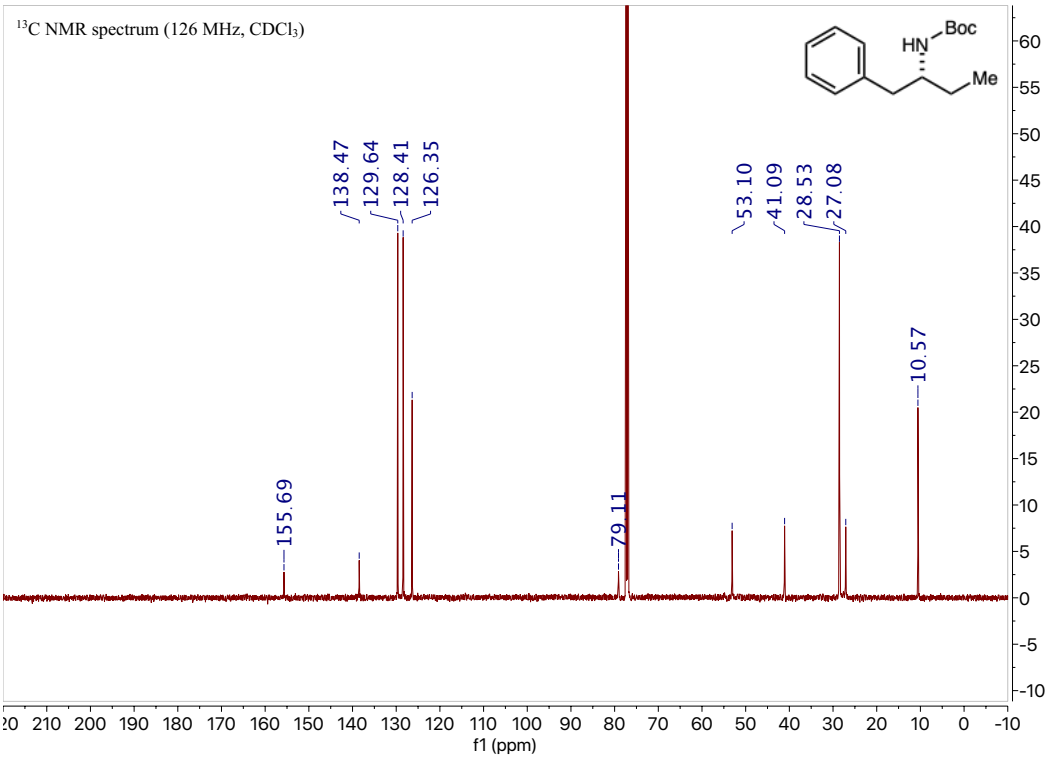


Figure S120. ^{1}H NMR assay of **47** with 1,3,5-trimethoxybenzene (0.359 equiv)

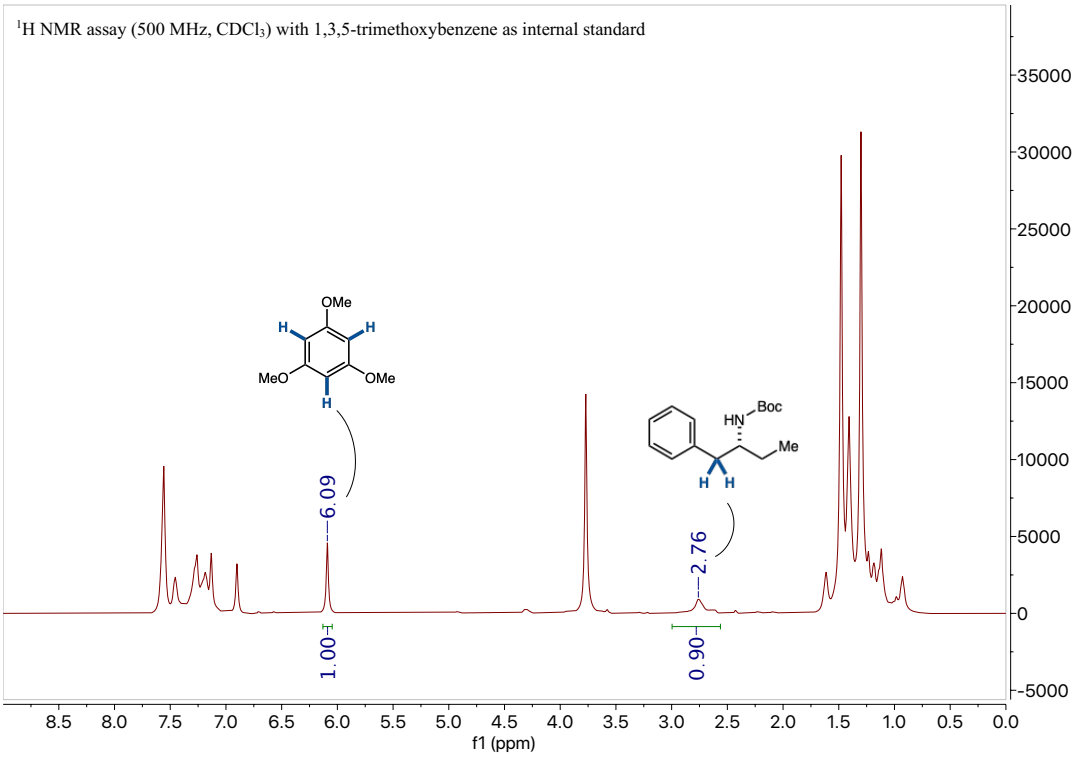


Figure S121. ^{1}H NMR spectrum of **48**

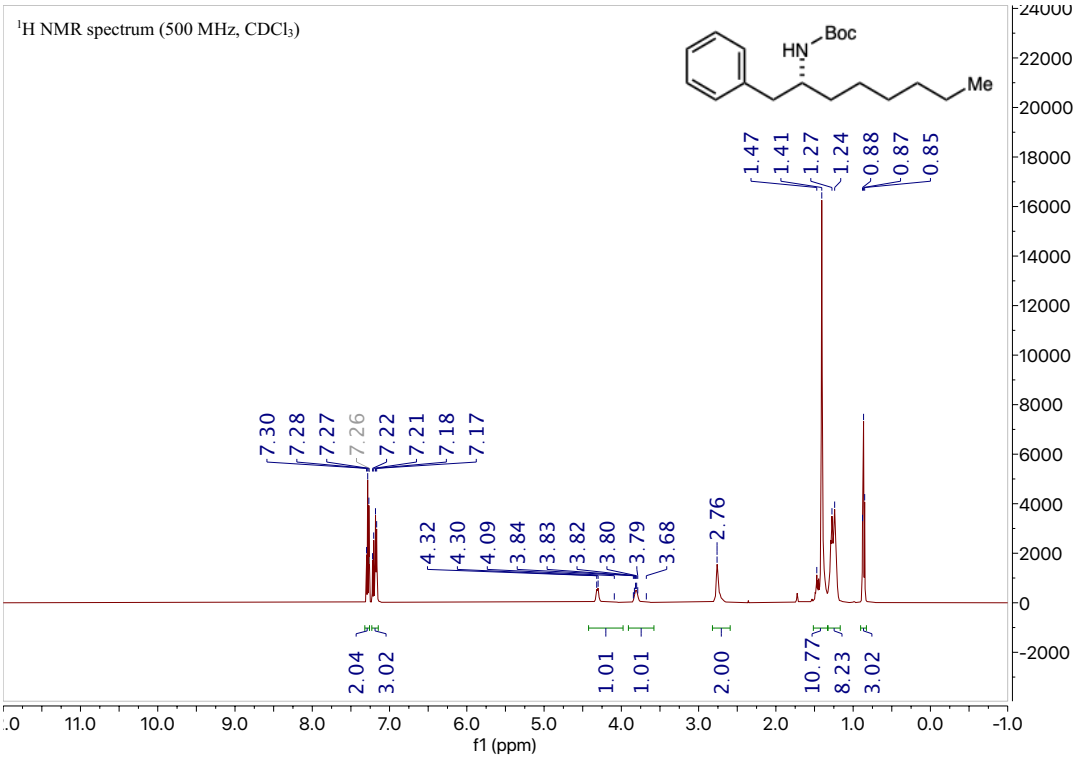


Figure S122. ^{13}C NMR spectrum of **48**

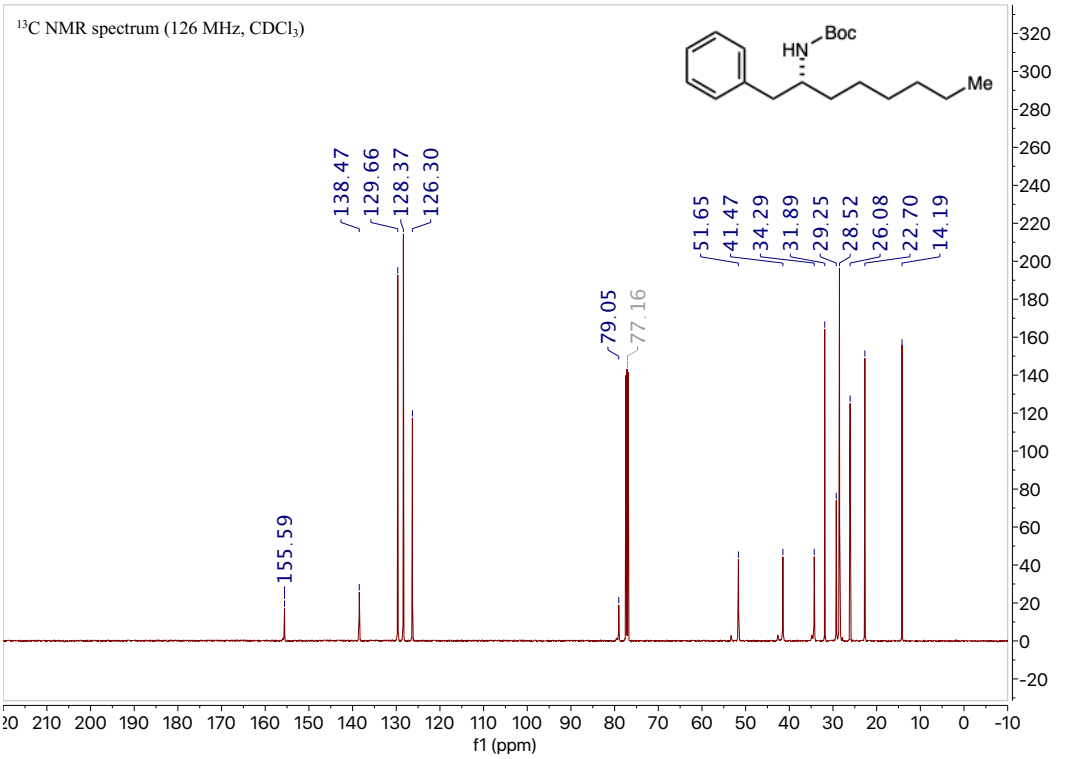


Figure S123. ^{1}H NMR assay of **48** with 1,3,5-trimethoxybenzene (0.370 equiv)

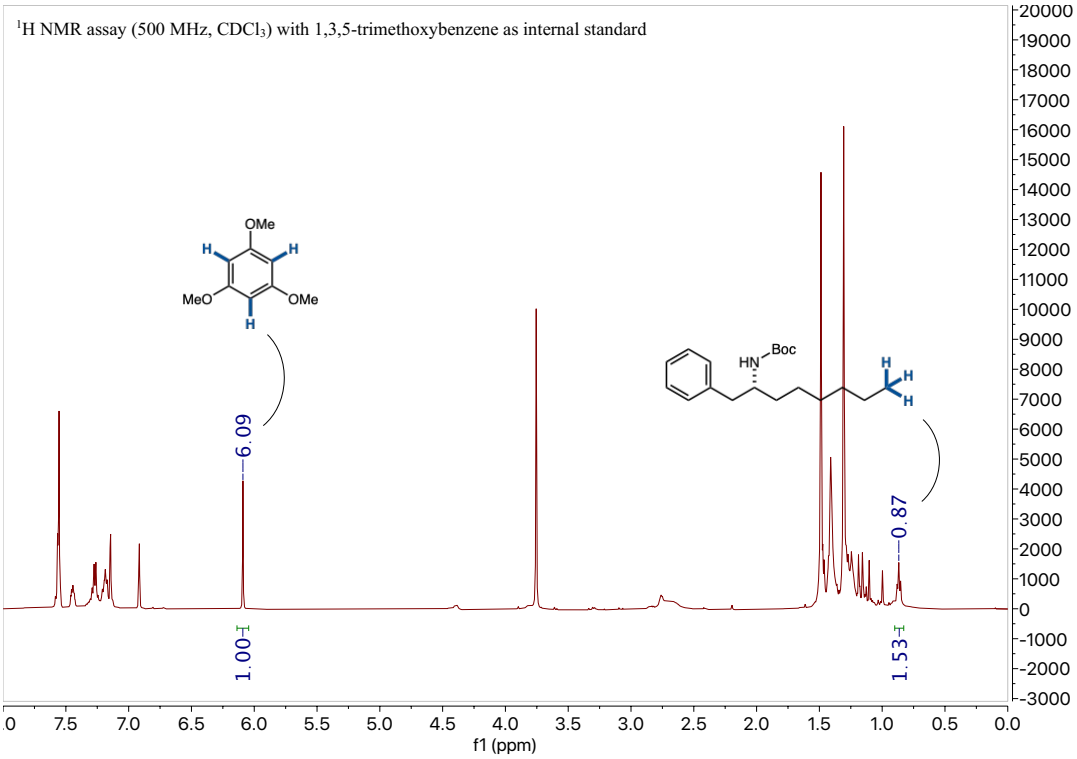


Figure S124. ^{1}H NMR spectrum of **49**

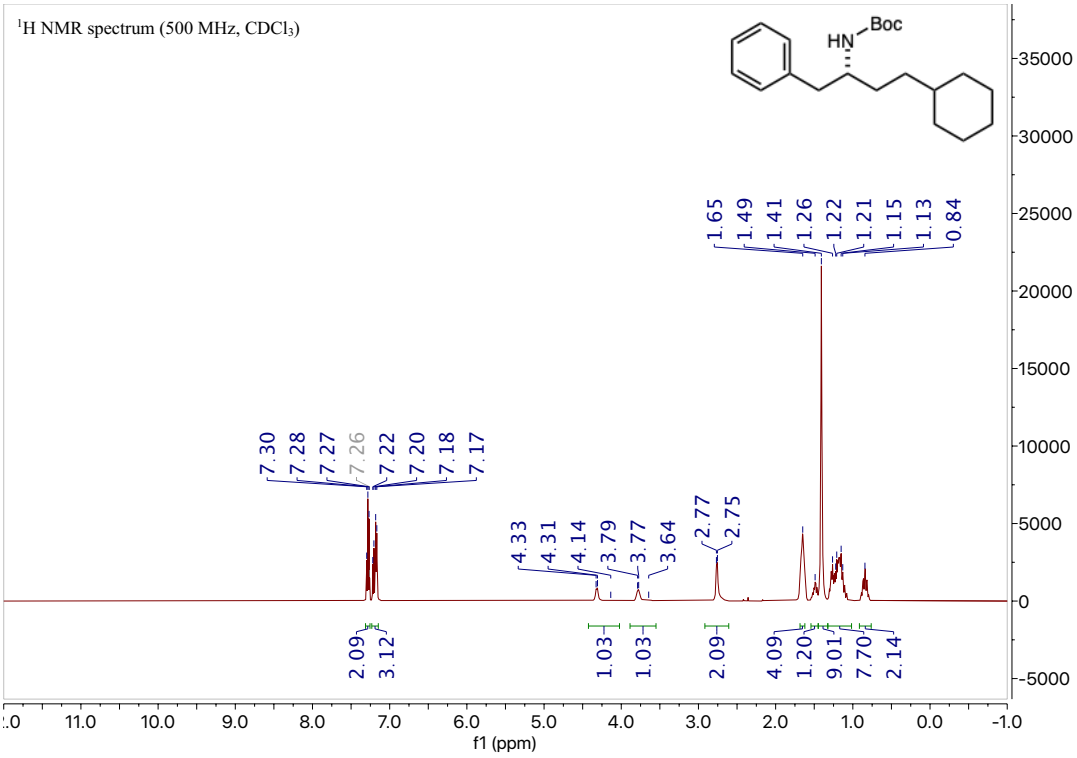


Figure S125. ^{13}C NMR spectrum of **49**

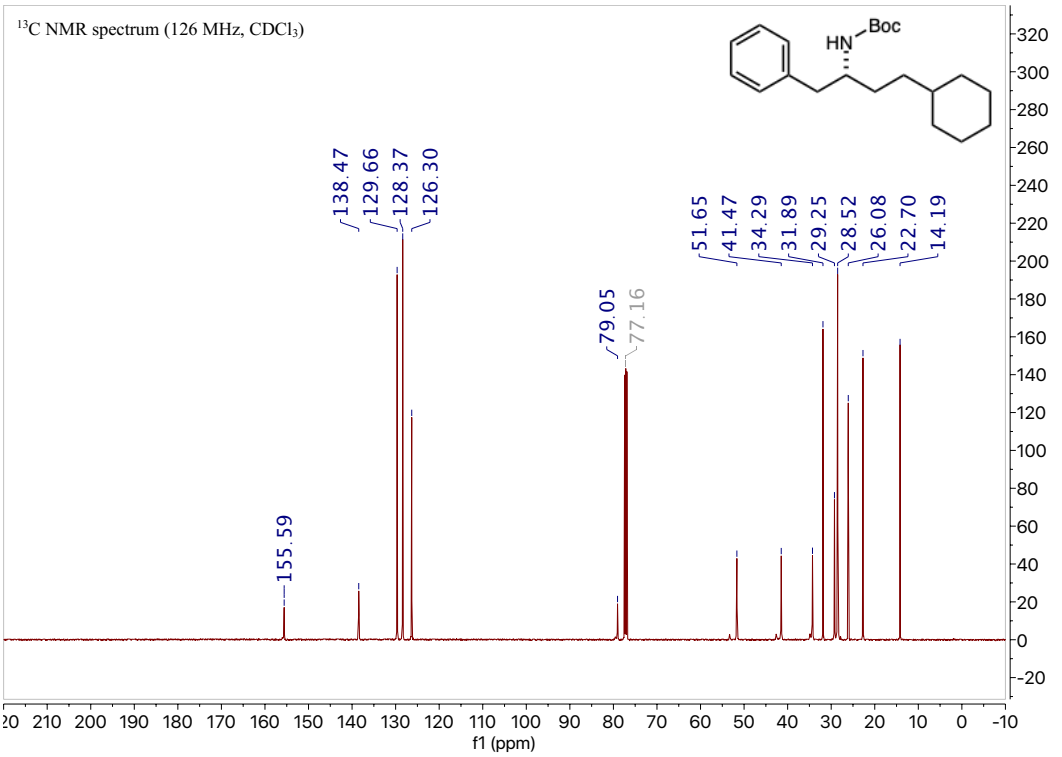


Figure S126. ^{1}H NMR spectrum of **50**

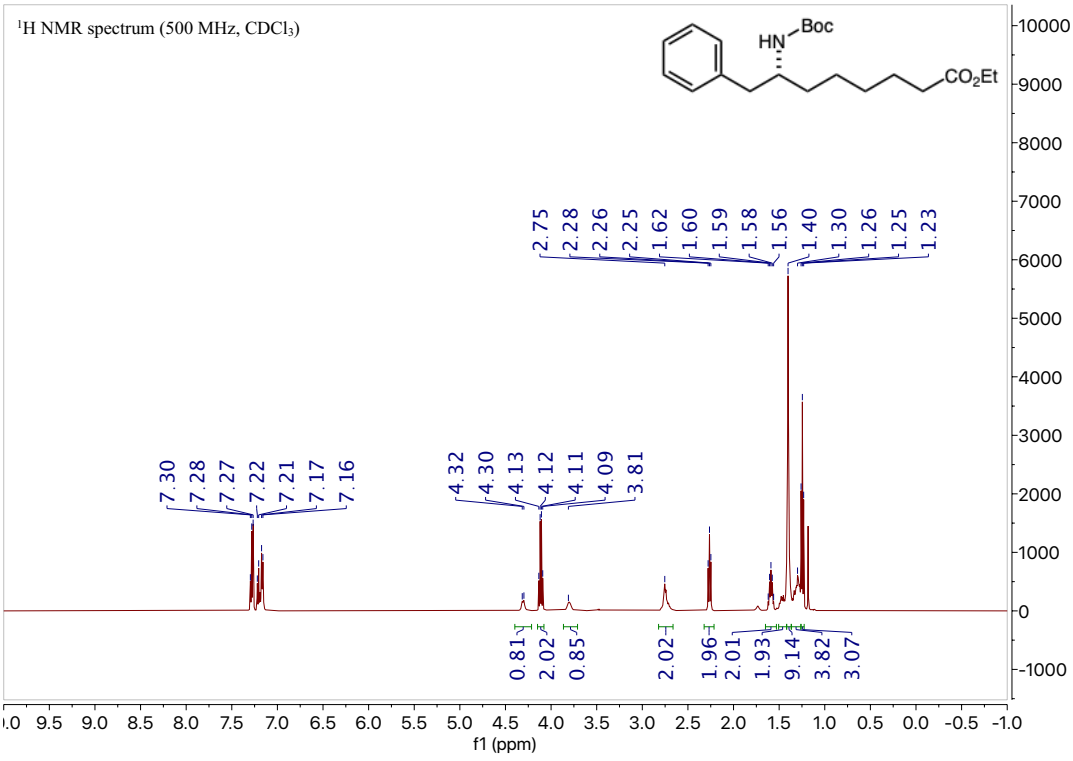


Figure S127. ^{13}C NMR spectrum of **50**

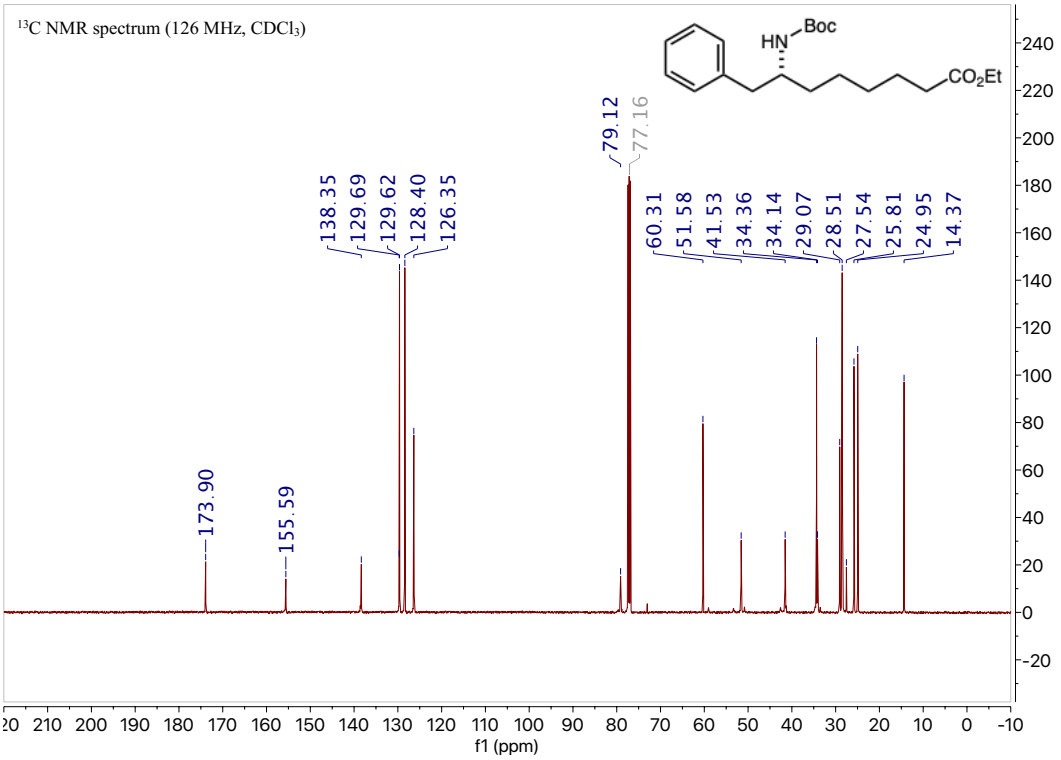


Figure S128. ^{1}H NMR assay of **50** with 1,3,5-trimethoxybenzene (0.354 equiv)

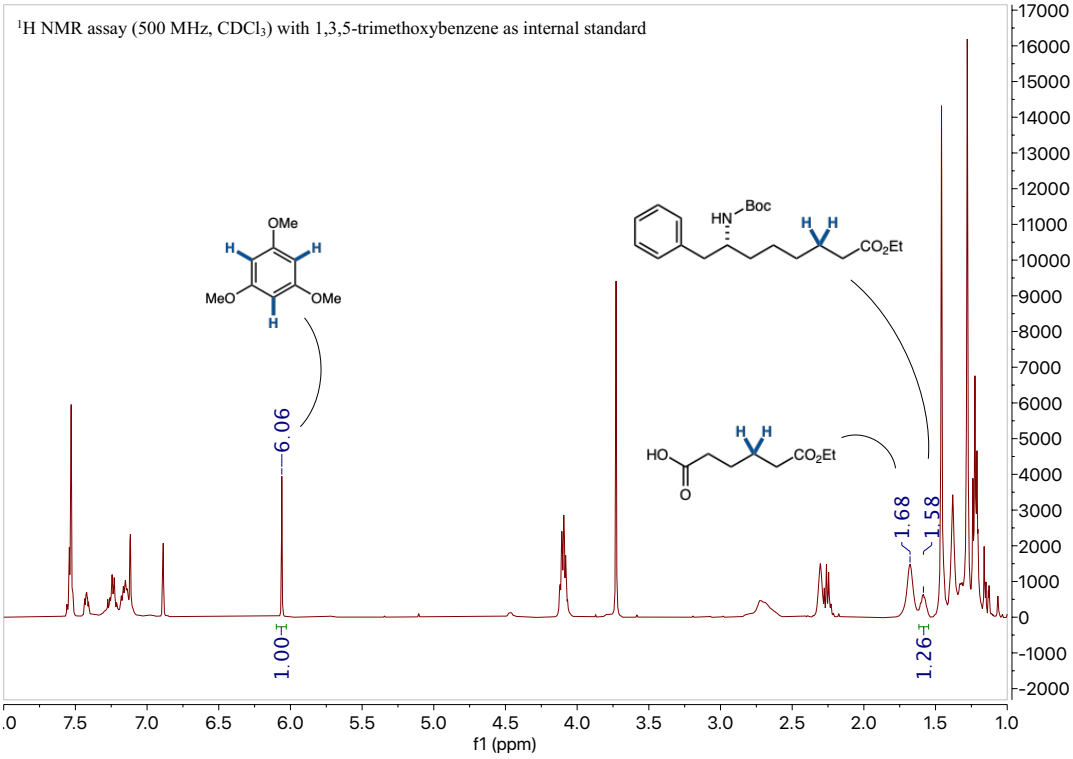


Figure S129. Chiral HPLC assay of **(±)-50**

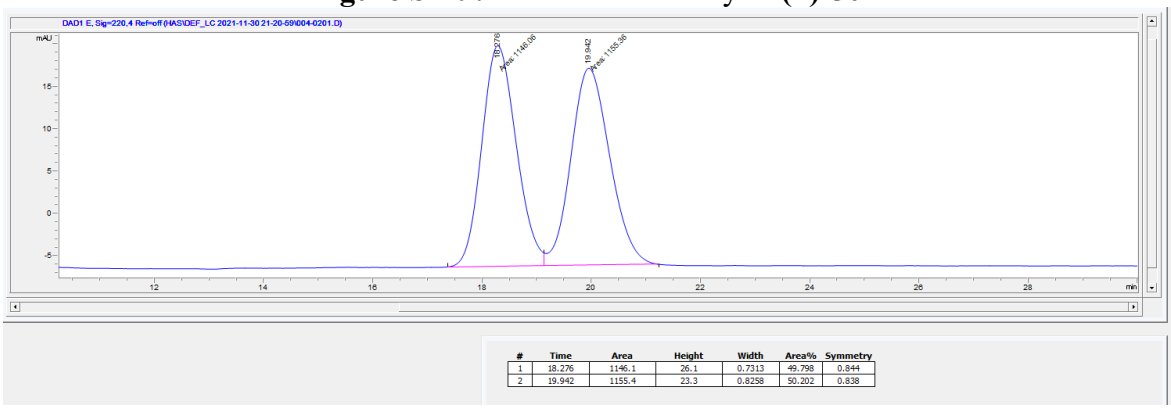


Figure S130. Chiral HPLC assay of isolated **50**

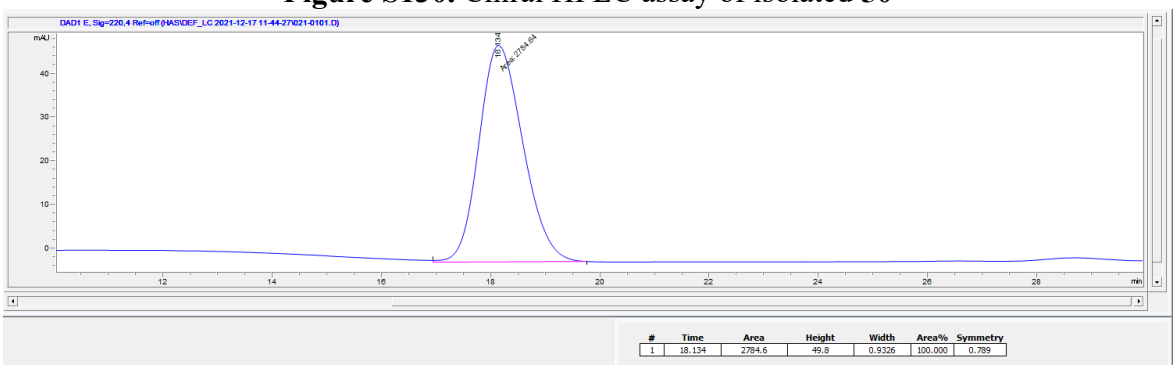


Figure S131. ^{1}H NMR spectrum of **51**

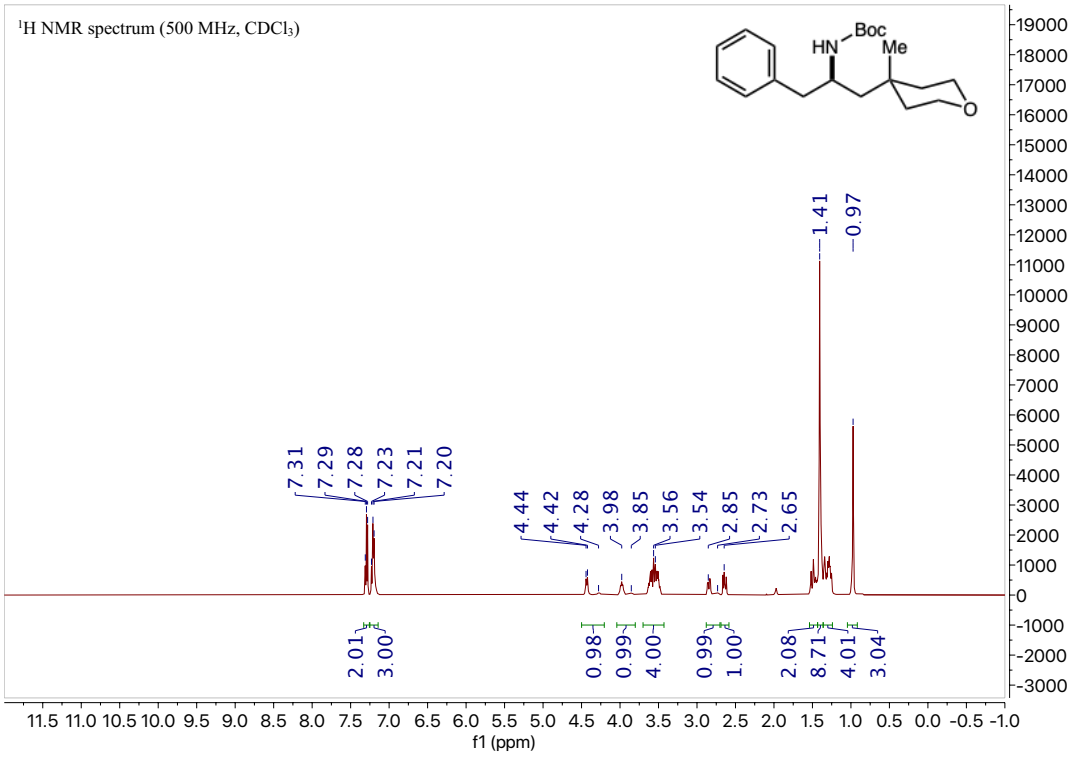


Figure S132. ^{13}C NMR spectrum of **51**

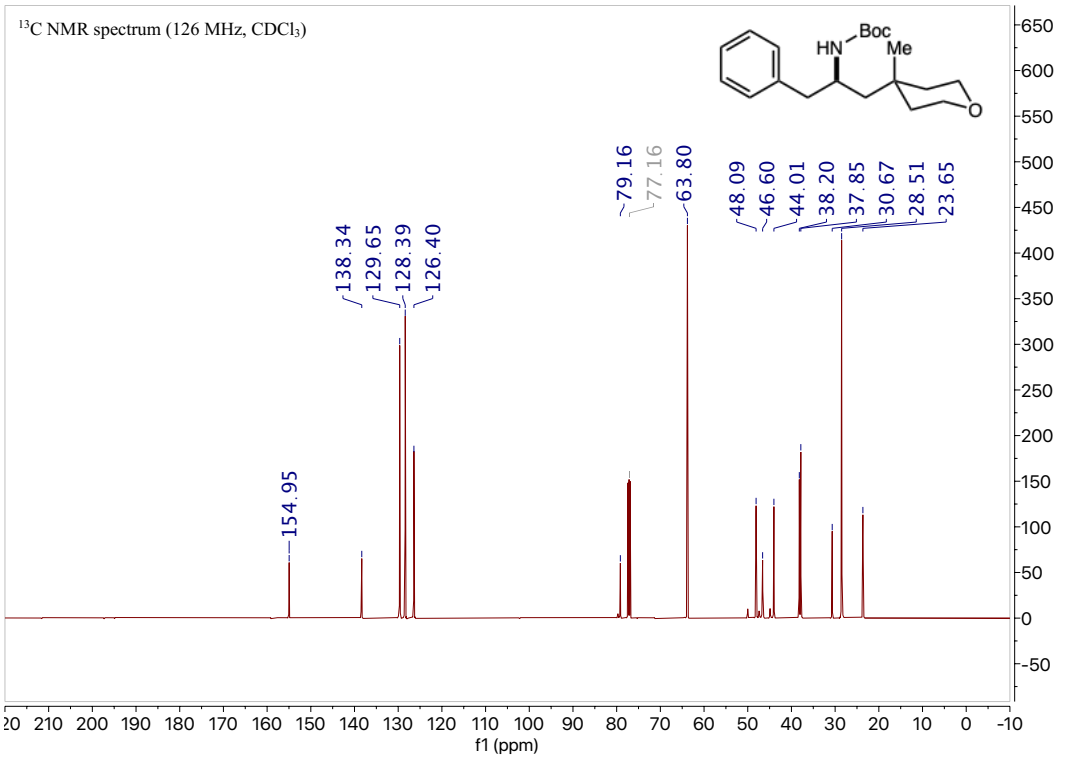


Figure S133. ^{1}H NMR spectrum of **52**

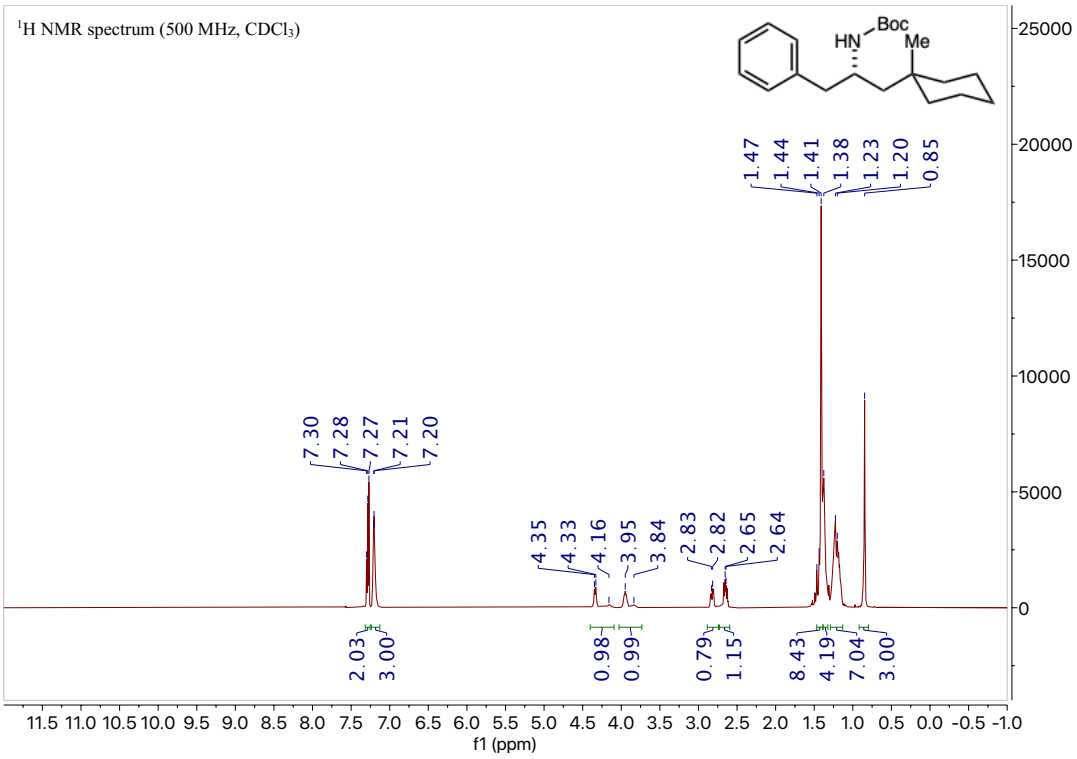


Figure S134. ^{13}C NMR spectrum of **52**

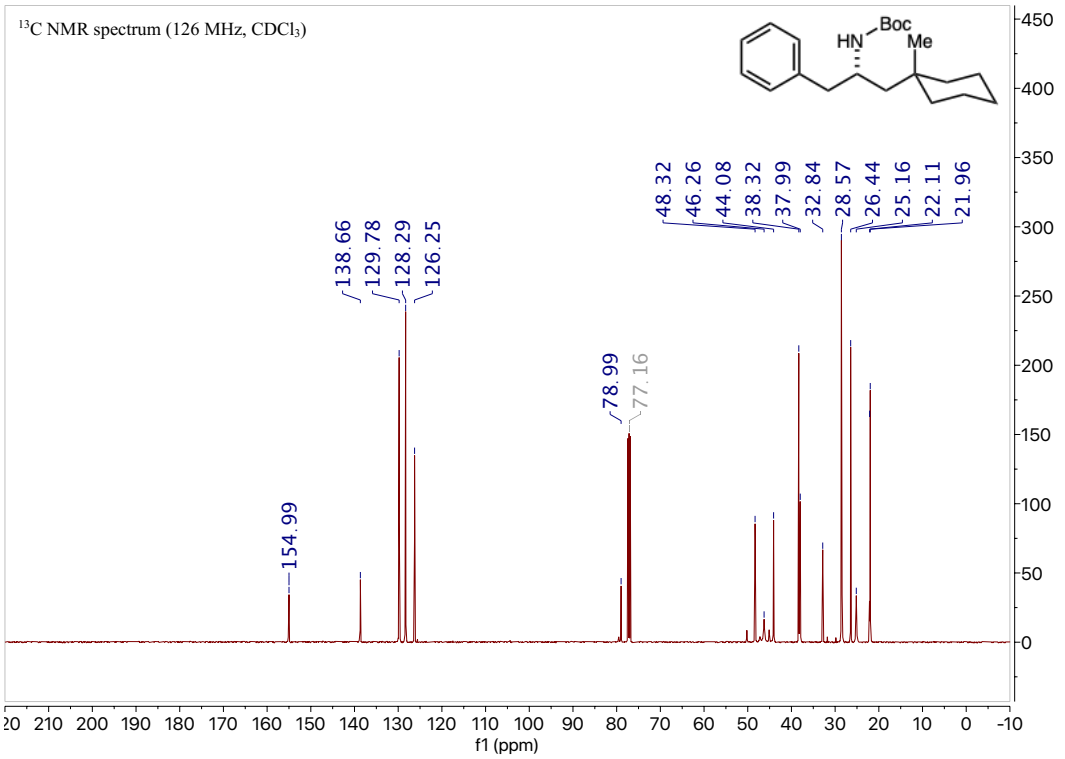


Figure S135. ^{1}H NMR spectrum of **53**

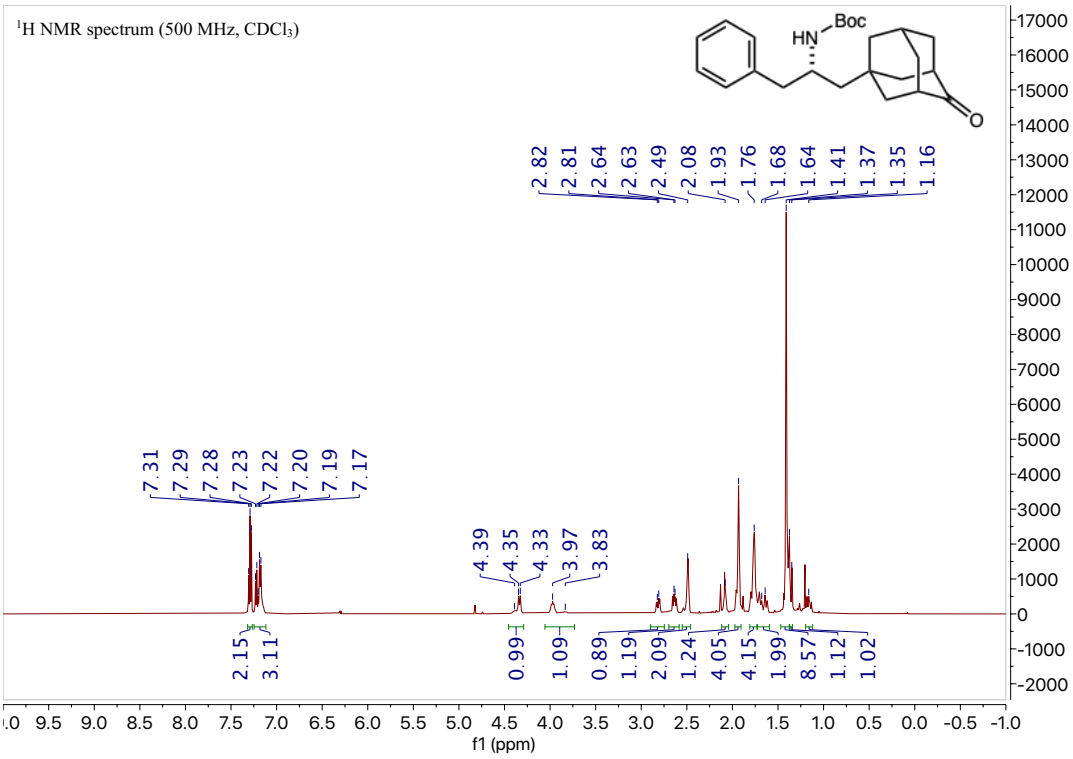


Figure S136. ^{13}C NMR spectrum of **53**

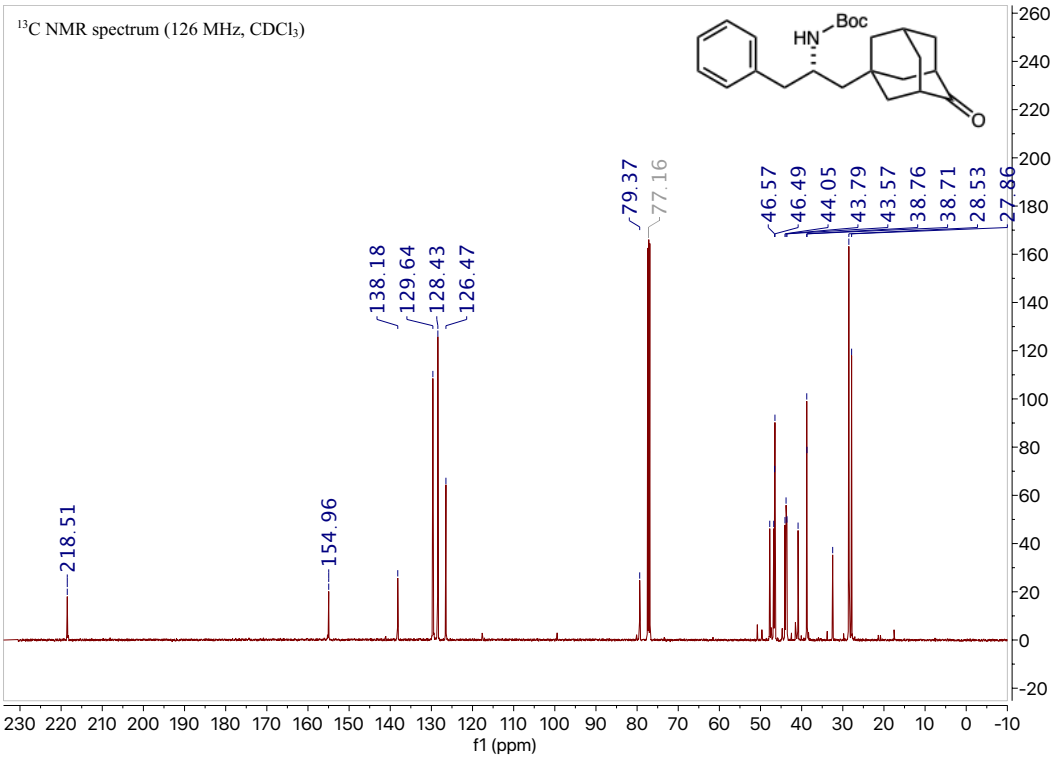


Figure S137. ^{1}H NMR spectrum of **54**

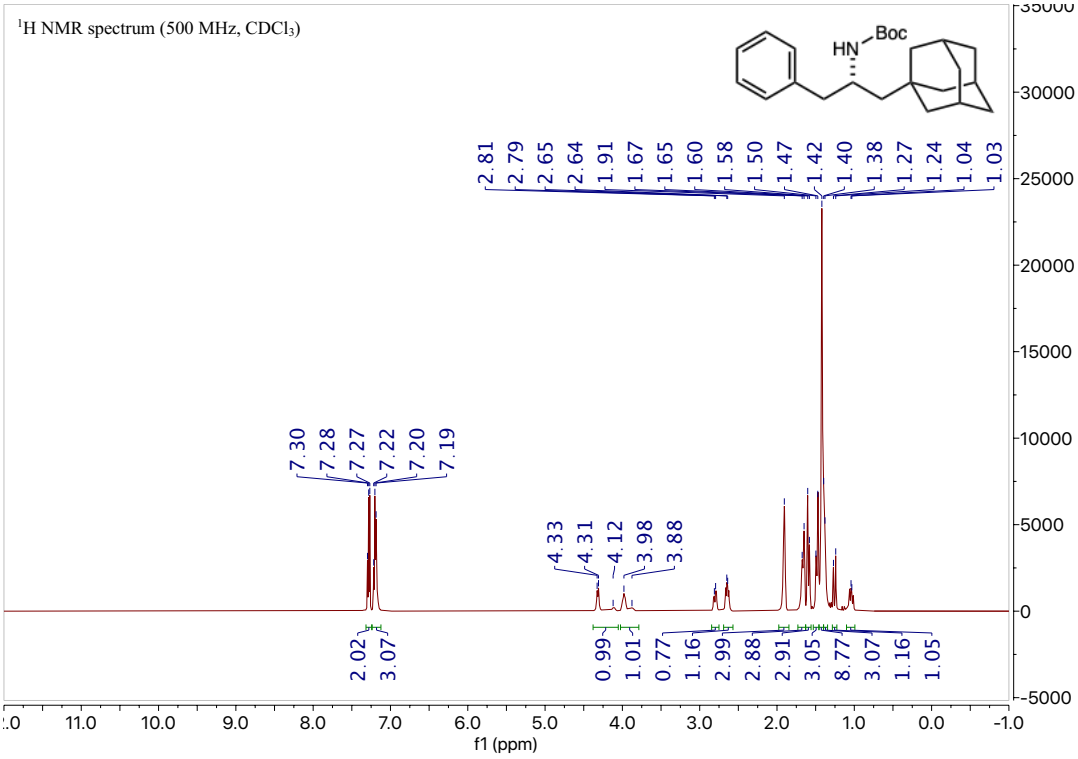


Figure S138. ^{13}C NMR spectrum of **54**

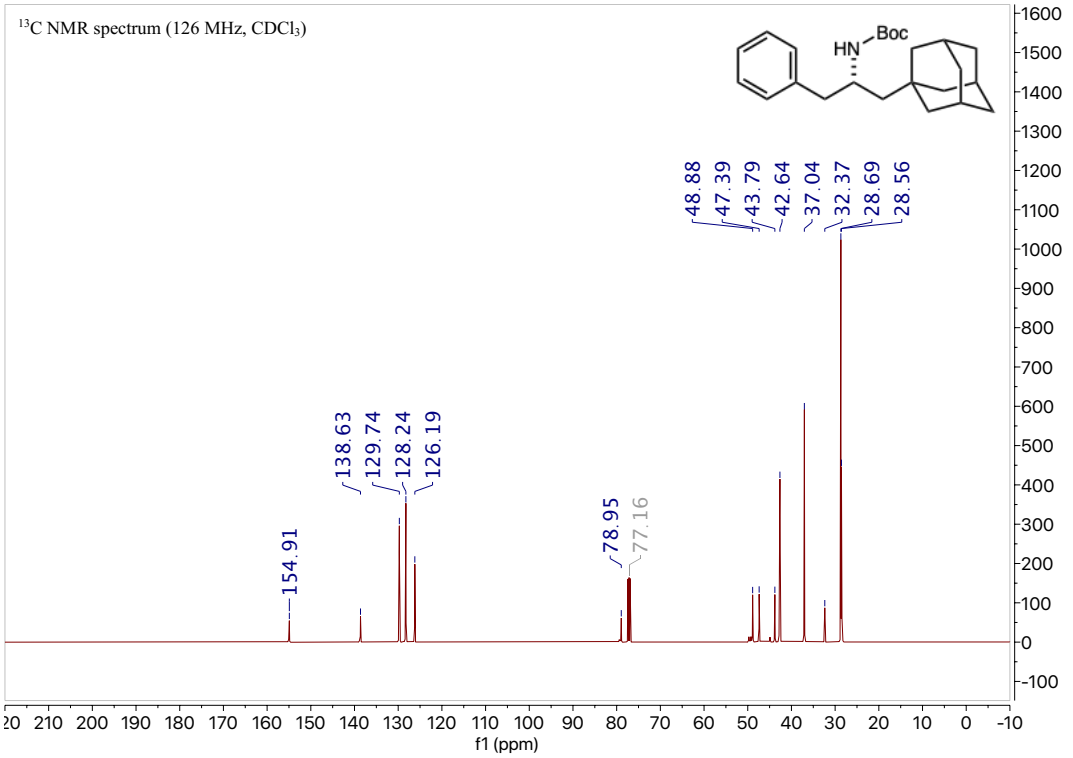


Figure S139. ^{1}H NMR spectrum of **55**

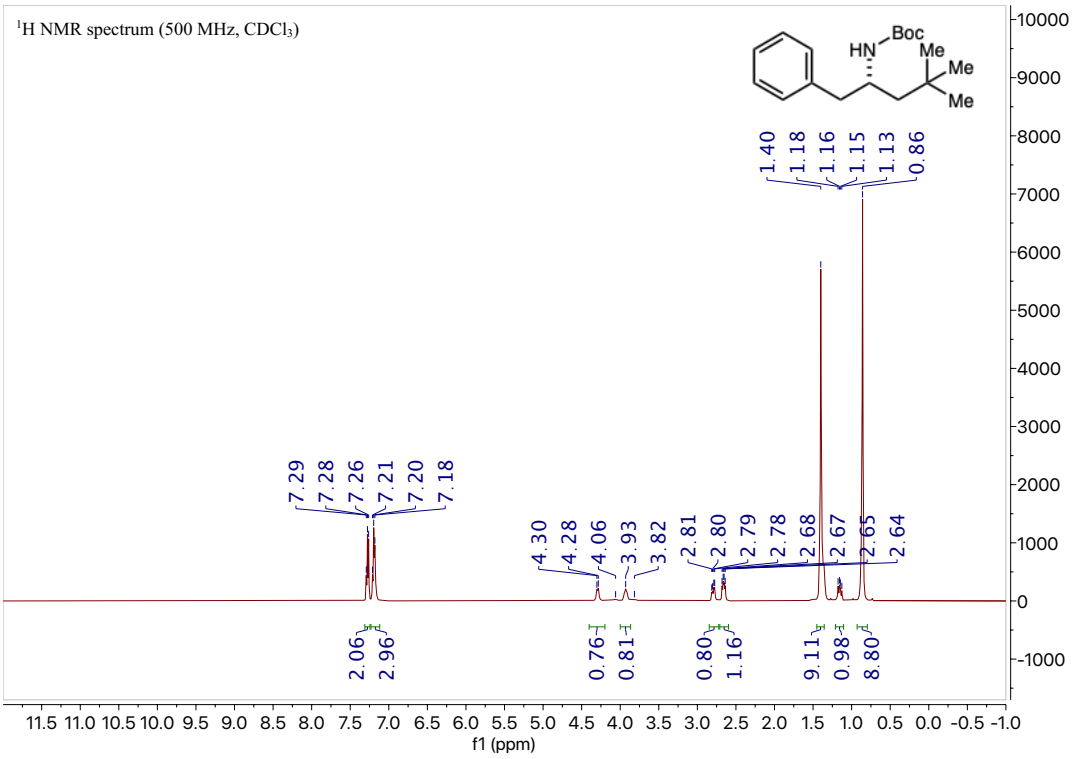


Figure S140. ^{13}C NMR spectrum of **55**

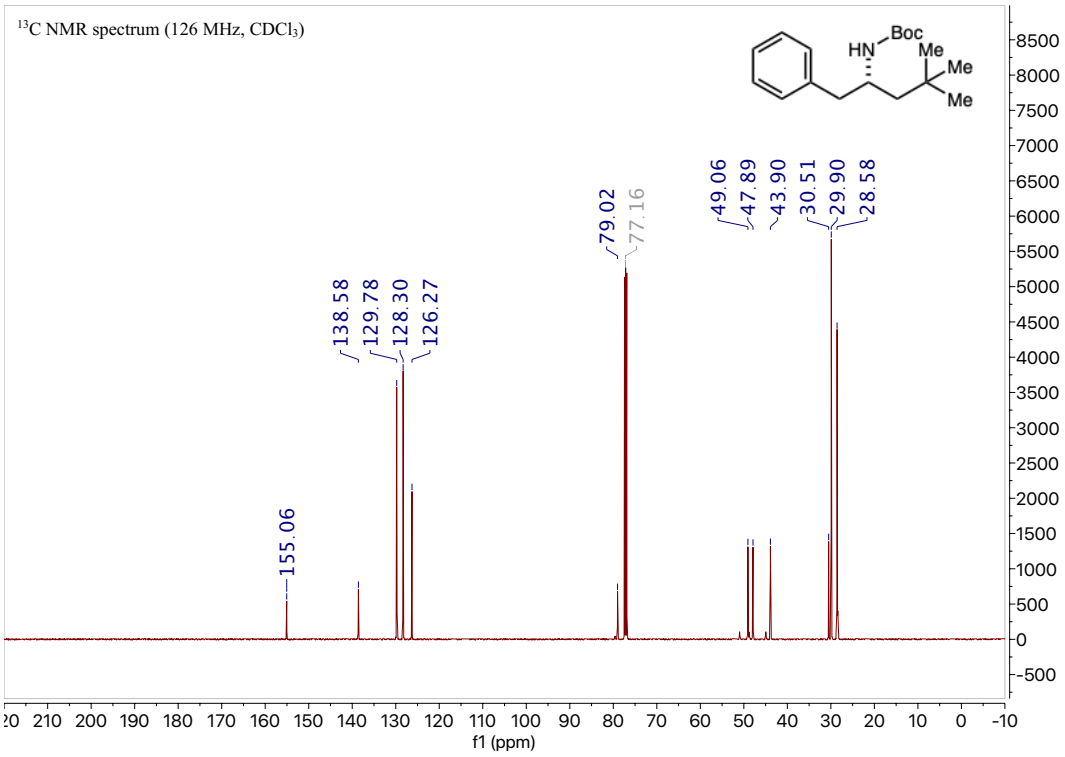
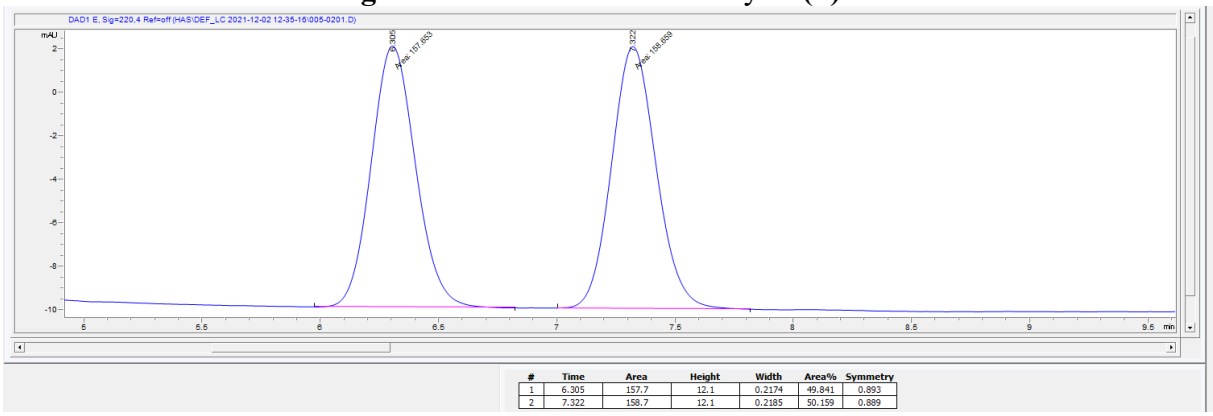
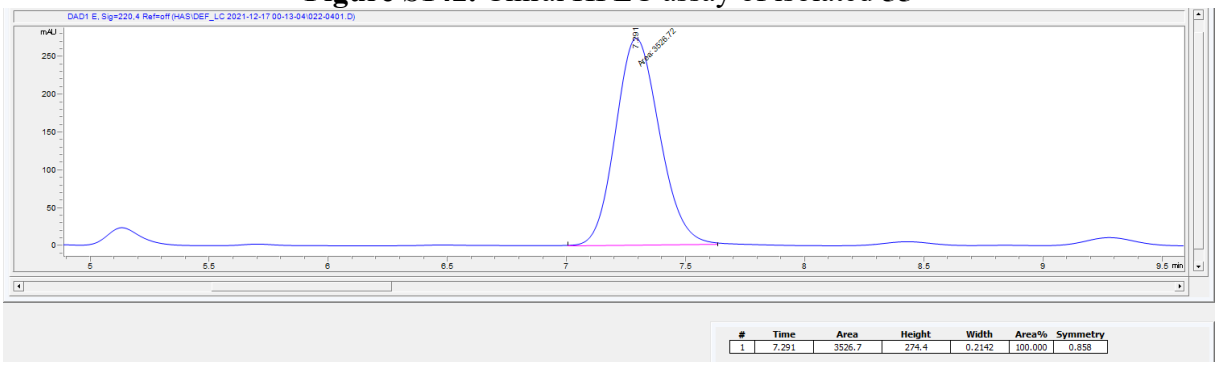


Figure S141. Chiral HPLC assay of **(±)-55**



#	Time	Area	Height	Width	Area%	Symmetry
1	6.305	157.7	12.1	0.2174	49.841	0.893
2	7.322	158.7	12.1	0.2185	50.159	0.889

Figure S142. Chiral HPLC assay of isolated **55**



#	Time	Area	Height	Width	Area%	Symmetry
1	7.291	3526.7	274.4	0.2142	100.000	0.858

Figure S143. ^{1}H NMR spectrum of **56**

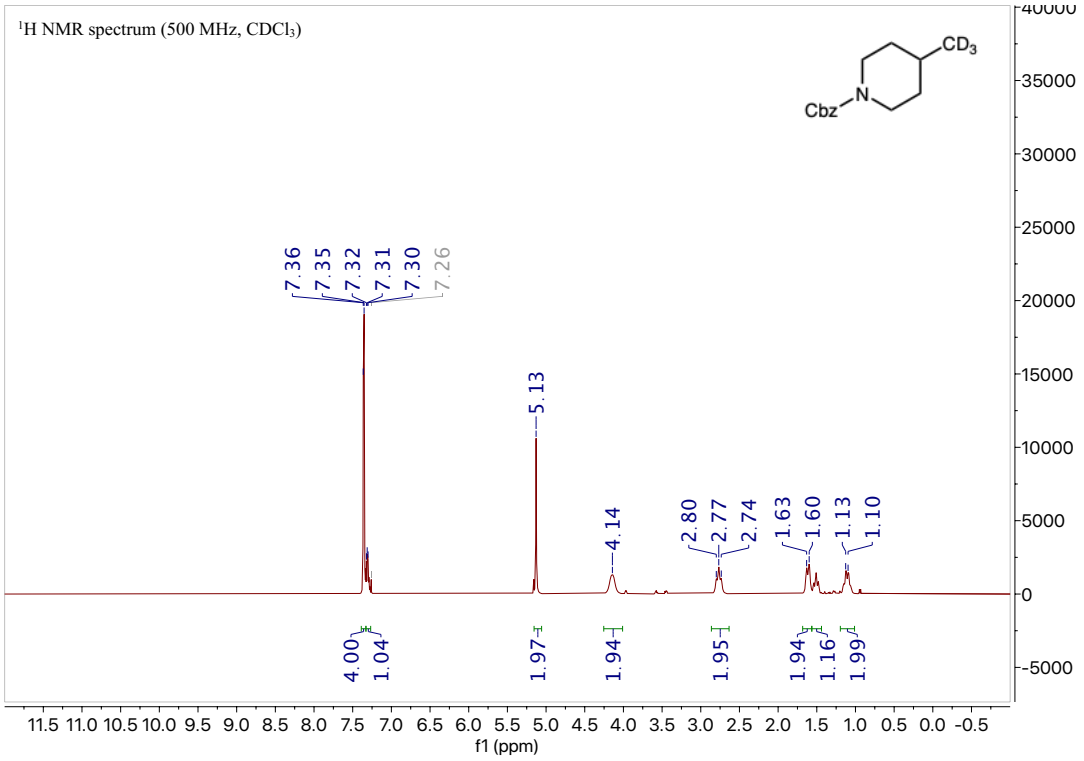


Figure S144. ^{13}C NMR spectrum of **56**

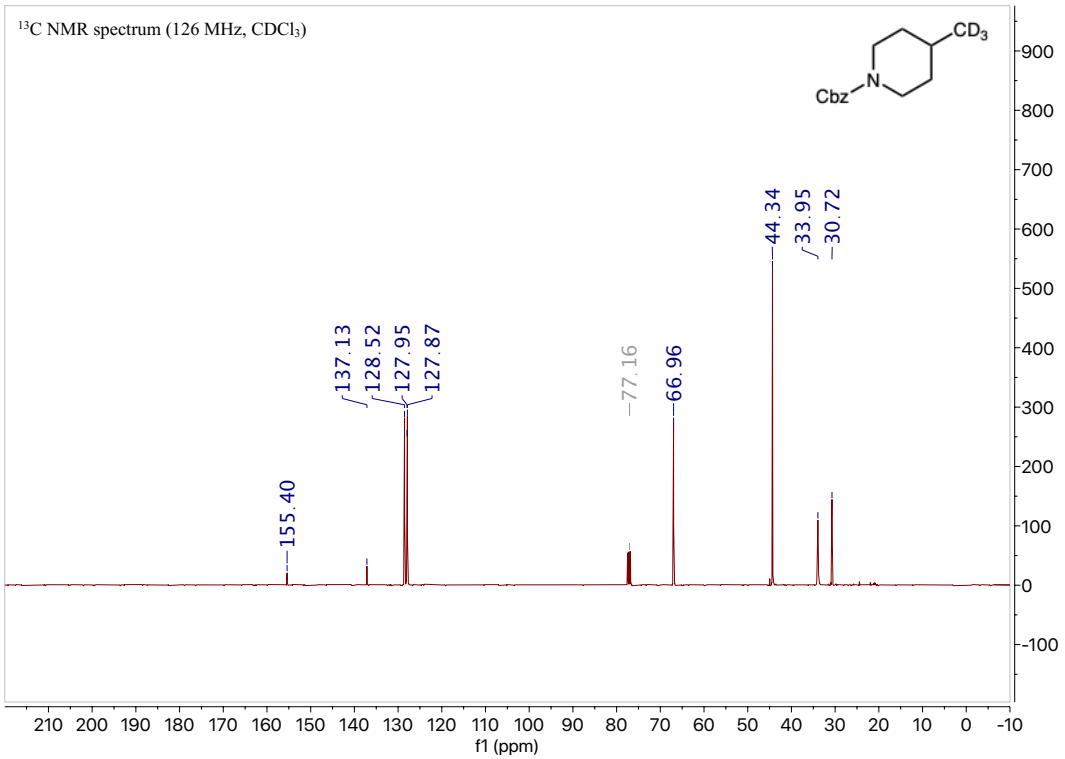


Figure S145. ^{1}H NMR spectrum of **57**

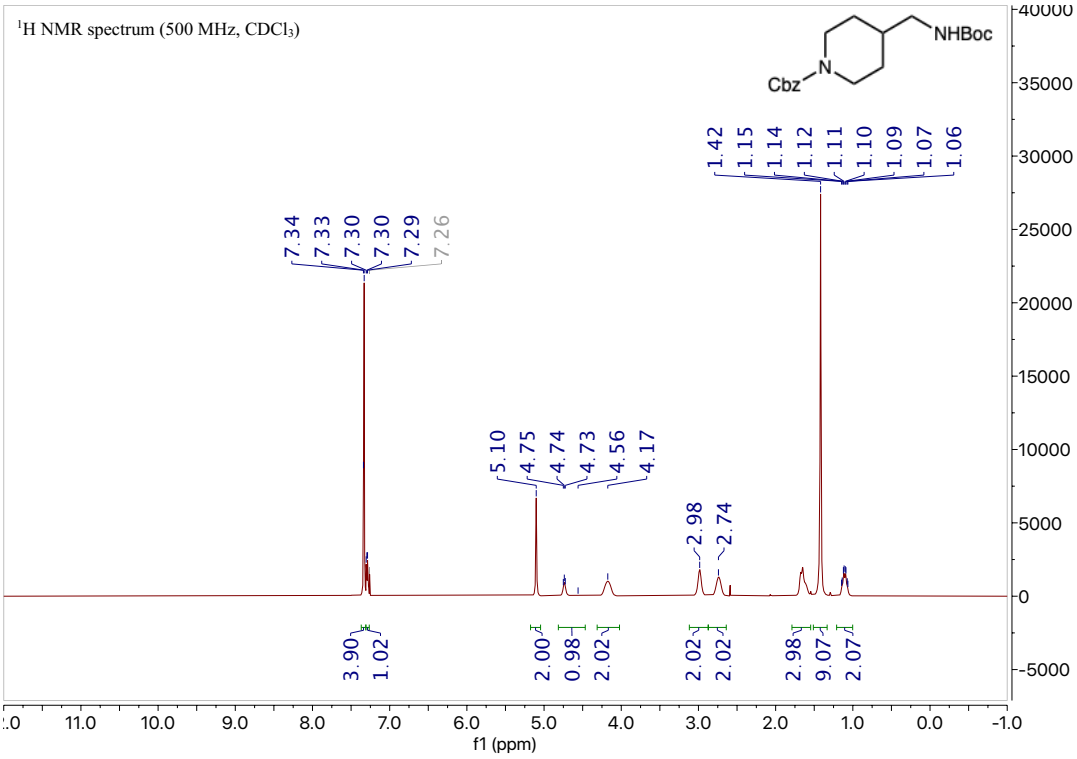


Figure S146. ^{13}C NMR spectrum of **57**

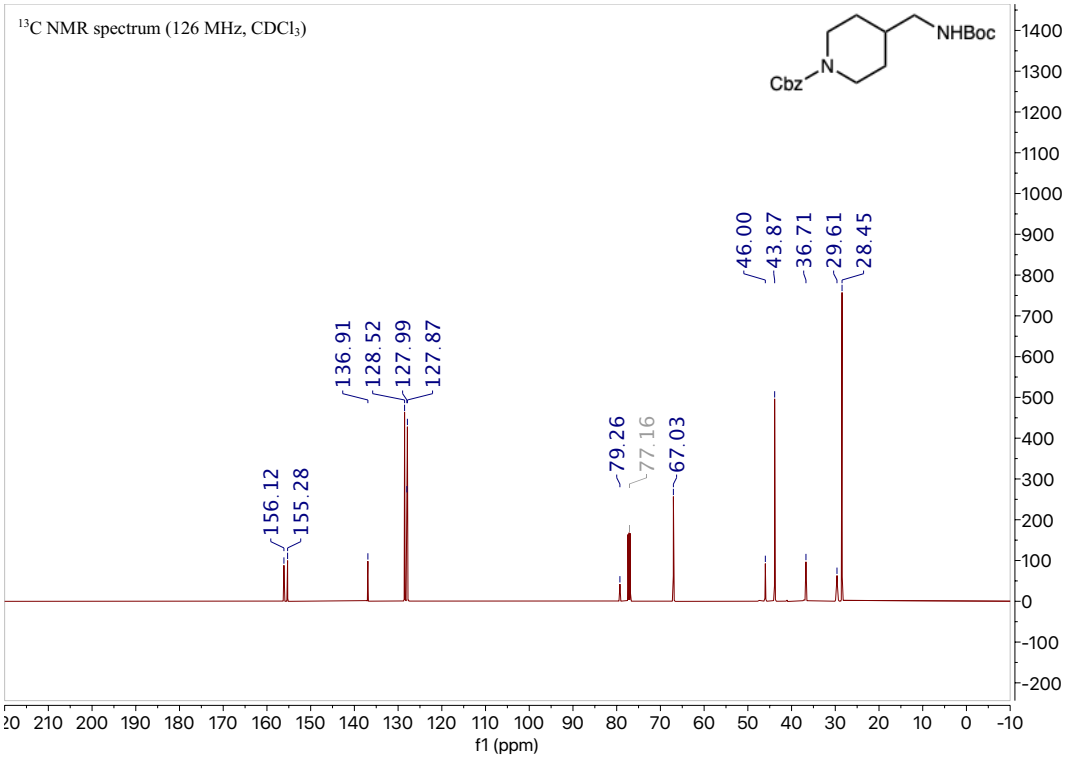


Figure S147. ^{1}H NMR spectrum of **58**

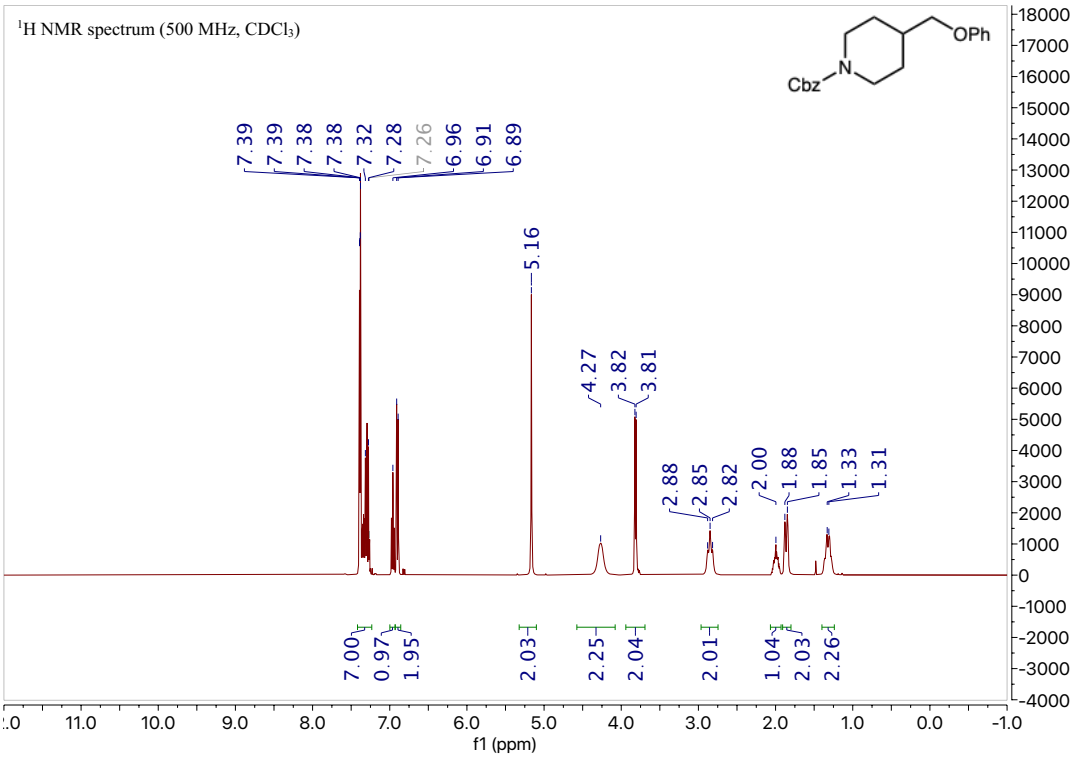


Figure S148. ^{13}C NMR spectrum of **58**

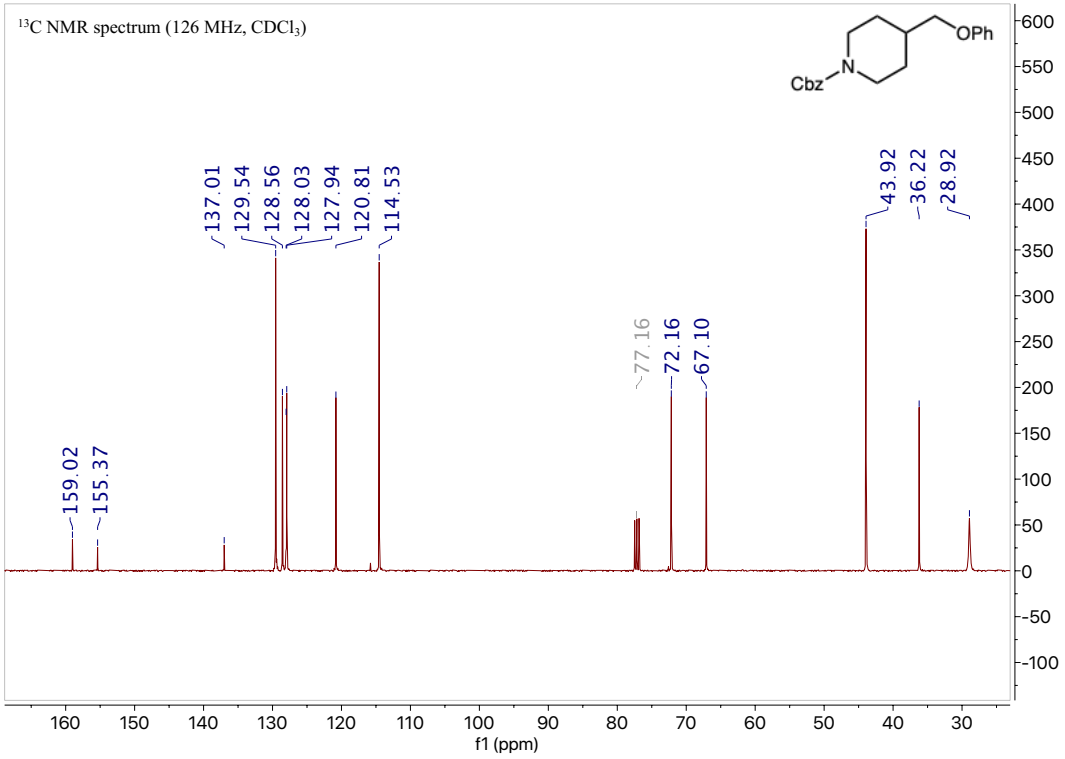


Figure S149. ^{1}H NMR spectrum of **59**

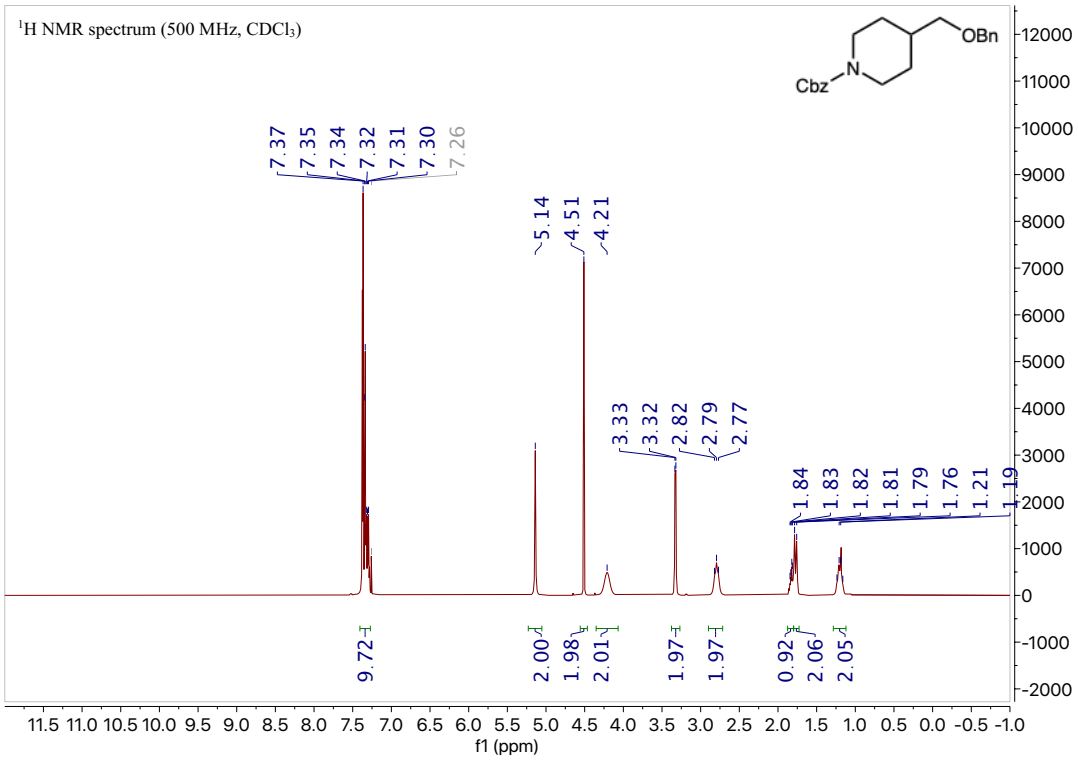


Figure S150. ^{13}C NMR spectrum of **59**

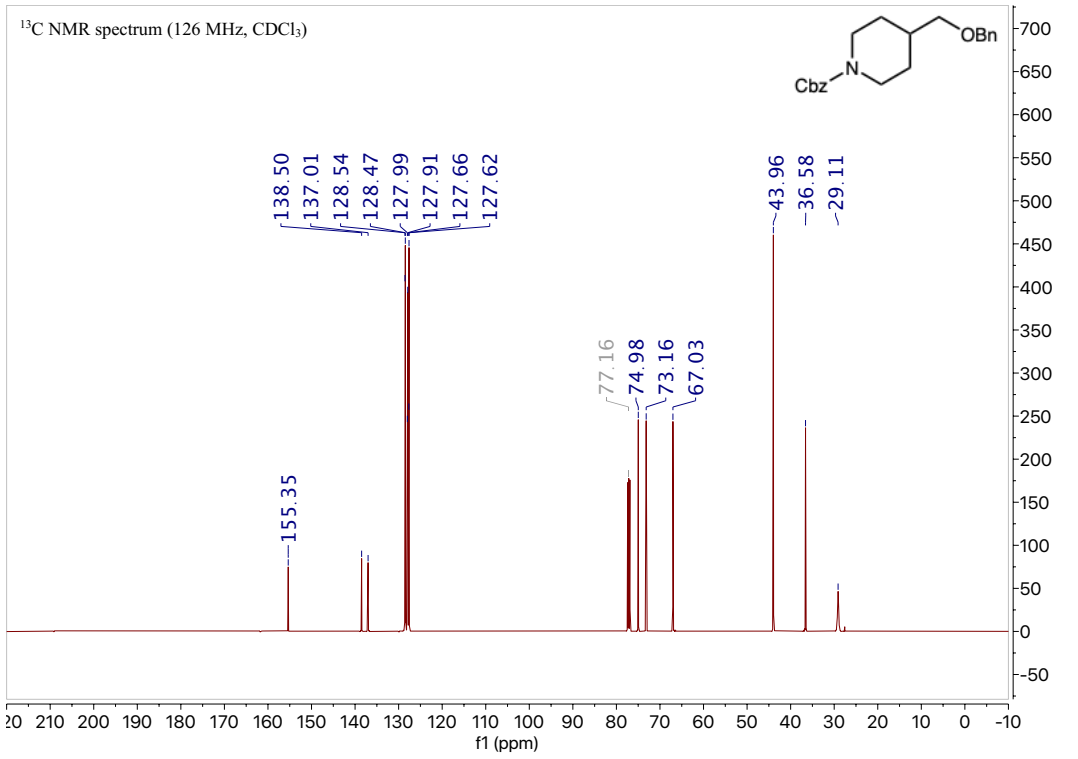


Figure S151. ^{1}H NMR spectrum of **60**

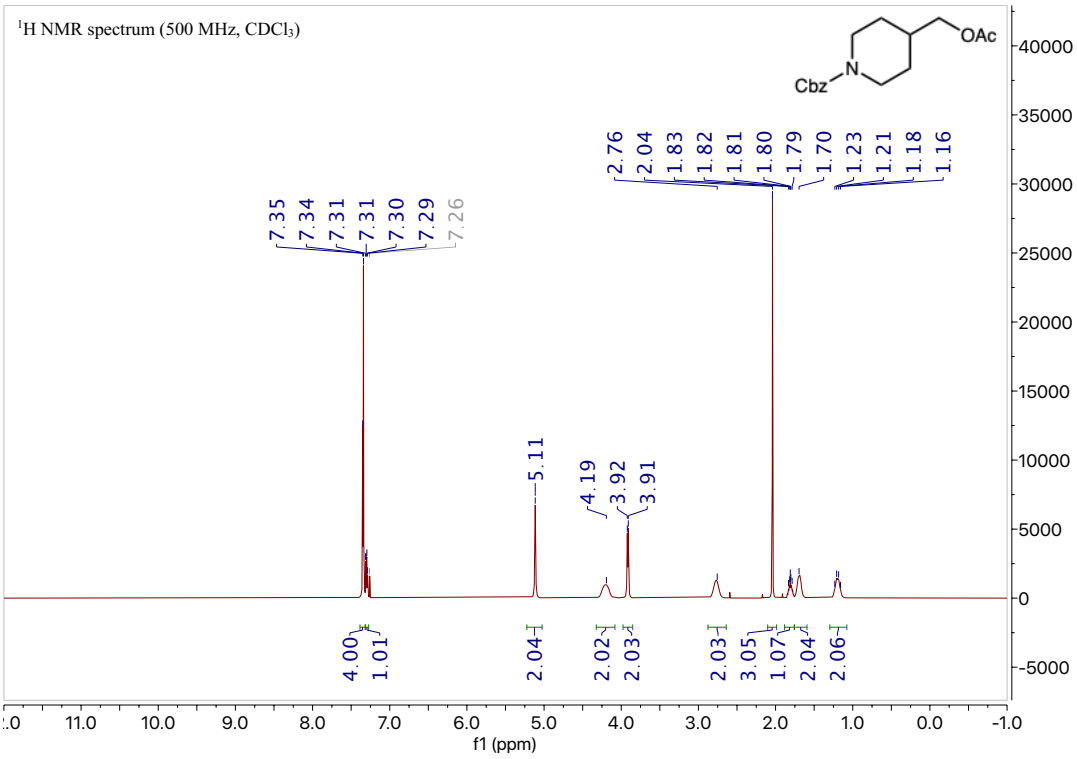


Figure S152. ^{13}C NMR spectrum of **60**

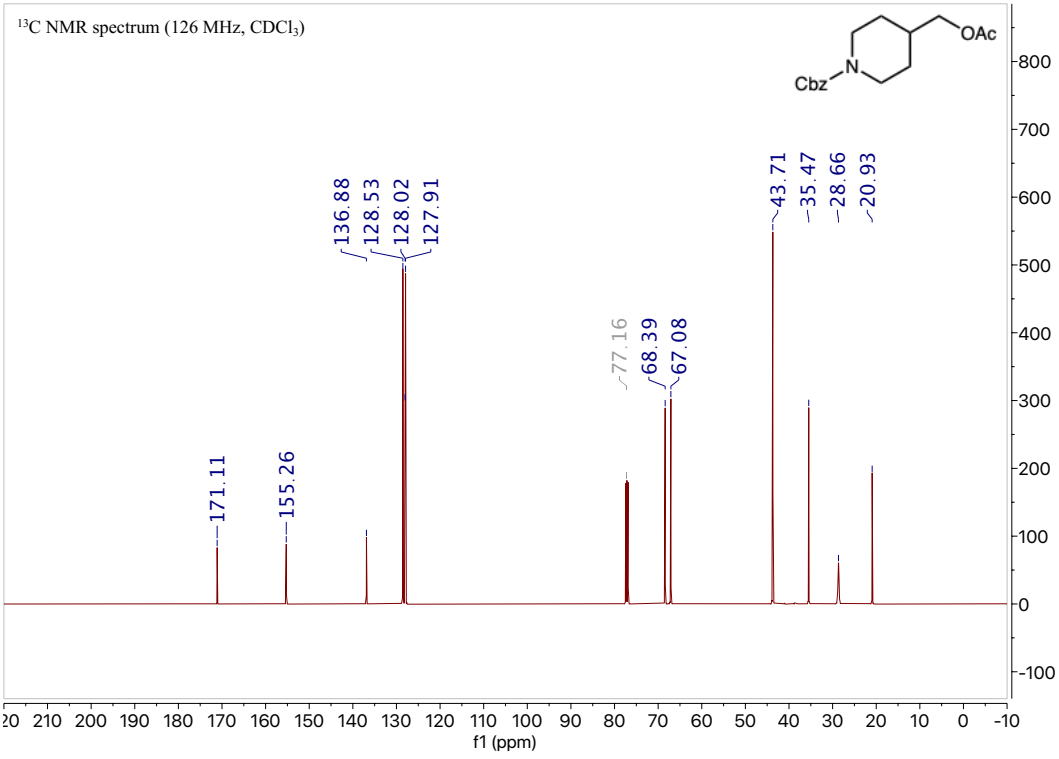


Figure S153. ^{1}H NMR spectrum of **61**

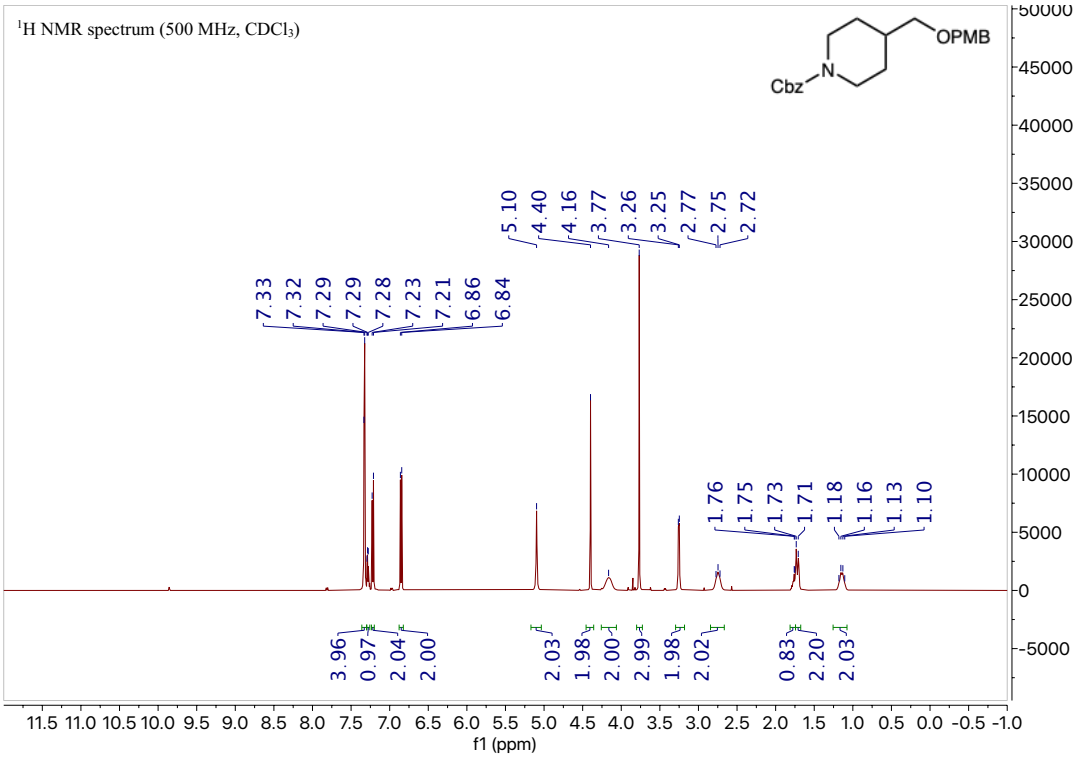


Figure S154. ^{13}C NMR spectrum of **61**

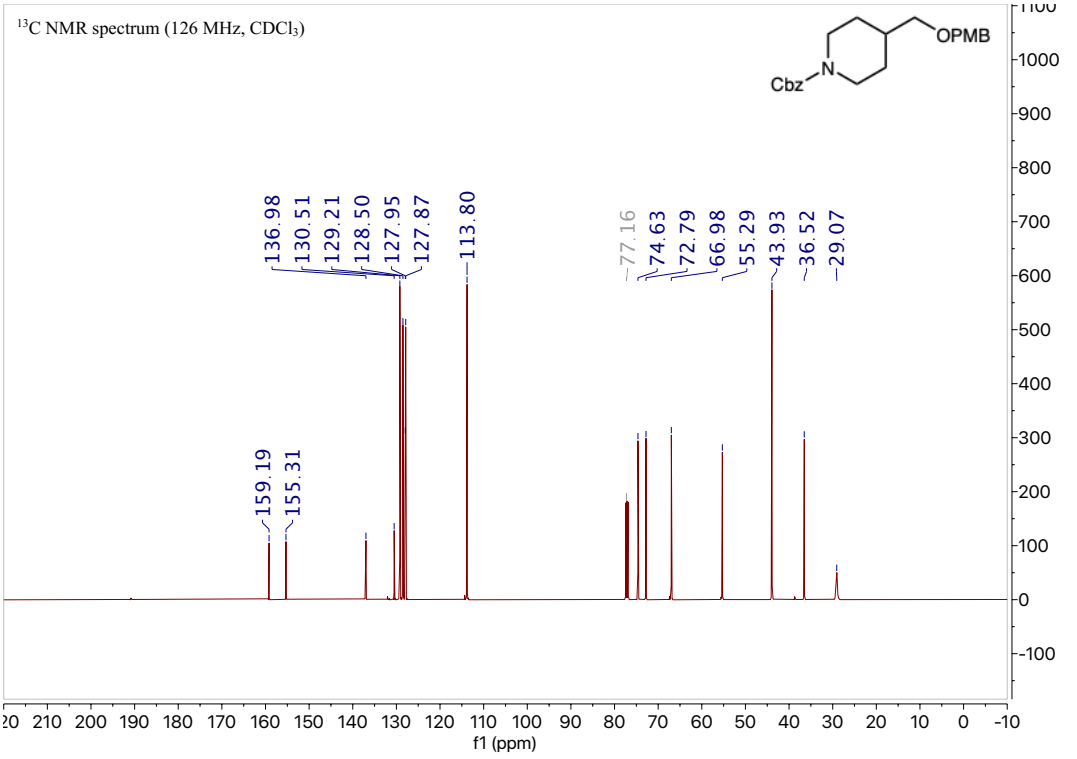


Figure S155. ^{1}H NMR spectrum of **62a**

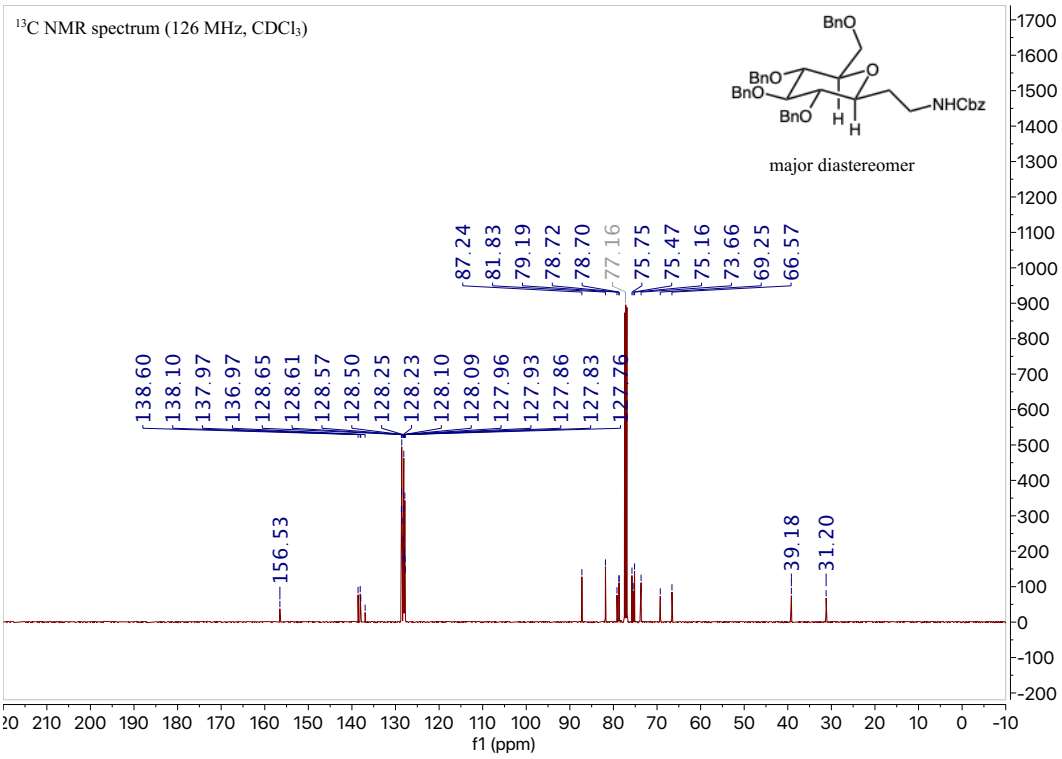


Figure S156. ^{13}C NMR spectrum of **62a**

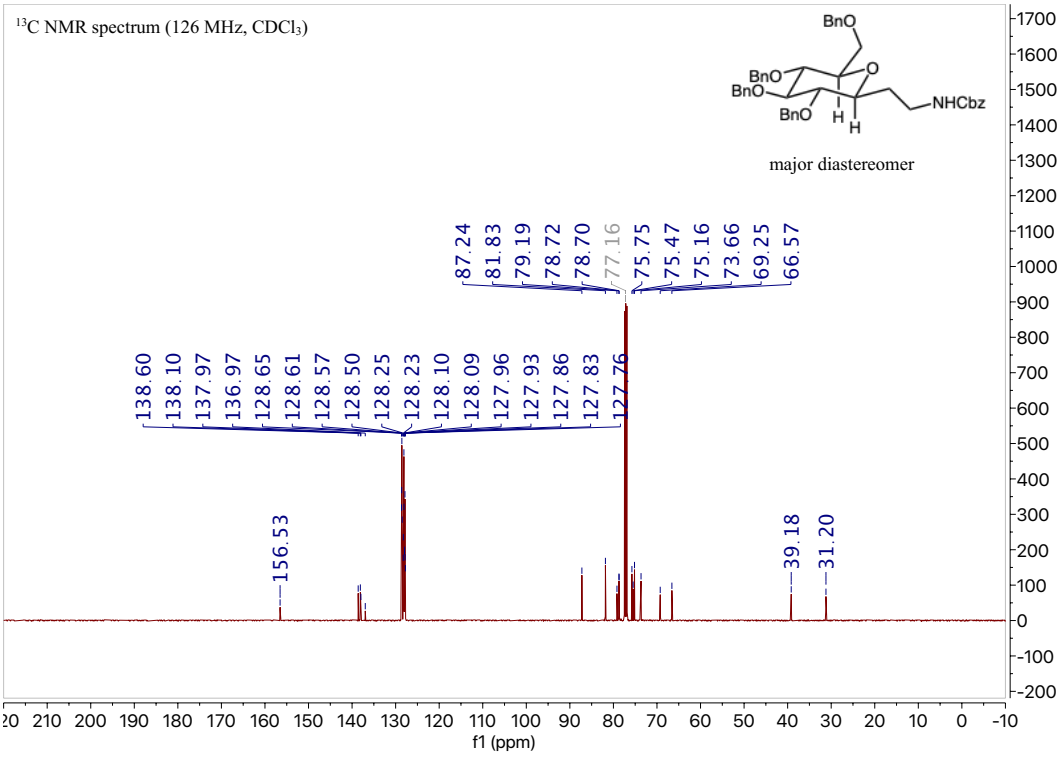


Figure S157. $^{1}H–^{1}H$ COSY NMR spectrum of **62a**

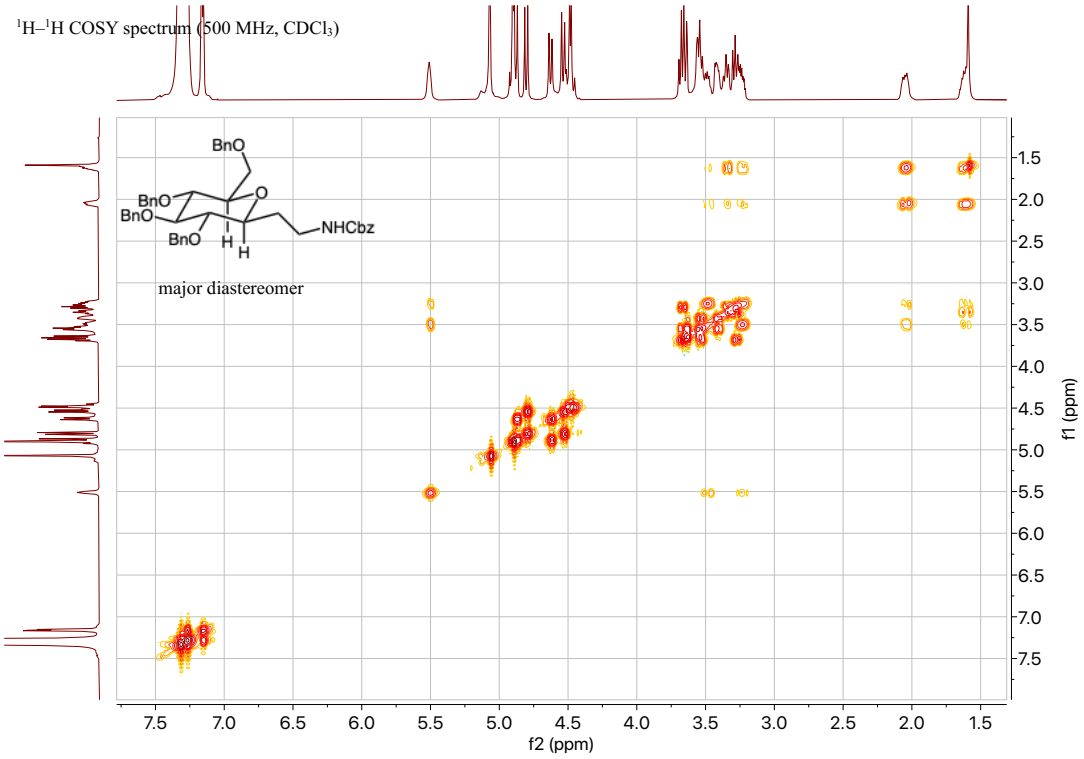


Figure S158. $^{1}H–^{13}C$ HSQC NMR spectrum of **62a**

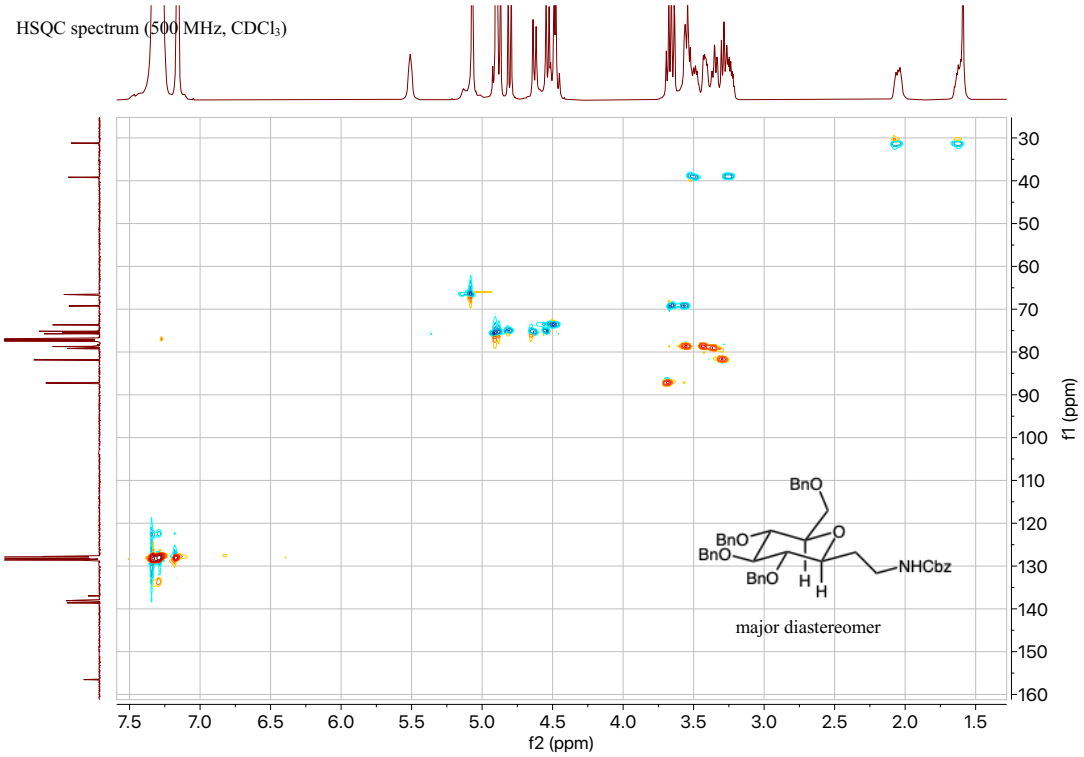


Figure S159. $^{1}H–^{13}C$ HMBC NMR spectrum of **62a**

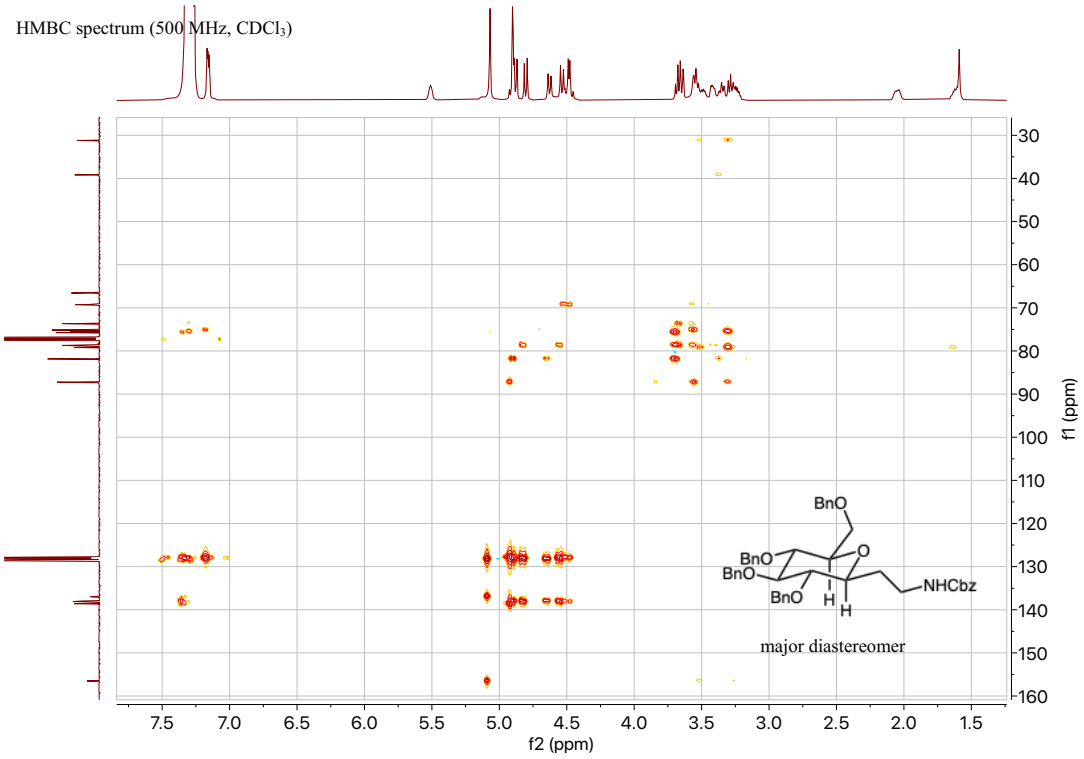


Figure S160. $^{1}H–^{1}H$ NOESY NMR spectrum of **62a**

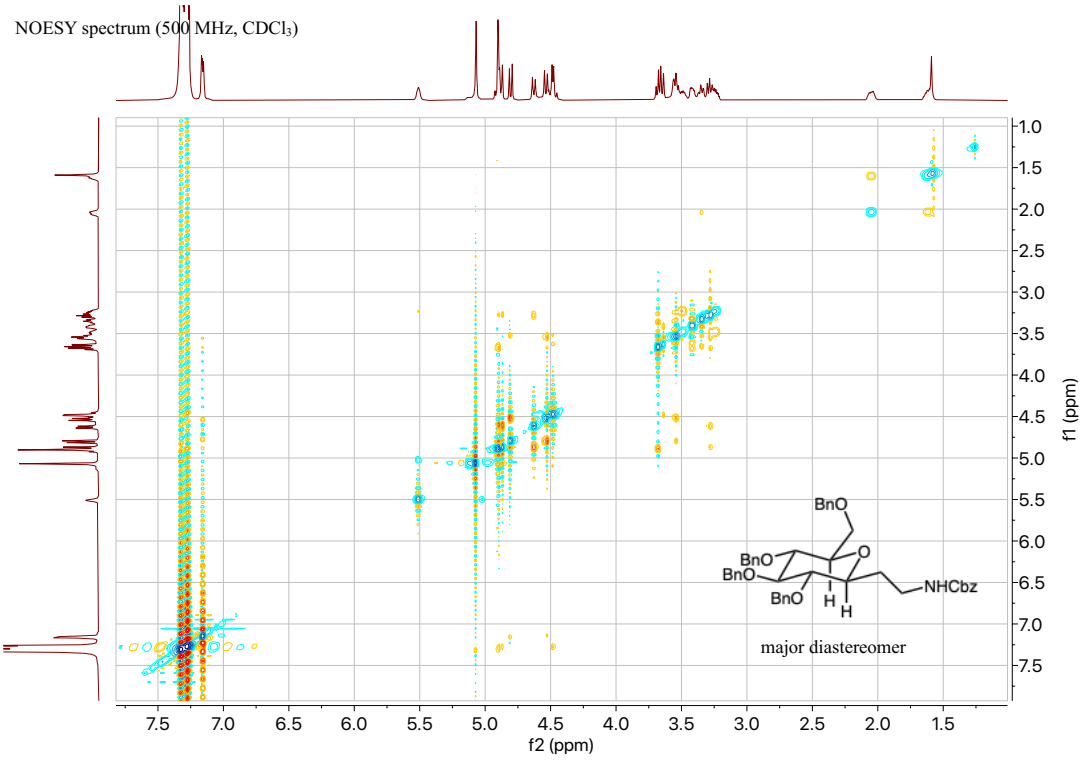


Figure S161. ^{1}H NMR spectrum of **62b**

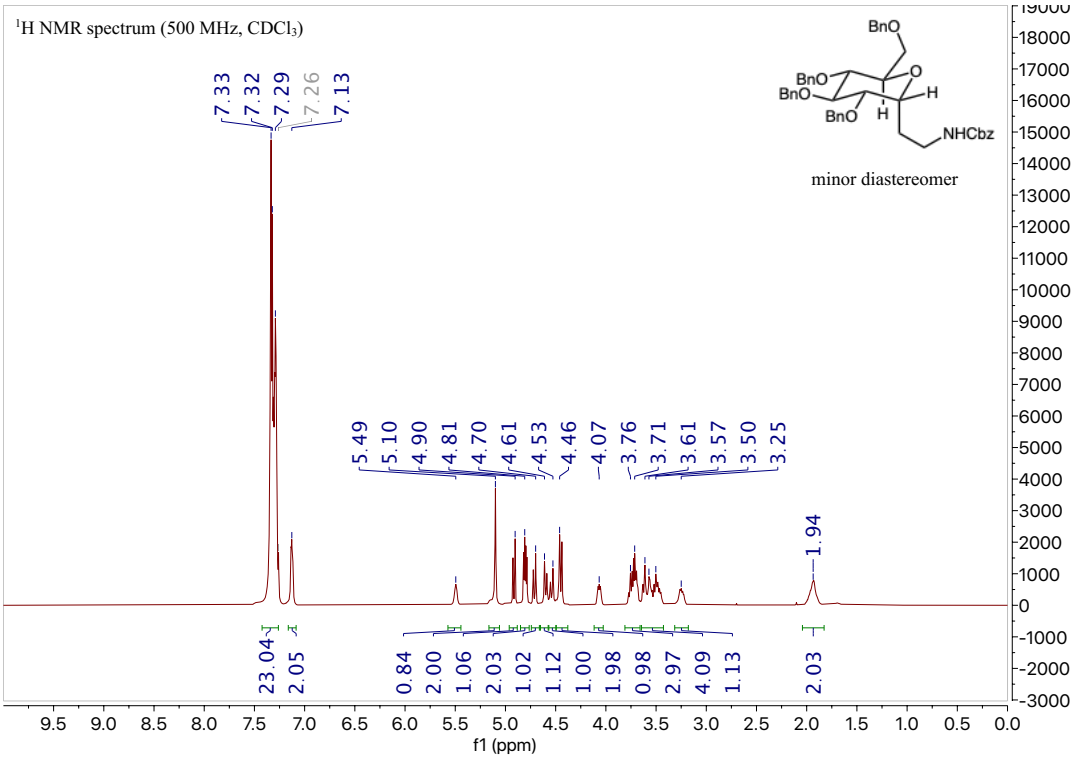


Figure S162. ^{13}C NMR spectrum of **62b**

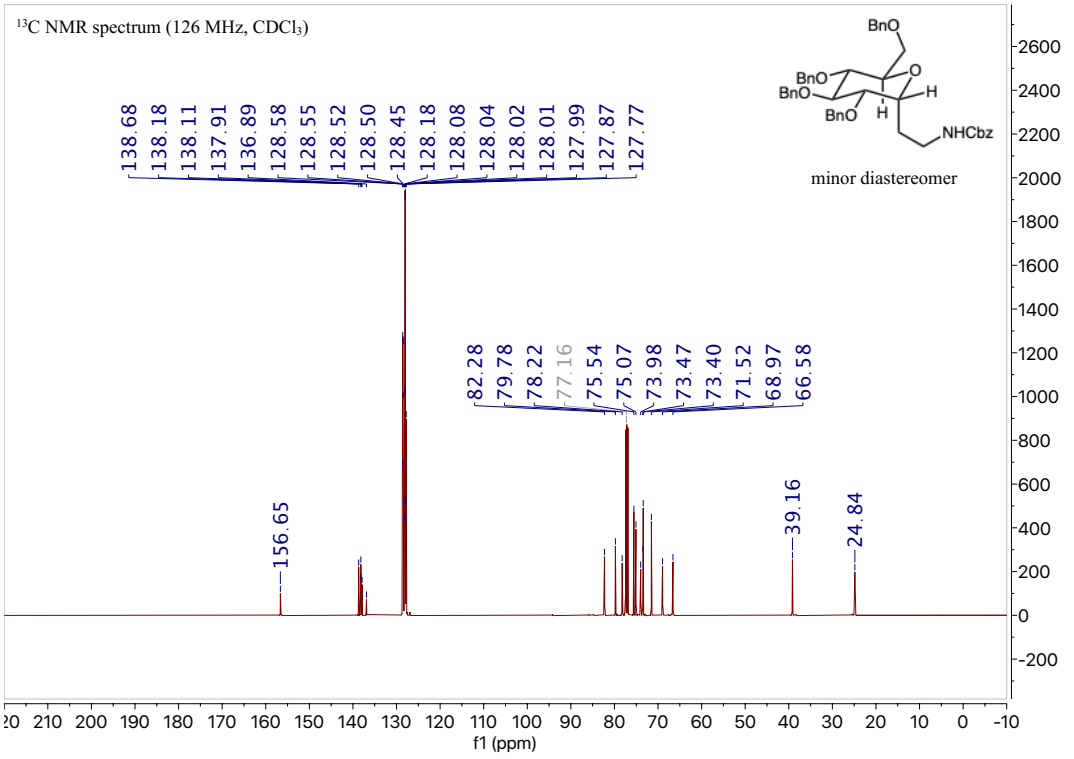


Figure S163. $^{1}H–^{1}H$ COSY NMR spectrum of **62b**

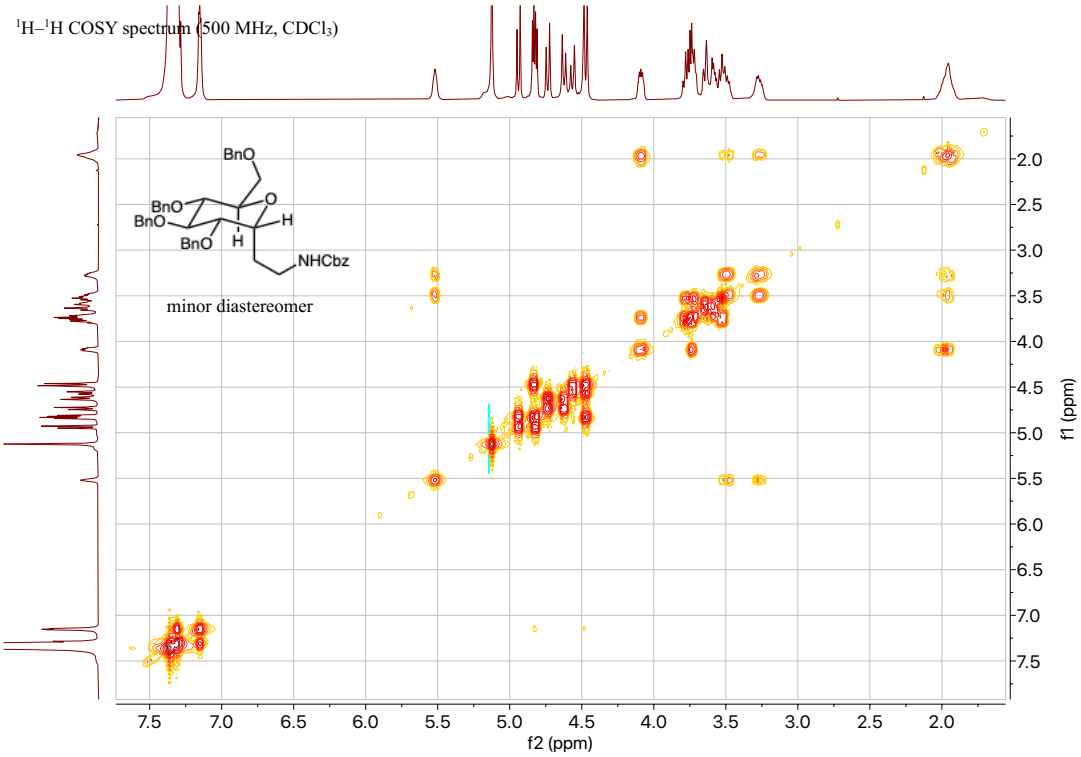


Figure S164. $^{1}H–^{13}C$ HSQC NMR spectrum of **62b**

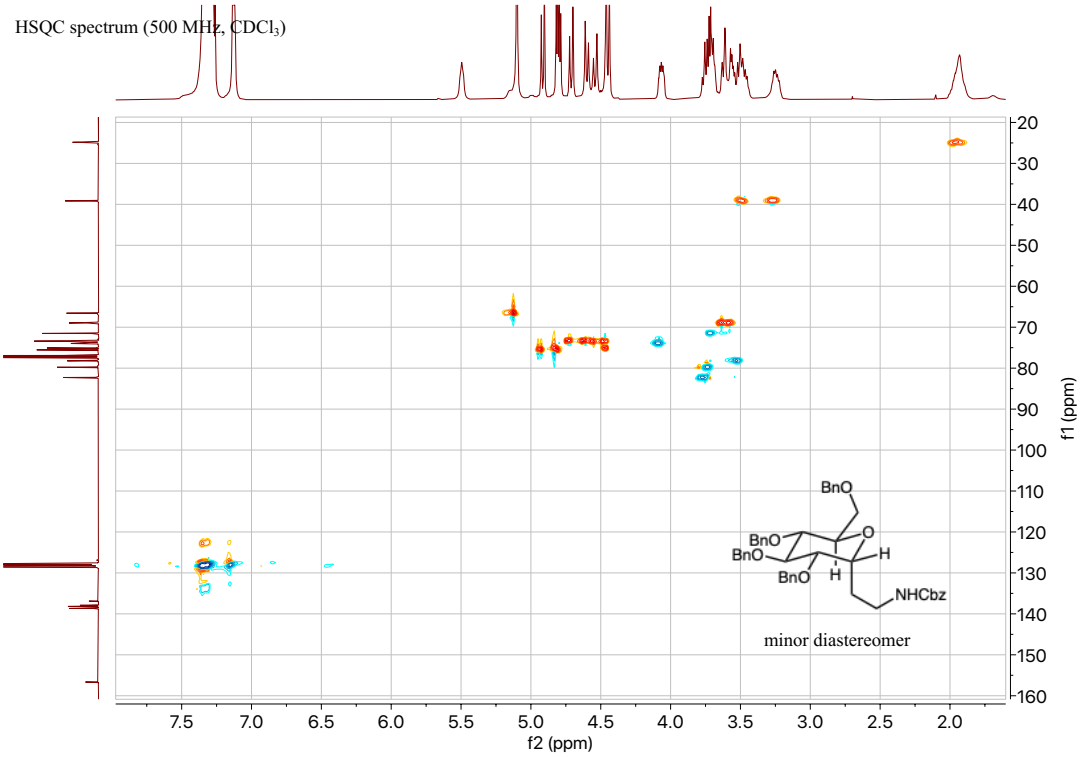


Figure S165. $^{1}H–^{13}C$ HMBC NMR spectrum of **62b**

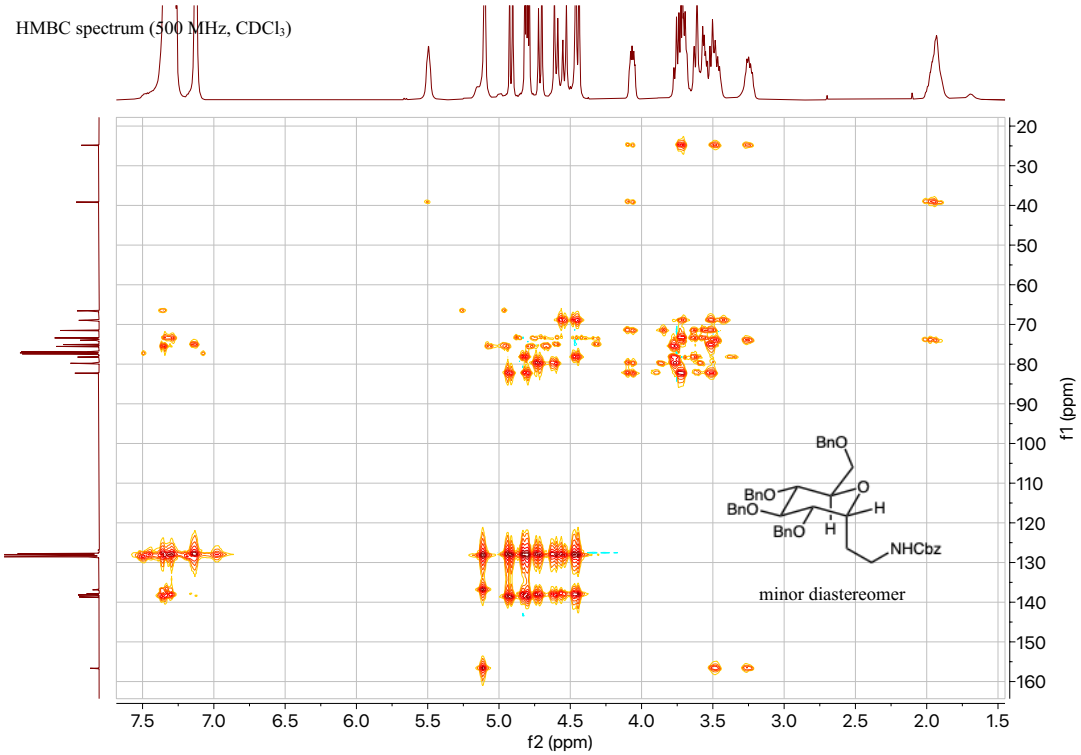


Figure S166. $^{1}H–^{1}H$ NOESY NMR spectrum of **62b**

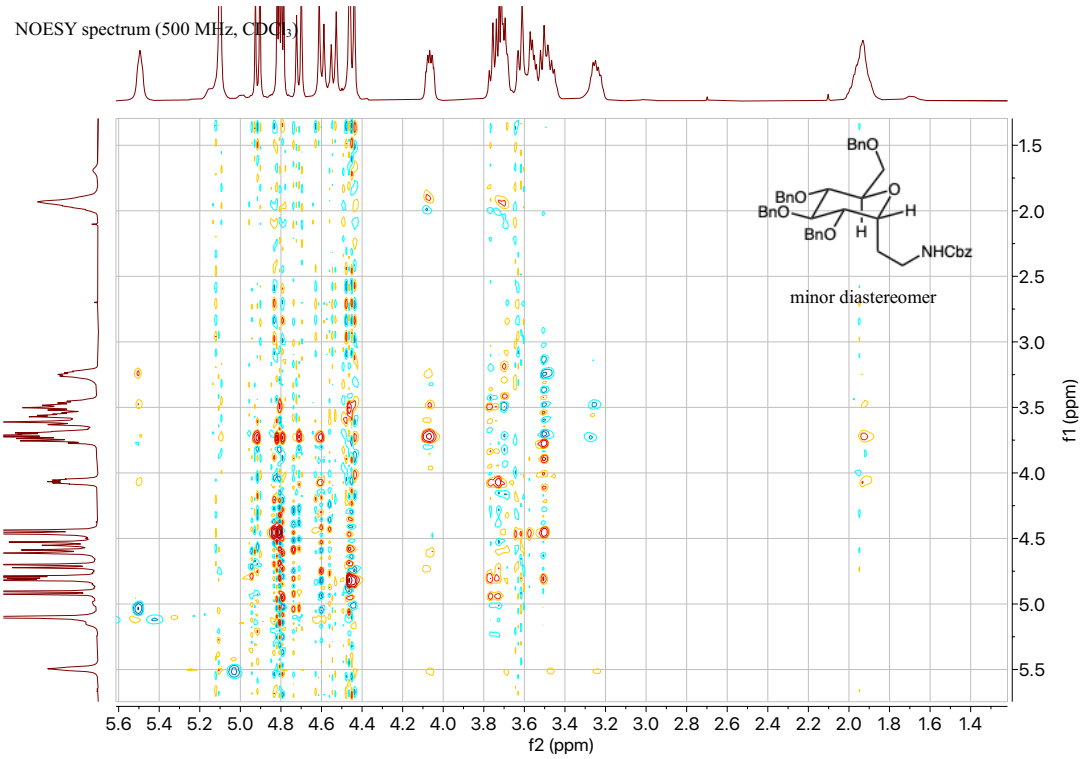


Figure S167. ^{1}H NMR spectrum of **63 (4.3:1 dr)**

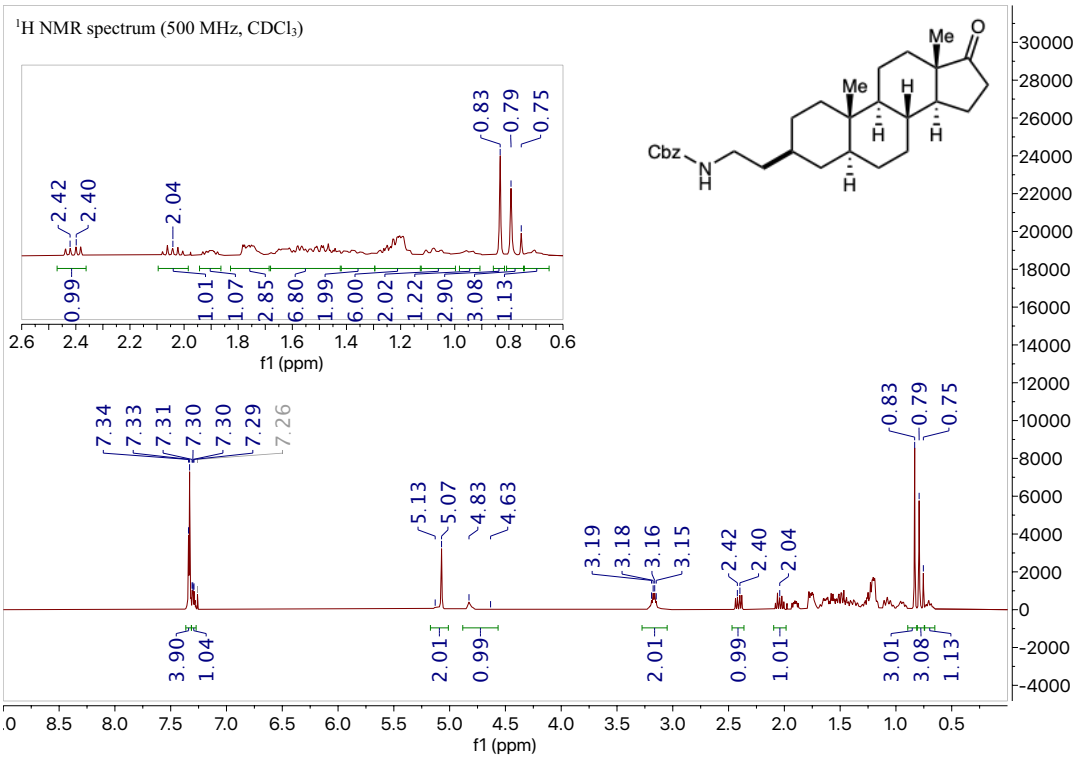


Figure S168. ^{13}C NMR spectrum of **63 (4.3:1 dr)**

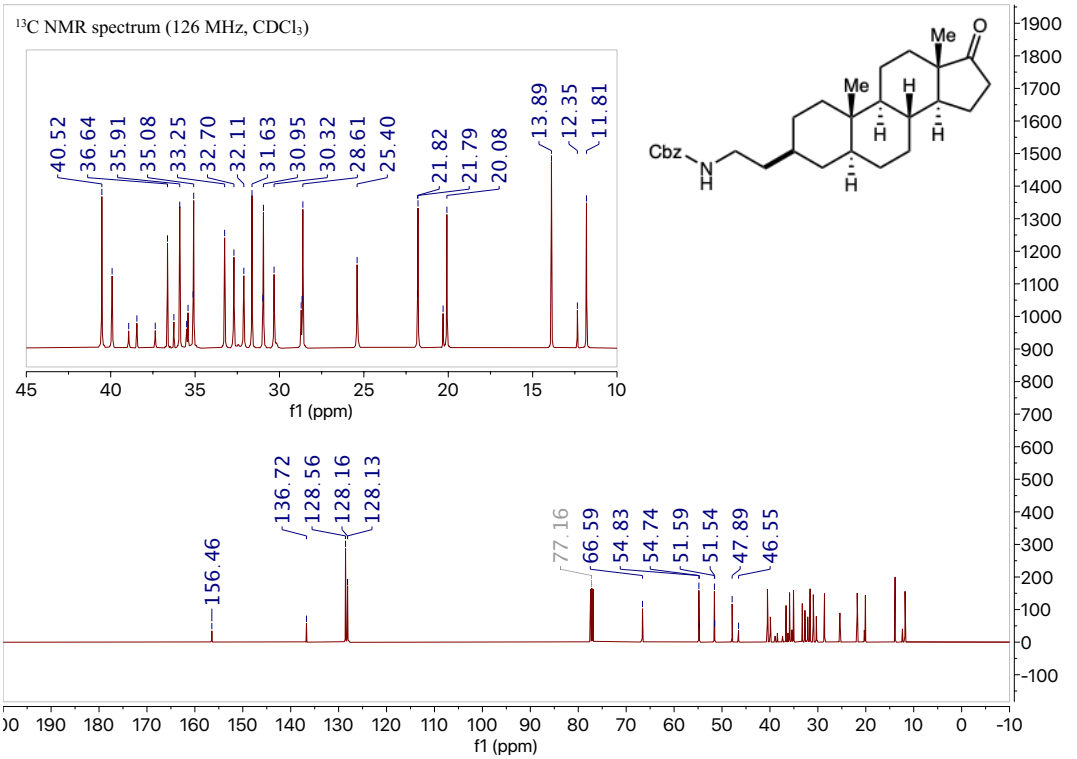


Figure S169. $^{1}H–^{1}H$ COSY NMR spectrum of **63 (4.3:1 dr)**

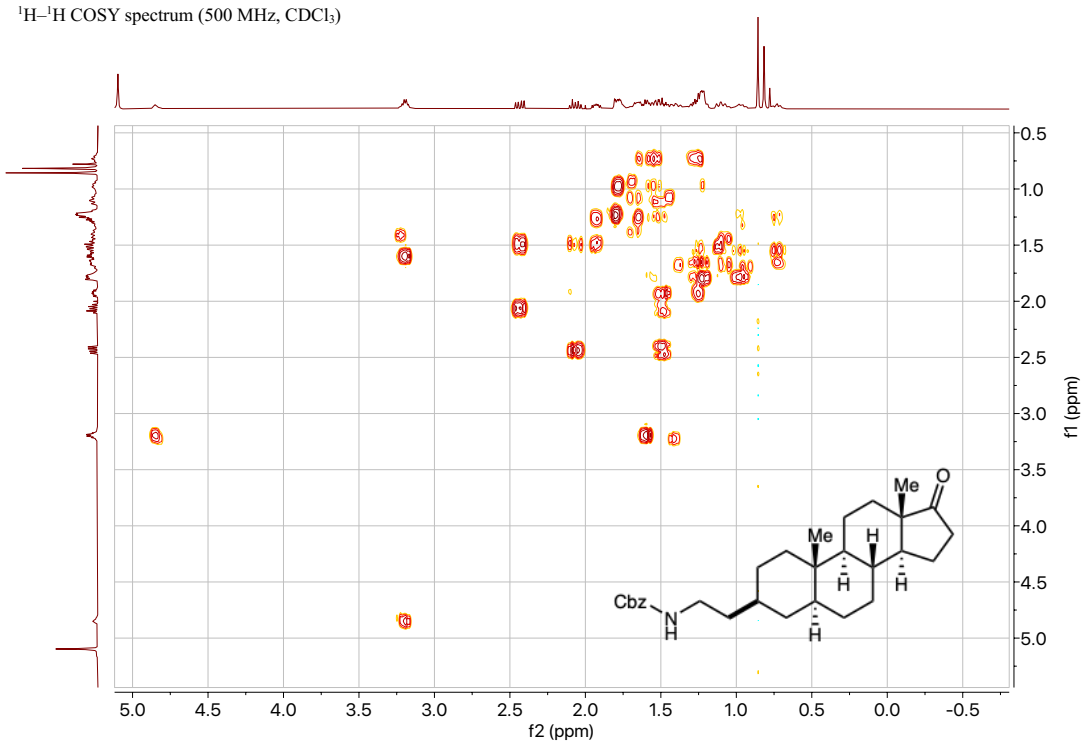


Figure S170. $^{1}H–^{13}C$ HSQC NMR spectrum of **63 (4.3:1 dr)**

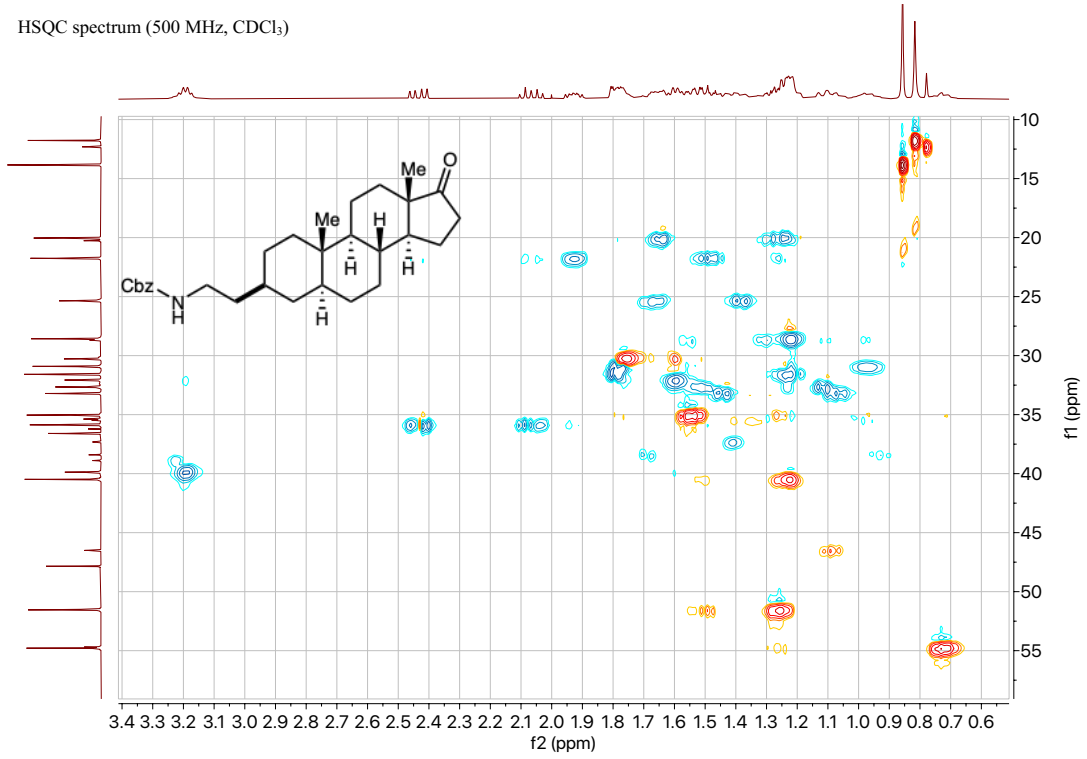


Figure S171. ^{1}H–^{1}H NOESY NMR spectrum of **63 (4.3:1 dr)**

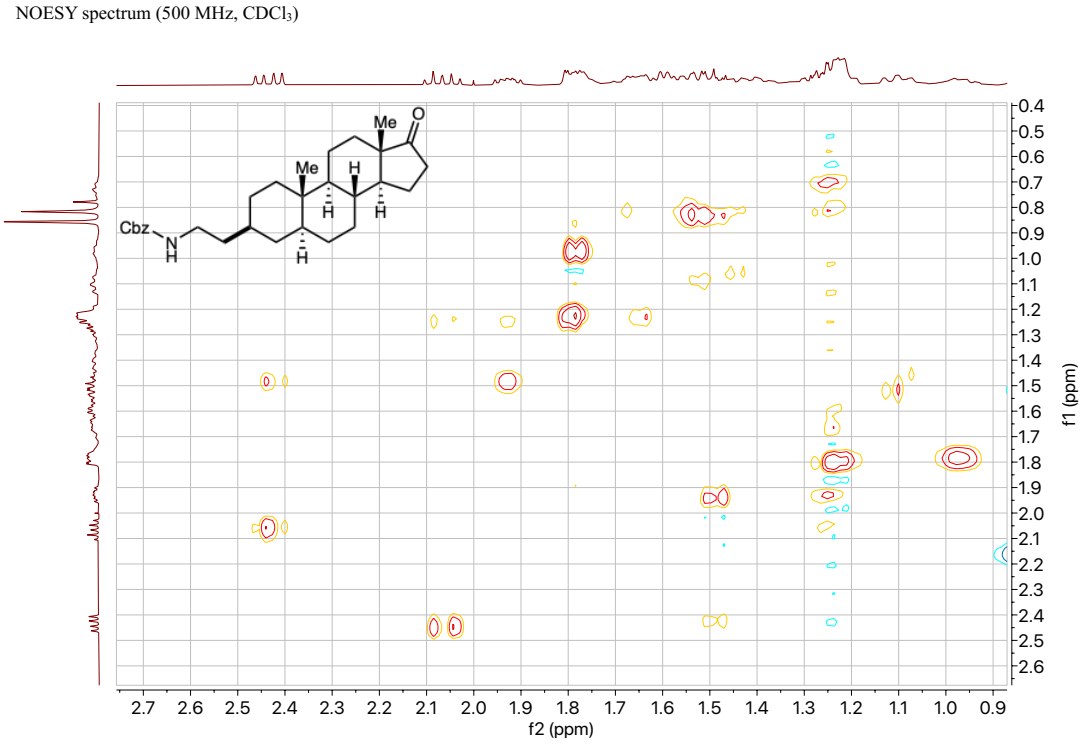


Figure S172. Diastereomeric analysis for **63** by quantitative ^{13}C NMR of isolated mixture.

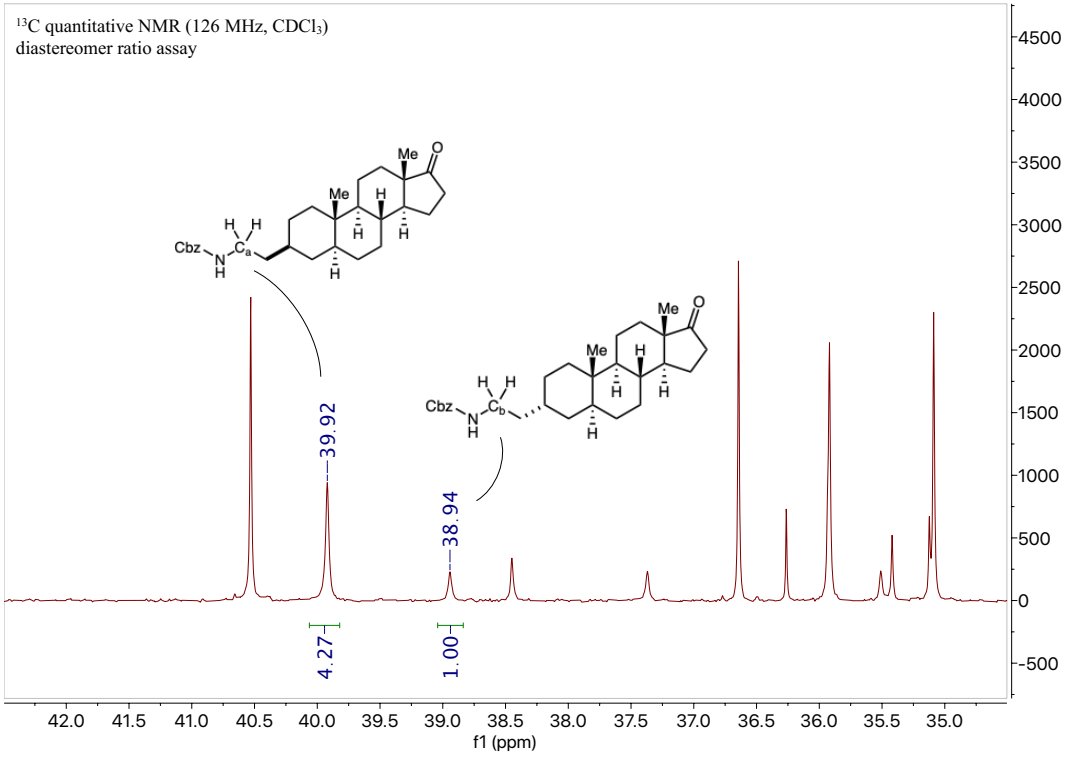


Figure S173. ^{1}H NMR spectrum of **64**

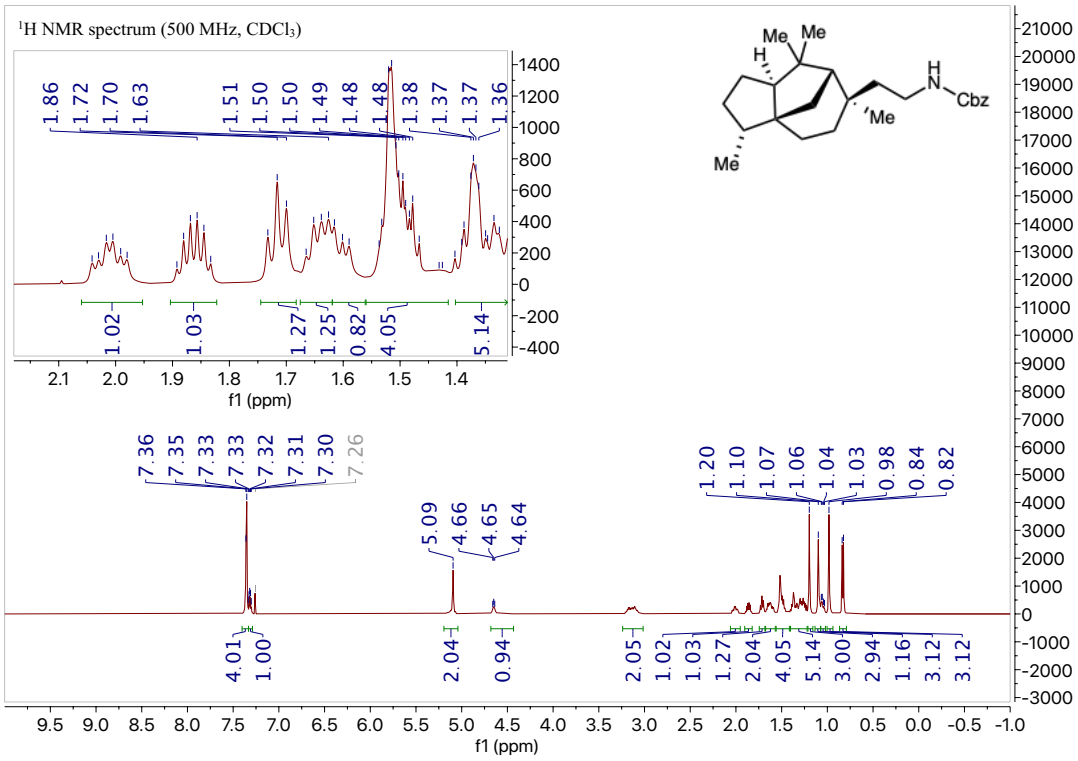


Figure S174. ^{13}C NMR spectrum of **64**

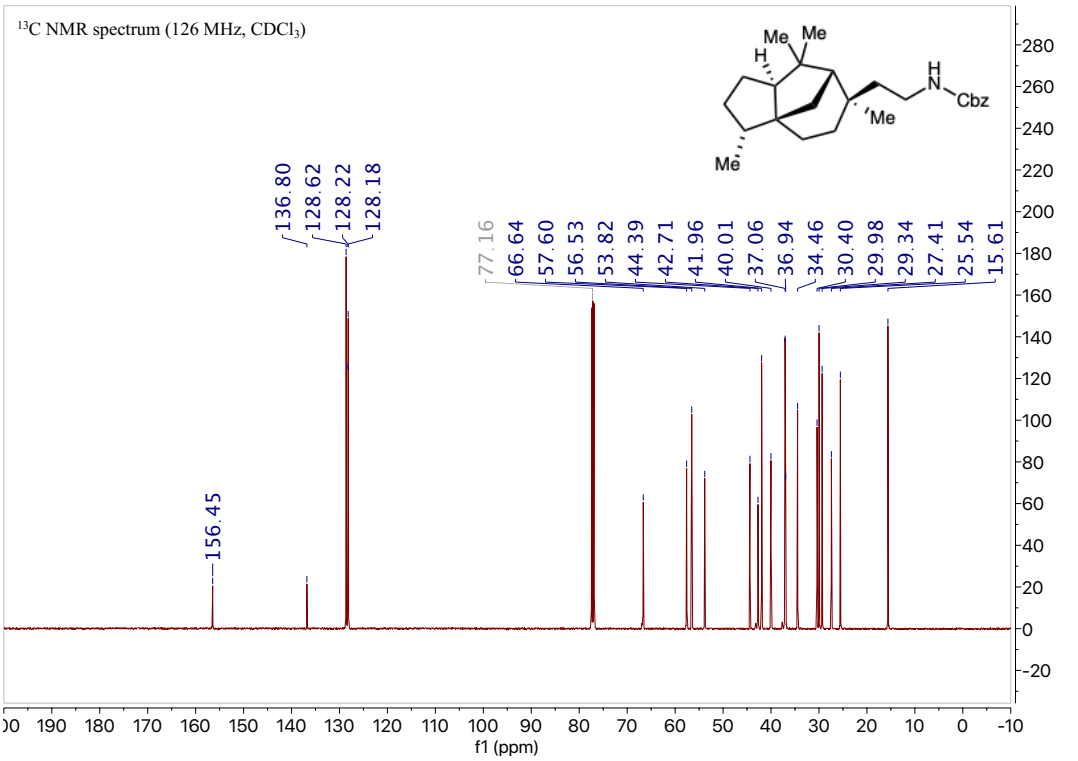


Figure S175. $^{1}H–^{1}H$ COSY NMR spectrum of **64**

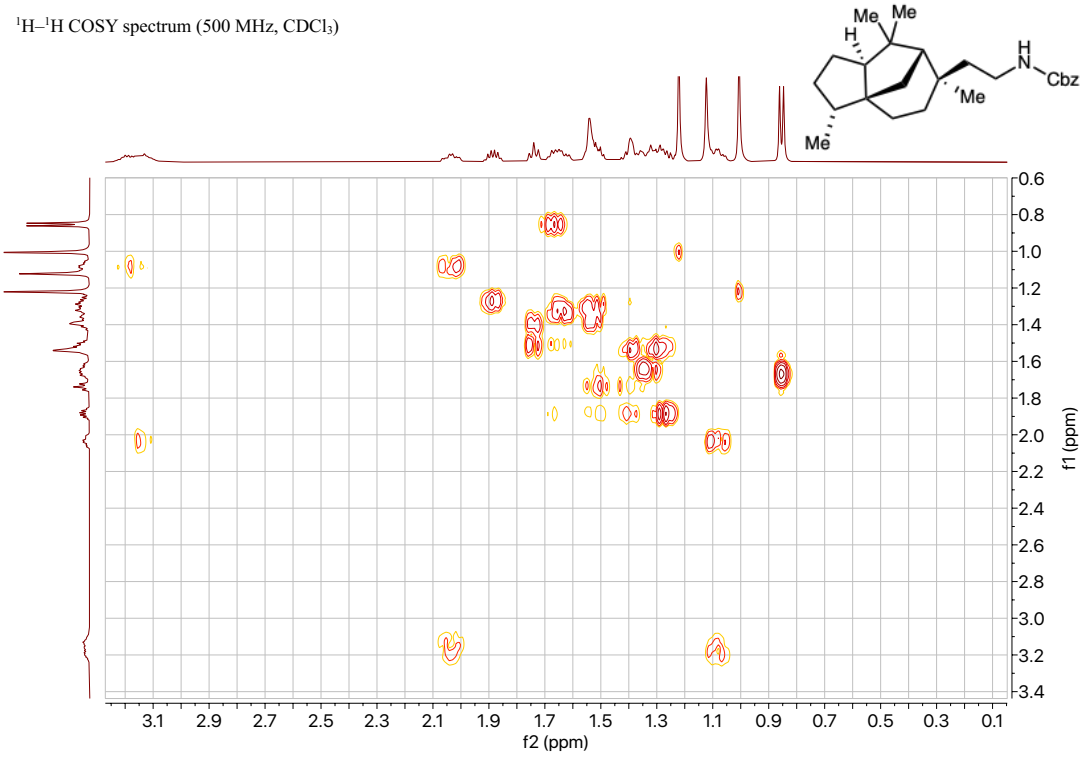


Figure S176. $^{1}H–^{13}C$ HSQC NMR spectrum of **64**

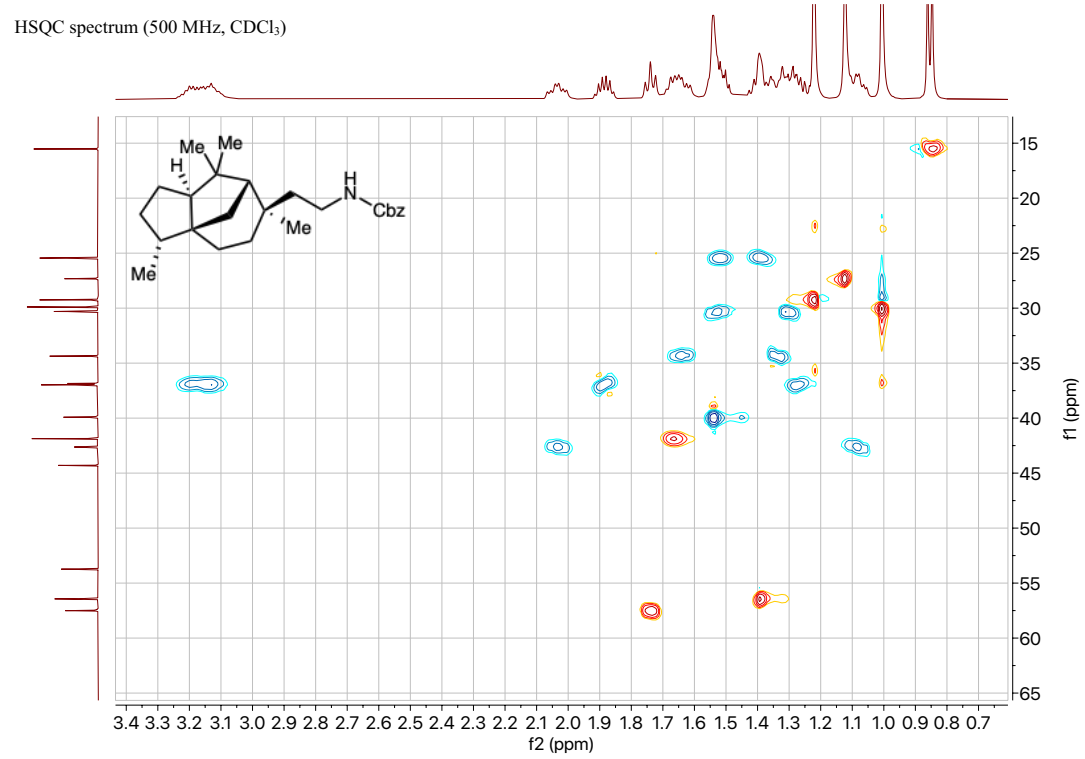


Figure S177. $^{1}H–^{13}C$ HMBC NMR spectrum of **64**

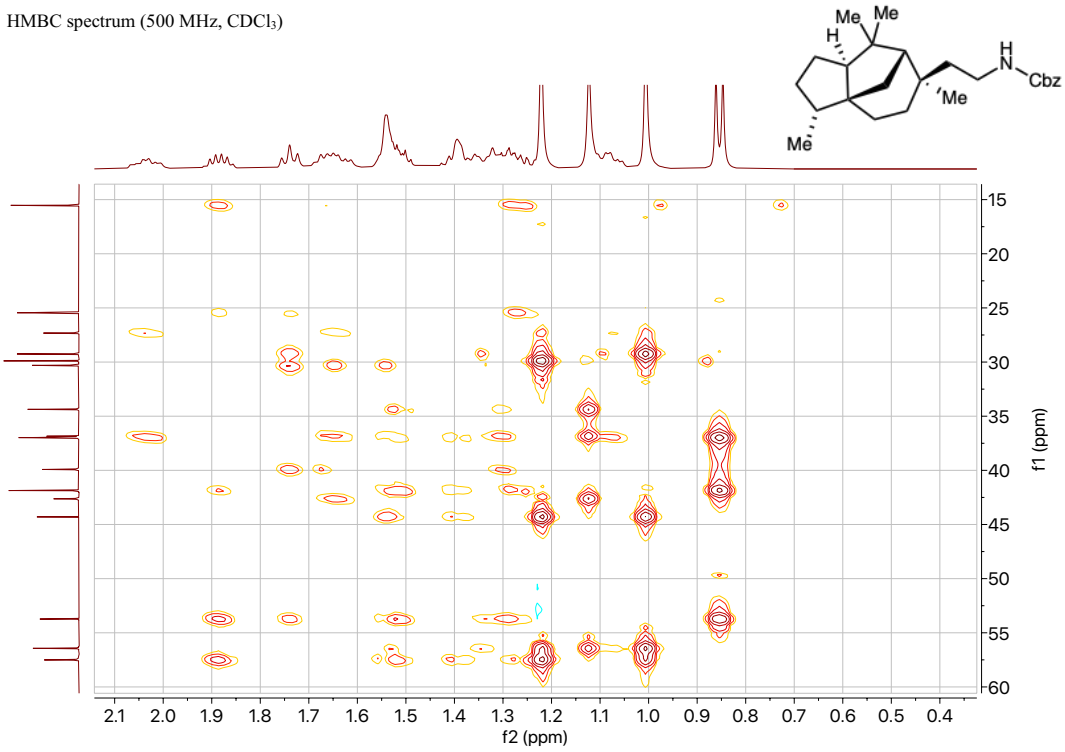


Figure S178. $^{1}H–^{1}H$ NOESY NMR spectrum of **64**

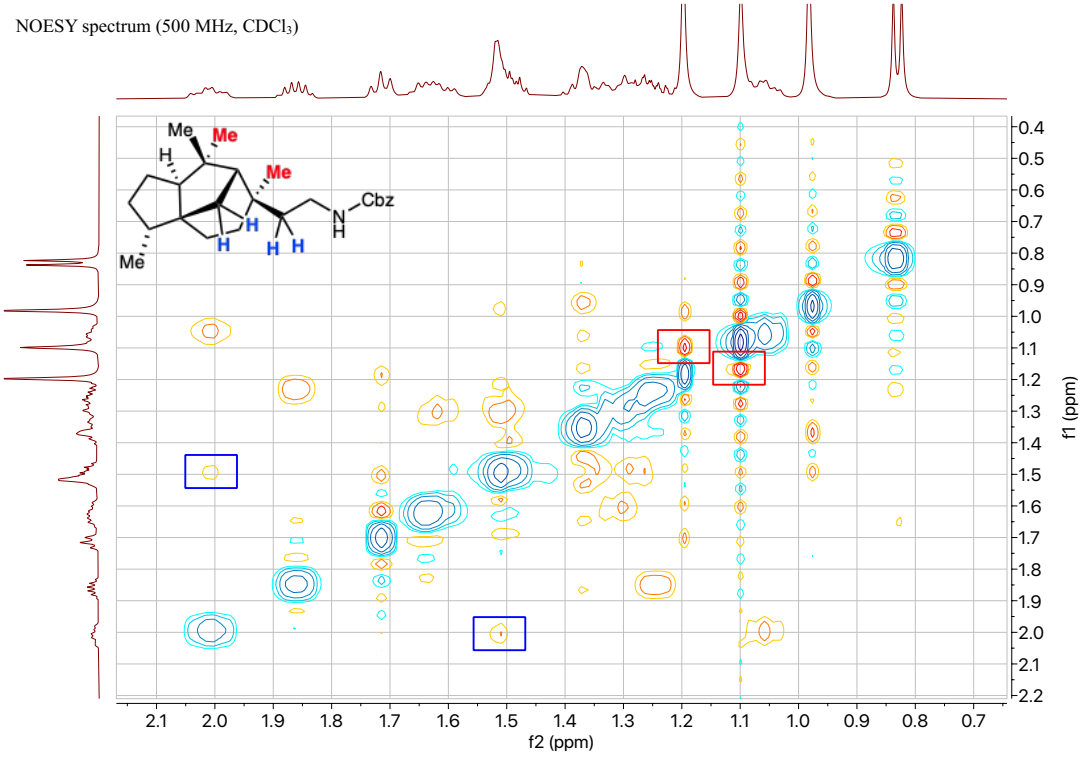
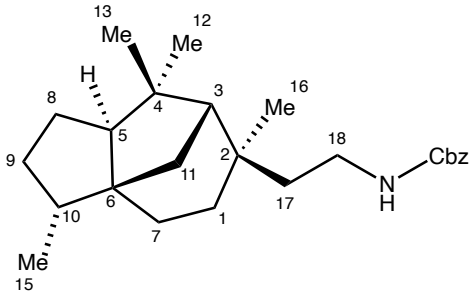


Figure S179. Assignment of key NMR peaks of **64** ^{1}H NMR (^{13}C NMR)



group(s)	^{1}H (ppm)	^{13}C (ppm)
18	3.15	36.94
17	1.09, 2.00	42.71
1	1.62, 1.32	34.46
16	1.10	27.41
3	1.37	56.53
12 & 13	0.98, 1.20	29.34, 29.98
5	1.71	57.60
8	1.37, 1.49	25.54
9	1.25, 1.86	37.06
10	1.64	41.96
15	0.83	15.61
6	—	53.82
7	1.28, 1.50	30.40
11	1.51	40.01

Figure S180. ^{1}H NMR spectrum of **65**

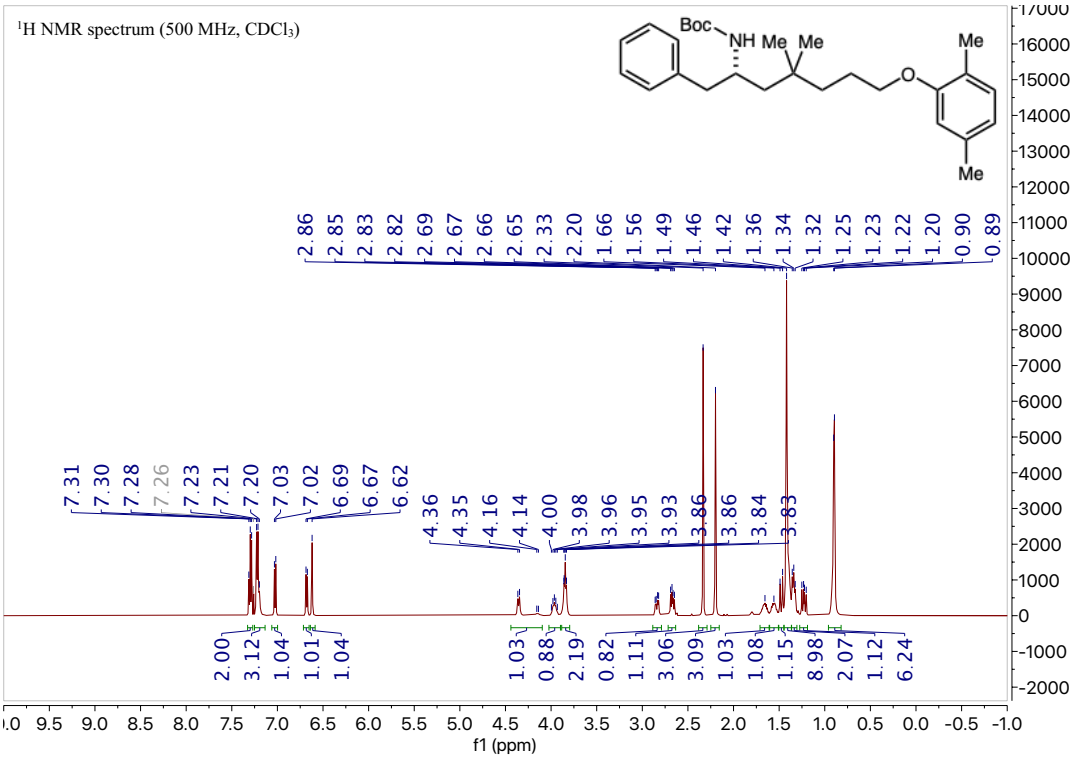
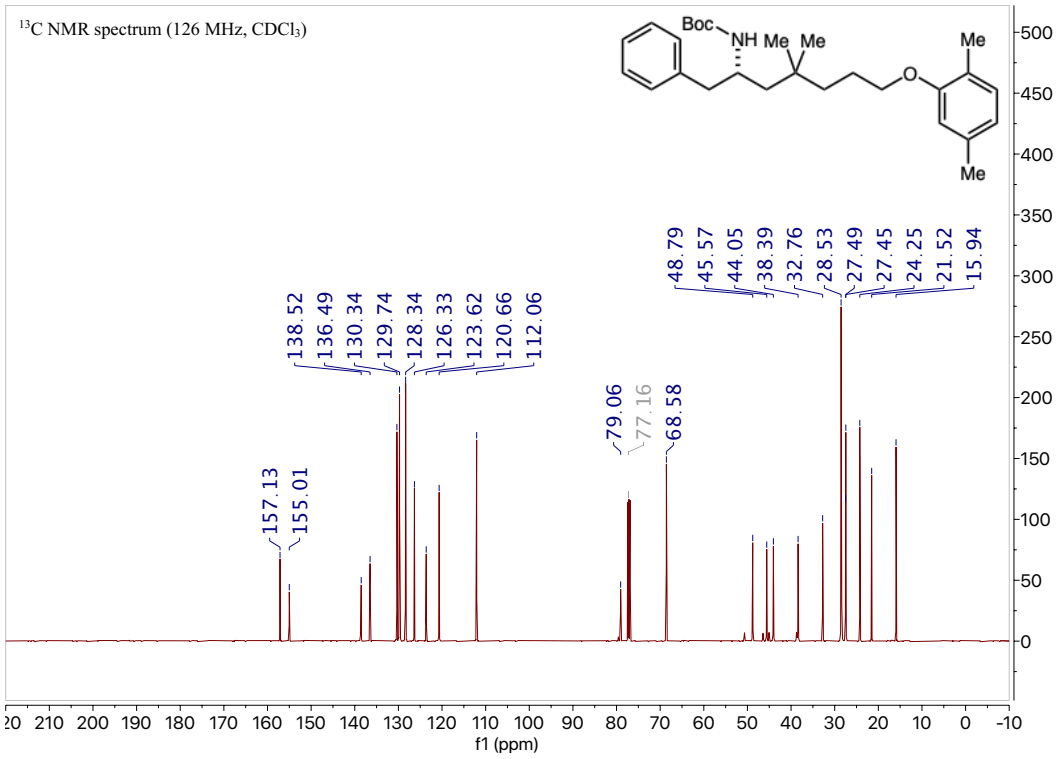


Figure S181. ^{13}C NMR spectrum of **65**



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