

Practical Ni-Catalyzed Aryl-Alkyl Cross-Coupling of Secondary Redox-active Esters

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SUPPORTING INFORMATION

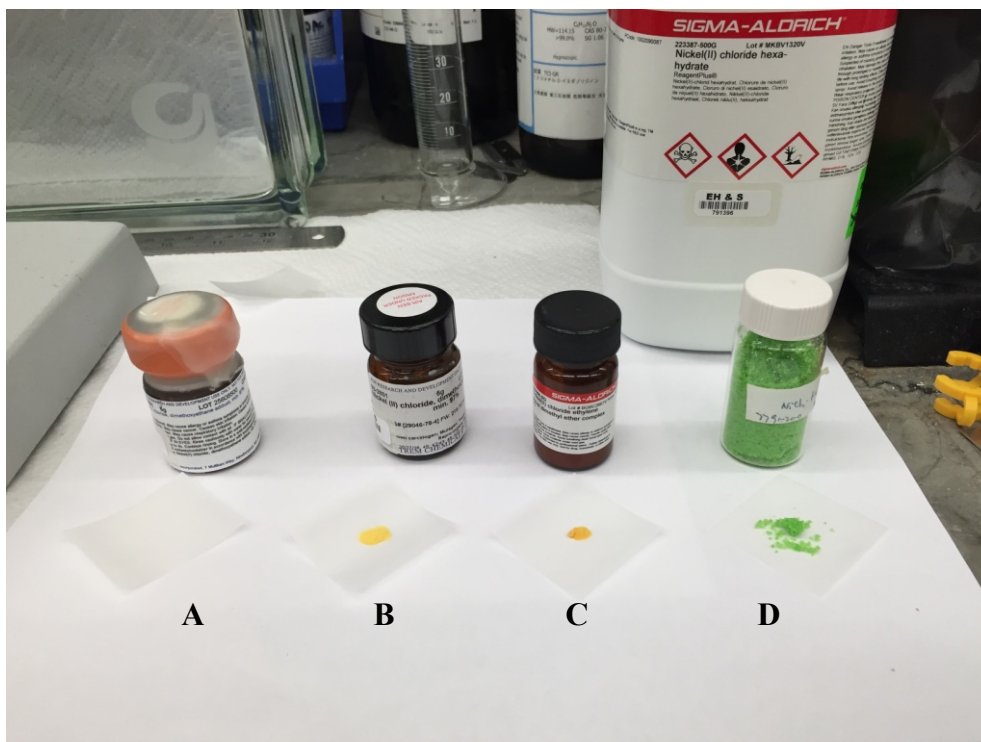
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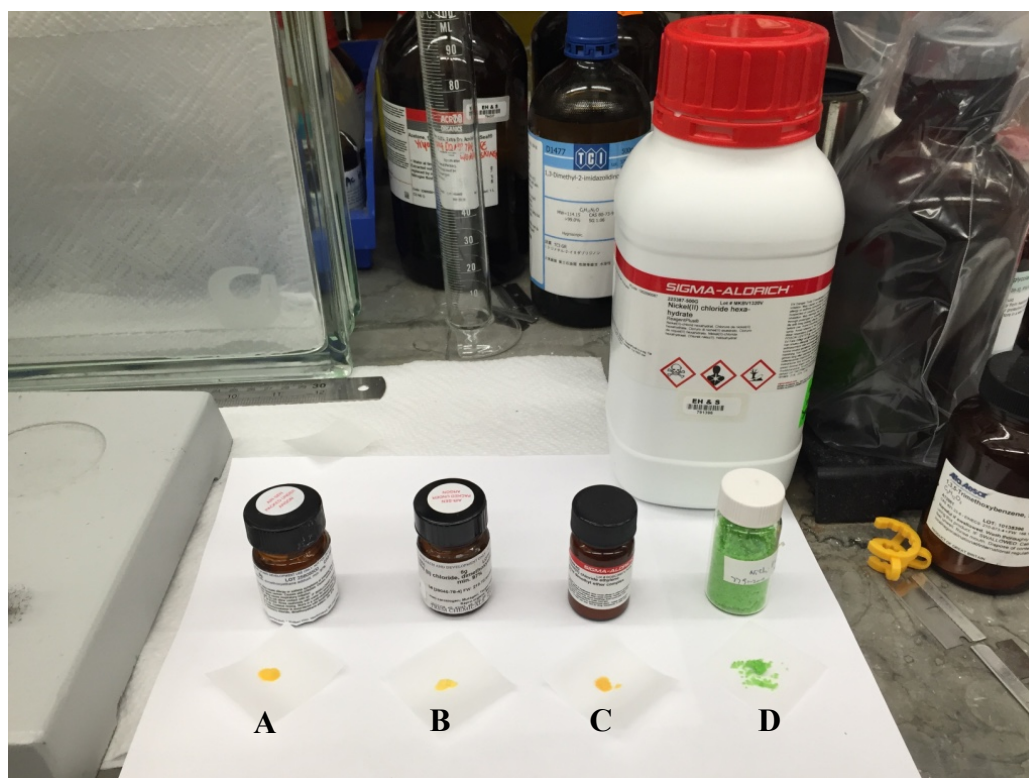
General Considerations. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dichloromethane (CH₂Cl₂) were obtained by passing the previously degassed solvents through an activated alumina column. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Nickel chloride glyme complex was purchased from Strem or Aldrich. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by GC/FID, GC/MS, and thin layer chromatography (TLC). TLC was performed using 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent or I₂ or KMnO₄ and heat as developing agents. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments and are calibrated using residual undeuterated solvent (CHCl₃ at 7.26 ppm ¹H NMR, 77.16 ppm ¹³C NMR) or TMS as an internal reference. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm), and preparative TLC was performed on Merck silica plates (60F-254). High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected.

Handling of [Ni] catalysts.

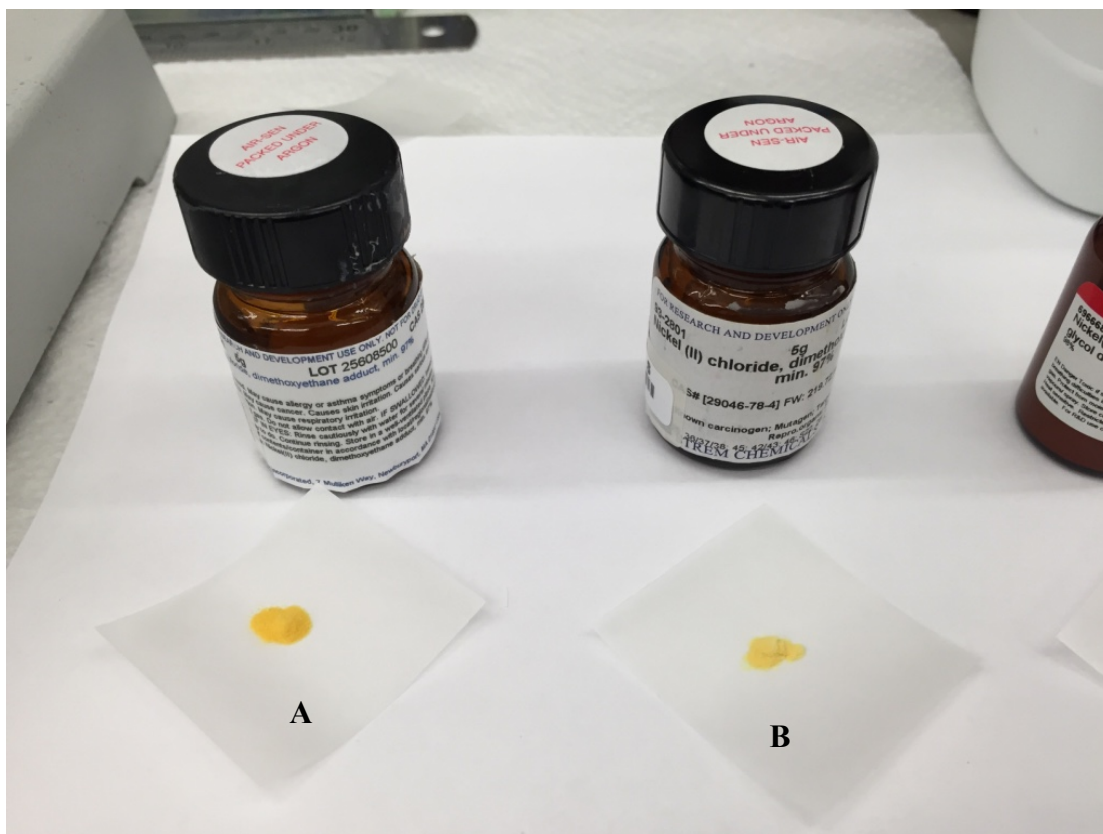
All Ni catalysts were handled open to air on the bench top, and the bottles were not stored under inert atmosphere. The initial studies were conducted using NiCl₂•glyme (Strem Chemicals, Inc., Lot # B9633065) that was stored with no precaution to exclude air or moisture. Upon receiving a new bottle of NiCl₂•glyme (Strem Chemicals, Inc., Lot # 25608500), the yields for some substrates were slightly diminished by approximately 10 – 15%. However, within a short period of 7 – 14 days, the yields recovered. The color of the Ni catalyst changed from gold to a lighter yellow over this period of time (see below).



A: Unopened and wax-sealed bottle of $\text{NiCl}_2\cdot\text{glyme}$ from Strem Chemicals, Inc. **B:** $\text{NiCl}_2\cdot\text{glyme}$ (opened approx. 1 month ago) from Strem Chemicals, Inc. **C:** Bottle of $\text{NiCl}_2\cdot\text{glyme}$ from Sigma-Aldrich. **D:** $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$.

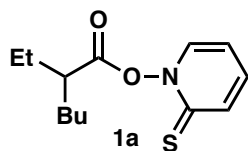


A: Recently opened bottle of $\text{NiCl}_2\cdot\text{glyme}$ from Strem Chemicals, Inc. **B:** $\text{NiCl}_2\cdot\text{glyme}$ (opened approx. 1 month ago) from Strem Chemicals, Inc. **C:** $\text{NiCl}_2\cdot\text{glyme}$ from Sigma-Aldrich. **D:** $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$.



(Above) Comparison of appearance of new (A) and older (B) $\text{NiCl}_2 \cdot \text{glyme}$.

Procedures for Figure 1.

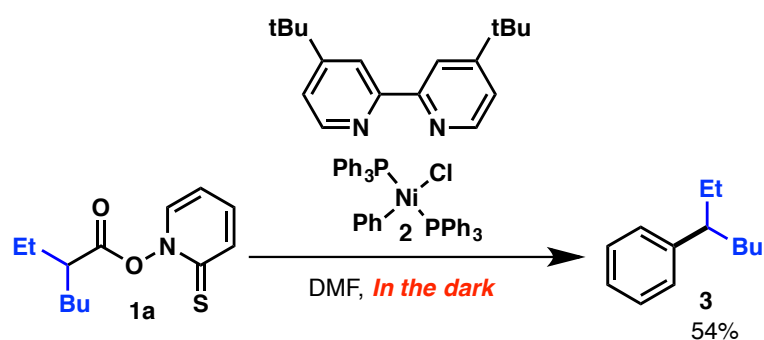


2-Thioxopyridin-1(2H)-yl 2-ethylhexanoate

Barton ester **1a** was prepared following the literature procedure.¹

In a round-bottom flask, 2-ethylhexanoic acid (0.160 mL, 1.0 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (anhydrous, 5.0 mL). Oxalyl chloride was added (0.10 mL, 1.1 mmol, 1.1 equiv.), and the reaction was cooled to 0 °C. DMF (anhydrous, 0.077 mL, 0.1 equiv) was added. After 5 minutes, the reaction was warmed to rt and stirred until all bubbling ceased (approximately 1 h). The flask was cooled again to 0 °C and wrapped in aluminum foil to shield the contents of the reaction vessel from light. DMAP (0.012 g, 0.1 mmol, 0.1 equiv.) and 2-mercaptopyridine *N*-oxide sodium salt (0.149 g, 1.0 mmol, 1.0 equiv.) were added in succession. After 5 min, the reaction was warmed to rt and stirred for 4 hours. The reaction was cooled to 0 °C, and H_2O (approx. 5 mL) was added. The mixture was poured into a separatory funnel wrapped

was diluted with EtOAc and an aliquot was removed, filtered through a short plug of silica gel, and analyzed by GC/FID.

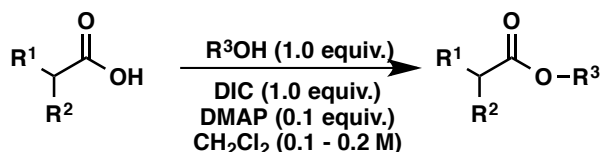


In the dark: A 25 mL culture tube was charged with Barton ester **1a** (25 mg, 0.10 mmol). DMF (anhydrous, 0.5 mL) was added, and the culture tube was wrapped with aluminum foil and sealed. In a separate 25 mL culture tube wrapped in aluminum foil, Ni-complex **2**² (34.8 mg, 0.05 mmol) and di-*t*Bubipy (13.4 mg, 0.05 mmol) were dissolved in DMF (anhydrous, 1.0 mL) under Ar. After 5 minutes the solution of **2** and di-*t*Bubipy became homogenous, and the solution containing **1a** was transferred to the Ni-complex solution via syringe. After 3 hours, the reaction was quenched with 1M HCl (approx. 2 mL) and diluted with Et₂O. Cyclooctane (1.0 equiv.) was added by micropipette. The mixture was diluted with EtOAc and an aliquot was removed, filtered through a short path of silica gel and analyzed by GC/FID.

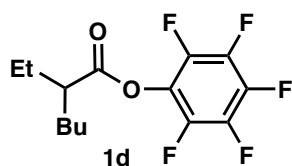


Left: reaction of **1a** with **2** in the presence of di-*t*Bubipy irradiated with a 300 W lamp. **Right:** reaction of **1a** with **2** in the presence of di-*t*Bubipy in the dark.

General Procedure for the synthesis of NHPI, NHS, TCNHP and pentafluorophenyl esters (General procedure A).



A round-bottom flask or culture tube was charged with (if solid) carboxylic acid (1.0 equiv), nucleophile (*N*-hydroxyphthalimide, *N*-hydroxysuccinimide tetrachloro-*N*-hydroxyphthalimide³ or pentafluorophenol, 1.0 equiv) and DMAP (0.1 equiv). Dichloromethane was added (0.1 – 0.2 M), and the mixture was stirred vigorously. Carboxylic acid (1.0 equiv) was added via syringe (if liquid). DIC (1.1 equiv) was then added dropwise via syringe, and the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. The mixture was filtered (over Celite, SiO₂, or through a fritted funnel) and rinsed with additional CH₂Cl₂. The solvent was removed under reduced pressure, and purification by column chromatography afforded corresponding activated esters, which were used without further purification unless otherwise noted. **Note:** Some esters are prone to hydrolysis on silica gel during column chromatography and should be purified as quickly as possible to obtain reasonable separation.



Perfluorophenyl 2-ethylhexanoate

Following the General Procedure A with 2-ethylhexanoic acid (320 μ L, 2.0 mmol) and pentafluorophenol (440 μ L, 2.2 mmol) in CH₂Cl₂ (10.0 mL) at rt for 2 h afforded 570 mg (92%) of the title compound after purification by column chromatography (9:1 hexanes:EtOAc).

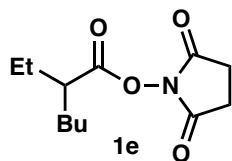
Physical State: colorless oil.

R_f = 0.64 (9:1 hexanes:EtOAc).

¹H NMR (400 MHz, CDCl₃): δ 2.77 – 2.55 (m, 1H), 1.92 – 1.59 (m, 4H), 1.40 (d, J = 6.0 Hz, 4H), 1.05 (td, J = 7.5, 1.5 Hz, 3H), and 0.98 – 0.87 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 171.8, 140.8 (m, 2C), 138.6 (m, 1C), 136.6 (m, 2C), 124.7 (t, J = 14.3 Hz, 1C), 46.7, 31.3, 28.9, 25.1, 22.1, 13.4, and 11.1.

HRMS (ESI-TOF): calc'd for C₁₄H₁₆F₅O₂ [M+H]⁺ 311.1065; found 311.1066.



2,5-Dioxopyrrolidin-1-yl 2-ethylhexanoate

Following the General Procedure A with 2-ethylhexanoic acid (320 μ L, 2.0 mmol) and *N*-hydroxysuccinimide (0.230 g, 2.0 mmol) in CH₂Cl₂ (5.0 mL) at rt for 2 h afforded 384 mg (80%) of the title compound after purification by column chromatography (gradient elution, hexanes to 4:1 hexanes:EtOAc).

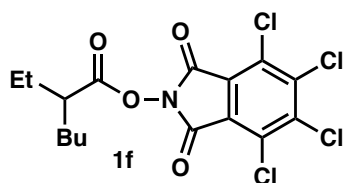
Physical State: colorless oil.

R_f = 0.27 (4:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 2.82 (d, *J* = 10.1 Hz, 4H), 2.58 (tt, *J* = 8.8, 5.4 Hz, 1H), 1.81 – 1.63 (m, 3H), 1.59 (ddt, *J* = 13.7, 10.1, 5.6 Hz, 1H), 1.48 – 1.28 (m, 4H), 1.03 (t, *J* = 7.5 Hz, 3H), and 0.91 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 171.6, 169.3, 44.9, 31.7, 29.3, 25.8, 25.6, 22.6, 14.0, and 11.7.

HRMS (ESI-TOF): calc'd for C₁₂H₂₀NO₄ [M+H]⁺ 242.1387; found 242.1378.



4,5,6,7-Tetrachloro-1,3-dioxoisindolin-2-yl 2-ethylhexanoate

Following the General Procedure A with 2-ethylhexanoic acid (800 μ L, 5.0 mmol), tetrachloro-*N*-hydroxyphthalimide (1.5 g, 5.0 mmol) in 10.0 mL of CH₂Cl₂ at rt for 2 h, afforded 1.3 g (61%) of the title compound after purification by column chromatography (gradient elution, hexanes to 4:1 hexanes:EtOAc). If desired, the title compound can be further purified by recrystallization with a small amount of CH₂Cl₂ in MeOH.

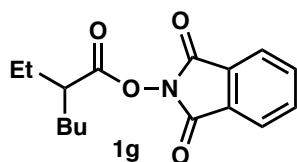
Physical State: white solid, mp: 91 – 94 °C.

R_f = 0.76 (4:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 2.65 (tt, *J* = 9.1, 5.2 Hz, 1H), 1.87 – 1.58 (m, 4H), 1.52 – 1.29 (m, 4H), 1.07 (t, *J* = 7.5 Hz, 3H), and 0.94 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 172.1, 157.8, 141.1, 130.6, 124.9, 45.0, 31.9, 29.3, 25.9, 22.6, 14.0, and 11.8.

HRMS (ESI-TOF): calc'd for C₁₆H₁₆Cl₄NO₄ [M+H]⁺ 425.9828; found 425.9829.



1,3-Dioxoisindolin-2-yl 2-ethylhexanoate

Following the General Procedure A with 2-ethylhexanoic acid (800 μL, 5.0 mmol) and *N*-hydroxyphthalimide (815 mg, 5.0 mmol) in CH₂Cl₂ (25.0 mL) at rt for 2 h afforded 1.18 g (82%) of the title compound after purification by column chromatography (gradient elution, hexanes to 4:1 hexanes:EtOAc).

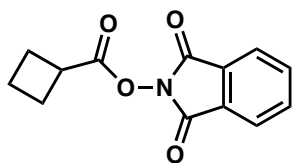
Physical State: colorless to slightly yellow oil.

R_f = 0.24 (9:1 hexanes:EtOAc).

¹H NMR (400 MHz, CDCl₃): δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.68 (tt, *J* = 8.9, 5.4 Hz, 1H), 1.95 – 1.29 (m, 8H), 1.10 (t, *J* = 7.4 Hz, 3H), and 0.96 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 172.6, 162.2, 134.8, 129.2, 124.0, 45.0, 31.9, 29.4, 25.8, 22.7, 14.0, and 11.7.

HRMS (ESI-TOF): calc'd for C₁₆H₂₀NO₄ [M+H]⁺ 290.1387; found 290.1387.



1,3-Dioxoisindolin-2-yl cyclobutanecarboxylate

Following the General Procedure A with cyclobutane carboxylic acid (0.383 mL, 4.0 mmol) and *N*-hydroxyphthalimide (0.653 g, 4.0 mmol) in CH₂Cl₂ (20.0 mL) at rt. Purification by column chromatography (9:1 hexanes:EtOAc) afforded 745 mg (76%) of the title compound.

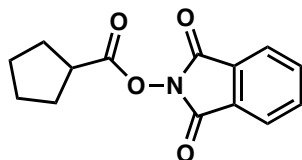
Physical State: white solid; mp: 58 °C.

R_f = 0.40 (3:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.91 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 3.56 – 3.46 (m, 1H), 2.57 – 2.46 (m, 2H), 2.46 – 2.36 (m, 2H), and 2.17 – 1.99 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 171.6, 162.2, 134.9, 129.1, 124.1, 35.2, 25.5, and 18.9.

HRMS (ESI-TOF): calc'd for C₁₃H₁₂NO₄ [M+H]⁺ 246.0761; found 246.0762.



1,3-Dioxoisindolin-2-yl cyclopentanecarboxylate

The title compound was prepared following the General Procedure A with cyclopentane carboxylic acid (0.95 mL, 8.76 mmol) and *N*-hydroxyphthalimide (1.43 g, 8.76 mmol) in CH₂Cl₂ (40.0 mL). The crude material was purified by column chromatography (9:1 hexanes:EtOAc) to yield the title compound (1.83 g, 80%) as a white solid.

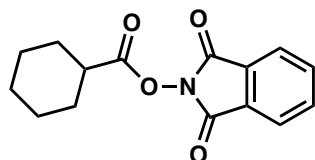
Physical State: white solid; mp: 58 °C.

R_f = 0.40 (3:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.92 – 7.85 (m, 2H), 7.83 – 7.76 (m, 2H), 3.17 – 3.01 (m, 1H), 2.15 – 1.99 (m, 4H), 1.85 – 1.74 (m, 2H), and 1.74 – 1.61 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 173.0, 162.3, 134.8, 129.1, 124.1, 40.8, 30.4, and 26.1.

HRMS (ESI-TOF): calc'd for C₁₄H₁₄NO₄ [M+H]⁺ 260.0917; found 260.0918.



1,3-Dioxoisindolin-2-yl cyclohexanecarboxylate

The title compound was prepared following the General Procedure A with cyclohexane carboxylic acid (513 mg, 4.0 mmol), *N*-hydroxyphthalimide (0.653 g, 4.0 mmol) in CH₂Cl₂ (20.0 mL). The crude material was purified by flash column chromatography (9:1 hexanes:EtOAc) to yield the title compound (863 mg, 79%) as a white solid.

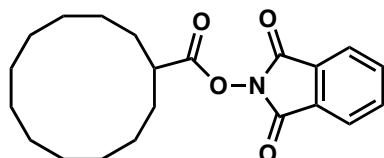
Physical State: white solid; mp: 66 °C.

R_f = 0.40 (3:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.92 – 7.83 (m, 2H), 7.82 – 7.74 (m, 2H), 2.79 – 2.66 (m, 1H), 2.15 – 2.02 (m, 2H), 1.89 – 1.77 (m, 2H), 1.76 – 1.55 (m, 3H), and 1.44 – 1.22 (m, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 172.0, 162.2, 134.8, 129.1, 124.0, 40.6, 28.9, 25.6, and 25.2.

HRMS (ESI-TOF): calc'd for C₁₅H₁₆NO₄ [M+H]⁺ 274.1074; found 274.1074.



1,3-Dioxoisindolin-2-yl cyclododecanecarboxylate

The title compound was prepared following the General Procedure A with cyclododecane carboxylic acid (65 mg, 0.31 mmol). The crude material was purified by column chromatography (9:1 hexanes:EtOAc) to yield the title compound (74 mg, 68%) as a white solid.

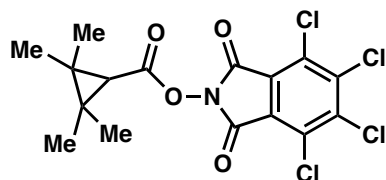
Physical State: white solid; mp: 145 °C.

R_f = 0.48 (3:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.91 – 7.82 (m, 2H), 7.81 – 7.74 (m, 2H), 2.93 – 2.84 (m, 1H), 1.88 – 1.72 (m, 4H), 1.61 – 1.52 (m, 2H), and 1.52 – 1.27 (m, 16H).

¹³C NMR (151 MHz, CDCl₃): δ 172.9, 162.3, 134.8, 129.1, 124.0, 38.3, 26.7, 23.9, 23.8, 23.6, 23.5, and 22.2.

HRMS (ESI-TOF): calc'd for C₂₁H₂₈NO₄ [M+H]⁺ 358.2013; found 358.2015.



Tetrachloro-1,3-dioxoisindolin-2-yl 2,2,3,3-tetramethylcyclopropanecarboxylate

The title compound was prepared following the General Procedure A with 2,2,3,3-tetramethylcyclopropane carboxylic acid (500 mg, 3.52 mmol) and tetrachloro-*N*-hydroxyphthalimide to afford the title compound in 659 mg (44%) after purification by column chromatography (9:1 hexanes:EtOAc) followed by recrystallization from CH₂Cl₂ and MeOH at 0 °C.

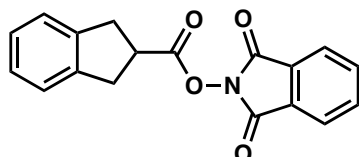
Physical State: white solid; mp: 135 °C.

R_f = 0.64 (3:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3): δ 1.52 (s, 1H), 1.31 (s, 6H), and 1.27 (s, 6H).

^{13}C NMR (150 MHz, CDCl_3): δ 167.3, 158.2, 140.9, 130.5, 125.0, 33.9, 32.3, 23.4, and 16.6.

HRMS (ESI-TOF): calc'd for $\text{C}_{16}\text{H}_{13}\text{Cl}_4\text{NO}_4$ $[\text{M}+\text{H}]^+$ 423.9677; found 423.9677.



1,3-Dioxoisindolin-2-yl 2,3-dihydro-1H-indene-2-carboxylate

Following the General Procedure A with 2,3-dihydro-1H-indene-2-carboxylic acid (162 mg, 1.0 mmol) and *N*-hydroxyphthalimide (163 mg, 1.0 mmol) in CH_2Cl_2 (10.0 mL) at rt for 2 h, afforded 261 mg (85%) of the title compound.

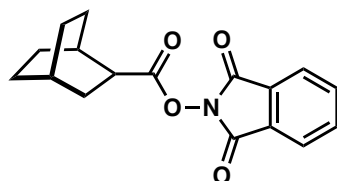
Physical State: white solid; mp: 165 – 167 °C.

R_f = 0.29 (4:1 hexanes:EtOAc).

^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, J = 5.5, 3.1 Hz, 2H), 7.81 (dd, J = 5.5, 3.1 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 – 7.10 (m, 2H), 3.80 – 3.65 (m, 1H), 3.56 – 3.31 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3): δ 171.6, 162.0, 140.6, 134.8, 129.0, 127.0, 124.4, 124.0, 40.5, and 36.3.

HRMS (ESI-TOF): calc'd for $\text{C}_{18}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 308.0917; found 308.0919.



1,3-Dioxoisindolin-2-yl bicyclo[2.2.2]octane-2-carboxylate

Following the General Procedure A with bicyclo[2.2.2]octane-2-carboxylic acid (90 mg, 0.58 mmol) and *N*-hydroxyphthalimide (95 mg, 0.58 mmol) in CH_2Cl_2 (5.0 mL) at rt for 2 h afforded 145 mg (84%) of the title compound after purification by column chromatography (4:1 hexanes:EtOAc).

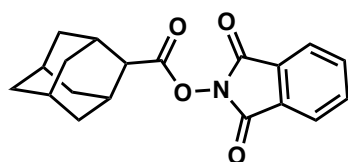
Physical State: white solid; mp: 111 – 113 °C.

R_f = 0.41 (4:1 hexanes:EtOAc).

^1H NMR (400 MHz, CDCl_3): δ 7.89 (dd, J = 5.4, 3.1 Hz, 2H), 7.80 (dd, J = 5.4, 3.2 Hz, 2H), 3.15 – 2.87 (m, 1H), 2.21 (t, J = 2.9 Hz, 1H), 2.14 – 2.00 (m, 1H), 1.92 – 1.79 (m, 2H), and 1.76 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.4, 162.2, 134.7, 129.0, 123.9, 39.5, 28.2, 27.8, 26.0, 24.9, 24.8, 23.4, and 21.4.

HRMS (ESI-TOF): calc'd for $\text{C}_{17}\text{H}_{18}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 300.1230; found 300.1232.



1,3-Dioxoisindolin-2-adamantane-2-carboxylate

Following the General Procedure A with 2-adamantane carboxylic acid (180 mg, 1.0 mmol) and *N*-hydroxyphthalimide (163 mg, 1.0 mmol) in CH_2Cl_2 (10.0 mL) at rt for 2 h afforded 244 mg (75%) of the title compound after purification by column chromatography (4:1 hexanes:EtOAc).

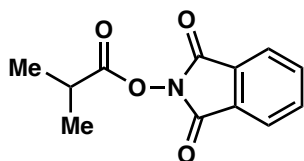
Physical State: white solid; mp: 143 – 145 °C.

R_f = 0.40 (4:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3): δ 7.91 (dd, J = 5.5, 3.1 Hz, 2H), 7.81 (dd, J = 5.5, 3.1 Hz, 2H), 3.11 (t, J = 2.1 Hz, 1H), 2.52 (q, J = 3.0 Hz, 2H), 2.13 (dd, J = 13.3, 3.0 Hz, 2H), 2.03 – 1.91 (m, 4H), 1.87 (dd, J = 12.4, 2.8 Hz, 2H), 1.81 (ddd, J = 4.3, 2.7, 1.5 Hz, 2H), and 1.75 (ddd, J = 13.3, 3.2, 1.7 Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 170.0, 161.8, 134.2, 128.6, 123.4, 47.0, 37.4, 36.7, 32.7, 29.3, 26.8, and 26.7.

HRMS (ESI-TOF): calc'd for $\text{C}_{19}\text{H}_{20}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 326.1387; found 326.1385.



1,3-Dioxoisindolin-2-yl isobutyrate

Following the General Procedure A with 2-ethylhexanoic acid (0.908 mL, 10.0 mmol, 1.0 equiv), *N*-hydroxyphthalimide (1.63 g, 10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (25.0

mL) at rt for 12 h afforded 1.83 g (7.8 mmol, 78%) of the title compound after purification by column chromatography (gradient elution, hexanes to 9:1 hexanes:EtOAc).

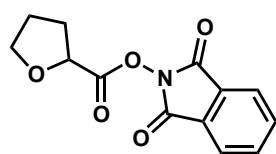
Physical State: white solid; mp: 49 – 53 °C.

R_f = 0.40 (4:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3): δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.96 (hept, J = 7.0 Hz, 1H), and 1.38 (d, J = 7.0 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 173.2, 162.2, 134.8, 129.2, 124.1, 31.9, and 19.0.

HRMS (ESI-TOF): calc'd for $\text{C}_{12}\text{H}_{12}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 234.0761; found 234.0762.



1,3-Dioxoisindolin-2-yl tetrahydrofuran-2-carboxylate

Following the General Procedure A with tetrahydrofuran-2-carboxylic acid (480 μL , 5.0 mmol) and *N*-hydroxyphthalimide (816 mg, 5.0 mmol) in CH_2Cl_2 (20.0 mL) at rt for 0.5 h afforded 1.12 g (82%) of the title compound after purification by column chromatography (2:1 hexanes:EtOAc).

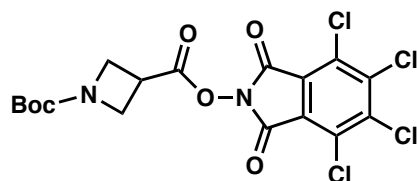
Physical State: white solid; mp = 44 – 45 °C.

R_f = 0.40 (2:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3): δ 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.80 (dd, J = 5.5, 3.1 Hz, 2H), 4.87 (dd, J = 8.6, 4.9 Hz, 1H), 4.14-4.06 (m, 1H), 4.04-3.98 (m, 1H), 2.49-2.35 (m, 2H), and 2.15-1.98 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 169.9, 161.9, 135.0, 129.0, 124.2, 75.1, 70.0, 31.0, and 25.2.

HRMS (ESI-TOF): calc'd for $\text{C}_{13}\text{H}_{12}\text{NO}_5^+$ $[\text{M}+\text{H}]^+$ 262.0710; found 262.0709.



1-(tert-Butyl) 3-(4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl) azetidine-1,3-dicarboxylate

Following the General Procedure A with *N*-Boc-2-azetidine acid (500 mg, 2.5 mmol) and tetrachloro-*N*-hydroxyphthalimide (750 mg, 2.5 mmol) in CH₂Cl₂ (20.0 mL) at rt for 2 h afforded 709 mg (59%) of the title compound following purification by column chromatography (10:1 CH₂Cl₂:Et₂O) followed by recrystallization from a small amount of CH₂Cl₂ with MeOH.

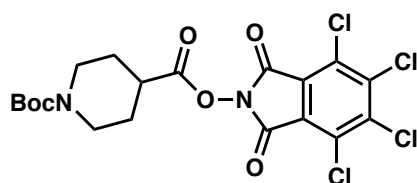
Physical State: white solid; mp: 148 – 149 °C.

R_f = 0.66 (2:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 4.27 (d, *J* = 7.4 Hz, 4H), 3.71 (p, *J* = 7.5 Hz, 1H), and 1.45 (s, 9H).

¹³C NMR (151 MHz, CDCl₃): δ 168.8, 157.5, 155.8, 141.4, 130.8, 124.7, 80.5, 51.6, 29.7, and 28.5.

HRMS (ESI-TOF): calc'd for C₁₇H₁₅Cl₄N₂O₆ [M+H]⁺ 482.9679; found 482.9679.



1-(tert-Butyl) 4-(4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl) piperidine-1,4-dicarboxylate

Following the General Procedure A with 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid (1.15 g, 5.0 mmol) and tetrachloro-*N*-hydroxyphthalimide (1.50 g, 5.0 mmol) in CH₂Cl₂ (25.0 mL) at rt for 2 h afforded 1.86 g (73%) of the title compound after purification by column chromatography (3:1 hexanes:EtOAc).

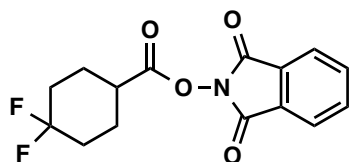
Physical State: white solid; mp: 190 – 192 °C.

R_f = 0.55 (3:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 4.00 (br s, 2H), 3.00 (t, *J* = 11.2 Hz, 2H), 2.90 (tt, *J* = 10.3, 4.0 Hz, 1H), 2.05-2.01 (m, 2H), 1.85-1.79 (m, 2H), and 1.44 (s, 9H).

¹³C NMR (151 MHz, CDCl₃): δ 170.3, 157.6, 154.6, 141.1, 130.6, 124.8, 80.0, 42.6 (br), 38.5, 28.5, and 27.8.

HRMS (ESI-TOF): calc'd for C₁₉H₁₉Cl₄N₂O₆ [M+H]⁺ 510.9992; found 510.9993.



1,3-dioxoisindolin-2-yl 4,4-difluorocyclohexane-1-carboxylate

Following the General Procedure A with 4,4-difluorocyclohexane-1-carboxylic acid (0.164 g, 1.0 mmol) and *N*-hydroxyphthalimide (0.163 g, 1.0 mmol) in CH₂Cl₂ (10.0 mL) at rt for 12 h afforded 223 mg (72%) of the title compound after purification by column chromatography (gradient elution, hexanes to 4:1 hexanes/EtOAc).

Physical State: white solid; mp: 109 – 111 °C.

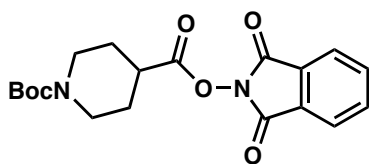
R_f = 0.32 (4:1 hexanes/EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.91 – 7.87 (m, 2H), 7.82 – 7.78 (m, 2H), 2.88 (ddt, *J* = 8.7, 7.4, 2.4 Hz, 1H), 2.25 – 2.14 (m, 4H), 2.13 – 2.06 (m, 2H), and 1.98 – 1.84 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 170.6, 162.0, 135.0, 129.1, 124.2, 122.3 (t, *J* = 242.3 Hz), 38.0, 32.2 (t, *J* = 24.8 Hz), and 25.1 (t, *J* = 5.0 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ -96.01 (d, *J* = 240.2 Hz), -98.80 (d, *J* = 240.3 Hz).

HRMS (ESI-TOF): calc'd for C₁₅H₁₄F₂NO₄ [M+H]⁺ 310.0885; found 310.0886.



1-(tert-Butyl) 4-(1,3-dioxoisindolin-2-yl) piperidine-1,4-dicarboxylate

Following the General Procedure A with 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid (229 mg, 1.0 mmol) and *N*-hydroxyphthalimide (163 mg, 1.0 mmol) in 5 mL of CH₂Cl₂ at rt for 2 h, afforded 242 mg (65%) of the title compound after purification by column chromatography (3:1 hexanes:EtOAc).

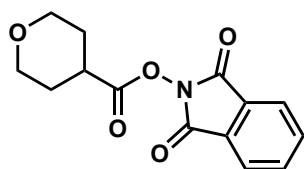
Physical State: white solid; mp: 102 – 105 °C.

R_f = 0.30 (3:1 hexanes:EtOAc).

¹H NMR (400 MHz, CDCl₃): δ 7.90-7.87 (m, 2H), 7.81-7.79 (m, 2H), 4.04 (br s, 2H), 3.01 (br s, 2H), 2.91 (tt, *J* = 10.4, 4.0 Hz, 1H), 2.08-2.04 (m, 2H), 1.88-1.82 (m, 2H), and 1.46 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 170.8, 162.1, 154.7, 134.9, 129.0, 124.1, 80.0, 42.7 (br), 38.7, 28.6, and 27.9.

HRMS (ESI-TOF): calc'd for C₁₉H₂₃N₂O₆ [M+H]⁺ 375.1551; found 375.1554.



1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate

Following the General Procedure A with tetrahydro-2H-pyran-4-carboxylic acid (260 mg, 2.0 mmol), and *N*-hydroxyphthalimide (391 mg, 2.4 mmol) in CH₂Cl₂ (20.0 mL) at rt for 0.5 h to afford 471 mg (85%) of the title compound following purification by column chromatography (2:1 hexanes:EtOAc).

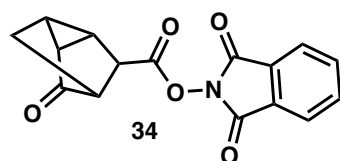
Physical State: white solid; mp = 118-119 °C.

R_f = 0.43 (2:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.02 (dt, *J* = 11.8, 3.8 Hz, 2H), 3.53 (ddd, *J* = 11.8, 10.4, 2.9 Hz, 2H), 3.10-2.93 (m, 1H), and 2.07-1.95 (m, 4H).

¹³C NMR (151 MHz, CDCl₃): δ 170.7, 162.1, 135.0, 129.1, 124.1, 66.7, 37.8, and 28.5.

HRMS (ESI-TOF): calc'd for C₁₄H₁₄NO₅⁺ [M+H]⁺ 276.0866; found 276.0868.



1,3-dioxoisindolin-2-yl 5-oxotricyclo[2.2.1.0^{2,6}]heptane-3-carboxylate

Following the General Procedure A with 5-oxotricyclo[2.2.1.0^{2,6}]heptane-3-carboxylic acid (152 mg, 1.0 mmol) and *N*-hydroxyphthalimide (163 mg, 1.0 mmol) in CH₂Cl₂ (10.0 mL) at rt for 2 h afforded 244 mg (82%) of the title compound **34** following purification by column chromatography (4:1 hexanes:EtOAc).

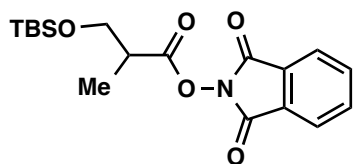
Physical State: white solid; mp: 128 – 130 °C.

R_f = 0.14 (4:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.92 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.43 (dd, *J* = 1.8, 1.2 Hz, 1H), 2.59 (tt, *J* = 5.2, 1.2 Hz, 1H), 2.50 (dd, *J* = 1.8, 1.0 Hz, 1H), 2.39 (dddd, *J* = 6.4, 4.1, 1.8, 1.2 Hz, 1H), 2.15 (qt, *J* = 11.6, 1.6 Hz, 2H), 1.62 (td, *J* = 5.4, 0.8 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 208.0, 167.1, 161.3, 134.4, 128.4, 123.6, 43.3, 40.7, 28.5, 20.6, 19.2, and 19.1.

HRMS (ESI-TOF): calc'd for $\text{C}_{16}\text{H}_{12}\text{NO}_5$ $[\text{M}+\text{H}]^+$ 298.0710; found 298.0711.



1,3-dioxisoindolin-2-yl 3-((tert-butyldimethylsilyl)oxy)-2-methylpropanoate

Following the General Procedure A with 3-((tert-butyldimethylsilyl)oxy)-2-methylpropanoic acid⁴ (1.00 g, 4.6 mmol) and *N*-hydroxyphthalimide (747mg, 4.6 mmol) in CH_2Cl_2 (15.0 mL) at rt for 2 h afforded 1.00 g (60%) of the title compound following purification by column chromatography (gradient elution, 19:1 hexanes:EtOAc to 9:1 hexanes:EtOAc).

Physical State: clear oil.

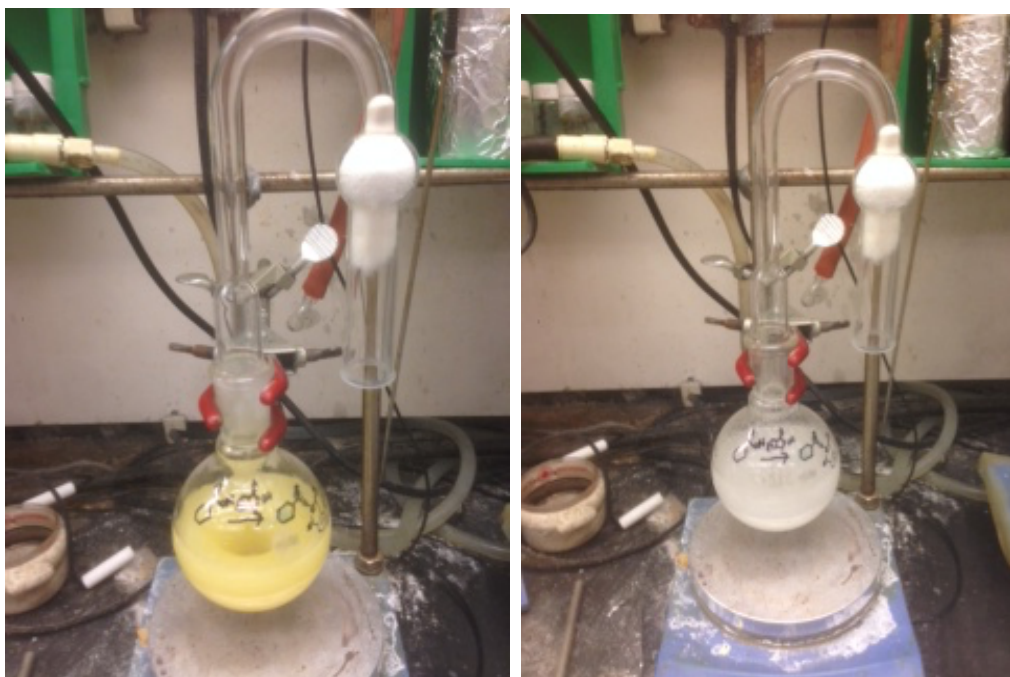
R_f = 0.46 (4:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3) δ 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 3.94 (dd, J = 9.9, 6.6 Hz, 1H), 3.80 (dd, J = 9.8, 6.1 Hz, 1H), 3.12 – 2.97 (m, 1H), 1.36 (d, J = 7.1 Hz, 3H), 0.92 (s, 9H), and 0.10 (d, J = 1.0 Hz, 6H, overlapping peaks).

^{13}C NMR (151 MHz, CDCl_3) δ 171.2, 134.8, 129.2, 124.0, 64.6, 40.6, 26.0, 18.4, 13.7, and -5.4 (2C).

HRMS (ESI-TOF): calc'd for $\text{C}_{18}\text{H}_{26}\text{NO}_5\text{Si}$ $[\text{M}+\text{H}]^+$ 364.1575; found 364.1576.

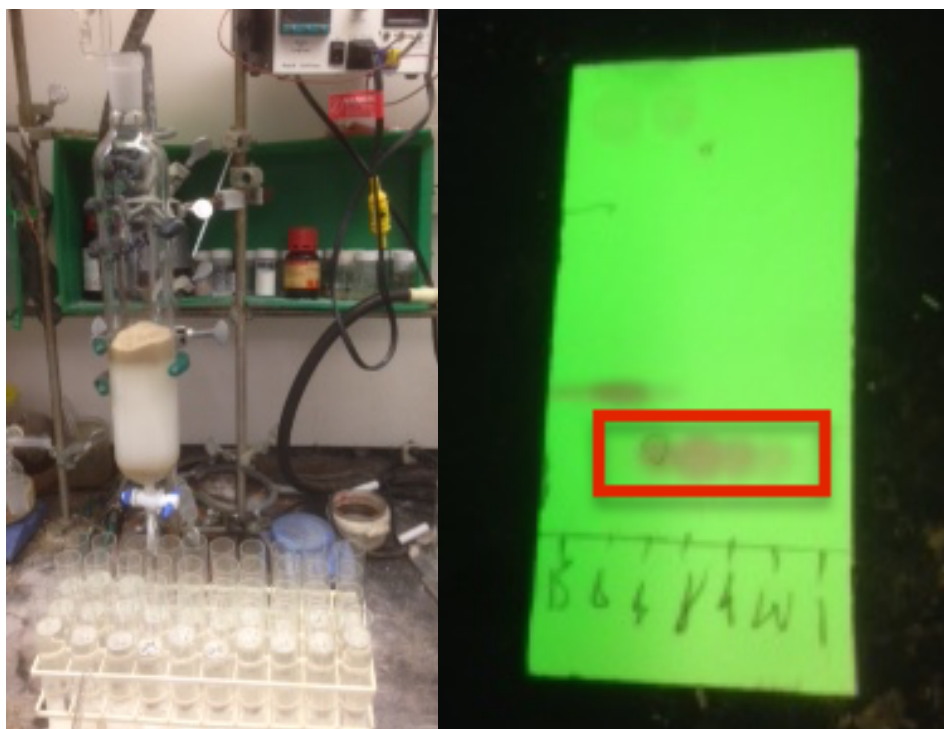
Graphical Supporting Information for the Synthesis of NHPI and 4Cl-NHPI Esters



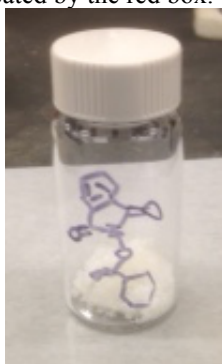
(Left) Reaction of *N*-hydroxyphthalamide with cyclohexane carboxylic acid in the presence of DIC at $t = 0$ min. **(Right)** Reaction of *N*-hydroxyphthalamide with cyclohexane carboxylic acid in the presence of DIC at $t = 2$ h.



(Left) TLC of reaction mixture after 2 h (9:1 hexanes:EtOAc). **(Right)** The reaction was passed over a pad of silica (rinsed with EtOAc).

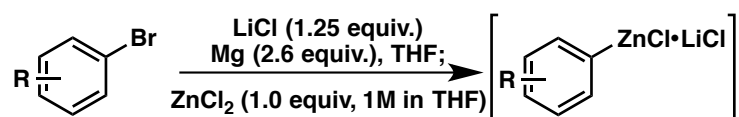


(Left) The crude organics were purified by silica gel chromatography (gradient elution, 95:5 hexanes:EtOAc to 9:1 hexanes:EtOAc). (Right) TLC of fractions from column chromatography; the fractions containing the product are indicated by the red box.



(Above) A pure sample of 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (white solid).

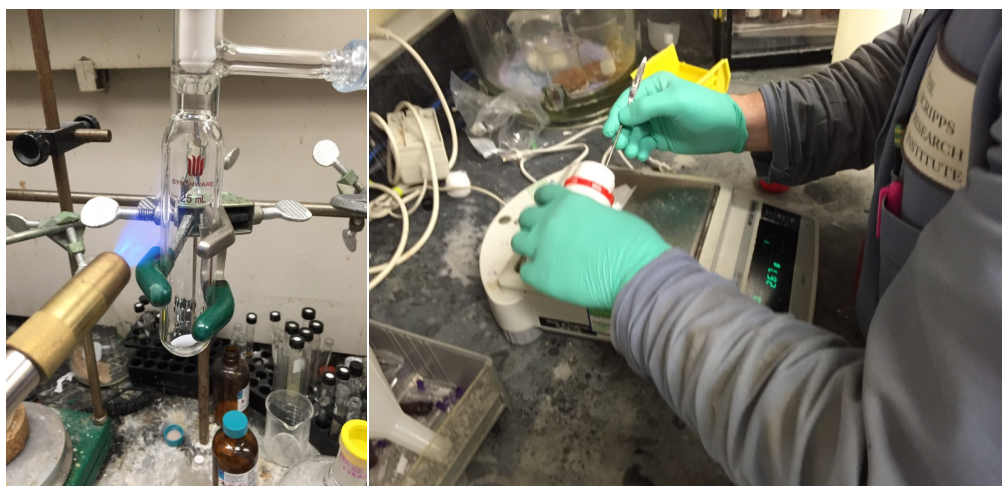
General Procedure for the Preparation of Aryl Zinc reagents from Aryl Bromides



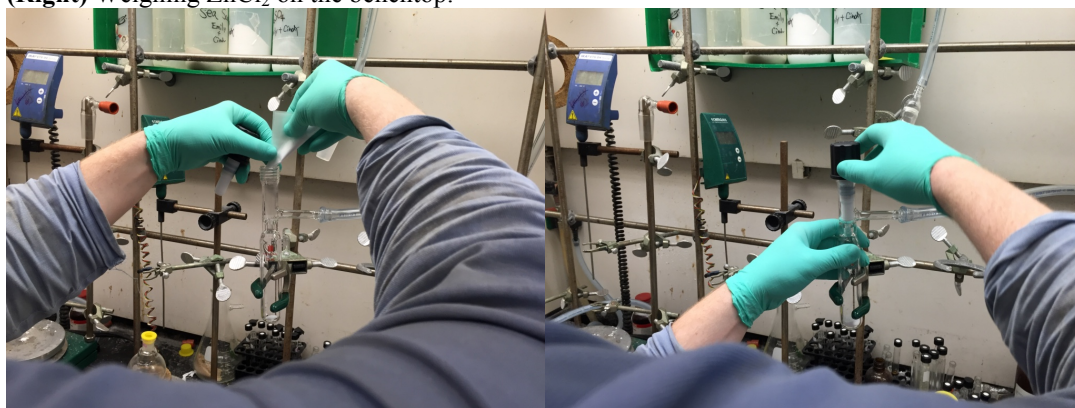
1. Preparation of ZnCl₂ Solution (1.0 M in THF)

A Schlenk flask equipped with stir bar was flame-dried and allowed to cool to rt under vacuum. The flask was backfilled with nitrogen, and ZnCl₂ (3.41 g, 25.0 mmol) was added. The flask was placed under vacuum and heated in an oil-bath preheated to 150 °C. After stirring for 2 – 12 h, the flask was removed from the oil bath and

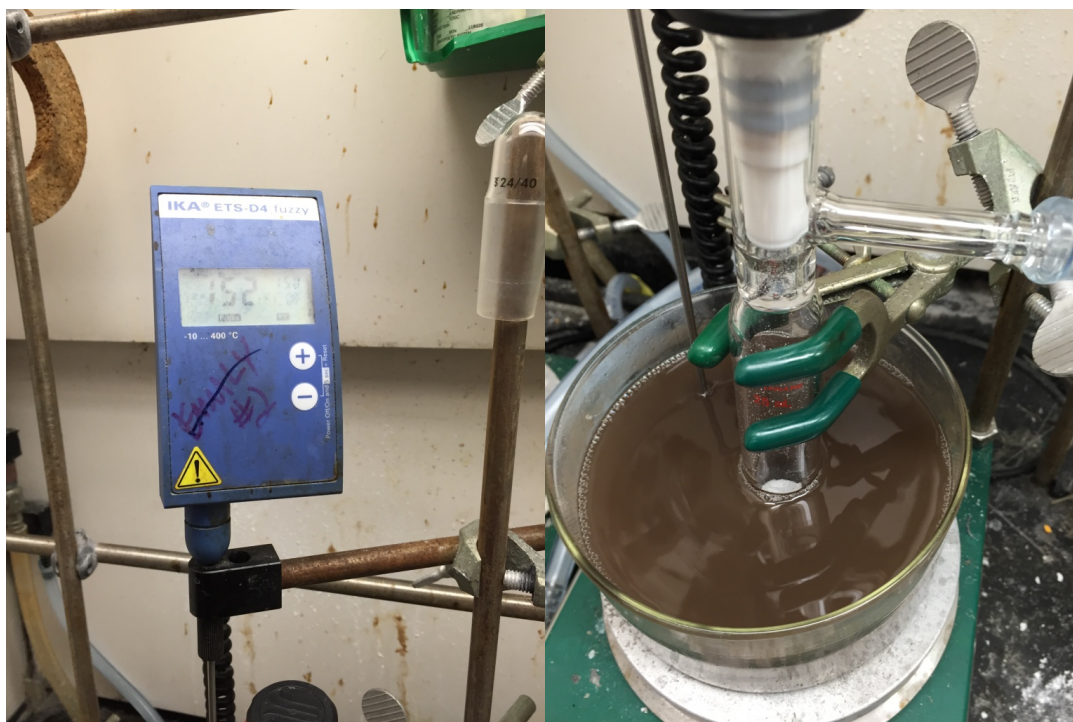
allowed to cool to rt. The flask was backfilled with nitrogen, and THF (anhydrous, 25 mL) was added. The mixture was vigorously stirred until all ZnCl_2 was dissolved (approximately 12 h). However, if necessary the solution can be used before all solids have completely dissolved without a decrease in yield of the subsequent reaction.



(Left) Flame-drying Schlenk flask under vacuum. The flask was backfilled with nitrogen upon cooling. **(Right)** Weighing ZnCl_2 on the benchtop.



(Left) Addition of ZnCl_2 to Schlenk flask under flow of nitrogen. **(Right)** Closing the Schlenk flask.



(Left) A preheated oil bath set to 150 °C. Small temperature fluctuations do not affect the quality of the drying. (Right) Schlenk flask under vacuum is heated in oil bath with stirring for 3 – 12 h.

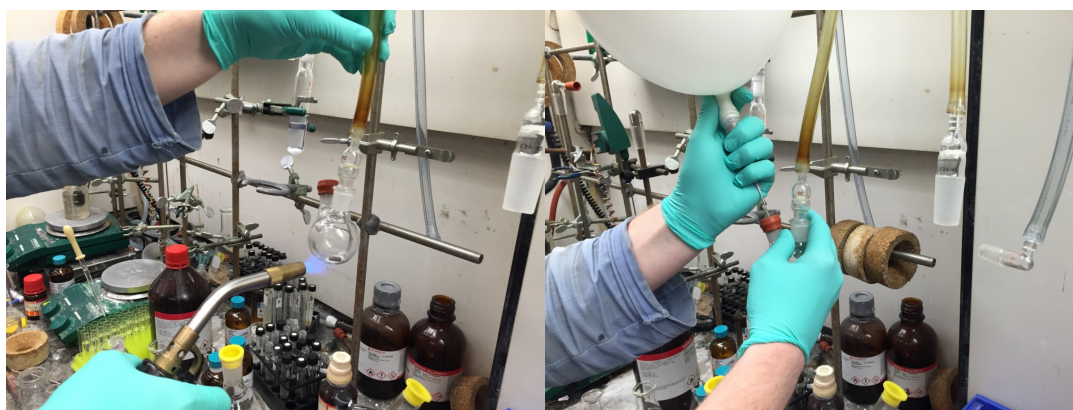


(Left) The Schlenk flask is removed from the oil bath and allowed to cool to rt. (Center) After 10 min of vigorous stirring. To fully dissolve all solids requires longer stirring times, but use of this solution at this stage in preparation of arylzinc does not result in subpar reaction performance. (Right) ZnCl_2 (1M in THF) after 12 h of stirring.

2. Arylzinc Reagent Preparation from Aryl Bromides

Arylzinc reagents were prepared in a manner similar to that report by Knochel and coworkers.⁵ LiCl (0.265 g, 6.25 mmol, 1.25 equiv.) was added to a round-bottom flask. The flask was placed under vacuum and flame-dried. Upon cooling the flask was backfilled with Ar from a balloon. Magnesium turnings (0.304 g, 12.5 mmol, 2.5 equiv.) were added by quickly removing the septum, adding the magnesium turnings, and replacing the septum. Tetrahydrofuran (anhydrous, 12.5 mL) was added, and the mixture was stirred vigorously for 5 min. DIBAL-H (1.0 M in THF, 0.05 mL, 0.01

equiv) was added via syringe, and the mixture was stirred vigorously for 5 min. The flask was then cooled to 0 °C in an ice/water bath, and aryl bromide (5.0 mmol, 1.0 equiv) was added via syringe if a liquid. If the aryl bromide was a solid, a septum was removed, the aryl bromide was quickly added, and the septum was replaced. After 10 minutes the ice/water bath was removed, and the mixture was stirred at rt until all aryl bromide was consumed (as determined by quenching an aliquot with water and observing the disappearance of the aryl bromide in the GC/MS spectrum; alternatively, an aliquot can be quenched into a solution of I₂ and conversion for aryl bromide to aryl iodide can be observed by GC/MS). ZnCl₂ solution (1.0 M in THF, 5.0 mL, 5.0 mmol) was added to a separate flame-dried flask. To this flask ArMgBr•LiCl was transferred via syringe. Often a white precipitate forms as the solution of ArMgBr•LiCl is added to the solution of ZnCl₂, but the precipitate dissolves over the course of the addition. After 10 minutes, the solution of ArZnCl•LiCl was titrated with I₂ in a manner similar to that reported by Knochel and coworkers (see below).



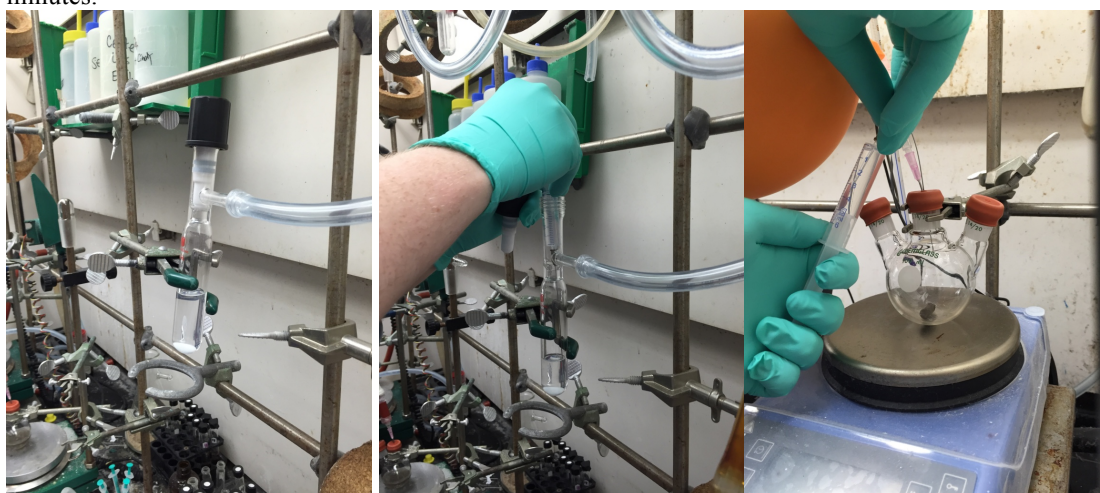
(Left) Flame-drying flask and LiCl under vacuum. **(Right)** Backfilling reaction vessel with Ar.



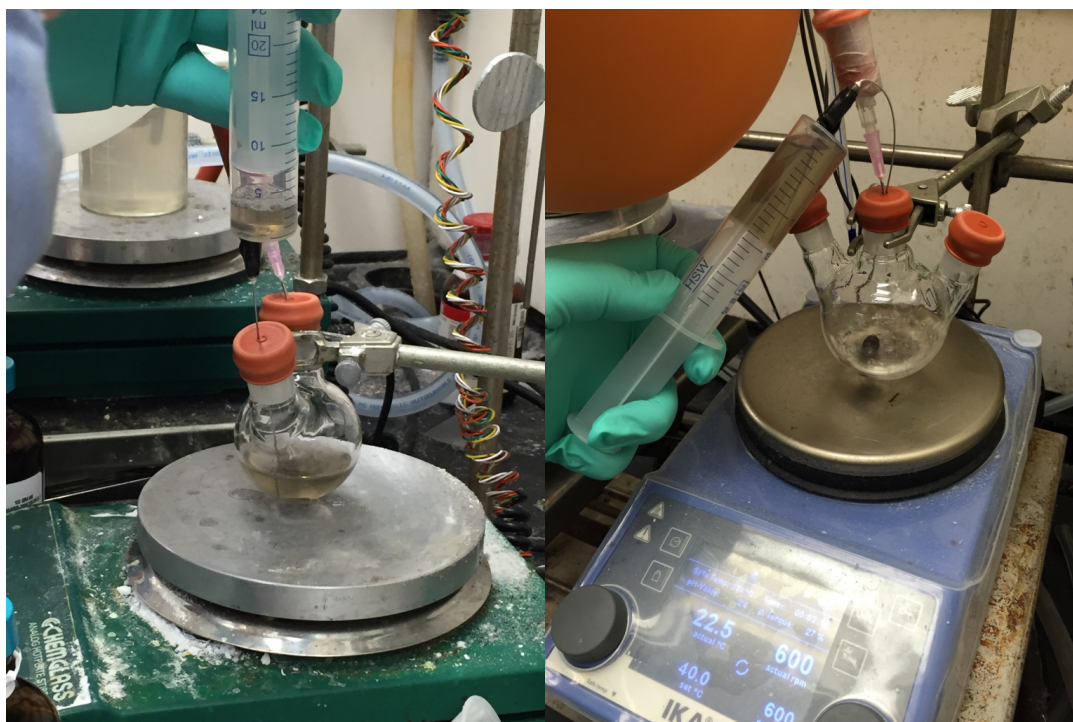
(Left) Addition of THF to Mg and LiCl. **(Center and Right)** Addition of DIBAL-H (1.0 M in THF) via syringe.



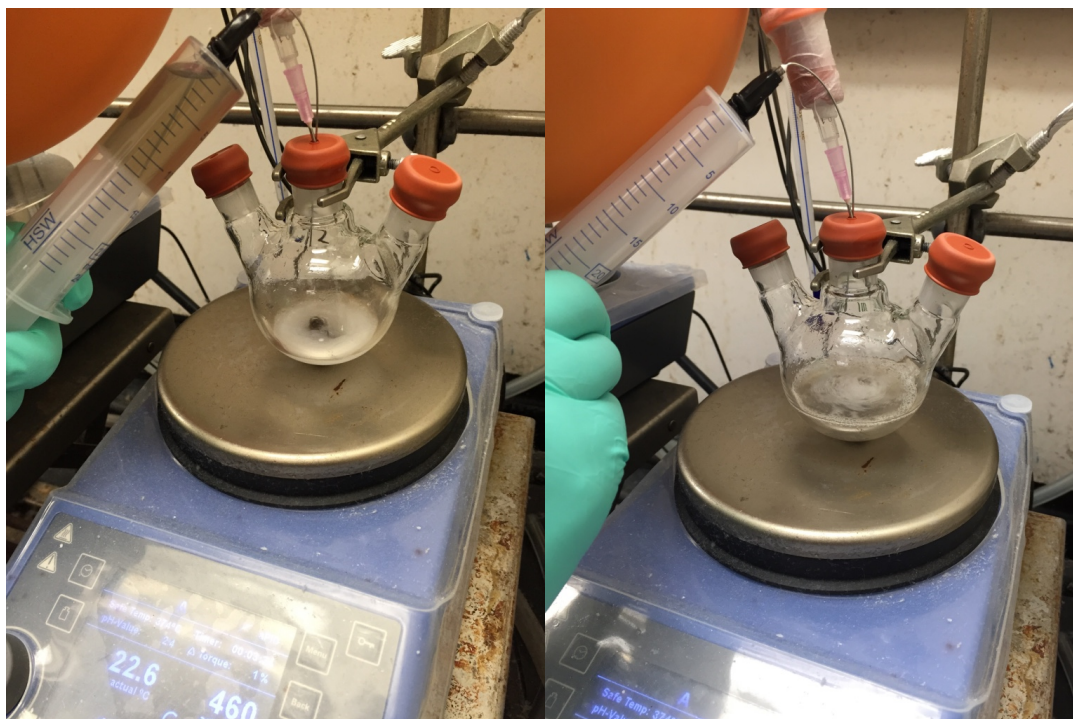
(Left) Addition of 3-bromoanisole at 0 °C (ice/water bath). **(Right)** Color change of solution after 30 minutes.



(Left) Schlenk-flask with ZnCl_2 (1M in THF) is attached to a manifold nitrogen line. **(Center and right)** Addition of ZnCl_2 solution to flame-dried flask under Ar atmosphere.



(Left) Removal of 3-OMePhMgBr•LiCl (Right) Addition of 3-OMePhMgBr•LiCl to ZnCl_2 solution



(Left) Formation of temporary white precipitate. (Right) Disappearance of precipitate by end of addition. **Note:** if preferred the ZnCl_2 solution can be directly added to the flask in which the Grignard reagent was prepared.



(Above) 3-OMePhZnCl•LiCl after 10 minutes of stirring.

3. Titration of Arylzinc Reagents

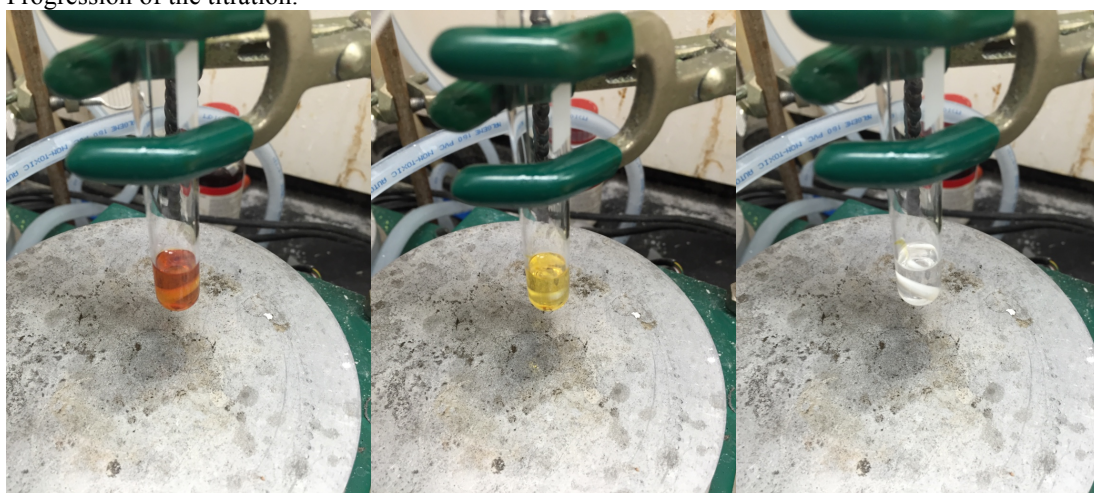
LiCl (0.021 g, 0.5 mmol) was added to a septum-containing screw-capped culture tube equipped with stir bar. The culture tube was flame-dried under vacuum and cooled under flow of Ar from a balloon. The cap was removed, I₂ (approximately 0.024 g, 0.1 mmol, 1.0 equiv.) was quickly added to the culture tube, and the cap was replaced. The exact amount of I₂ added was recorded. THF (anhydrous, 1.0 mL) was added, and the mixture was stirred for 5 min to give a dark brown solution. A 1.00 mL syringe was filled with approximately 0.90 mL of ArZnCl•LiCl, and the solution was added dropwise via the syringe. The exact volume of ArZnCl•LiCl solution in the syringe was recorded (titration start point). Over the course of the titration the color changes from dark brown to light brown to yellow to clear, indicating complete consumption of I₂, and upon consumption of I₂, the titration end point was recorded. The concentration of the ArZnCl•LiCl solution was then calculated. Typical concentrations of arylzinc reagents ranged from 0.18 M to 0.24 M in THF.



(Left) Flame-drying a culture tube equipped with stir bar and LiCl (0.5 mmol). **(Center)** Backfilling culture tube with Ar. **(Right)** Culture tube after cooling and addition of I_2 (0.1 mmol).



(Left) After addition of THF (1.0 mL) to I_2 and LiCl. **(Center)** Beginning of the titration. **(Right)** Progression of the titration.



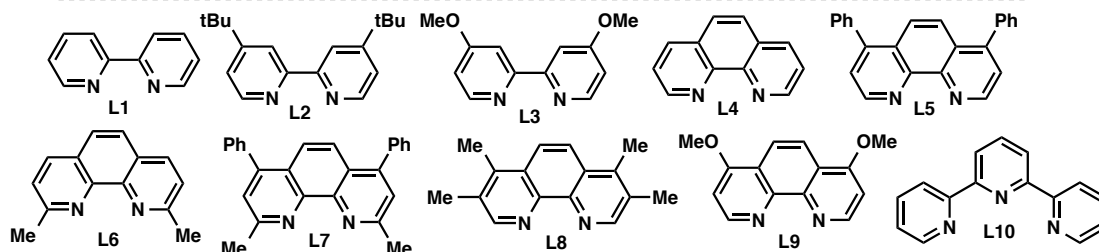
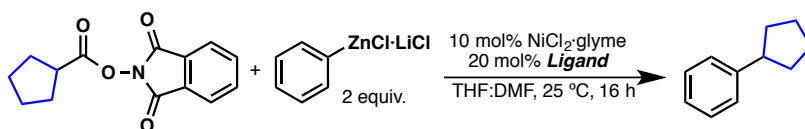
(Left and Center) Progression of the titration. **(Right)** All I_2 has been consumed.

Optimization details

Determining the yield by GC/FID: A screw-capped culture tube with Teflon™ septum containing a stirring bar was charged with NiCl₂·glyme or NiCl₂·6H₂O, ligand and 1,3-dioxoisindolin cyclopentylcarboxylate *N*-hydroxyphthalimide ester (0.25 mmol, 1.0 equiv.) on the bench top. The tube was evacuated and back-filled with Ar. DMF (anhydrous) was added via syringe, and the mixture stirred for 2 minutes at 25 °C. Then, ArZnCl•LiCl in THF was added in one portion, and the mixture was stirred for 14 – 16 h at rt. The mixture was then quenched with 1M HCl (approx. 2 mL) and cyclooctane (1 equiv.) was added. The mixture was diluted with EtOAc, and an aliquot was taken, filtered through a short path of silica gel, and analyzed by GC/FID.

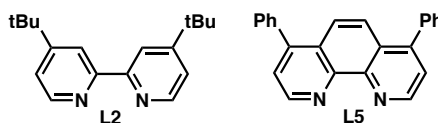
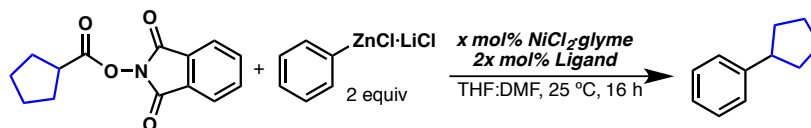
Determining the yield by ¹H NMR: The reaction was set up as above on 0.1 mmol scale with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (EtBu-NHPI ester), 4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2-ethylhexanoate (EtBu-4Cl-NHPI ester), or 2-ethylhexanoic acid with DIC (1.5 equiv.) and HOAt (1.0 equiv.) or HATU (1.0 equiv.) and Et₃N (1.0 equiv.). For activated esters formed *in situ*, the reaction mixture was stirred for 1 h prior to addition of [Ni] and ligand to the reaction mixture. After 16 h, 1M HCl was added, and the mixture was diluted with Et₂O. The two layers were separated and the organic layer was washed with brine or 10% LiCl (aq) to remove DMF. The organic layer was dried over anhydrous NaSO₄ or MgSO₄, filtered, and evaporated to dryness. CDCl₃ (1 – 2 mL) was added by pipette to the crude reaction mixture, CH₂Br₂ (0.125 mmol, 0.5 equiv) was added via microliter syringe, and the crude mixture was analyzed by ¹H NMR spectroscopy.

Optimization with Cyclopentyl-NHPI ester^a



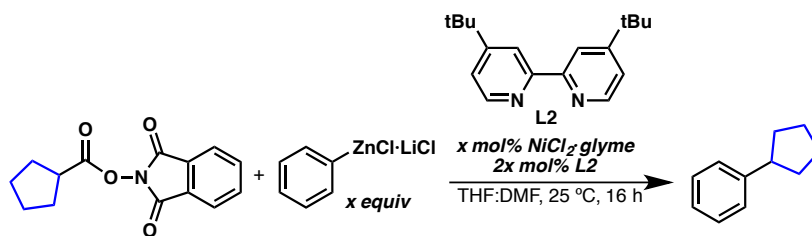
Ligand	Yield (%) ^a	Ph-Ph (%) ^a
L1	11	7
L2	16	3
L3	10	4
L4	14	4
L5	29	3
L6	23	3
L7	13	11
L8	16	12
L9	7	7

^aYields determined by GC/FID with cyclooctane as an internal standard



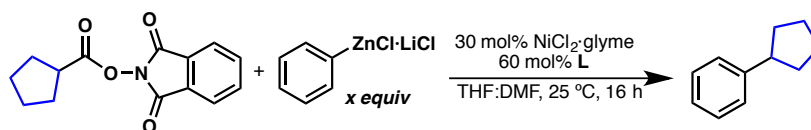
Ligand	Ni/L ratio	Yield (%) ^a	Ph-Ph (%) ^a
L2	15:30	39	3
L2	20:40	47	3
L5	15:30	45	7
L5	20:40	61	4

^aYields determined by GC/FID with cyclooctane as an internal standard.



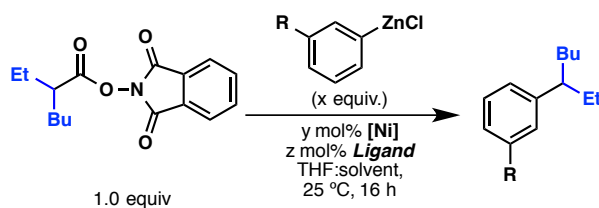
Equiv. $\text{PhZnCl} \cdot \text{LiCl}$	Ni:L ratio	Yield (%) ^a	Ph-Ph (%) ^a
3.0	10:20	67	6
3.0	15:30	55	16
3.0	20:40	91	11
4.0	10:20	93	30
4.0	15:30	85	22
4.0	20:40	99	2

^aYields determined by GC/FID with cyclooctane as an internal standard.



x equiv $\text{PhZnCl} \cdot \text{LiCl}$	Ligand	Yield (%) ^a	Ph-Ph (%) ^a
2.0	L2	41	3
3.0	L2	96	70
4.0	L2	90	99
3.0	L1	77	6
4.0	L1	99	40
3.0	L5	99	5
4.0	L5	99	15

Optimization with Et,Bu-NHPI ester^{a,b}

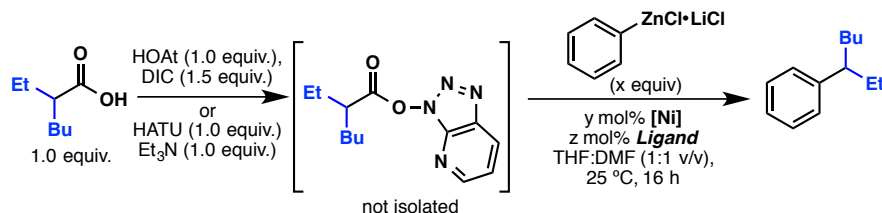


R	[Ni]	Mol %	L	Mol % L	Equiv. $\text{PhZnCl} \cdot \text{LiCl}$	THF:DMF	Yield (%)
OMe	$\text{NiCl}_2 \cdot \text{glyme}$	15	L1	15	2.0	1:1	43
OMe	$\text{NiCl}_2 \cdot \text{glyme}$	15	L1	18.75	2.0	1:1	30
OMe	$\text{NiCl}_2 \cdot \text{glyme}$	15	L1	30	2.0	1:1	63
OMe	$\text{NiCl}_2 \cdot \text{glyme}$	15	L1/L2	15/15	2.0	1:1	67

OMe	NiCl ₂ •glyme	20	L2	40	3.0	1:1	65 ^b
H	NiCl ₂ •glyme	30	L1	60	3.0	1:1	80
H	NiCl ₂ •glyme	30	L2	60	3.0	1:1	86
H	NiCl ₂ •glyme	20	L2	40	3.0	2:1	92 ^b
H	NiCl ₂ •6H ₂ O	20	L2	40	3.0	2:1	93 ^b

^a Yield determined by ¹H NMR analysis with CH₂Br₂ as an internal standard ^b Isolated yield (0.25 mmol scale).

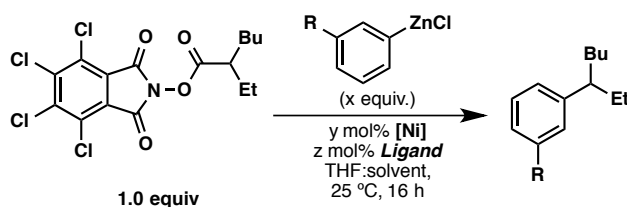
Optimization with –OAt Esters Generated *in situ*^{a,b}



[Ni]	Mol %	L	Mol % L	[Ni]/L	Equiv. PhZnCl•LiCl	Additive (equiv.)	Yield (%)
NiCl ₂ •glyme	1	L2	1	1:1	4.0	-	11
NiCl ₂ •glyme	2.5	L2	2.5	1:1	4.0	-	21
NiCl ₂ •glyme	5.0	L2	5.0	1:1	4.0	-	23
NiCl ₂ •glyme	7.5	L2	10	1:1	4.0	-	27
NiCl ₂ •glyme	10	L2	10	1:1	1.0	-	11
NiCl ₂ •glyme	10	L2	10	1:1	2.0	-	27
NiCl ₂ •glyme	10	L2	10	1:1	3.0	-	29
NiCl ₂ •glyme	10	L2	10	1:1	4.0	-	33
NiCl ₂ •glyme	10	L4	10	1:1	4.0	-	35
NiCl ₂ •glyme	10	L7	10	1:1	4.0	-	24
NiCl ₂ •glyme	10	L9	10	1:1	4.0	-	20
NiCl ₂ •glyme	10	L10	10	1:1	4.0	-	15
NiCl ₂ •glyme	10	L1	10	1:1	4.0	-	36
NiCl ₂ •glyme	10	L5	10	1:1	4.0	-	40
NiCl ₂ •glyme	10	-	-	1:1	4.0	-	8
NiCl ₂ •glyme	10	L2	10	1:1	2.0	TMEDA (0.1)	35
Ni(acac) ₂	10	L2	10	1:1	2.0	-	30
NiCl ₂ •glyme	10	L2	20	1:2	2.0	-	48 (41) ^b

^a Yield determined by ¹H NMR analysis with CH₂Br₂ as an internal standard. ^b Isolated yield (0.25 mmol scale).

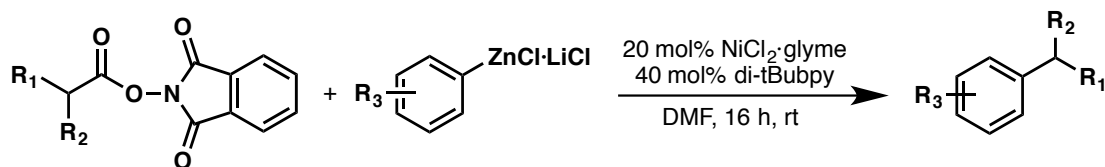
Optimization with 4Cl-NHPI esters^{a,b}



R	[Ni]	Mol %	L	Mol % L	Equiv. PhZnCl·LiCl	THF:DMF	Additive (0.2 equiv.)	Yield (%)
H	NiCl ₂ ·glyme	10	L1	20	2.0	1:1	-	61
H	NiCl ₂ ·glyme	10	L2	20	2.0	1:1	-	45
H	NiCl ₂ ·glyme	20	L2	20	2.0	1:0	-	50
H	NiCl ₂ ·glyme	10	L3	20	2.0	1:1	-	58
H	NiCl ₂ ·glyme	10	L4	20	2.0	1:1	-	59
H	NiCl ₂ ·glyme	10	L5	20	2.0	1:1	-	49
H	NiCl ₂ ·glyme	10	L6	20	2.0	1:1	-	35
H	NiCl ₂ ·glyme	10	L7	20	2.0	1:1	-	46
H	NiCl ₂ ·glyme	10	L8	20	2.0	1:1	-	35
H	NiCl ₂ ·glyme	10	L9	20	2.0	1:1	-	34
H	NiCl ₂ ·glyme	10	L10	20	2.0	1:1	-	64
OMe	NiCl ₂ ·glyme	10	L1	20	2.0	1:1	-	58
OMe	NiCl ₂ ·glyme	10	L1	20	2.0	1:0	-	54
OMe	NiCl ₂ ·glyme	10	L1	10	2.0	1:1	TMEDA	45
OMe	NiCl ₂ ·glyme	15	L1	30	2.0	1:1	-	71
OMe	NiCl ₂ ·glyme	20	L1	40	2.0	1:1	-	70

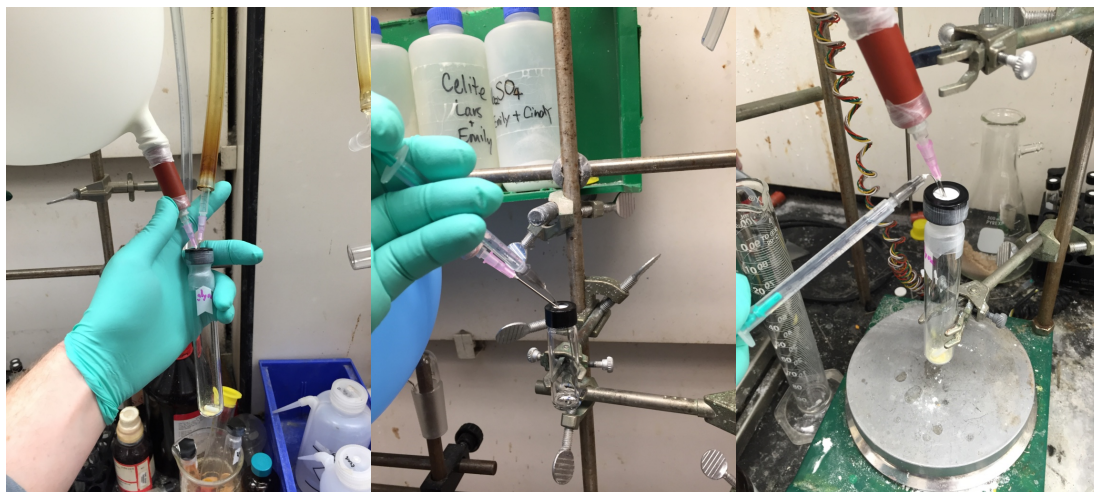
^a Yield determined by ¹H NMR analysis with CH₂Br₂ as an internal standard.

General Procedure for the Ni-catalyzed cross-coupling reaction (General Procedure B).

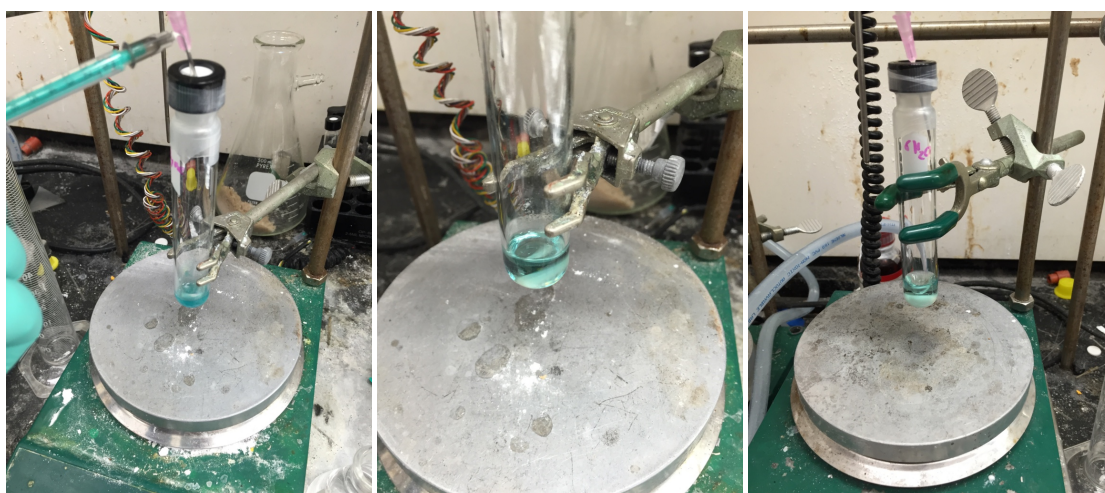


A culture tube with a Teflon™ septum screw-cap and stir bar was charged with NiCl₂·glyme or NiCl₂·6H₂O (20 mol%), di-*t*Bubpy (40 mol%) and (if solid) NHPI-ester (1.0 equiv.). The tube was evacuated and backfilled with Ar. Reactions were run with a 3:2 ratio of THF:DMF. The volume of DMF used was calculated based on the titre of the THF solution of the arylzinc reagent. DMF (anhydrous) was added via syringe, and the mixture stirred for 2 minutes at rt for solid NHPI-esters. NHPI-ester (if liquid) was dissolved in DMF (anhydrous) and added to the culture tube containing [Ni] and di-*t*Bubpy, and the mixture was stirred for 2 minutes at rt. Then, arylzinc

reagent in THF (3.0 equiv.) was added in one portion, and the mixture was stirred for 12 – 16 h at rt. The mixture was diluted with EtOAc or Et₂O and quenched with 1M HCl (aq). The reaction can also be quenched with H₂O or half-saturated NH₄Cl (aq) solution for acid-sensitive substrates. The organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure (*CAUTION*: some of the products are volatile). The crude material was purified by silica gel column chromatography or preparative TLC. **Note**: for *in situ* preparation of –OAt or –OBt esters with HATU or HBTU, respectively, see **25**.



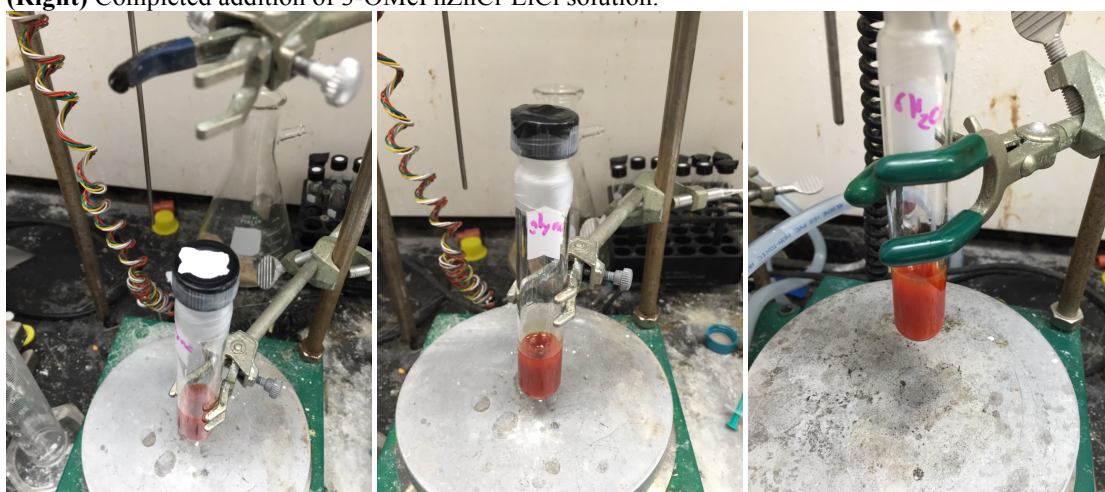
(Left) Backfilling with Ar a culture tube containing NiCl₂•glyme, di-*t*Bubipy, and a stir bar. **(Center)** A solution of 1,3-dioxoisindolin-2-yl 2-ethylhexanoate in DMF **(Right)** Adding the solution of DMF and redox-active ester to the culture tube.



(Left) Blue color develops as the DMF solution is added. **(Center)** After all of the redox-active ester solution has been added and stirred for 5 min. **(Right)** Same as before with NiCl₂•6H₂O.



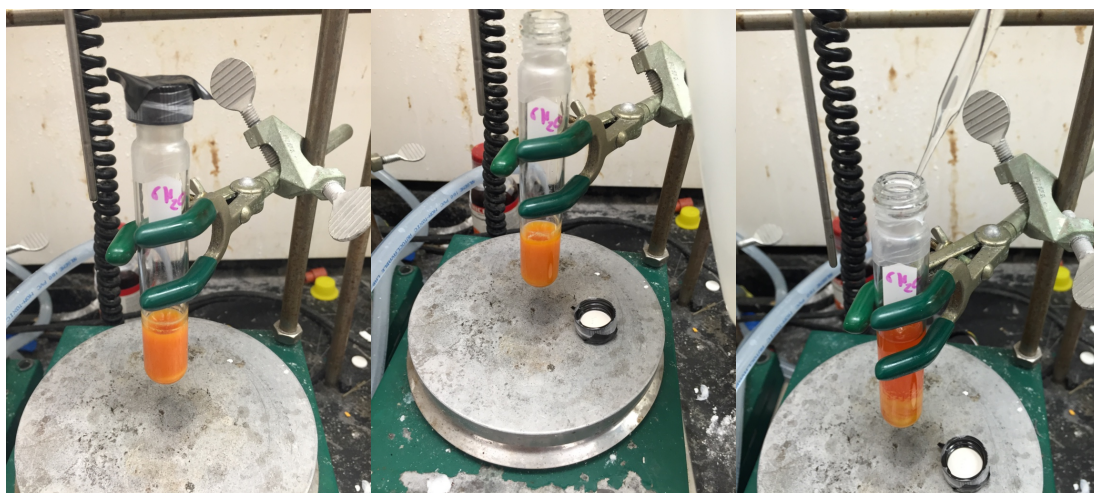
(Left) Prior to addition of 3-OMePhZnCl•LiCl. **(Center)** A red/brown color is immediately evident. **(Right)** Completed addition of 3-OMePhZnCl•LiCl solution.



(Left) Removal of Ar balloon and covering septum with Teflon™ tape. **(Center)** Covering the Teflon™ tape with electrical tape. **(Right)** Same as before with NiCl₂•6H₂O.



(Left) Reaction with NiCl₂•glyme after 12 hr. A black color is often observed but is not imperative to the success of the reaction. **(Center)** Dilution with Et₂O. **(Right)** Slow addition of 1M HCl (aq).



(All) As above with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.



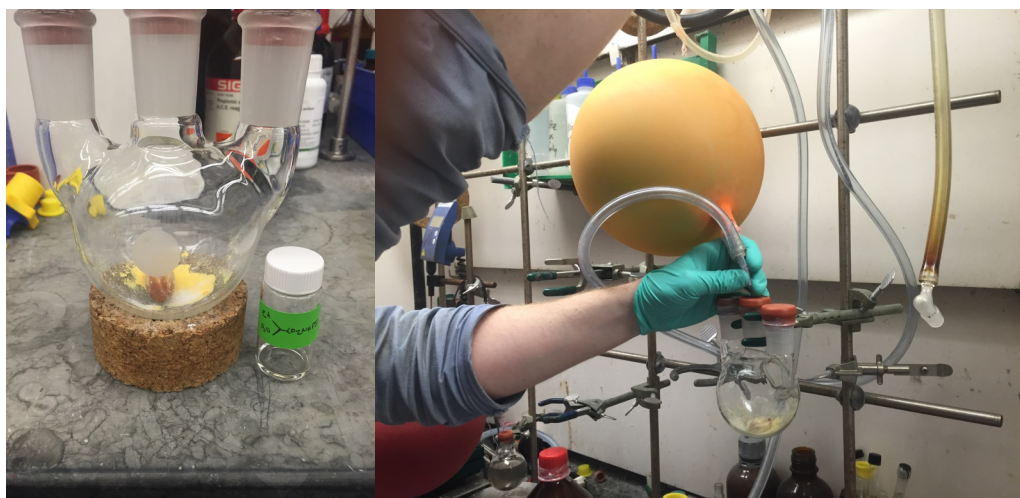
(Left) After 1M HCl (aq) wash. (Center) After brine wash. (Right) Filtering the drying agent.



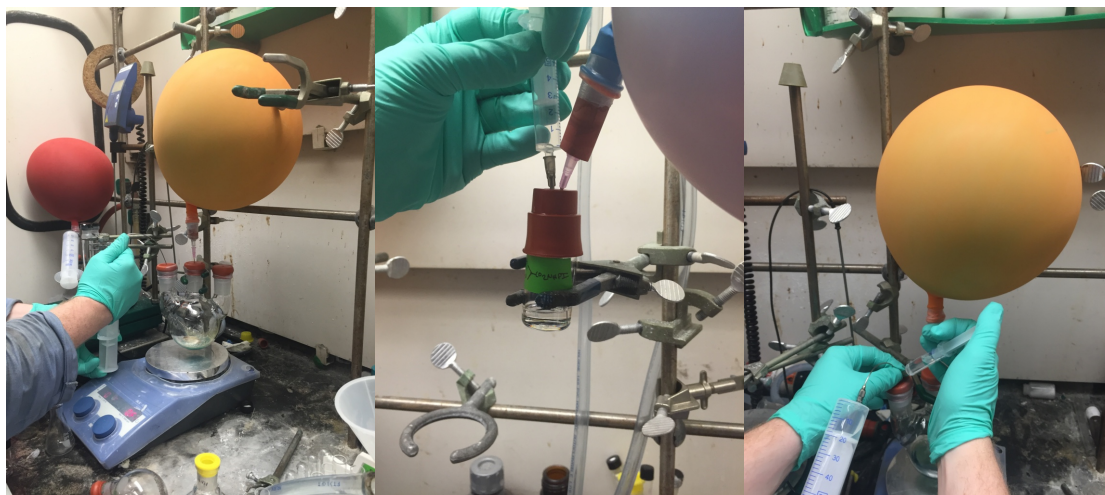
(Left) TLC (4:1 hexanes:EtOAc). Lane 1: 1,3-dioxoisindolin-2-yl 2-ethylhexanoate; Lane 2: Co-spot; Lane 3: Reaction mixture (Center and Right) TLC (9:1 hexanes:DCM) Lane 1: Reaction mixture; Lane 2: Co-spot; Lane 3: Authentic sample of 1-(heptan-3-yl)-3-methoxybenzene.

Gram-scale Procedure for the Ni-catalyzed cross-coupling (*Heptan-3-ylbenzene*).

The gram-scale coupling procedure is modified from General Procedure B. A three-neck 250 mL round-bottomed flask was charged with $\text{NiCl}_2\cdot\text{glyme}$ (20 mol %) and di-*t*Bubipy (40 mol %). The flask was fitted with three septa, evacuated by a needle attached to a vacuum line, and placed under positive pressure of argon from a balloon. Reactions were run with a 3:2 ratio of THF:DMF. The volume of DMF (30.0 mL) used was calculated based on the titre of the THF solution of the arylzinc reagent. Approximately 20 mL of the volume of DMF was added to the flask containing $\text{NiCl}_2\cdot\text{glyme}$ and di-*t*Bubipy. The remaining 10 mL of DMF was used to transfer 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (1.00 g, 3.5 mmol, 1 equiv.) to the reaction flask quantitatively (three rinses). The mixture was stirred for 2 minutes at rt. The flask was then placed in a water bath at ambient laboratory temperature. The $\text{PhZnCl}\cdot\text{LiCl}$ in THF (45.1 mL, 3.0 equiv., 0.23 M) was added in one portion over the course of approximately 30 seconds. The flask was removed from the water bath, and the mixture was stirred for 16 h at rt under positive pressure of argon from a balloon. The mixture was then slowly quenched with 1M HCl (aq) and stirred until clear, diluted with Et_2O , and transferred to a separatory funnel. The organic layer was washed with H_2O (3x) and brine, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (pentanes) to yield 483 mg (79%) of *heptan-3-ylbenzene*.



(Left) Reaction flask containing $\text{NiCl}_2\cdot\text{glyme}$ and di-*t*Bubipy and vial of NHPI-ester. **(Right)** Evacuation of reaction flask and backfilling with Ar balloon.



(Left) Addition of DMF to reaction flask. **(Center)** A solution of 1,3-dioxoisindolin-2-yl 2-ethylhexanoate in DMF **(Right)** Adding the solution of redox-active ester (in DMF) to the reaction flask.



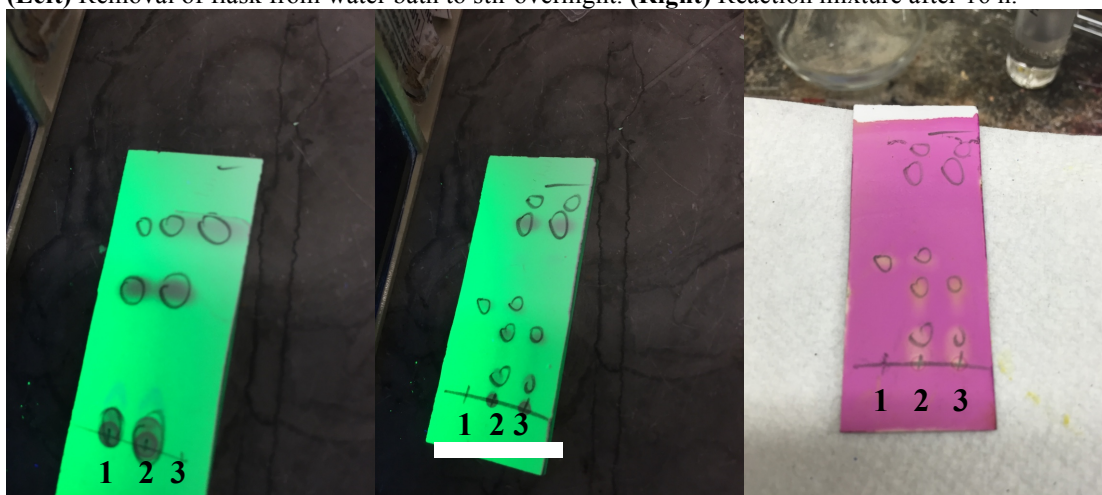
(Left) Reaction flask after addition of redox-active ester. **(Center)** Reaction flask placed in water bath. **(Right)** Addition of $\text{PhZnCl} \cdot \text{LiCl}$ in THF.



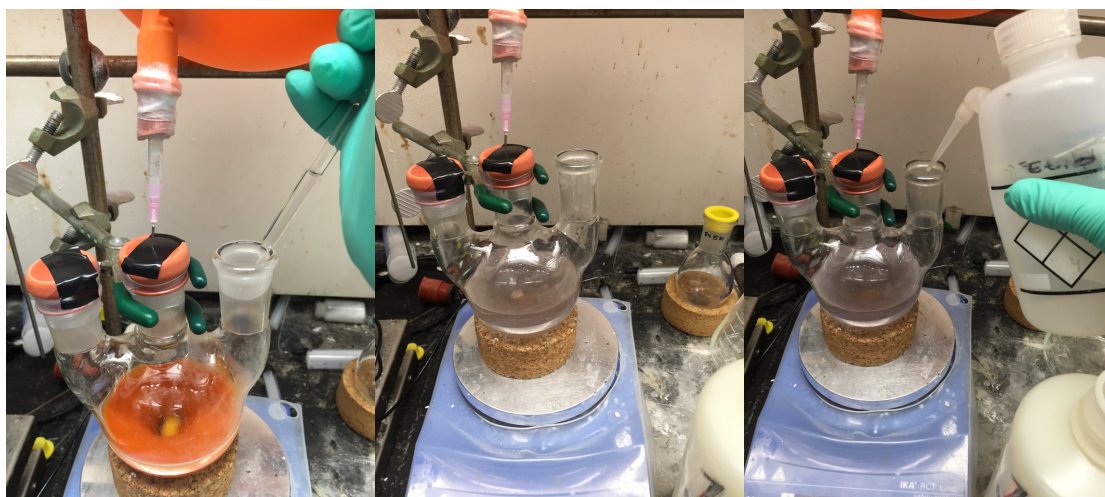
(Left and Center) Progression of addition of $\text{PhZnCl} \cdot \text{LiCl}$ in THF **(Right)** After addition of $\text{PhZnCl} \cdot \text{LiCl}$ in THF.



(Left) Removal of flask from water bath to stir overnight. **(Right)** Reaction mixture after 16 h.



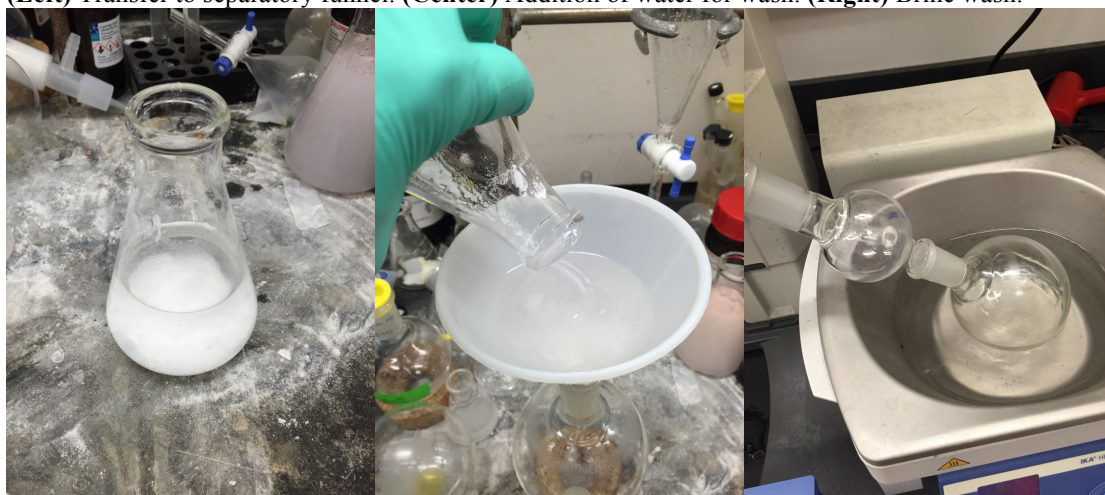
(Left) TLC (hexanes). *Lane 1*: Reaction mixture; *Lane 2*: Co-spot; *Lane 3*: Pure *heptan-3-ylbenzene*
(Center) TLC (4:1 hexanes:EtOAc). *Lane 1*: 1,3-dioxoisindolin-2-yl 2-ethylhexanoate; *Lane 2*: Co-spot; *Lane 3*: Reaction mixture **(Right)** As center with KMnO_4 visualization.



(Left) Quench with 1M HCl. **(Center)** After quench. **(Right)** Dilution with diethyl ether.



(Left) Transfer to separatory funnel. **(Center)** Addition of water for wash. **(Right)** Brine wash.

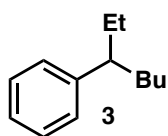


(Left) Drying over MgSO_4 . **(Center)** Filtration of drying agent. **(Right)** Concentration of organic layer.



(Left) Crude product. (Right) Pure product after column chromatography.

Procedures and characterization data



Heptan-3-ylbenzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and PhZnCl·LiCl (0.17 M in THF). Column chromatography with pentane afforded 46 mg (92%) of the title compound **3**.

From NiCl₂·glyme [gram-scale]: 483 mg (79%)

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and PhZnCl·LiCl (0.17 M in THF). Column chromatography with pentane afforded 47 mg (93%) of the title compound **3**.

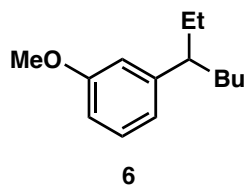
Physical State: colorless oil.

R_f = 0.76 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.15 (m, 1H), 7.15 – 7.07 (m, 2H), 2.39 (tt, *J* = 9.5, 5.3 Hz, 1H), 1.75 – 1.59 (m, 2H), 1.59 – 1.46 (m, 2H), 1.33 – 1.00 (m, 4H), 0.83 (t, *J* = 7.3 Hz, 3H), and 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 146.5, 128.5, 128.1, 126.1, 48.2, 36.61, 30.2, 30.1, 23.2, 14.4, and 12.6.

GC/MS (m/z (rel int)): 176 (M^+ , 0.16), 147 (0.18), 119 (0.30), 91 (1.00).



1-(Heptan-3-yl)-3-methoxybenzene

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol), 3-OMePhZnCl \cdot LiCl (0.21 M in THF), and di-*tert*-butylbipyridine (0.3 equiv). Purification by PTLC (0.5:99.5 acetone:hexanes) afforded **6** (34 mg, 66% yield).

From $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 3-OMePhZnCl \cdot LiCl (0.23 M in THF). Purification by PTLC (0.5:99.5 acetone:hexanes) afforded **6** (33 mg, 64% yield).

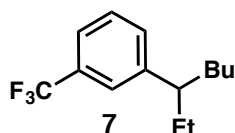
Physical State: colorless oil.

R_f = 0.33 (0.5:99.5 acetone/hexanes).

^1H NMR (600 MHz, CDCl_3): δ 7.20 (t, J = 7.8 Hz, 1H), 6.82 – 6.71 (m, 2H), 6.69 (d, J = 1.9 Hz, 1H), 3.81 (s, 3H), 2.36 (tt, J = 9.6, 5.3 Hz, 1H), 1.73 – 1.58 (m, 2H), 1.57 – 1.49 (m, 2H), 1.39 – 1.19 (m, 2H), 1.20 – 1.01 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H), and 0.77 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 159.6, 148.1, 129.1, 120.5, 113.9, 110.7, 55.2, 48.1, 36.4, 30.0, 29.8, 23.0, 14.2, and 12.4.

HRMS (ESI-TOF): calc'd for $\text{C}_{14}\text{H}_{23}\text{O}$ [$\text{M}+\text{H}$] $^+$ 207.1743; found 207.1753.



1-(Heptan-3-yl)-3-(trifluoromethyl)benzene

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 3-CF $_3$ -PhZnCl \cdot LiCl (0.25 M in THF). Column chromatography with pentane afforded 39 mg (66%) of the title compound **7**.

From NiCl₂ · 6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 3-CF₃-PhZnCl•LiCl (0.25 M in THF). Column chromatography with pentane afforded 42 mg (69%) of the title compound **7**.

Physical State: colorless oil.

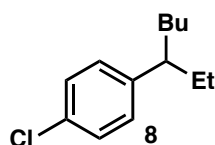
R_f = 0.79 (Hexane).

¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 2.49 (m, 1H), 1.79 – 1.63 (m, 2H), 1.56 (m, 2H), 1.37 – 0.99 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H), and 0.78 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 146.6, 130.7, 123.00 (q, *J* = 32.0 Hz, 1C), 128.1, 124.0 (q, *J* = 272.4 Hz, 1C), 124.0 (q, *J* = 3.4 Hz, 1C), 122.2 (q, *J* = 4.3 Hz, 1C), 47.4, 35.6, 29.3, 29.1, 22.3, 13.5, and 11.6.

¹⁹F NMR (376 MHz, CDCl₃): δ – 62.73.

HRMS (APCI): calc'd for C₁₄H₁₈F₃ [M–H][–] 243.1366; found 243.1.



1-Chloro-4-(heptan-3-yl)benzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 4-Cl-PhZnCl•LiCl (0.21 M in THF). Column chromatography with pentane afforded 30 mg (71%) of the title compound **8**.

From NiCl₂ · 6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 4-Cl-PhZnCl•LiCl (0.21 M in THF). Column chromatography with pentane afforded 41 mg (77%) of the title compound **8**.

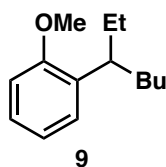
Physical State: colorless oil.

R_f = 0.74 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.31 – 7.20 (m, 2H), 7.14 – 6.96 (m, 2H), 2.40 (tt, *J* = 9.6, 5.2 Hz, 1H), 1.75 – 1.61 (m, 2H), 1.58 – 1.46 (m, 2H), 1.36 – 1.03 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 3H), and 0.78 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 144.1, 130.8, 128.6, 127.8, 46.9, 35.8, 29.3, 29.2, 22.3, 13.6, and 11.7.

HRMS (APCI): calc'd for C₁₃H₁₉Cl [M] 210.1175; found 210.1162.



1-(Heptan-3-yl)-2-methoxybenzene

From $\text{NiCl}_2 \cdot \text{glyme}$: Following the General Procedure B with 4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 3-OMePhZnCl•LiCl (0.23 M) at 60 °C. Purification by column chromatography with gradient elution (hexanes to 19:1 hexanes:DCM) afforded **9** (27mg, 52% yield).

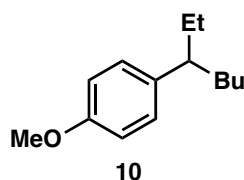
Physical State: colorless oil.

R_f = 0.38 (5:95 DCM/hexanes).

^1H NMR (400 MHz, CDCl_3): δ 7.21 – 7.09 (m, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 3.80 (s, 3H), 3.00 (ddd, J = 14.5, 8.7, 5.9 Hz, 1H), 1.72 – 1.48 (m, 4H), 1.42 – 1.02 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H), and 0.77 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 157.9, 134.6, 127.6, 126.4, 120.6, 110.7, 55.6, 39.2, 35.2, 29.9, 28.6, 23.0, 14.2, and 12.2.

HRMS (ESI-TOF): calc'd for $\text{C}_{14}\text{H}_{23}\text{O}$ [$\text{M}+\text{H}^+$] 207.1743; found 207.1739.



1-(Heptan-3-yl)-3-methoxybenzene

From $\text{NiCl}_2 \cdot \text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 4-OMePhZnCl•LiCl (0.20 M). Purification by column chromatography with gradient elution (hexanes to 9:1 hexanes: CH_2Cl_2) afforded **10** (35 mg, 68% yield).

From $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.25 mmol) and 4-OMePhZnCl•LiCl (0.20 M). Purification by column chromatography with gradient elution (hexanes to 9:1 hexanes: CH_2Cl_2) afforded **10** (42 mg, 81% yield).

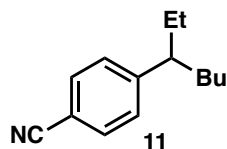
Physical State: colorless oil.

R_f = 0.25 (9:1 hexanes: CH_2Cl_2).

^1H NMR (600 MHz, CDCl_3): δ 7.08 – 7.02 (m, 2H), 6.90 – 6.80 (m, 2H), 3.79 (s, 3H), 2.33 (tt, J = 9.3, 5.3 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.53 – 1.45 (m, 2H), 1.33 – 1.04 (m, 4H), 0.83 (t, J = 7.3 Hz, 3H), and 0.75 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 157.8, 138.3, 128.7, 113.6, 55.3, 47.1, 36.6, 30.0 (2C), 23.0, 14.2, and 12.3.

HRMS (ESI-TOF): calc'd for $\text{C}_{14}\text{H}_{22}\text{O}$ [MH^+] 207.1743; found 207.1750.



4-(heptan-3-yl)benzonitrile

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with **1f** (4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2-ethylhexanoate, 0.25 mmol) and 4-CN-PhZnCl•LiCl in THF. This organozinc reagent could not be titrated due to its dark color (see picture below), so quantitative yield of the reagent was assumed (3 mL, 0.25 M). Purification by column chromatography (9:1 hexanes:EtOAc) and PTLC in the same solvent system afforded **11** (27 mg, 54% yield).

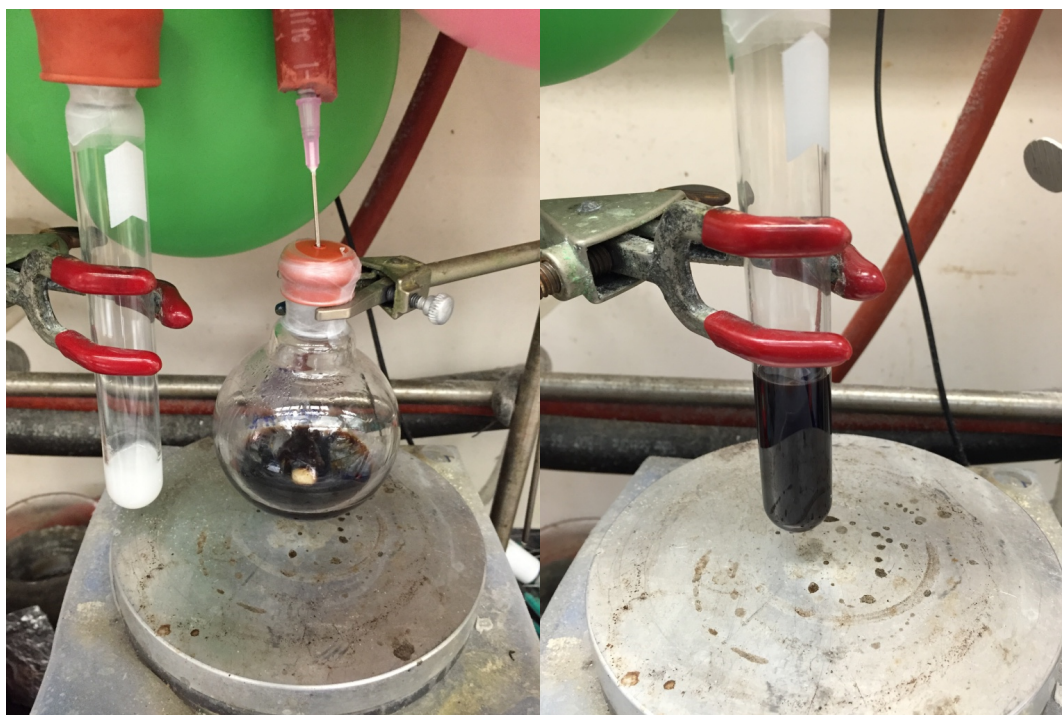
Physical State: colorless oil.

R_f = 0.71 (4:1 hexanes:EtOAc).

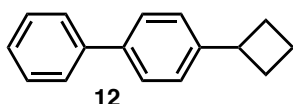
^1H NMR (600 MHz, CDCl_3) δ 7.59 – 7.55 (m, 2H), 7.25 – 7.22 (m, 2H), 2.46 (tt, J = 9.3, 5.3 Hz, 1H), 1.74 – 1.61 (m, 2H), 1.57 – 1.48 (m, 2H), 1.32 – 1.18 (m, 2H), 1.13 (dddt, J = 13.1, 10.3, 8.7, 5.8 Hz, 1H), 1.08 – 0.98 (m, 1H), 0.82 (t, J = 7.3 Hz, 3H), and 0.75 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 152.1, 132.2, 128.7, 119.4, 109.8, 48.3, 36.1, 29.9, 29.6, 22.8, 14.1, and 12.2.

HRMS (ESI-TOF): calc'd for $\text{C}_{14}\text{H}_{20}$ [MH^+] 202.1590; found 202.1590.



(Left) ZnCl_2 solution in THF (left) and $4\text{-CNMgBr}\cdot\text{LiCl}$ (right). (Right) $4\text{-CNZnCl}\cdot\text{LiCl}$ in THF.



4-Cyclobutyl-1,1'-biphenyl

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclobutylcarboxylate (0.25 mmol) and 4-Ph-Ph $\text{ZnCl}\cdot\text{LiCl}$ complex (0.22 M in THF). PTLC (hexanes) afforded 20.3 mg (65%) of the title compound **12**.

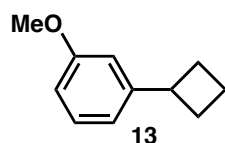
Physical State: white solid; mp: 28 °C.

R_f = 0.30 (hexanes).

^1H NMR (600 MHz, CDCl_3): δ 7.60 – 7.57 (m, 2H), 7.55 – 7.52 (m, 2H), 7.45 – 7.41 (m, 2H), 7.34 – 7.32 (m, 1H), 7.32 – 7.28 (m, 2H), 3.64 – 3.55 (m, 1H), 2.42 – 2.32 (m, 2H), 2.25 – 2.14 (m, 2H), 2.10 – 1.99 (m, 1H), and 1.93 – 1.84 (m, 1H).

^{13}C NMR (150 MHz, CDCl_3): δ 145.5, 141.3, 138.8, 128.8, 127.2, 127.1, 127.1, 126.9, 40.2, 30.0, and 18.5.

HRMS (ESI-TOF): calc'd for $\text{C}_{16}\text{H}_{17}$ $[(\text{M}+\text{H})^+]$ 209.1325; found 209.1326.



1-Cyclobutyl-3-methoxybenzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclobutanecarboxylate (0.25 mmol) and 3-MeOPhZnCl·LiCl (0.23 M in THF). Column chromatography with hexanes afforded 25 mg (62%) of the title compound **13**.

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclobutanecarboxylate (0.25 mmol) and 3-OMePhZnCl·LiCl (0.23 M in THF). Column chromatography with hexane afforded 26 mg (64%) of the title compound **13**.

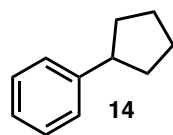
Physical State: colorless oil.

R_f = 0.34 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.83 (m, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 6.73 (ddd, *J* = 7.9, 2.9, 0.9 Hz, 1H), 3.82 (s, 3H), 3.58 – 3.50 (m, 1H), 2.39 – 2.31 (m, 2H), 2.21 – 2.11 (m, 2H), 2.07 – 1.97 (m, 1H), and 1.86 (dddd, *J* = 10.8, 8.8, 6.2, 2.5, 1.0 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 159.7, 148.1, 129.3, 118.8, 112.3, 111.0, 55.3, 40.5, 29.8, and 18.4.

HRMS (APCI): calc'd for C₁₁H₁₅O [M+H]⁺ 163.1117; found 163.1119.



Cyclopentylbenzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclopentancarboxylate (0.25 mmol) and PhZnCl·LiCl (0.17 M in THF). Column chromatography with pentane afforded 30 mg (81%) of the title compound **14**.

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclopentancarboxylate (0.25 mmol) and PhZnCl·LiCl (0.17 M in THF). Column chromatography with pentane afforded 23 mg (77%) of the title compound **14**.

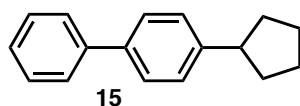
Physical State: colorless oil.

R_f = 0.69 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.33 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 3.02 (tt, *J* = 9.8, 7.5 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.89 – 1.79 (m, 2H), 1.77 – 1.66 (m, 2H), and 1.66 – 1.58 (m, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 146.1, 127.8, 126.6, 125.2, 45.5, 34.2, and 25.1.

HRMS (APCI): calc'd for C₁₁H₁₃ [M-H]⁻ 145.1023; found 145.1005.



4-Cyclopentyl-1,1'-biphenyl

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclopentancarboxylate (0.25 mmol) and 4-Ph-PhZnCl·LiCl (0.22 M in THF). Purification by PTLC (hexanes) afforded 22 mg (66%) of the title compound **15**.

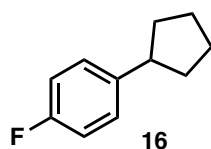
Physical State: white solid; mp: 35 °C.

R_f = 0.30 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.60 – 7.57 (m, 2H), 7.54 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.35 – 7.30 (m, 3H), 3.09 – 2.99 (m, 1H), 2.15 – 2.05 (m, 2H), 1.90 – 1.79 (m, 2H), 1.77 – 1.67 (m, 2H), and 1.67 – 1.57 (m, 2H).

¹³C NMR (150 MHz, CDCl₃): δ 145.8, 141.3, 138.8, 128.8, 127.7, 127.2, 127.1, 127.1, 45.8, 34.8, and 25.7.

HRMS (ESI-TOF): calc'd for C₁₇H₁₉ [M+H]⁺ 223.1481; found 223.1481.



1-Cyclopentyl-4-fluorobenzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclopentancarboxylate (0.25 mmol) and 4-F-PhZnCl·LiCl (0.25 M in THF). Column chromatography with pentane afforded 32 mg (78%) of the title compound **16**.

Physical State: colorless oil.

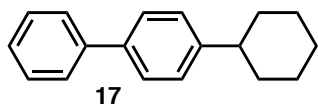
R_f = 0.78 (hexanes).

¹H NMR (600 MHz, CDCl₃): δ 7.26 – 7.16 (m, 2H), 7.04 – 6.93 (m, 2H), 2.99 (tt, *J* = 9.9, 7.4 Hz, 1H), 2.14 – 1.97 (m, 2H), 1.91 – 1.78 (m, 2H), 1.75 – 1.65 (m, 2H), and 1.62 – 1.50 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 160.6 (d, J = 242.1 Hz, 1C), 141.6 (d, J = 7.5 Hz, 1C), 127.9 (d, J = 7.5 Hz, 2C), 114.4 (d, J = 20.9 Hz, 2C), 44.8, 34.3, and 25.0.

^{19}F NMR (376 MHz, CDCl_3): δ -118.49.

HRMS (APCI): calc'd for $\text{C}_{11}\text{H}_{12}\text{F}$ $[\text{M}-\text{H}]^-$ 163.0929; found 163.0910.



4-Cyclohexyl-1,1'-biphenyl

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclohexancarboxylate (0.25 mmol) and 4-Ph-PhZnCl·LiCl (0.22 M in THF). PTLC (hexanes) afforded 27.7 mg (78%) of the title compound **17**.

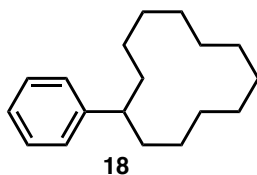
Physical State: white solid; mp: 55 °C.

R_f = 0.30 (hexanes).

^1H NMR (600 MHz, CDCl_3): δ 7.60 – 7.57 (m, 2H), 7.54 – 7.50 (m, 2H), 7.44 – 7.40 (m, 2H), 7.34 – 7.30 (m, 1H), 7.30 – 7.27 (m, 2H), 2.59 – 2.51 (m, 1H), 1.96 – 1.89 (m, 2H), 1.90 – 1.83 (m, 2H), 1.81 – 1.73 (m, 1H), 1.51 – 1.36 (m, 4H), and 1.33 – 1.22 (m, 1H).

^{13}C NMR (150 MHz, CDCl_3): δ 147.4, 141.3, 138.9, 128.8, 127.4, 127.1, 127.2, 127.1, 44.4, 34.6, 27.1, and 26.3.

HRMS (ESI-TOF): calc'd for $\text{C}_{18}\text{H}_{21}$ $[\text{M}+\text{H}]^+$ 237.1638; found 237.1638.



Phenylcyclododecyl

From $\text{NiCl}_2\cdot\text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl cyclododecylcarboxylate (0.13 mmol) and PhZnCl·LiCl complex (0.25 M in THF). Purification by PTLC (hexanes) afforded 16.1 mg (50%) of the title compound **18**.

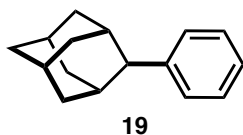
Physical State: white solid; mp: 45–47 °C.

R_f = 0.76 (hexanes).

^1H NMR (600 MHz, CDCl_3): δ 7.32 (t, J = 7.6 Hz, 2H), 7.26 – 7.17 (m, 3H), 2.80 (p, J = 6.5 Hz, 1H), 1.94 – 1.71 (m, 2H), and 1.64 – 1.00 (m, 20H).

¹³C NMR (151 MHz, CDCl₃): δ 147.2, 127.7, 127.2, 125.2, 39.2, 31.1, 23.5, 23.5, 23.0, 22.8, and 22.3.

HRMS (APCI): calc'd for C₁₈H₂₇ [M-H]⁻ 243.2118; found 243.2104.



2-Phenyladamantane

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl adamantane 2-carboxylate (0.20 mmol) and PhZnCl·LiCl (0.25 M in THF). Column chromatography with pentane afforded 30 mg (73%) of the title compound **19**.

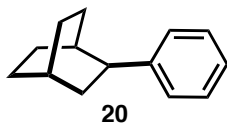
Physical State: colorless oil.

R_f = 0.69 (hexanes).

¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.31 (m, 4H), 7.22 (t, *J* = 7.1 Hz, 1H), 3.06 (s, 1H), 2.52 (s, 2H), 2.09 – 1.74 (m, 10H), and 1.60 (d, *J* = 12.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 144.4, 128.1, 126.9, 125.2, 46.8, 39.2, 37.9, 32.0, 31.1, 28.1, and 27.8.

HRMS (APCI): calc'd for C₁₆H₁₉ [M-H]⁻ 211.1492; found 211.1494.



2-Phenyl bicyclo[2.2.2]octane

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl bicyclo[2.2.2]octane 2-carboxylate (0.20 mmol) and PhZnCl·LiCl (0.25 M in THF). Column chromatography with pentane afforded 25 mg (67%) of the title compound **20**.

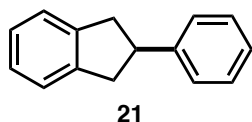
Physical State: colorless oil.

R_f = 0.70 (hexanes).

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.30 (m, 4H), 7.26 – 7.17 (m, 1H), 3.02 (ddd, *J* = 10.9, 7.4, 1.7 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.90 – 1.48 (m, 10H), and 1.41 – 1.26 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 146.6, 128.1, 127.7, 125.5, 41.9, 32.3, 31.0, 27.6, 26.0, 25.4, 24.8, and 20.5.

HRMS (APCI): calc'd for C₁₄H₁₇ [M-H]⁻ 185.1330; found 185.1325.



2-Phenyl-2,3-dihydro-1H-indene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 2,3-dihydro-1H-indene-2-carboxylate (0.20 mmol) and PhZnCl·LiCl (0.22 M in THF). Column chromatography with pentane afforded 20 mg (52%) of the title compound **21**.

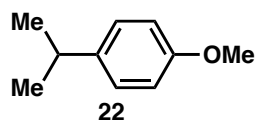
Physical State: colorless oil.

R_f = 0.38 (hexanes).

¹H NMR (400 MHz, CDCl₃): δ 7.46 – 6.92 (m, 9H), 3.74 (p, *J* = 8.6 Hz, 1H), 3.40 (dd, *J* = 15.6, 8.2 Hz, 2H), and 3.14 (dd, *J* = 15.6, 9.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 145.5, 143.0, 128.5, 127.1, 126.5, 126.2, 124.3, 45.5, and 40.9.

HRMS (APCI): calc'd for C₁₅H₁₃ [M-H]⁺ 193.1017; found 193.1012.



1-isopropyl-4-methoxybenzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl isobutyrate (0.25 mmol) and 4-OMePhZnCl·LiCl (0.20 M in THF). Purification by PTLC (99:1 hexanes:Et₂O) afforded **22** (19 mg, 51% yield).

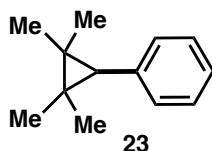
Physical State: clear oil.

R_f = 0.31 (9:1 hexanes/CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃): δ 7.19 – 7.13 (m, 2H), 6.86 – 6.83 (m, 2H), 3.79 (s, 3H), 2.87 (hept, *J* = 6.9 Hz, 1H), and 1.23 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃): δ 157.8, 141.2, 127.4, 113.8, 55.4, 33.4, and 24.4.

HRMS (ESI-TOF): calc'd for C₁₀H₁₅O [M+H]⁺ 151.1117; found 151.1118



(2,2,3,3-Tetramethylcyclopropyl)benzene

From NiCl₂·glyme: Following the General Procedure B with 4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2,2,3,3-tetramethylcyclopropane-1-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.25 M in THF). Column chromatography with pentane afforded 15 mg (35%) of the title compound **23**.

From NiCl₂·6H₂O: Following the General Procedure B with 4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2,2,3,3-tetramethylcyclopropane-1-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.25 M in THF). Column chromatography with pentane afforded 12 mg (31%) of the title compound **23**.

Physical State: colorless oil.

R_f = 0.76 (hexanes).

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.29 (m, 3H), 7.27 – 7.12 (m, 2H), 1.62 (s, 1H), 1.33 (s, 6H), and 1.01 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 139.4, 131.0, 127.9, 125.5, 37.8, 23.9, 23.2, and 19.1.

HRMS (APCI): calc'd for C₁₃H₁₇ [M–H]⁺ 174.1408; found 174.1402.



tert-Butyl 2-phenylpyrrolidine-1-carboxylate

From NiCl₂·glyme: A screw-cap culture tube with Teflon™ septum and stir bar was charged with 1-(tert-butoxycarbonyl)pyrrolidine-2-carboxylic acid (54 mg, 0.25 mmol) and HATU (95 mg, 0.25 mmol) in DMF (anhydrous, 1.0 mL) followed by the addition of Et₃N (35 μ L, 0.25 mmol). The mixture was stirred at rt for 30 min.⁶ A solution of NiCl₂·glyme (20 mol %) and di-*t*Bubipy (40 mol %) in 1.0 mL of DMF was added to the reaction mixture and stirred at rt for 5 min. PhZnCl·LiCl (0.25 M in THF) was added dropwise to the reaction mixture, which was stirred for 12 h. Normal work up and purification by column chromatography (20:3 hexanes:EtOAc) to provide 35 mg (56%) of the title compound **24**.

From NiCl₂·6H₂O: A screw-cap culture tube with Teflon™ septum and stir bar was charged with 1-(*tert*-butoxycarbonyl)pyrrolidine-2-carboxylic acid (54 mg, 0.25 mmol) and HATU (95 mg, 0.25 mmol) in DMF (anhydrous, 1.0 mL) followed by the addition of Et₃N (35 μL, 0.25 mmol). The mixture was stirred at rt for 30 min.⁶ A solution of NiCl₂·glyme (20 mol %) and di-*t*Bubipy (40 mol %) in 1.0 mL of DMF was added to the reaction mixture and stir at rt for 5 min. PhZnCl·LiCl (0.25 M in THF) was added dropwise to the reaction mixture, which was stirred for 12 h. Normal work up and purification by column chromatography (20:3 hexanes:EtOAc) to provide 36 mg (58%) of the title compound **24**.

Physical State: colorless oil.

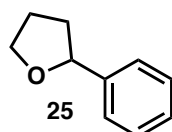
R_f = 0.53 (20:3 hexanes:EtOAc).

The product gives two sets of NMR signals, owing to the presence of rotamers.

¹H NMR (600 MHz, CDCl₃): δ 7.27-7.23 (m, 2H), 7.19-7.13 (m, 3H), 4.93 (brs, 0.3H), 4.73 (brs, 0.7H), 3.60-3.49 (m, 2H), 2.30 (br, 1H), 1.89 (br, 1H), 1.85-1.75 (m, 2H), 1.43 (s, 3H), and 1.15 (s, 6H).

¹³C NMR (151 MHz, CDCl₃): δ 154.7, 145.3, 144.2, 128.4, 128.2, 126.6, 125.6, 125.5, 79.3, 61.5, 60.8, 47.5, 47.2, 36.2, 35.0, 28.7, 28.3, 23.6, and 23.3.

HRMS (ESI-TOF): calc'd for C₁₅H₂₂NO₂⁺ [M+H]⁺ 248.1645; found 248.1645.



2-Phenyltetrahydrofuran

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl tetrahydrofuran-2-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.21 M in THF). Purification by column chromatography (10:1 hexanes:EtOAc) to afford 20 mg (55%) of the title compound **25**.

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.18 M in THF). Purification by column chromatography (10:1 hexanes:EtOAc) to afford 9 mg (25%) of the title compound **25**.

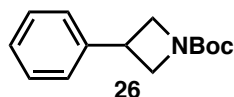
Physical State: colorless oil.

R_f = 0.53 (10:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.35-7.32 (m, 4H), 7.26–7.24 (m, 1H), 4.90 (t, *J* = 7.2, Hz, 1H), 4.20-4.05 (m, 1H), 3.94 (td, *J* = 7.9, 6.4 Hz, 1H), 2.33 (ddd, *J* = 12.4, 7.2, 5.5 Hz, 1H), 2.07-1.94 (m, 2H), and 1.81 (dq, *J* = 12.3, 7.7 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃): δ 143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.8, and 26.2.

HRMS (ESI-TOF): calc'd for C₁₀H₁₃O [M+H]⁺ 149.0961; found 149.0959.



***tert*-Butyl 3-phenylazetidine-1-carboxylate**

From NiCl₂glyme: Following the General Procedure B with 1-(*tert*-butyl) 3-(4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl) azetidine-1,3-dicarboxylate (0.25 mmol), 2,2'-bipyridine (40 mol%, in place of di-*t*Bubipy), and PhZnCl·LiCl (0.28 M in THF). Purification by column chromatography (4:1 hexanes:EtOAc) afforded 33 mg (56%) of the title compound **26**.

From NiCl₂·6H₂O: Following the General Procedure B with 1-(*tert*-butyl) 3-(4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl) azetidine-1,3-dicarboxylate (0.25 mmol), 2,2'-bipyridine (40 mol%, in place of di-*t*Bubipy), and PhZnCl·LiCl (0.25 M in THF). Purification by column chromatography (4:1 hexanes:EtOAc) afforded 27 mg (46%) of the title compound **26**.

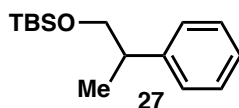
Physical State: colorless oil.

R_f = 0.63 (4:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.37 – 7.33 (m, 2H), 7.32 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 4.33 (dd, *J* = 8.6, 8.6 Hz, 2H), 3.98 (dd, *J* = 8.6, 6.1 Hz, 2H), 3.73 (tt, *J* = 8.7, 6.0 Hz, 1H), and 1.47 (s, 9H).

¹³C NMR (151 MHz, CDCl₃): δ 156.6, 142.4, 128.9, 127.1, 126.9, 79.7, 56.6, 33.7, and 28.6.

HRMS (ESI-TOF): calc'd for C₁₄H₂₀NO₂ [M+H]⁺ 234.1488; found 234.1489.



***tert*-butyldimethyl(2-phenylpropoxy)silane**

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 3-((*tert*-butyldimethylsilyl)oxy)-2-methylpropanoate (0.25 mmol) and PhZnCl·LiCl (0.21 M in THF). Purification by PTLC (hexanes) afforded 32 mg (51%) of the title compound **27**.

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.29 M in THF). Purification by column chromatography (gradient elution, hexanes to 9:1 hexanes:EtOAc) afforded 40 mg (64%) of the title compound **27**.

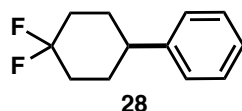
Physical State: clear oil.

R_f = 0.33 (9:1 hexanes:EtOAc).

¹H NMR (600 MHz, CDCl₃): δ 7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 3.69 (dd, J = 9.8, 5.9 Hz, 1H), 3.59 (dd, J = 9.8, 7.6 Hz, 1H), 2.94 – 2.84 (m, 1H), 1.29 (d, J = 7.0 Hz, 3H), 0.86 (s, 9H), -0.03 (s, 3H), and -0.04 (s, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 144.7, 128.3, 127.7, 126.4, 69.4, 42.6, 26.1, 18.5, 17.6, and -5.3 (2C).

HRMS (ESI-TOF): calc'd for C₁₅H₂₇OSi [M+H]⁺ 251.1826; found 251.1828.



(4,4-Difluorocyclohexyl)benzene

From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 4,4-difluorocyclohexane-1-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.25 M in THF). Purification by column chromatography (pentane) afforded 36 mg (73%) of the title compound **28**.

From NiCl₂·6H₂O: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 4,4-difluorocyclohexane-1-carboxylate (0.25 mmol) and PhZnCl·LiCl (0.25 M in THF). Column chromatography (pentane) afforded 15 mg (31%) of the title compound **28**.

Physical State: white solid; mp: 40 – 42 °C.

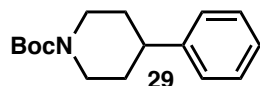
R_f = 0.51 (Hexanes:EtOAc 9:1);

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 3H), 2.66 – 2.61 (m, 1H), 2.27 – 2.21 (m, 2H), 2.02 – 1.71 (m, 6H).

^{13}C NMR (151 MHz, CDCl_3): δ 144.7 (d, $J = 2.0$ Hz), 128.1, 126.3, 126.0, 122.7 (dd, $J = 242.5, 239.2$ Hz, 1C), 42.1, 33.6 (dd, $J = 25.6, 22.4$ Hz, 2C), and 29.8 (d, $J = 9.9$ Hz, 2C).

^{19}F NMR (376 MHz, CDCl_3): δ -91.86 (d, $J = 235.8$ Hz), and -102.61 (d, $J = 235.8$ Hz).

GC/MS (m/z): 196 (M^+), 117, 104, 91.



tert-Butyl 4-phenylpiperidine-1-carboxylate

Following the General Procedure B with 1-(*tert*-butyl) 4-(4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl) piperidine-1,4-dicarboxylate (0.1 mmol) and $\text{PhZnCl} \cdot \text{LiCl}$ (0.20 M in THF). Purification by column chromatography (30:1 hexanes:EtOAc) afforded 14 mg (54%) of the title compound **29**.

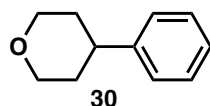
Physical State: colorless oil.

$R_f = 0.55$ (6:1 hexanes:EtOAc).

^1H NMR (400 MHz, CDCl_3): δ 7.32 – 7.30 (m, 2H), 7.22 – 7.20 (m, 3H), 4.24 (d, $J = 13.3$ Hz, 2H), 2.85 – 2.76 (m, 2H), 2.64 (tt, $J = 12.2, 3.6$ Hz, 1H), 1.89 – 1.78 (m, 2H), 1.67 – 1.58 (m, 2H), and 1.48 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3): δ 155.0, 146.0, 128.7, 126.9, 126.5, 79.6, 44.6, 42.9, 33.3, and 28.7.

Spectroscopic data matches that reported in the literature.⁷



4-phenyltetrahydro-2H-pyran

From $\text{NiCl}_2 \cdot \text{glyme}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate (0.25 mmol) and $\text{PhZnCl} \cdot \text{LiCl}$ (0.21 M in THF). Purification by column chromatography (10:1 hexanes:EtOAc) afforded 26 mg (65%) of the title compound **30**.

From $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: Following the General Procedure B with 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate (0.25 mmol) and $\text{PhZnCl} \cdot \text{LiCl}$ (0.18 M in THF). Purification by column chromatography with (10:1 hexanes:EtOAc) afforded 12 mg (30%) of the title compound **30**.

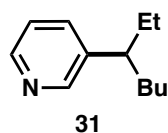
Physical State: white solid; mp: 49-50 °C.

R_f = 0.53 (10:1 hexanes:EtOAc).

^1H NMR (600 MHz, CDCl_3): δ 7.34 – 7.31 (m, 2H), 7.24 – 7.21 (m, 3H), 4.09 (dd, J = 11.3, 4.0 Hz, 2H), 3.54 (td, J = 11.7, 2.0 Hz, 2H), 2.79 – 2.73 (m, 1H), and 1.91 – 1.71 (m, 4H);

^{13}C NMR (151 MHz, CDCl_3): δ 146.0, 128.7, 126.9, 126.5, 68.6, 41.7, and 34.1.

HRMS (ESI-TOF): calc'd for $\text{C}_{11}\text{H}_{15}\text{O}^+$ $[\text{M}+\text{H}]^+$ 163.1117; found 163.1116.



Preparation of 3-pyridylzinc chloride lithium chloride reagent.

A dry and argon-charged 10-mL flask was charged with *i*PrMgCl·LiCl (1.06 mL, 1.04 M in THF, 1.10 mmol) and diluted with THF (1 mL). The reaction mixture was cooled to 0 °C and 3-bromopyridine (96 μL , 1.0 mmol) was added in one portion. The resulting solution was kept stirring at room temperature for 30 min before ZnCl_2 (1.2 mL, 1.0 M in THF, 1.2 mmol) was added in. After 30 min stirring, the 3-PyZnCl·LiCl solution was titrated as 0.21 M in THF.

From phthalimide ester: Following the General Procedure with 1-(tert-butyl) 4-(1,3-dioxoisindolin-2-yl) piperidine-1,4-dicarboxylate (0.1 mmol) and 33-PyZnCl·LiCl (0.21 M in THF). Column chromatography (10:1 hexanes:EtOAc) afforded 6 mg (34%) of the title compound **31**.

From HATU ester: Following the General Procedure with 2-ethylhexanoic acid (0.1 mmol), HATU, and 3-PyZnCl·LiCl (0.21 M in THF). Column chromatography (10:1 hexanes:EtOAc) afforded 9.6 mg (54%) of the title compound **31**.

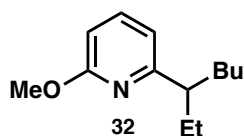
Physical State: colorless oil.

R_f = 0.50 (5:1 hexanes:EtOAc).

^1H NMR (400 MHz, CDCl_3): δ 8.43 (dd, J = 4.7, 1.7 Hz, 1H), 8.41 – 8.37 (m, 1H), 7.45 (dt, J = 7.8, 2.0 Hz, 1H), 7.22 (ddd, J = 7.9, 4.8, 0.9 Hz, 1H), 2.41 (td, J = 9.3, 4.8 Hz, 1H), 1.69 (dddt, J = 21.6, 13.5, 10.7, 5.5 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.32 – 1.19 (m, 2H), 1.19 – 1.11 (m, 1H), 1.10-1.03 (m, 1H), 0.82 (t, J = 7.3 Hz, 3H), and 0.76 (t, J = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 150.0, 147.5, 141.3, 134.9, 123.5, 45.4, 36.0, 29.8, 29.6, 22.8, 14.1, and 12.2.

HRMS (ESI-TOF): calc'd for C₁₂H₂₀N [M+H]⁺ 178.1590; found 178.1590.



2-(heptan-3-yl)-6-methoxypyridine

Following the General Procedure with 4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2-ethylhexanoate (0.1 mmol) and 6-methoxy-2-PyZnCl·LiCl (0.05 M in THF). Purification by column chromatography (10:1 hexanes:CH₂Cl₂) afforded 9 mg (42%) of the title compound **32**.

Physical State: colorless oil.

R_f = 0.4 (10:1 hexanes:CH₂Cl₂).

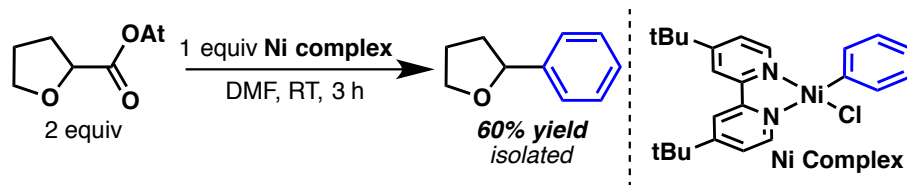
¹H NMR (400 MHz, CDCl₃): δ 7.44 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.64 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.51 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.90 (s, 3H), 2.48 (tt, *J* = 9.1, 5.2 Hz, 1H), 1.75 – 1.68 (m, 2H), 1.66 – 1.56 (m, 2H), 1.32 – 1.22 (m, 2H), 1.20 – 1.13 (m, 1H), 1.11 – 1.03 (m, 1H), 0.83 (t, *J* = 7.3 Hz, 3H), and 0.76 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 163.8, 163.3, 138.4, 115.7, 107.2, 53.2, 49.3, 34.9, 30.00, 28.4, 23.0, 14.2, and 12.3.

HRMS (ESI-TOF): calc'd for C₁₃H₂₂NO [M+H]⁺ 208.1696; found 208.1695.

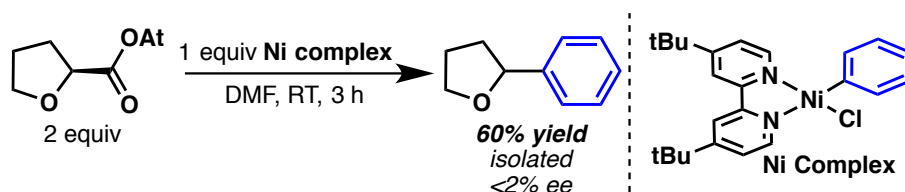
Mechanistic investigations

Stoichiometric reaction of activated tetrahydrofuran-2-carboxylic acid and Ni complex 2.

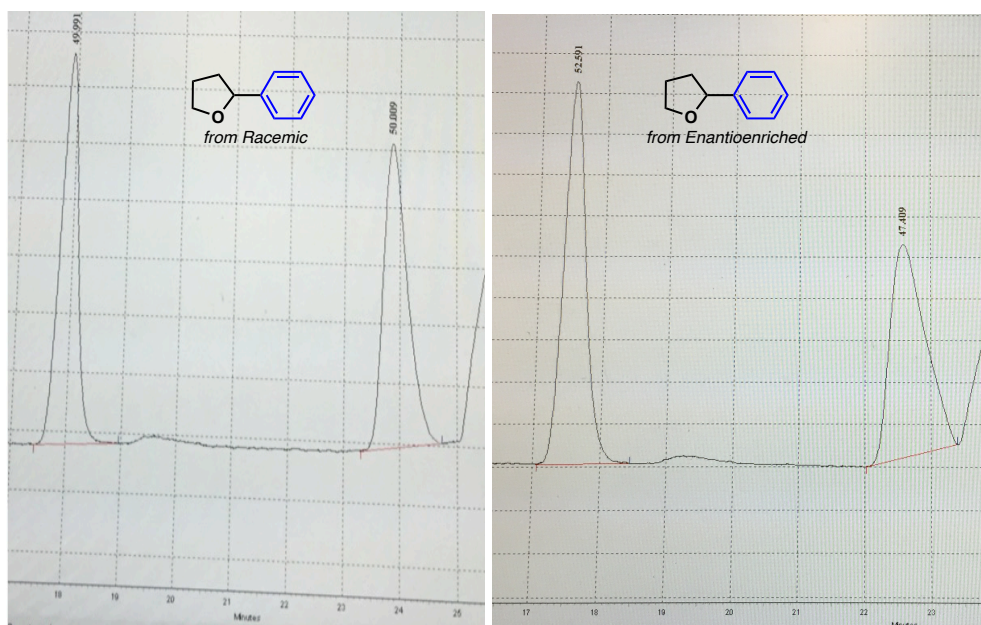


From racemic acid. A 25 mL Teflon™ screw-capped test tube was charged with 2-tetrahydrofuran-2-carboxylic acid (46 μL, 0.50 mmol), HATU (190 mg, 0.50 mmol) and Et₃N (70 μL, 0.50 mmol). The tube was sealed and evacuated and back-filled with Ar. Anhydrous DMF (1 mL) was added and stirred for 15 minutes. In another 25 mL Teflon™ screw capped, **2**² (174 mg, 0.25 mmol) and di-*t*Bubipy (67 mg, 0.25 mmol)

were dissolved in DMF under Ar. The solution with the activated ester was then added via syringe to the Nickel complex solution at room temperature. The mixture slowly turned from red-yellow to clear green. After 3 hours, the reaction was quenched with HCl 1N (2 mL), and Et₂O was added. The organic layer was dried over NaSO₄ (anh), filtered and concentrated. Column chromatography (hexanes:EtOAc 9:1) afforded 22 mg (60% yield) of compound **25** as a yellowish oil.

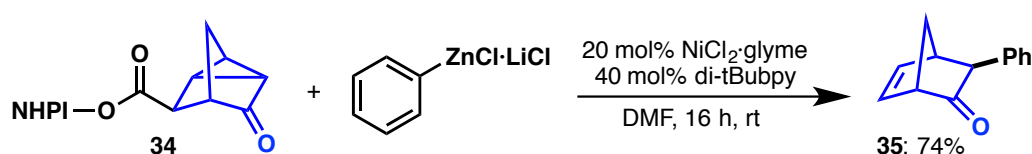


From enantiopure acid: A 25 mL screw-cap culture tube with Teflon™ septum was charged with (*S*)-2-tetrahydrofuroic acid (99% ee, 46 μL, 0.50 mmol), HATU (190 mg, 0.50 mmol) and Et₃N (70 μL, 0.50 mmol). The tube was sealed, evacuated, and back-filled with Ar. DMF (anhydrous, 1.0 mL) was added and stirred for 15 minutes. In a separate 25 mL Teflon™ screw-cap culture tube, **2** (174 mg, 0.25 mmol) and di-*t*Bubipy (67 mg, 0.25 mmol) were dissolved in DMF under Ar. The solution containing the activated ester was then added via syringe to the solution of **2** and di-*t*Bubipy at rt. The color of the reaction mixture slowly turned from red-yellow to clear green. After 3 h, the reaction was quenched with 1M HCl (2 mL), and Et₂O was added. The organic layer was dried over NaSO₄, filtered and concentrated. Column chromatography (hexanes:EtOAc 9:1) afforded 22 mg (60% yield) of compound **25** as a yellow oil.

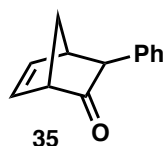


Left: HPLC chromatogram of **26** from the racemic acid. **Right:** from enantiopure acid.

Ring opening experiment



From NiCl₂·glyme: Following the General Procedure B with 1,3-dioxoisindolin-2-yl 5-oxotricyclo[2.2.1.0^{2,6}]heptane-3-carboxylate (59 mg, 0.20 mmol) and PhZnCl·LiCl complex (0.25 M in THF). Purification by column chromatography (pentane) afforded 25 mg (74%) of the rearranged product **35**.



3-Phenylbicyclo[2.2.1]hept-5-en-2-one

Physical State: yellow oil.

R_f = 0.42 (Hexanes:EtOAc 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.31 (m, 4H), 7.31 – 7.19 (m, 1H), 6.75 (dd, J = 5.6, 2.8 Hz, 1H), 6.30 (t, J = 4.4 Hz, 1H), 3.43 (s, 1H), 3.26 (d, J = 3.5 Hz, 1H), 3.17 – 3.06 (m, 1H), 2.34 (d, J = 9.7 Hz, 1H), and 2.29 – 2.17 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 214.1, 143.7, 138.1, 132.9, 128.5, 127.8, 126.6, 55.6, 49.3, 47.3, and 46.0.

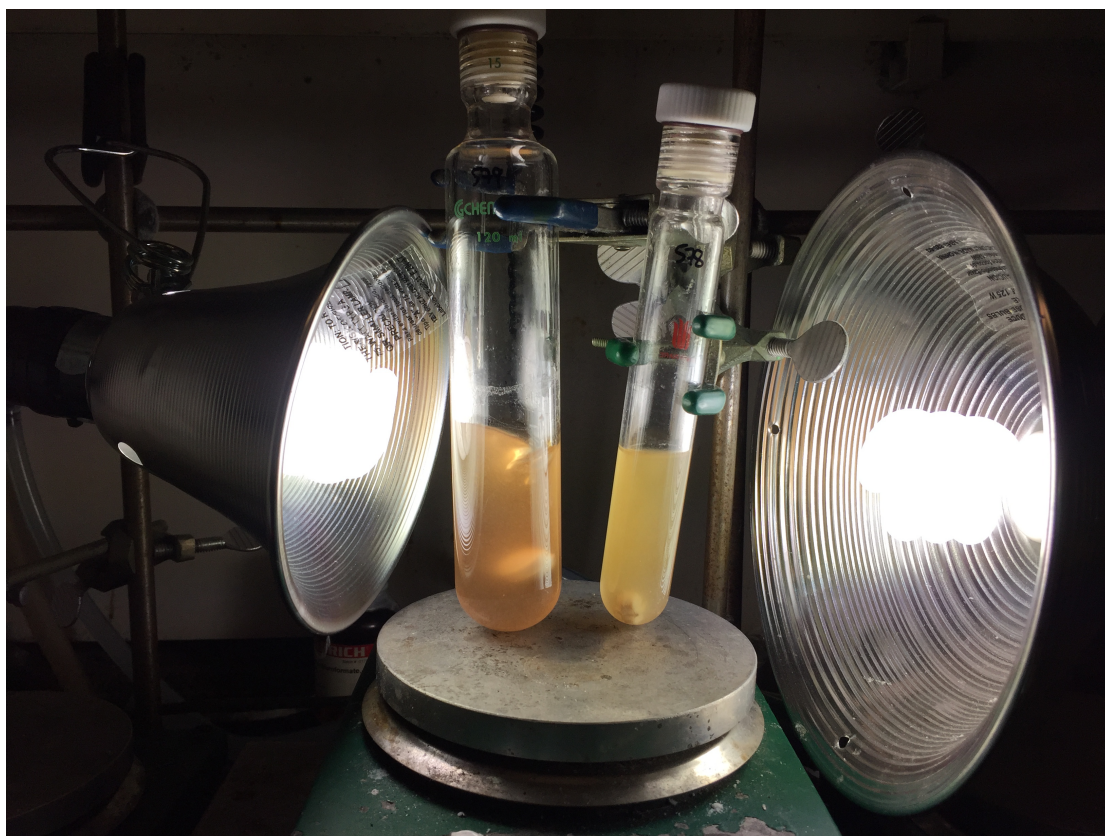
HRMS (ESI-TOF): calc'd for $\text{C}_{15}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 185.0961; found 185.0961.

TEMPO experiment

An oven-dried test tube containing a stirring bar was charged with $\text{NiCl}_2\cdot\text{glyme}$ (20 mol %), di-*t*Bubipy (40 mol %), TEMPO (39 mg, 0.1 mmol), and 2-ethylhexanoic phthalimide ester (0.1 mmol, 1.0 equiv). The tube was sealed evacuated and back-filled with Ar. DMF was then added via syringe and the mixture stirred for 2 minutes at rt. Then, $\text{PhZnCl}\cdot\text{LiCl}$ (0.21 M in THF) was added at rt and the mixture was stirred for 14 – 16 h at rt. The mixture was then diluted with EtOAc (2 mL) and a solution of HCl (1 M). No trace of product **3** was detected after evaporation of the organic layer and analysis using GC/MS).

Photocatalysis and Nickel catalysis

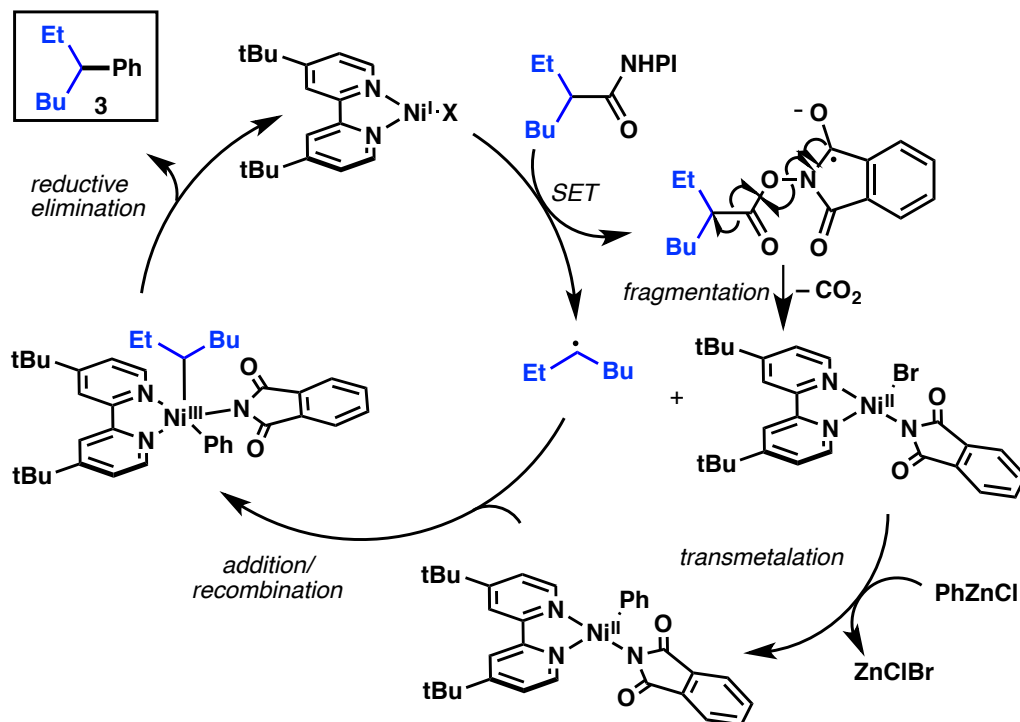
A 50 mL pyrex glass high-pressure tube was charged with $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbpy}))\text{PF}_6$ (4.5 mg, 0.004 mmol), $\text{NiCl}_2\cdot\text{glyme}$ (8.8 mg, 0.04 mmol), di-*tert*-butylbipyridine (16 mg, 0.06 mmol), 4-chloro-1-iodobenzene (95 mg, 0.4 mmol), anhydrous Cs_2CO_3 (195 mg, 0.6 mmol) and 2-ethylhexanoic acid (0.6 mmol) and dissolved in 20 mL of anhydrous DMF. The mixture was then sparged with Ar for 30 minutes and then sealed under Ar. The tube was then placed in a stirring plate and irradiated with two 60 W lamps for 3 days (72 h). After this time, the mixture was quenched with Na_2CO_3 saturated and extracted with Et_2O (20 mL x 4). No trace of product **8** was detected after evaporation of the organic layer and analysis by GC/MS and NMR.



(Left) Performed with 0.8 mmol of aryl iodide (40 mL DMF). **Right:** reaction performed with 0.4 mmol of aryl iodide (20 mL DMF).

Alternative mechanism for the Ni-catalyzed decarboxylative arylation of secondary carboxylic activated esters and arylzinc reagents.

A. Bimetallic

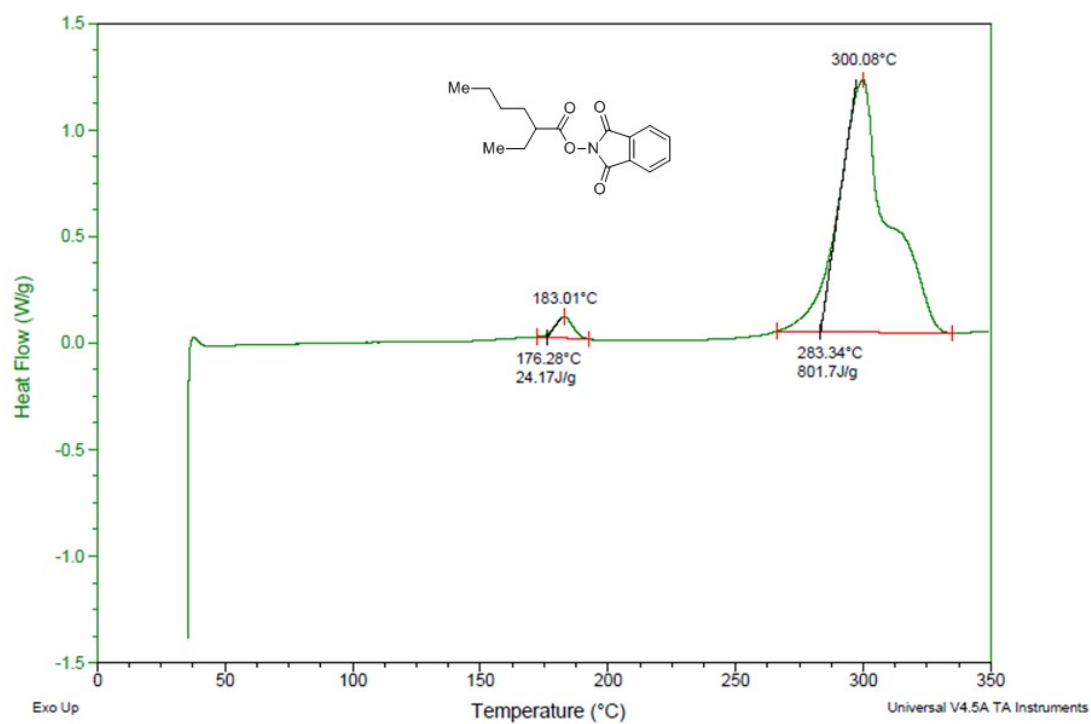


At present, a putative mechanism based on a bimetallic system where Ni(I) species act as radical carrier as proposed by Fu *et al* could not be ruled out.⁸

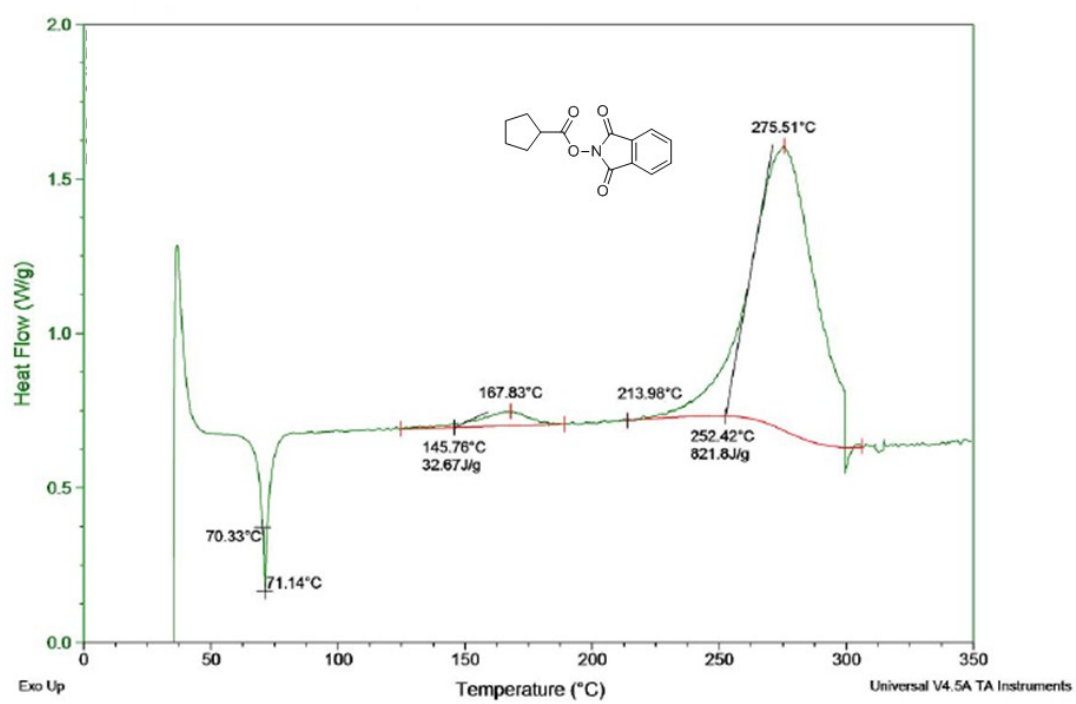
Differential Scanning Calorimetry of NHPI-Esters.

Both esters were stable well within the reaction operating ranges. The cyclopentyl substrate showed a small onset at 145.76 deg C (32.76 J/g), then a much larger one at 213.98 °C (821.8 J/g). The exact melting point was at 71.14 °C. The 2-ethylhexanoyl substrate showed a similar pattern; a small onset at 176.28 °C (24.17 J/g), then a larger one at 283.34 °C (801.7 J/g).

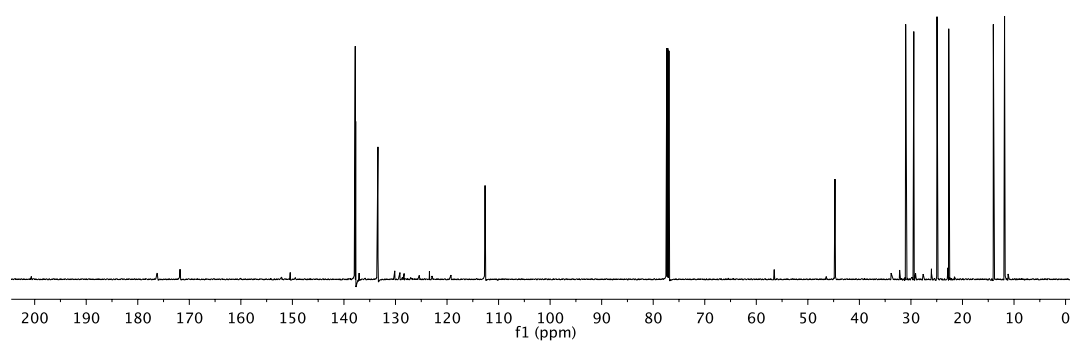
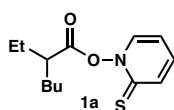
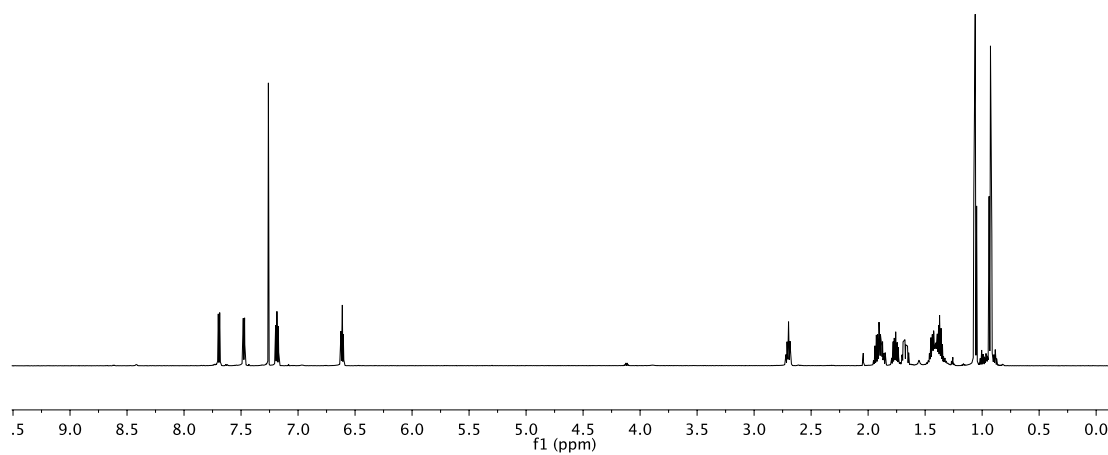
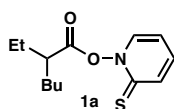
DSC

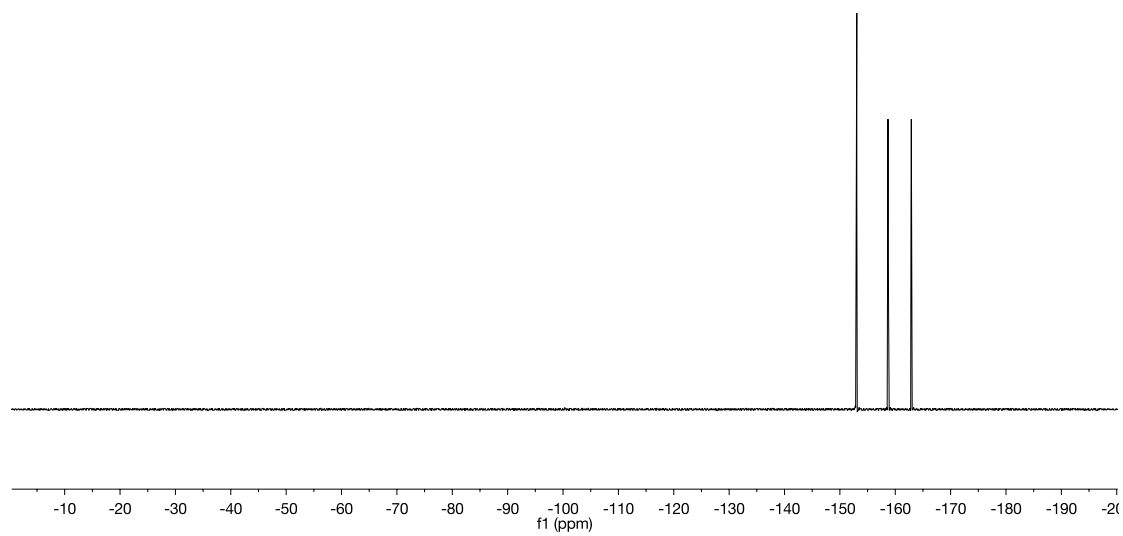
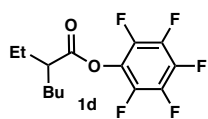
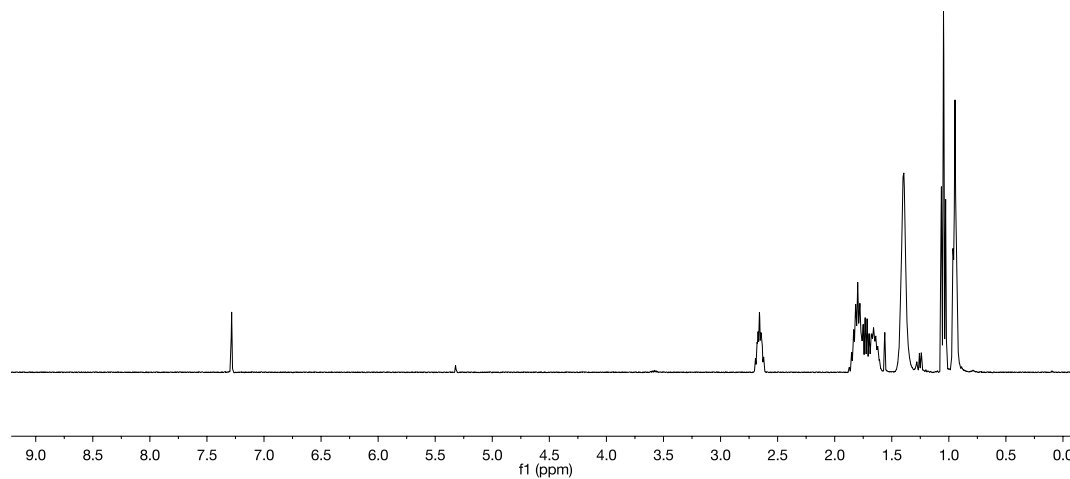
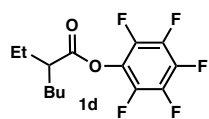


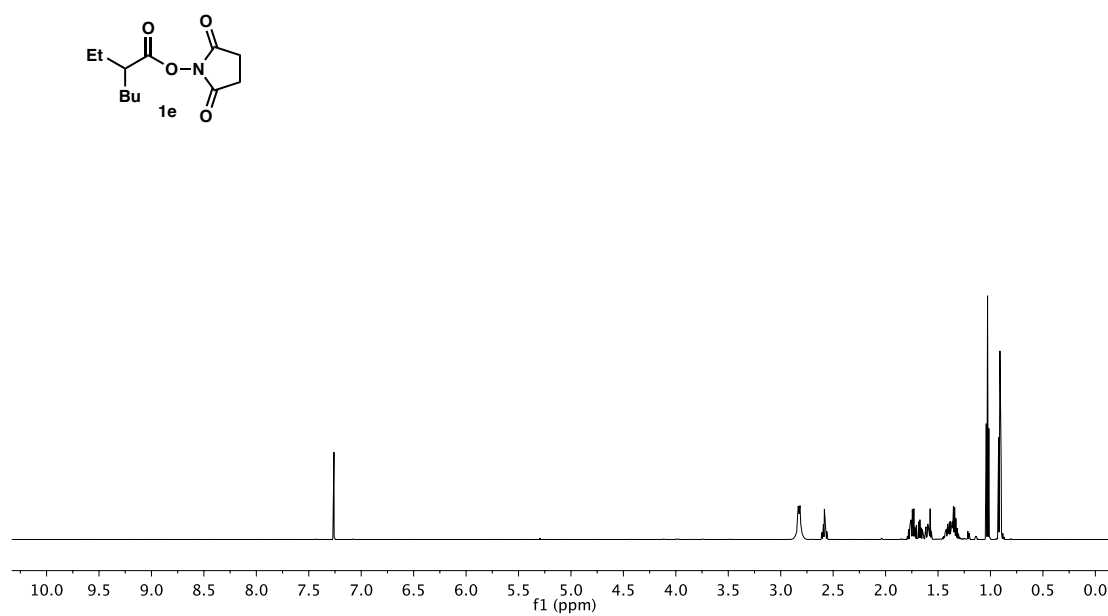
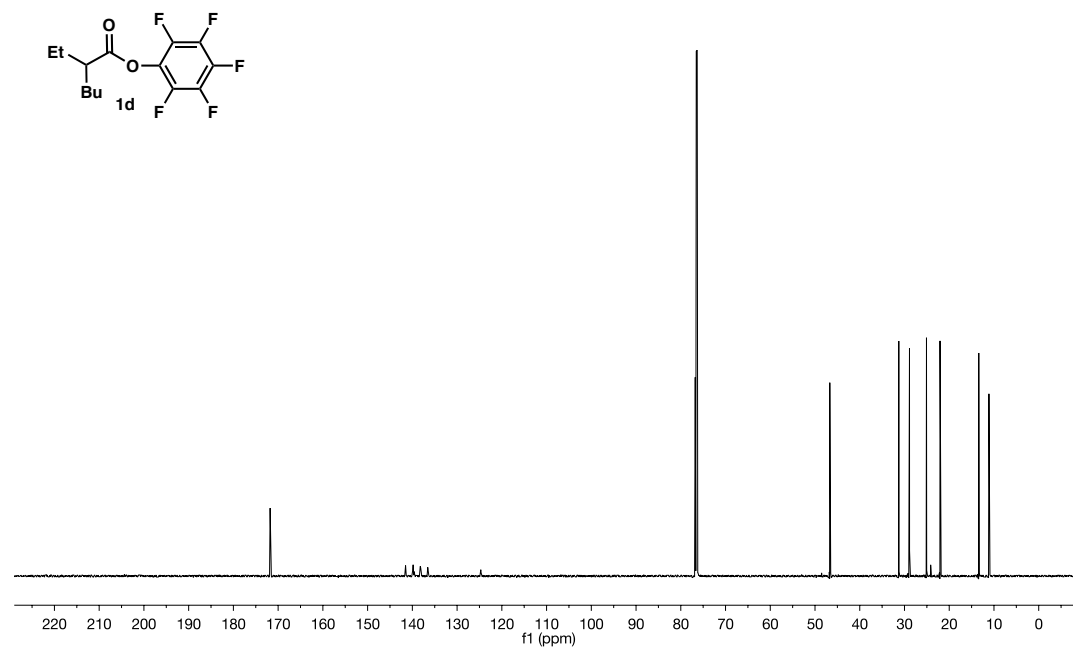
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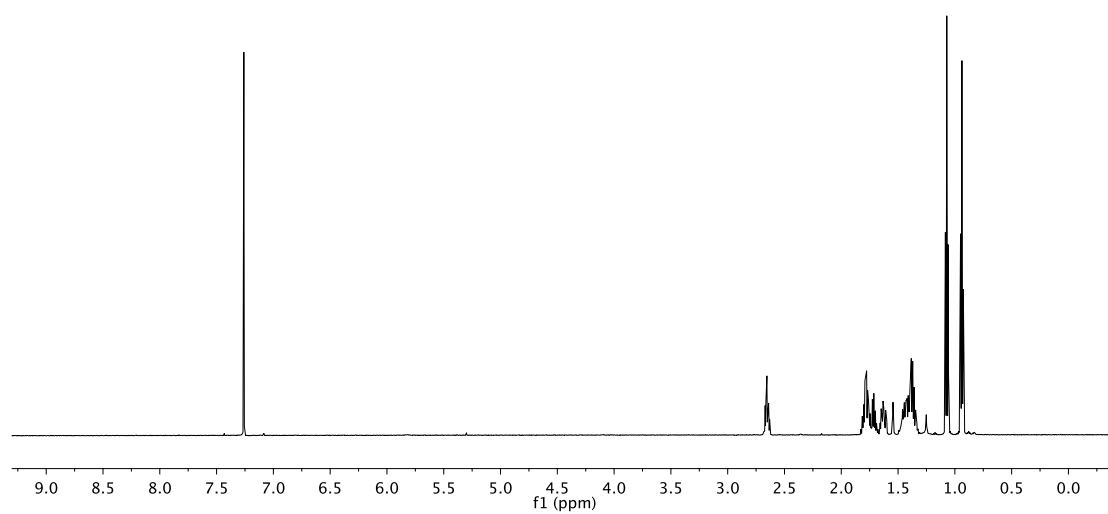
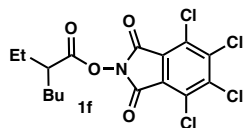
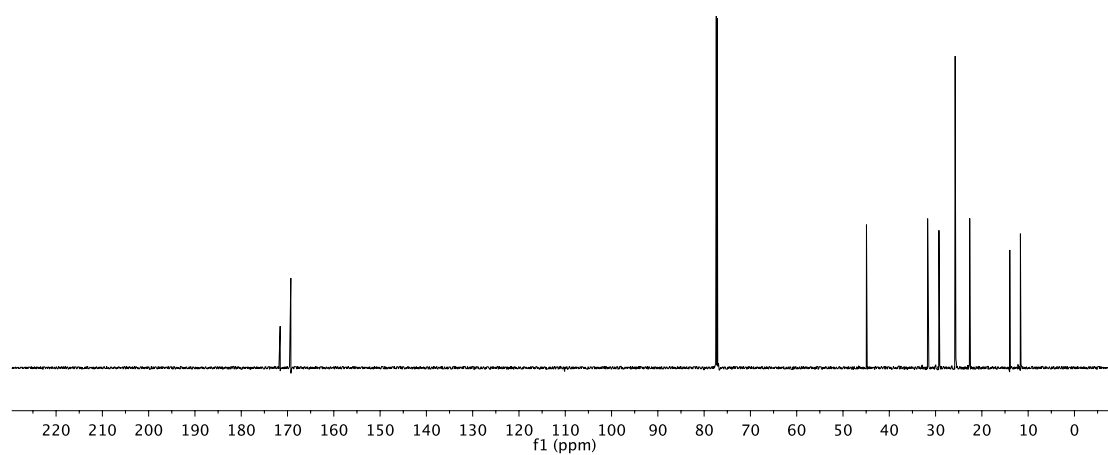
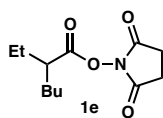


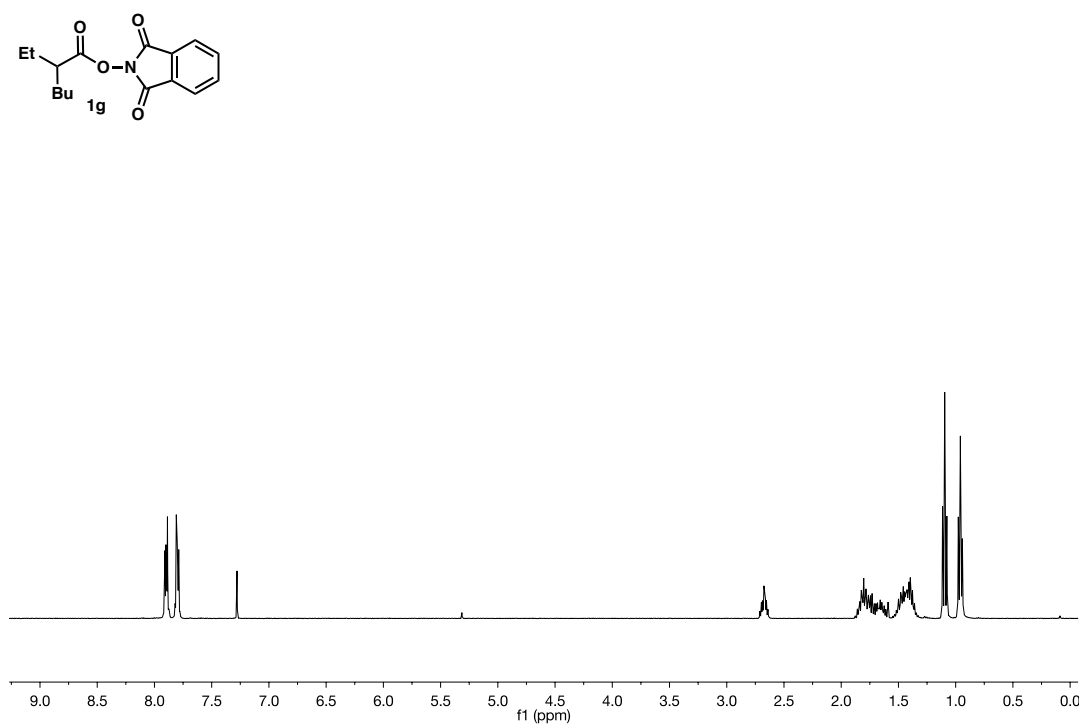
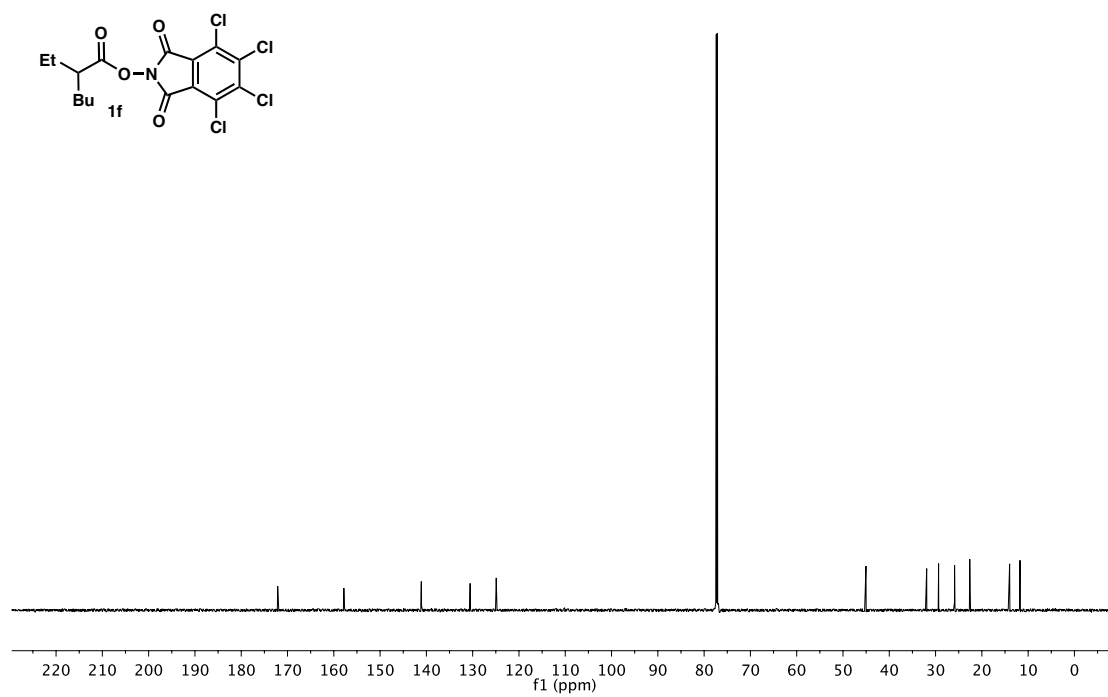
NMR Spectra

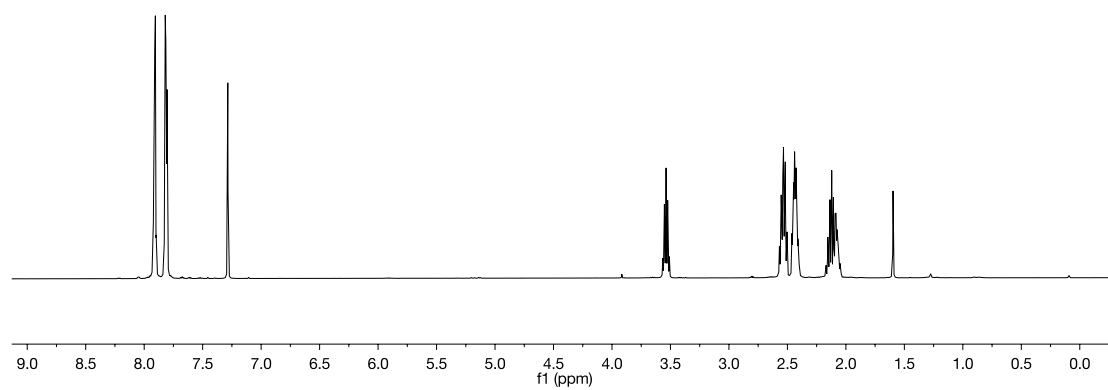
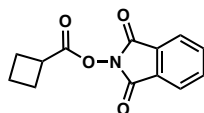
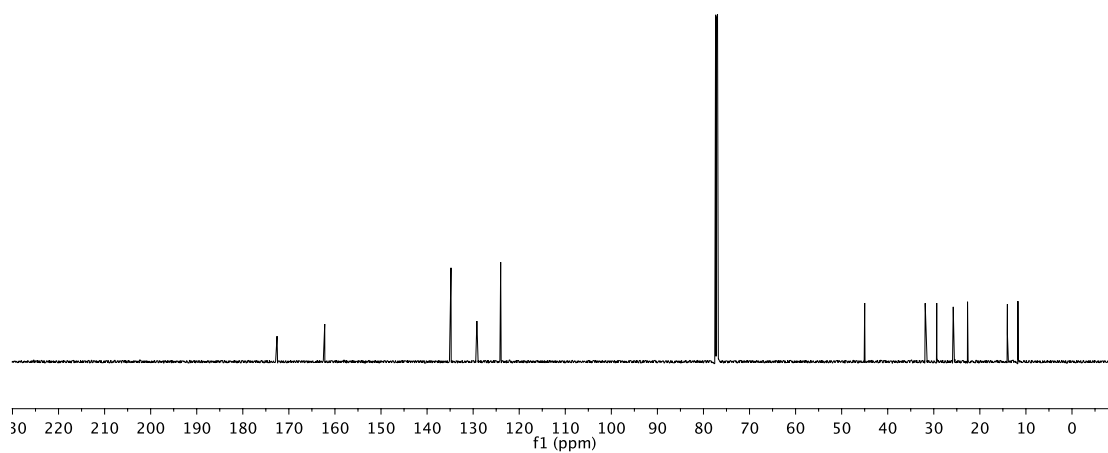
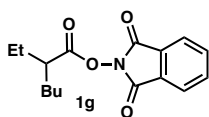


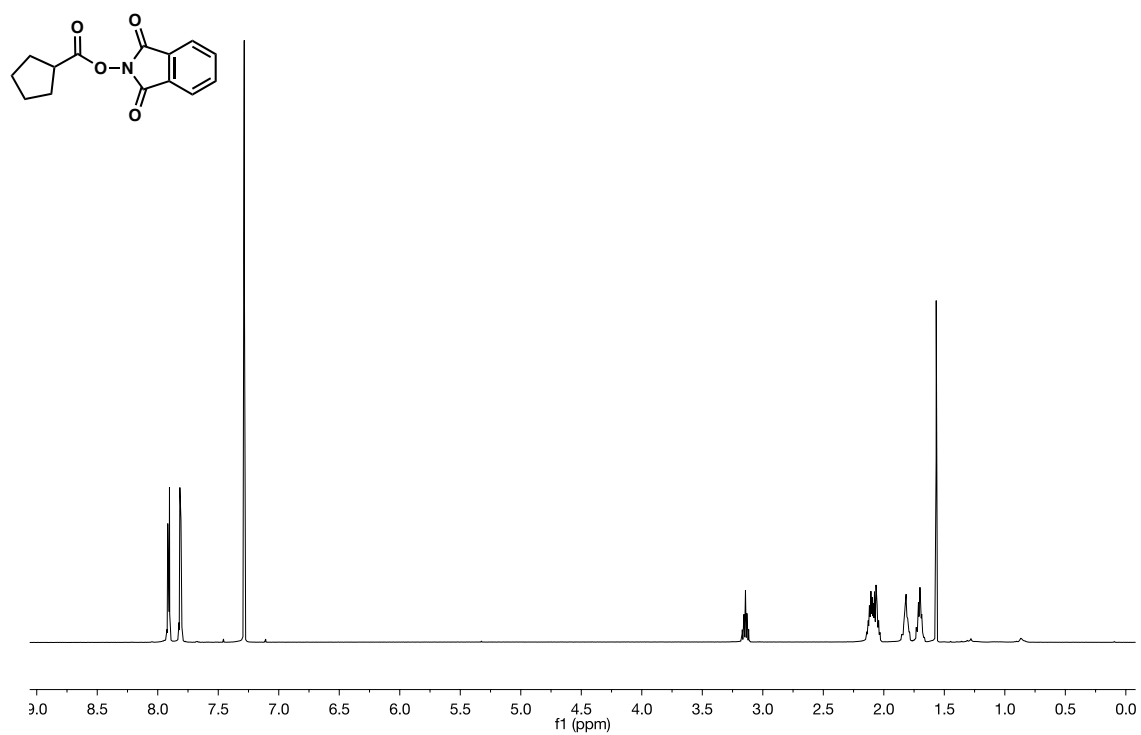
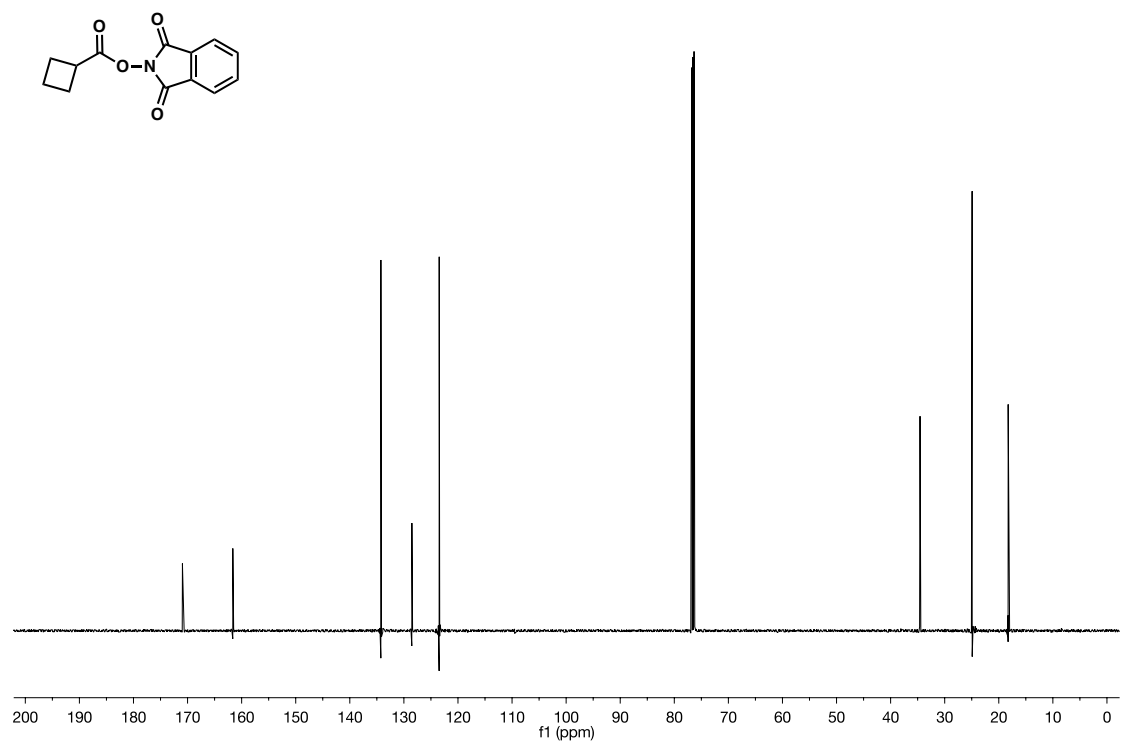


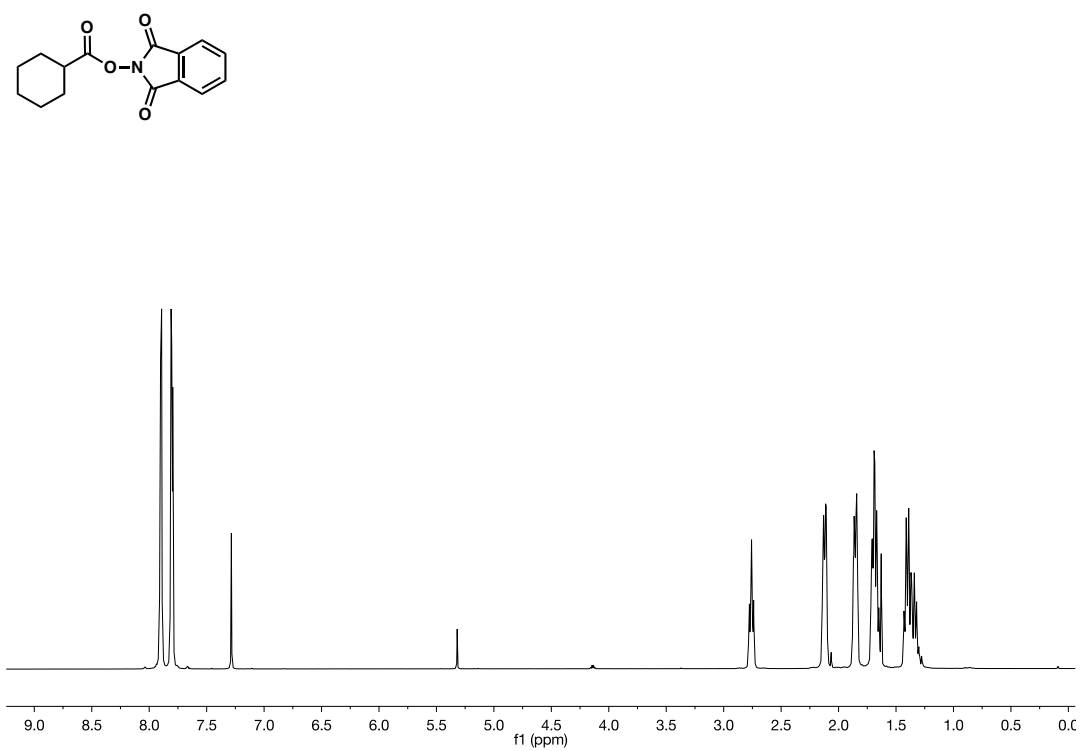
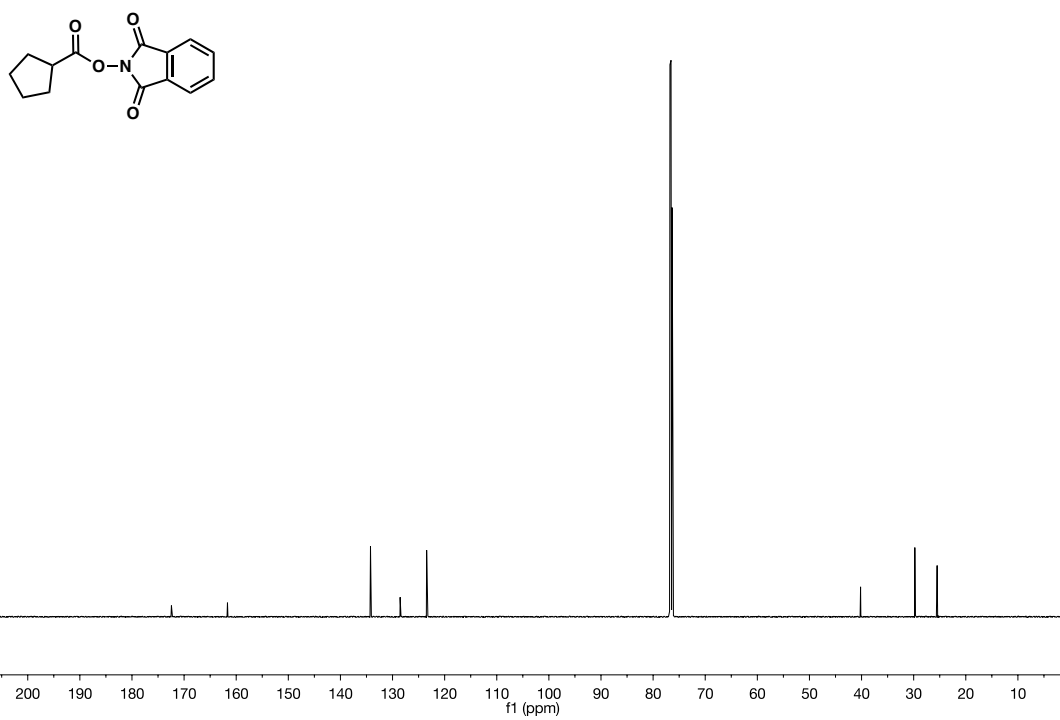


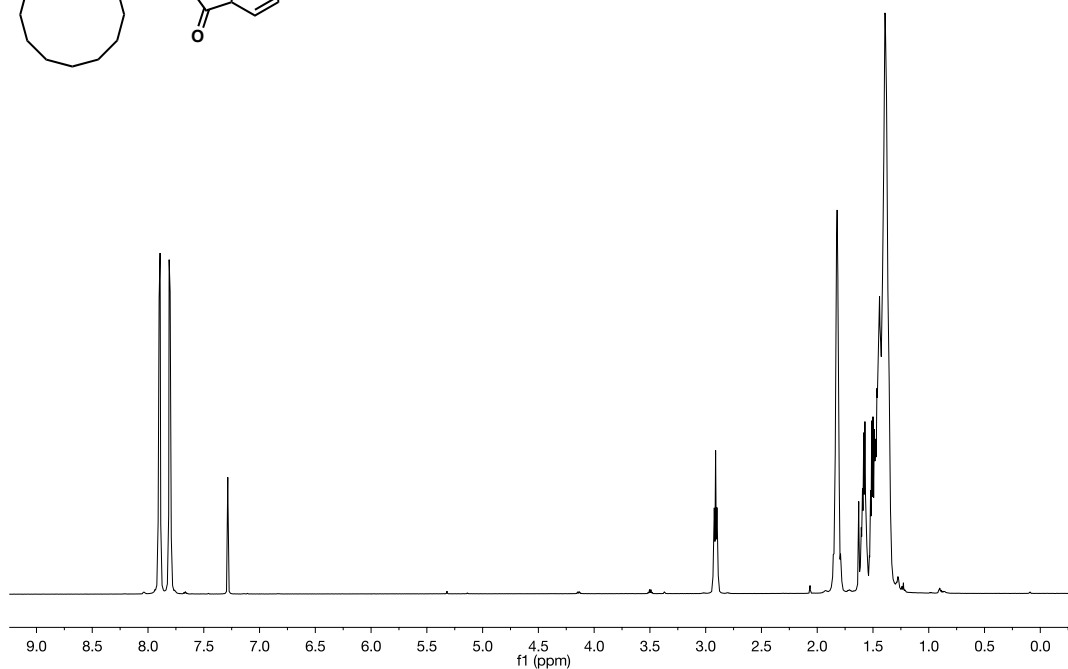
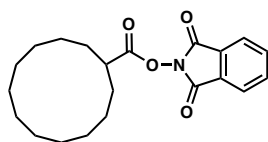
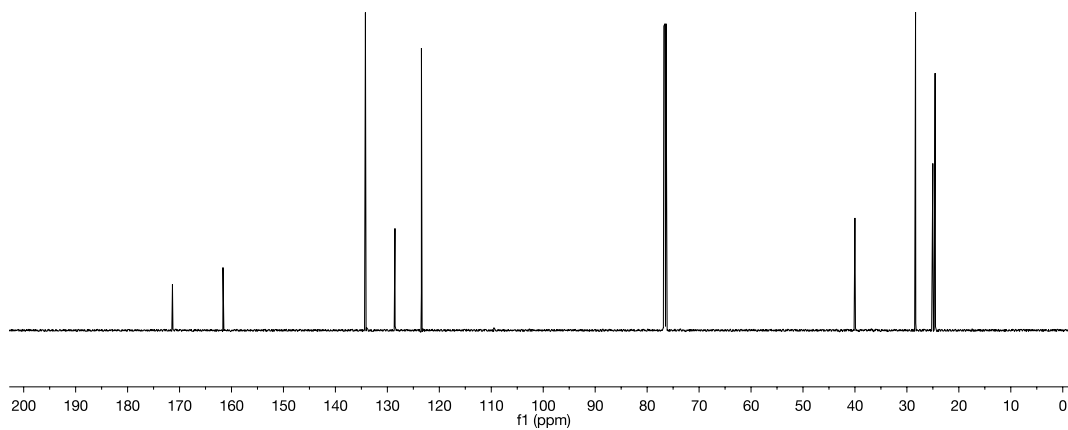
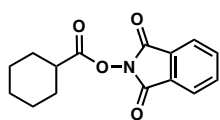


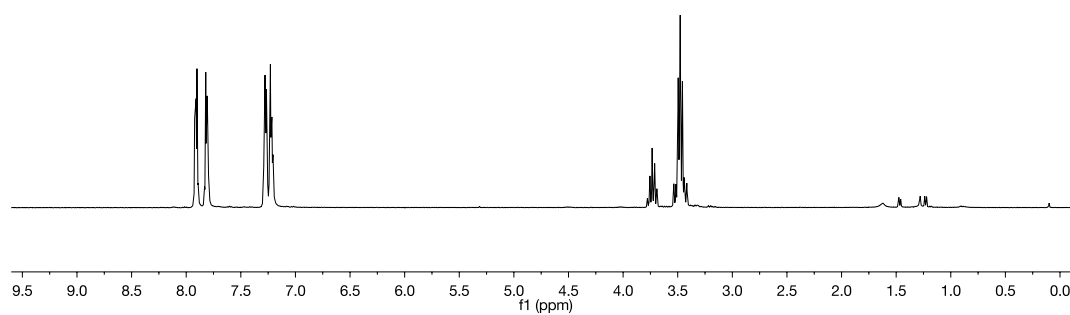
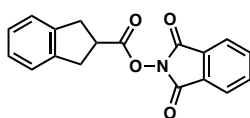
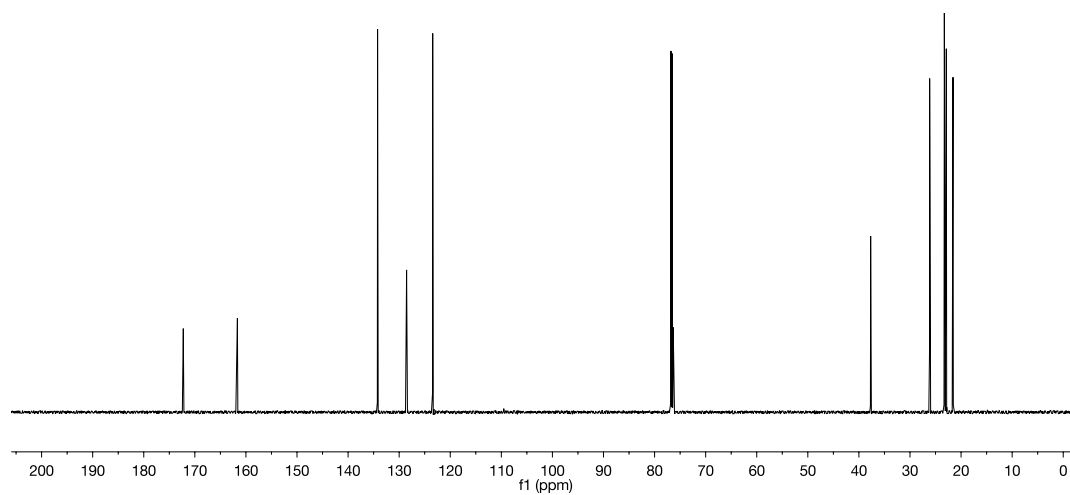
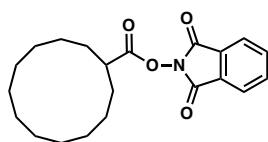


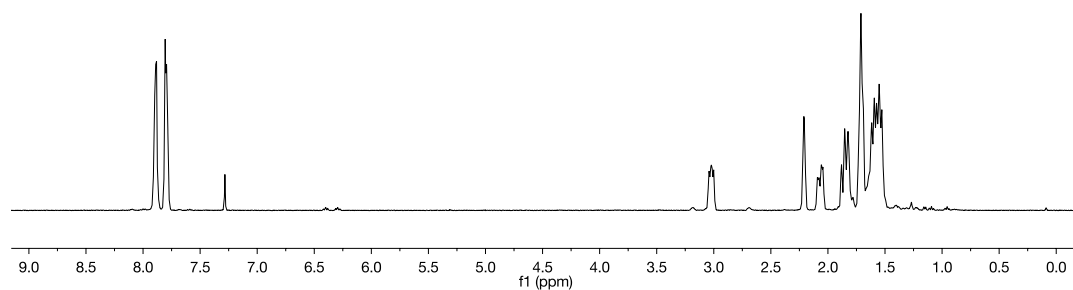
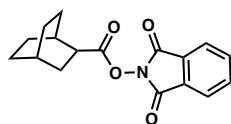
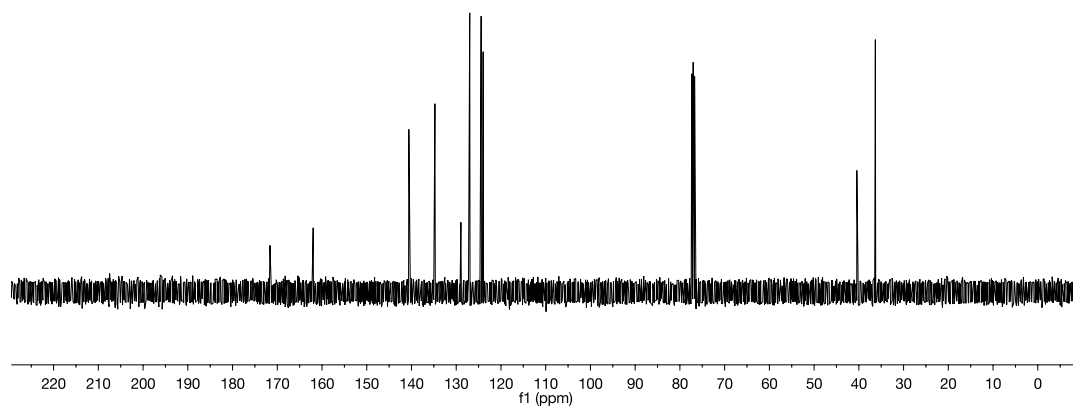
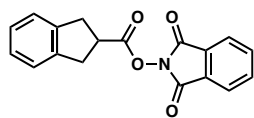


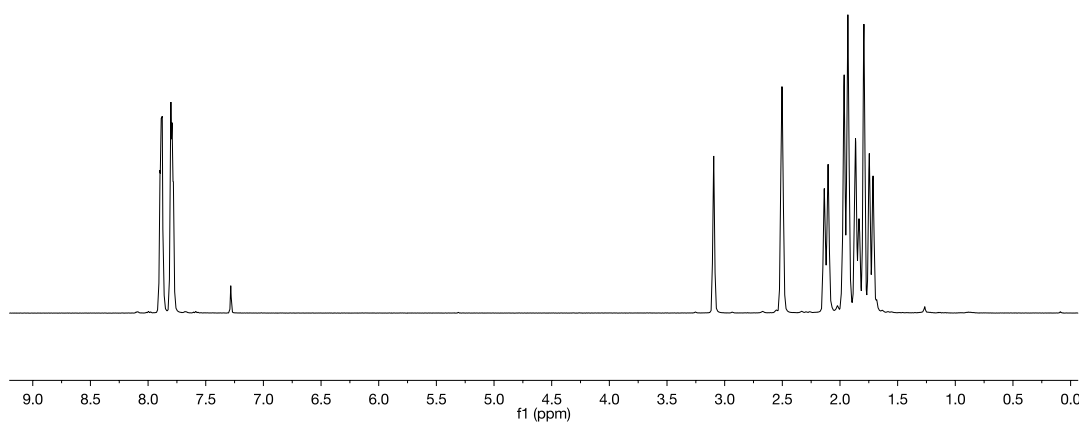
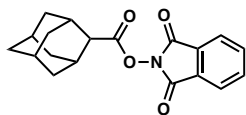
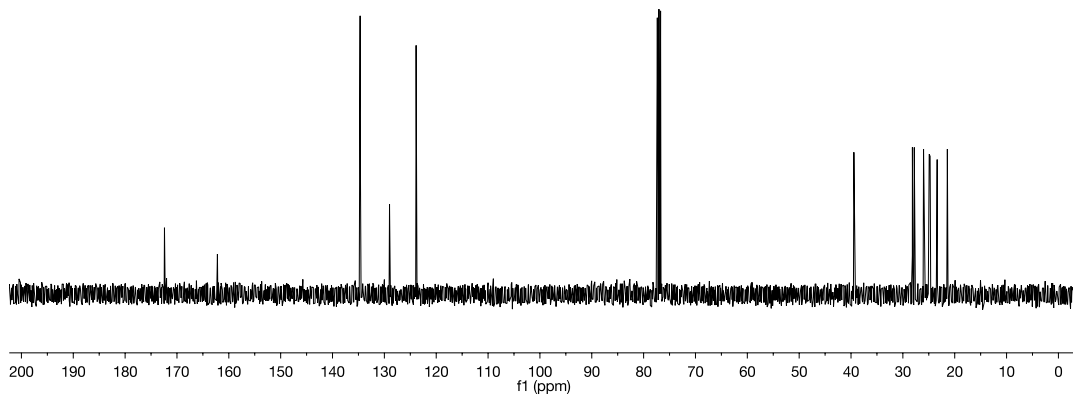
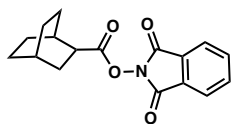


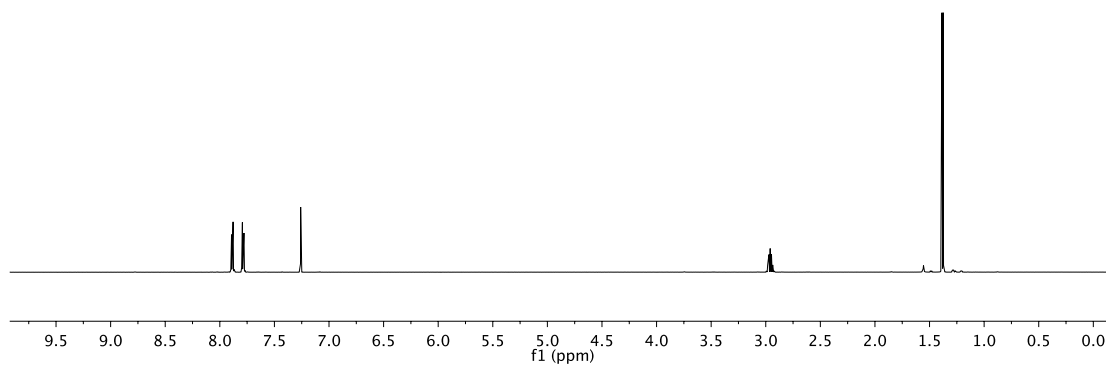
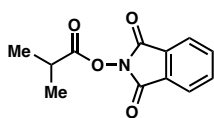
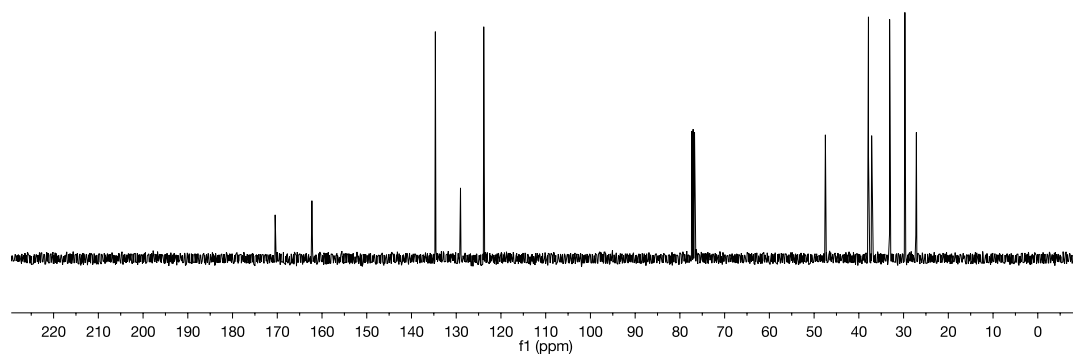
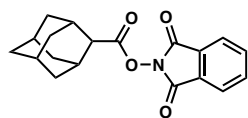


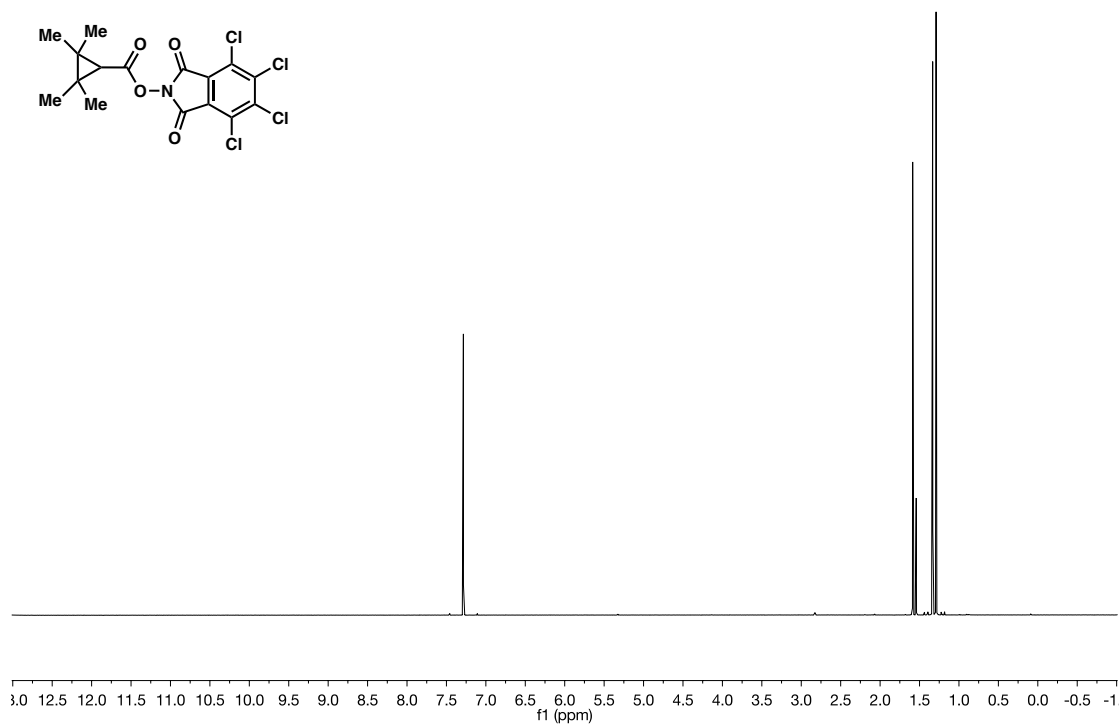
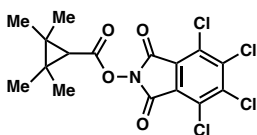
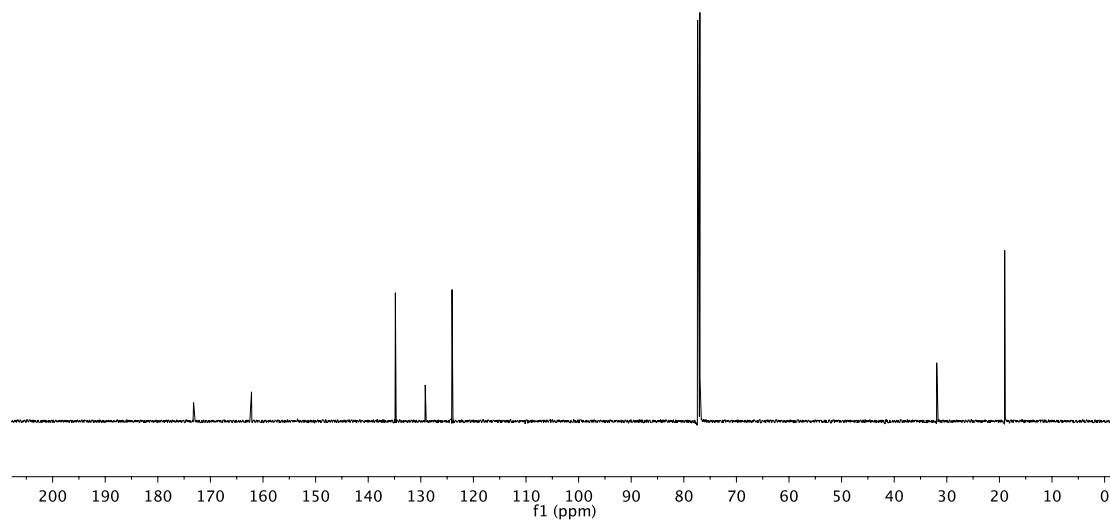
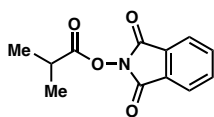


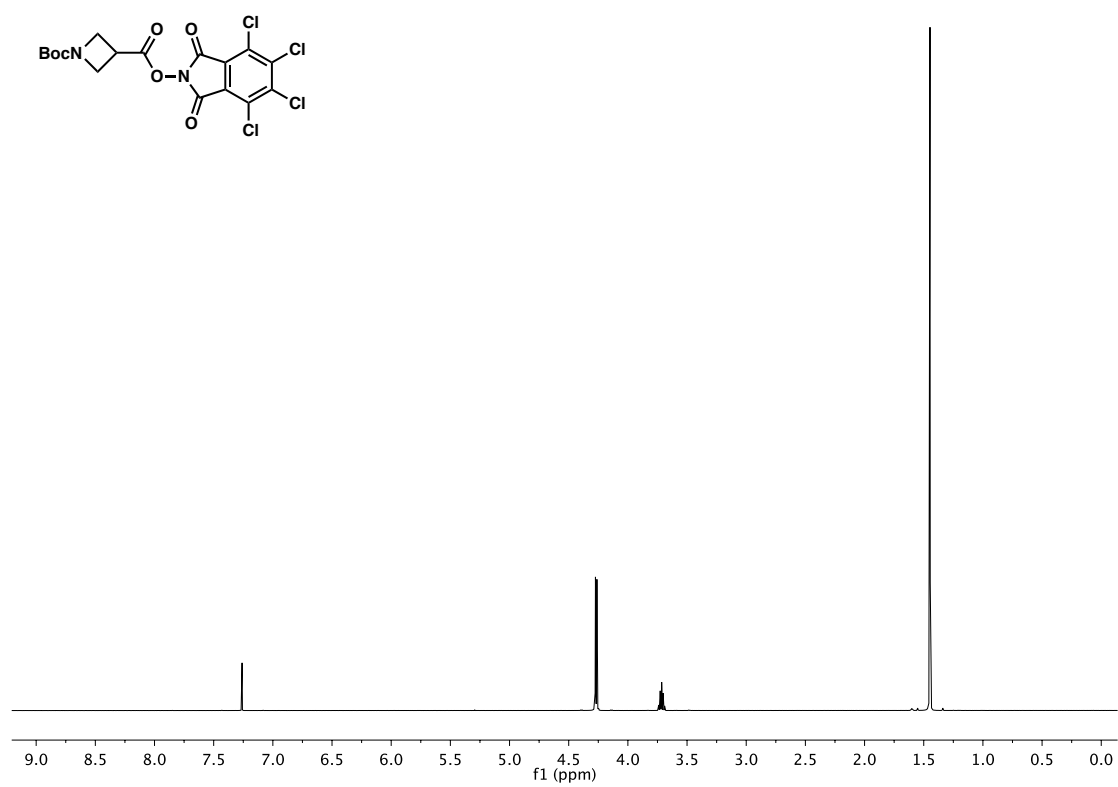
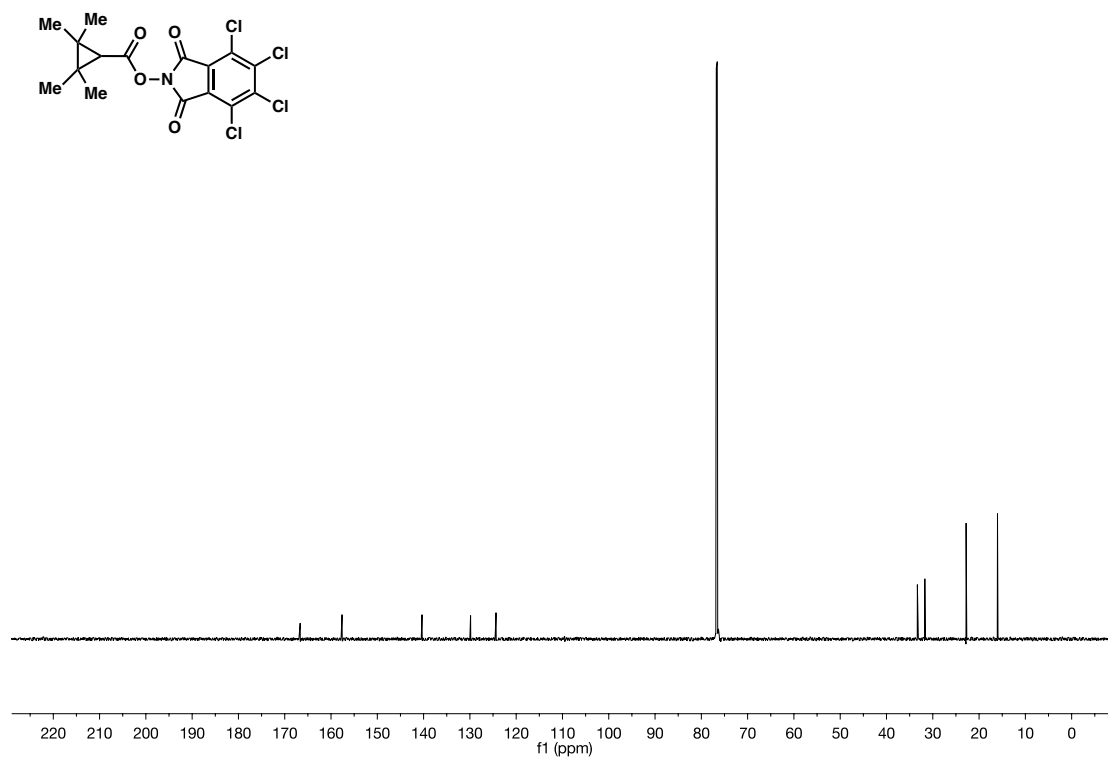


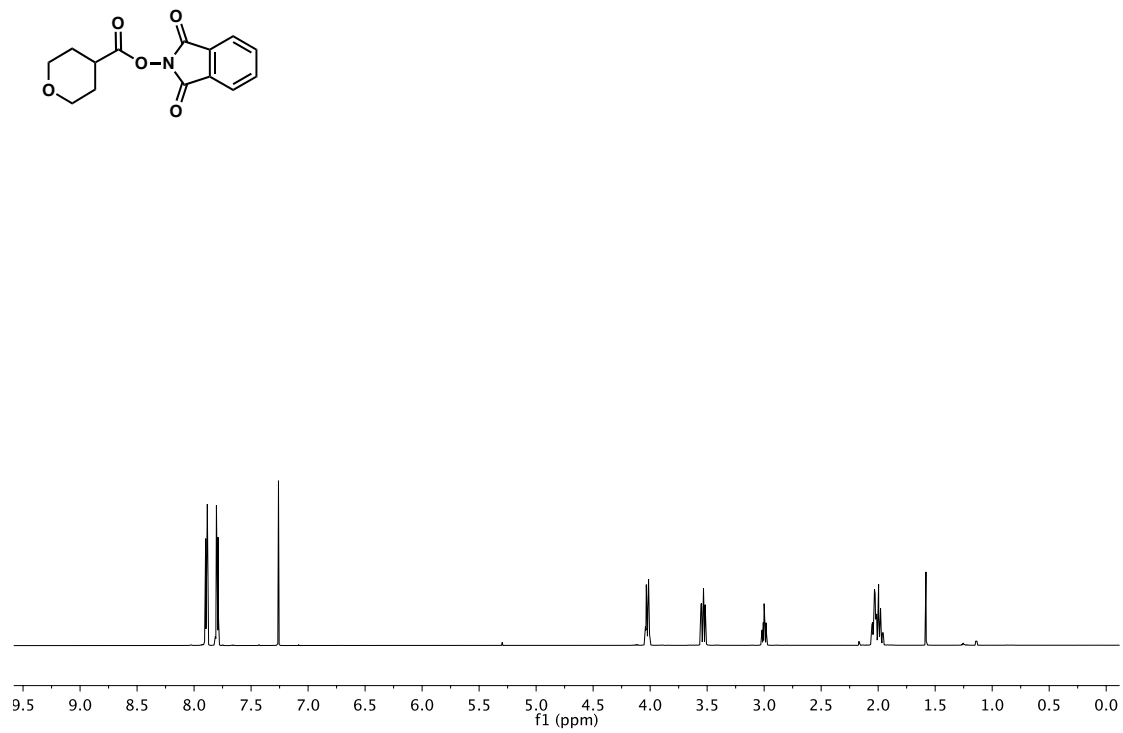
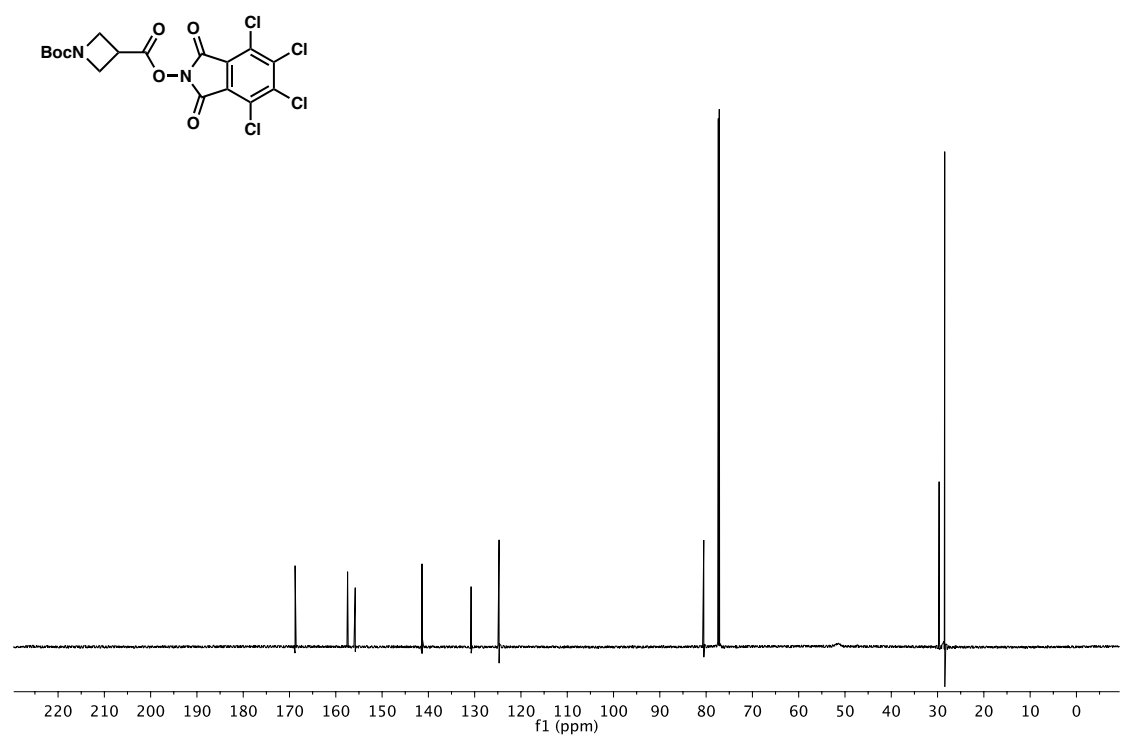


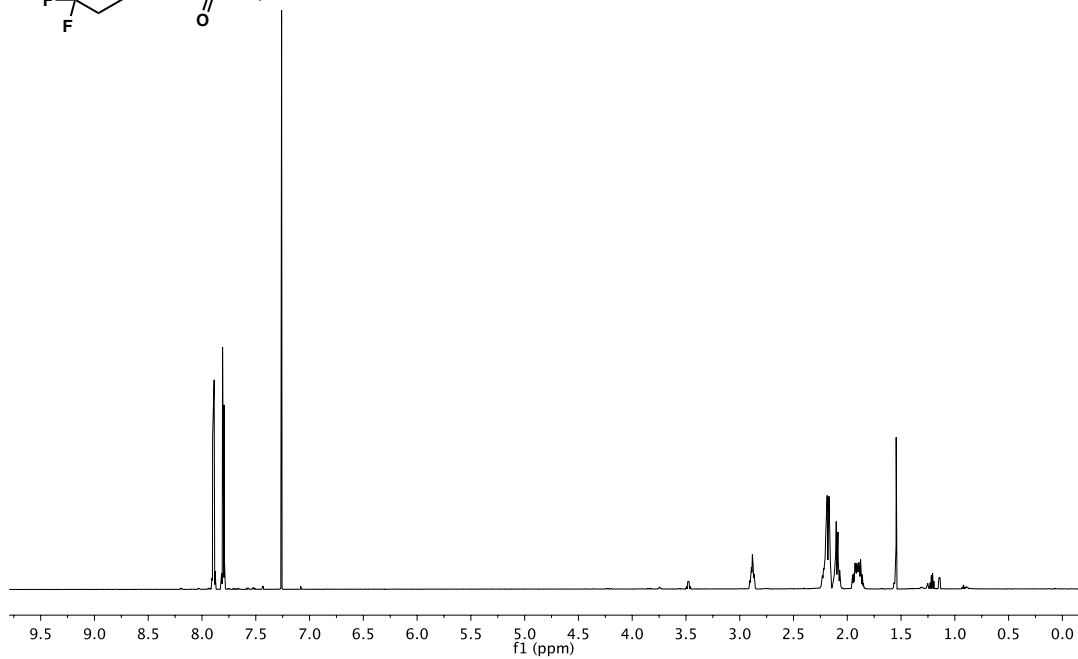
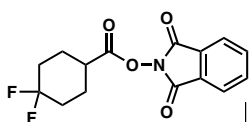
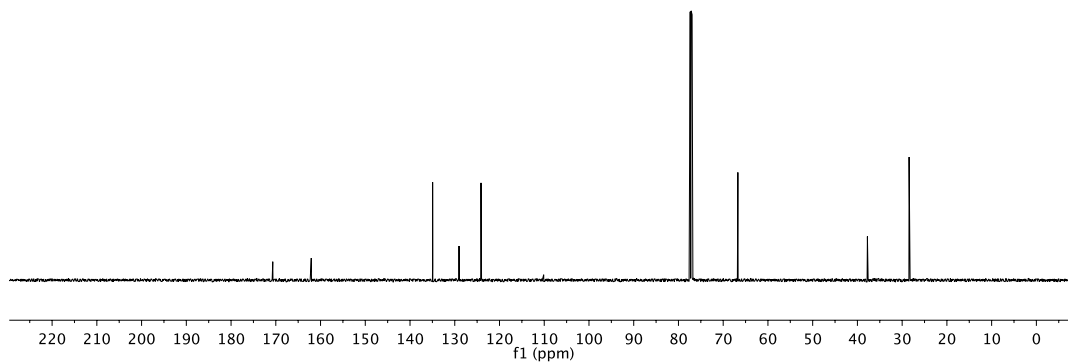
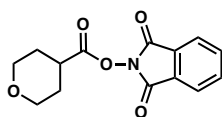


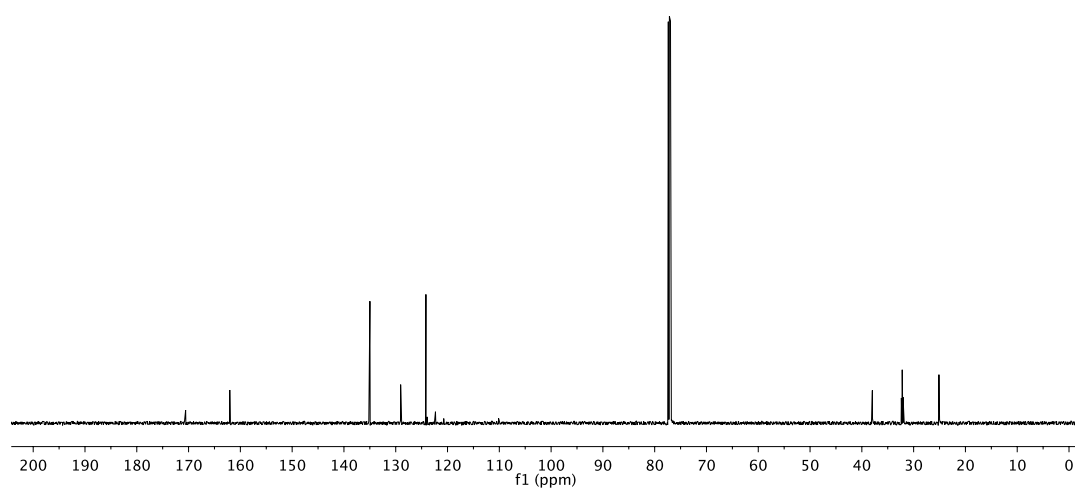
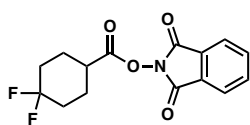
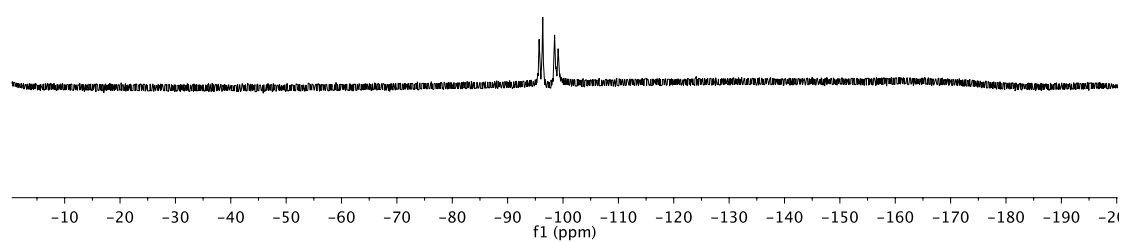
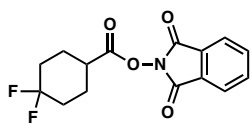


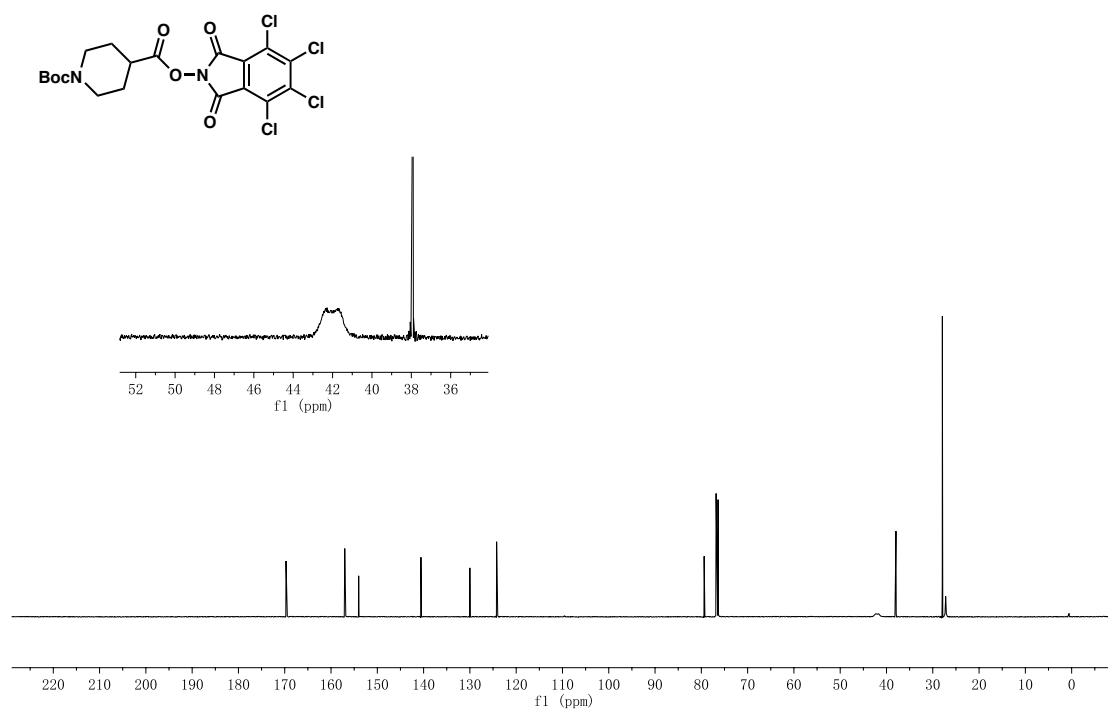
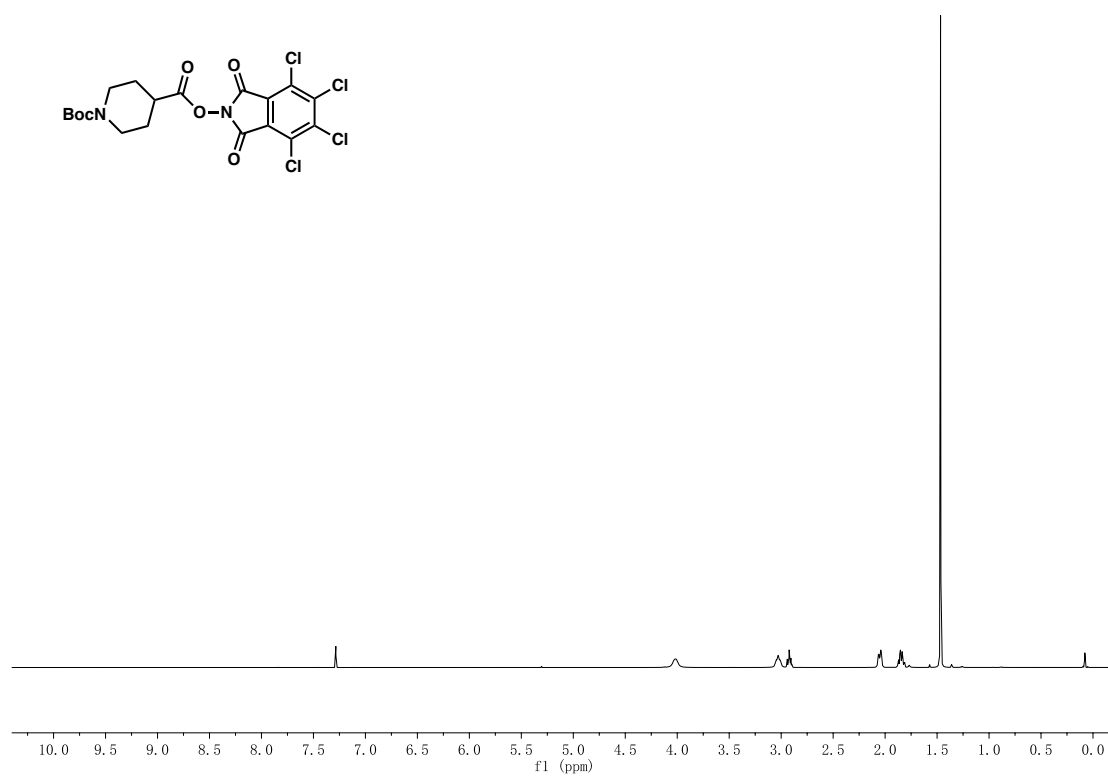


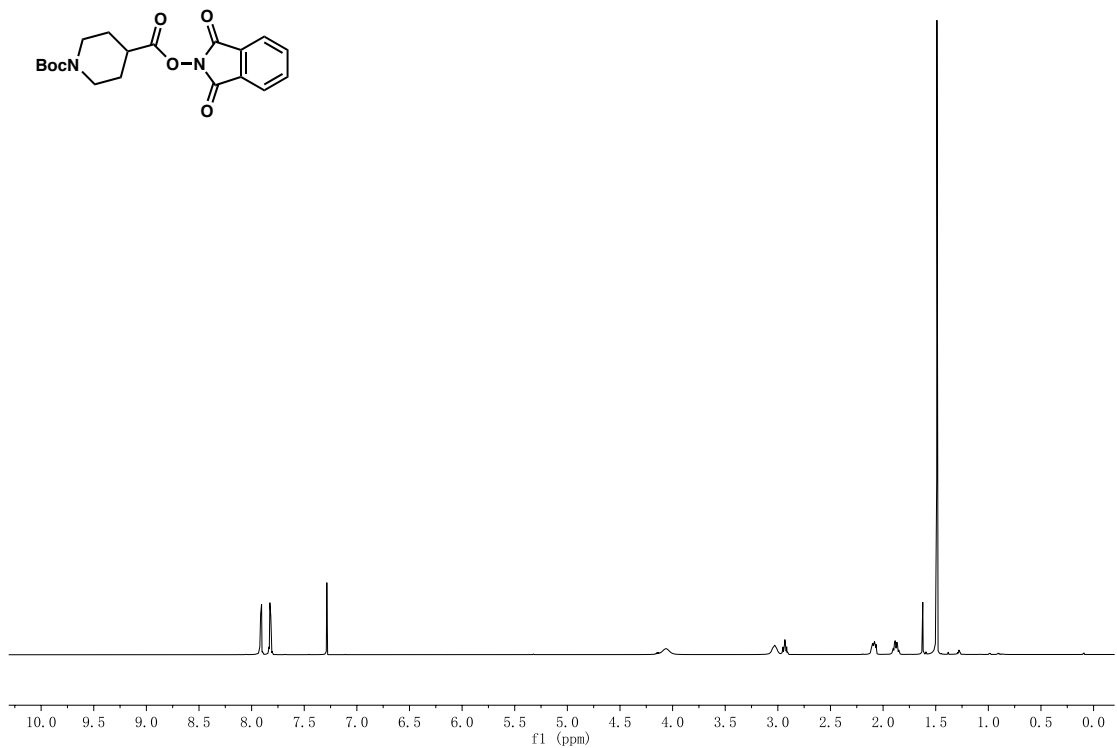
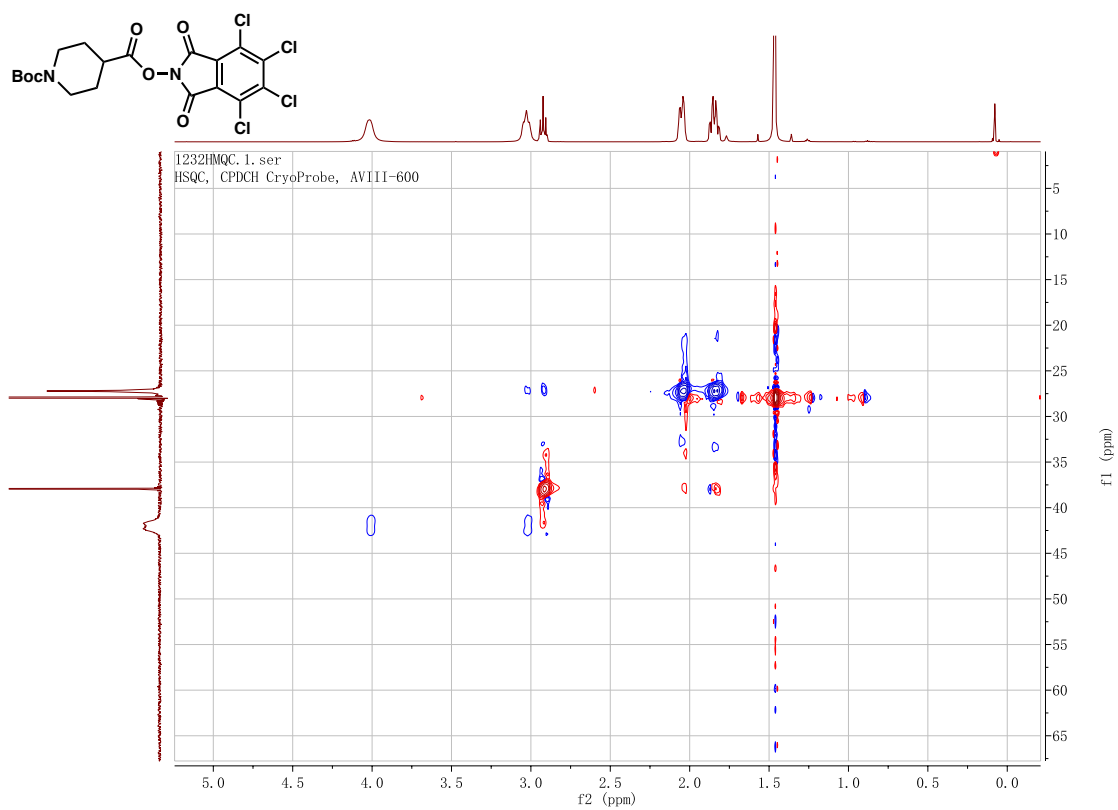


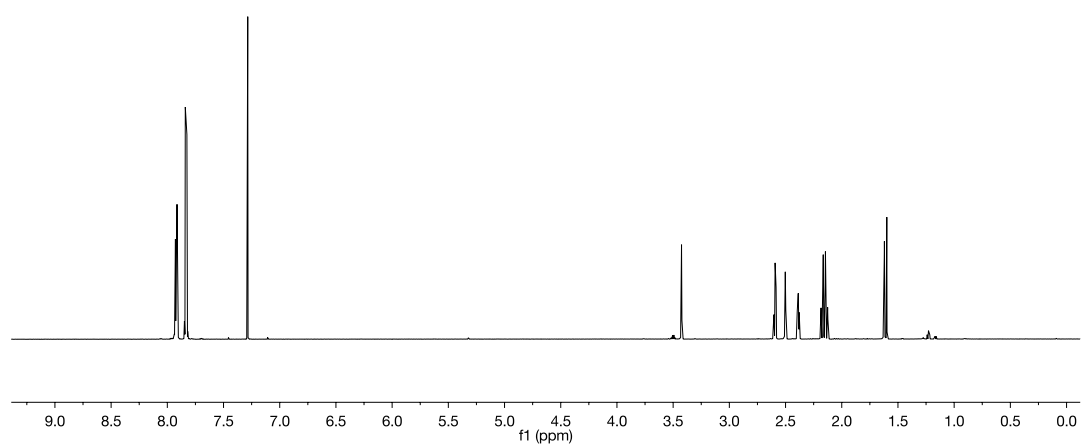
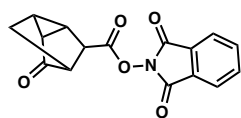
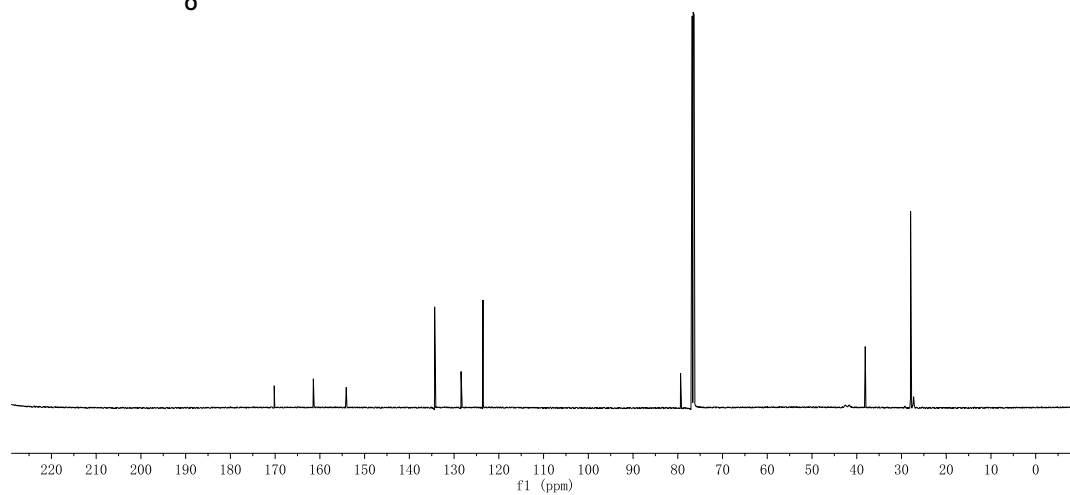
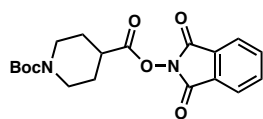


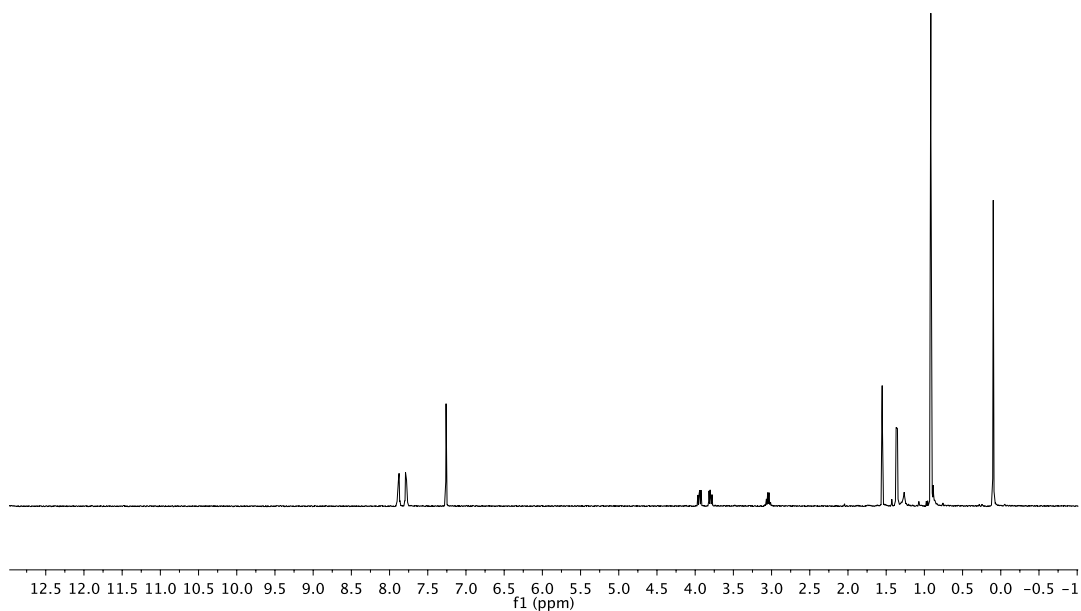
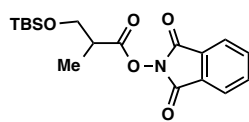
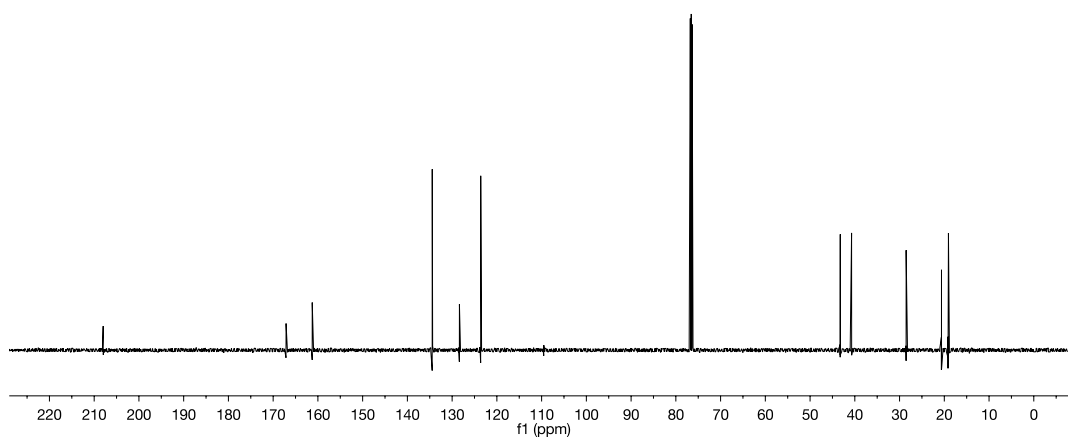
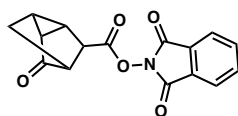


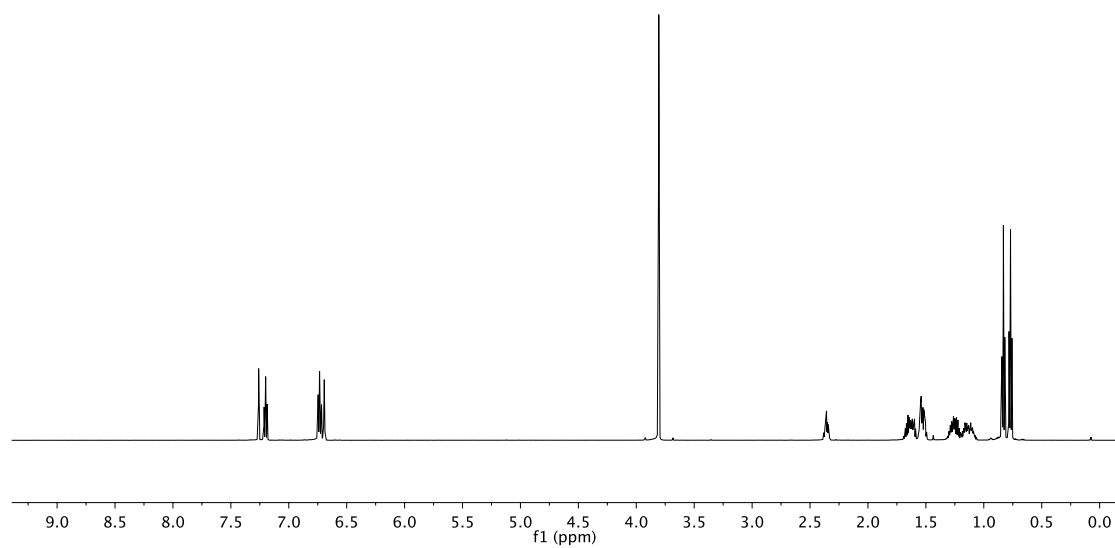
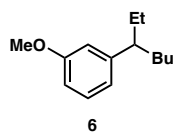
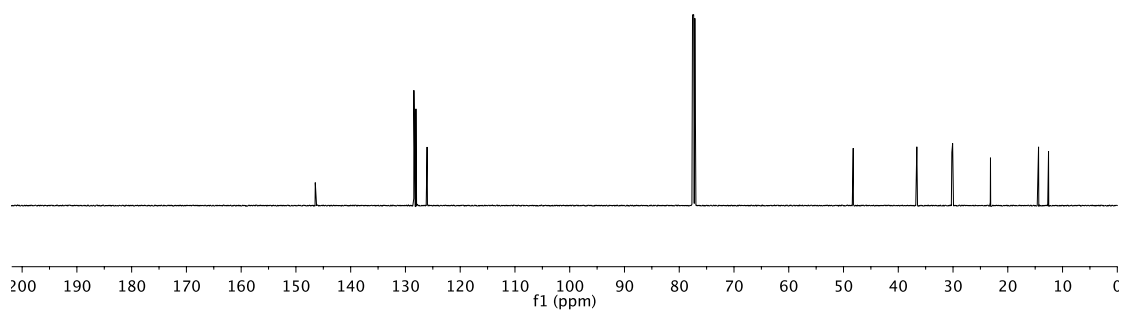
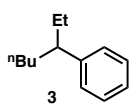


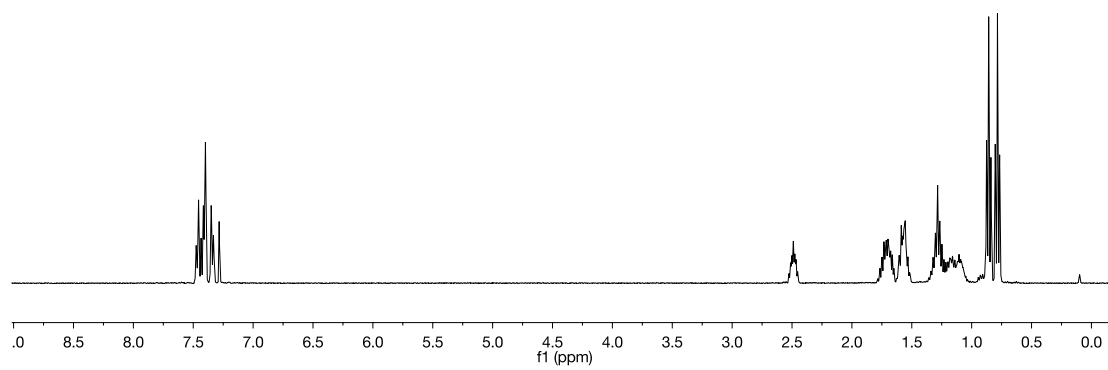
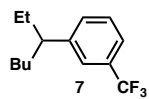
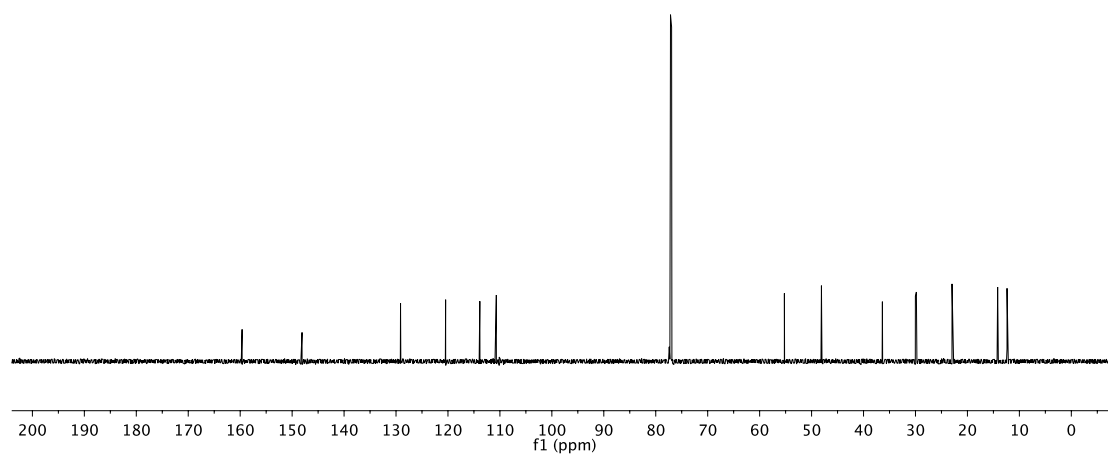
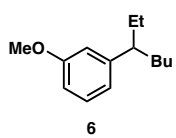


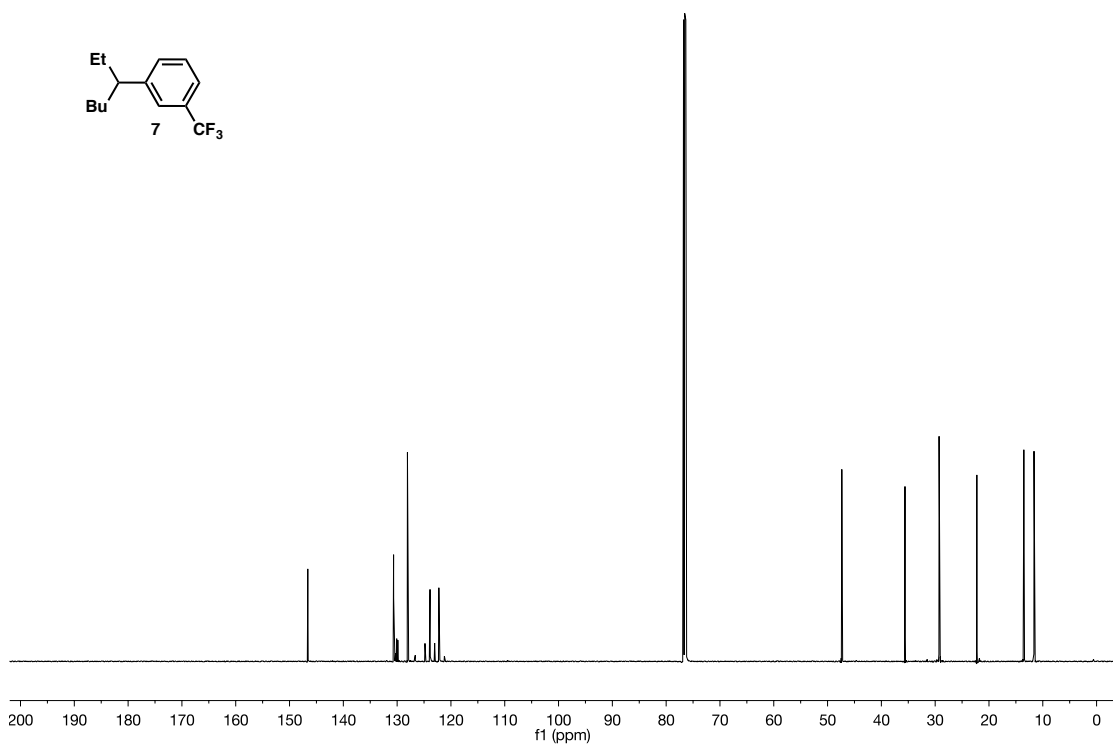
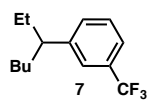
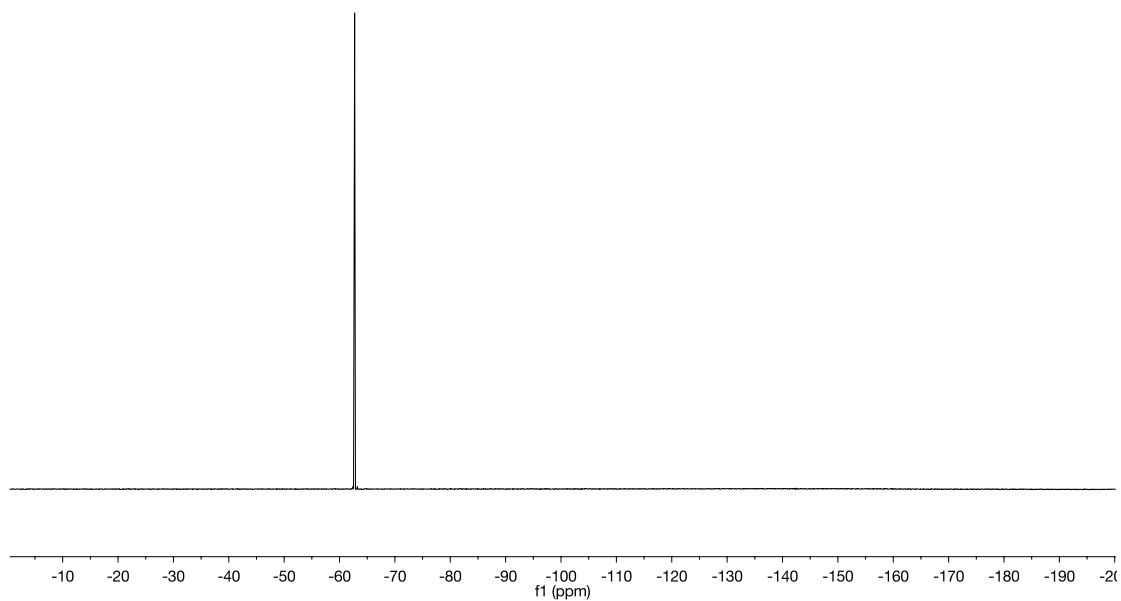
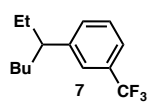


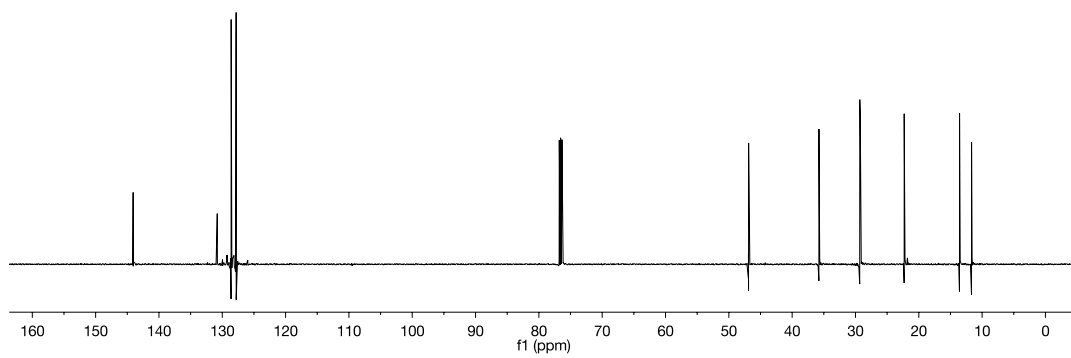
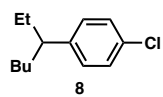
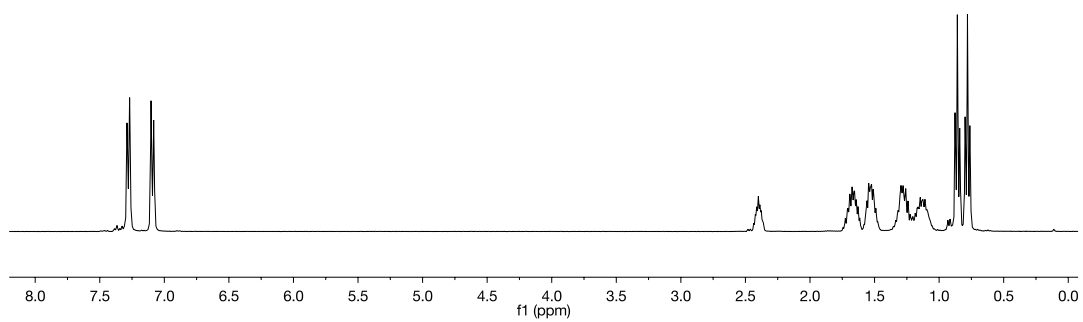
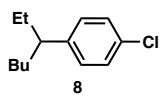


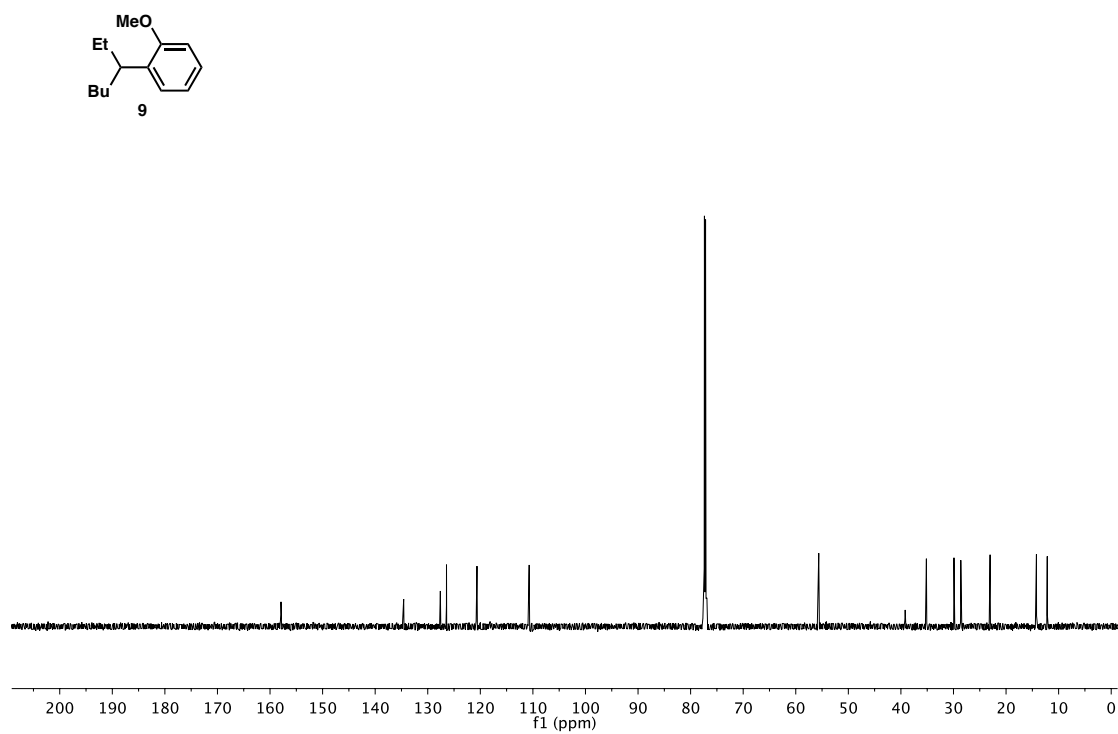
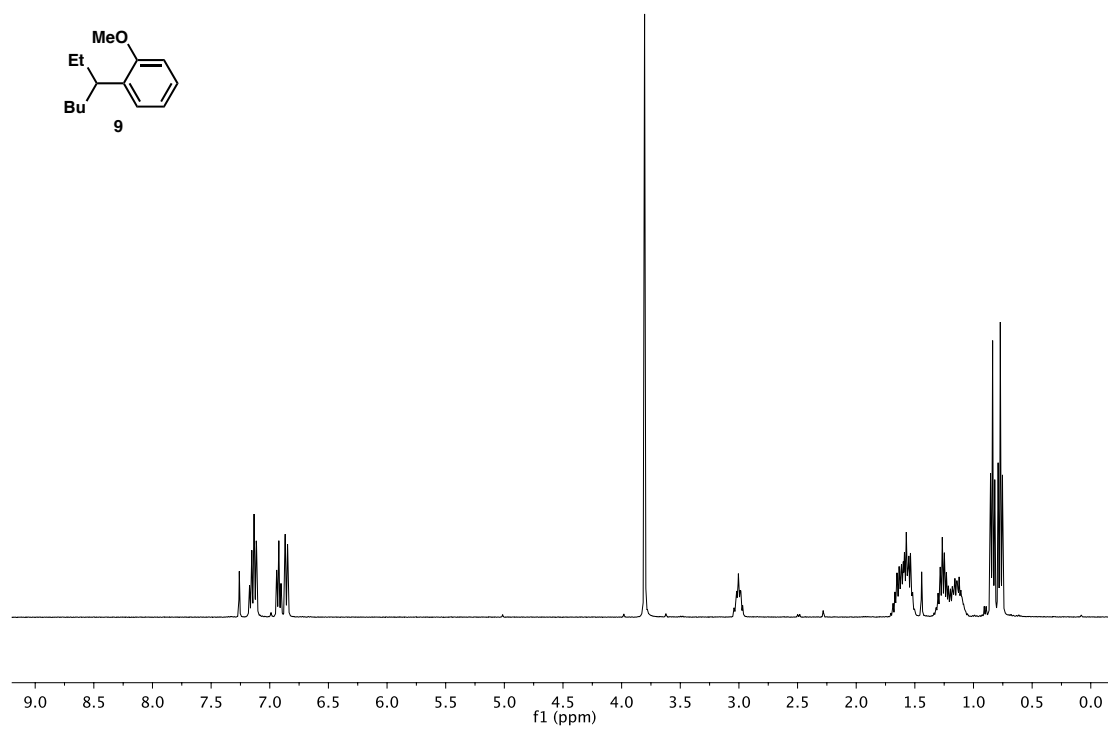


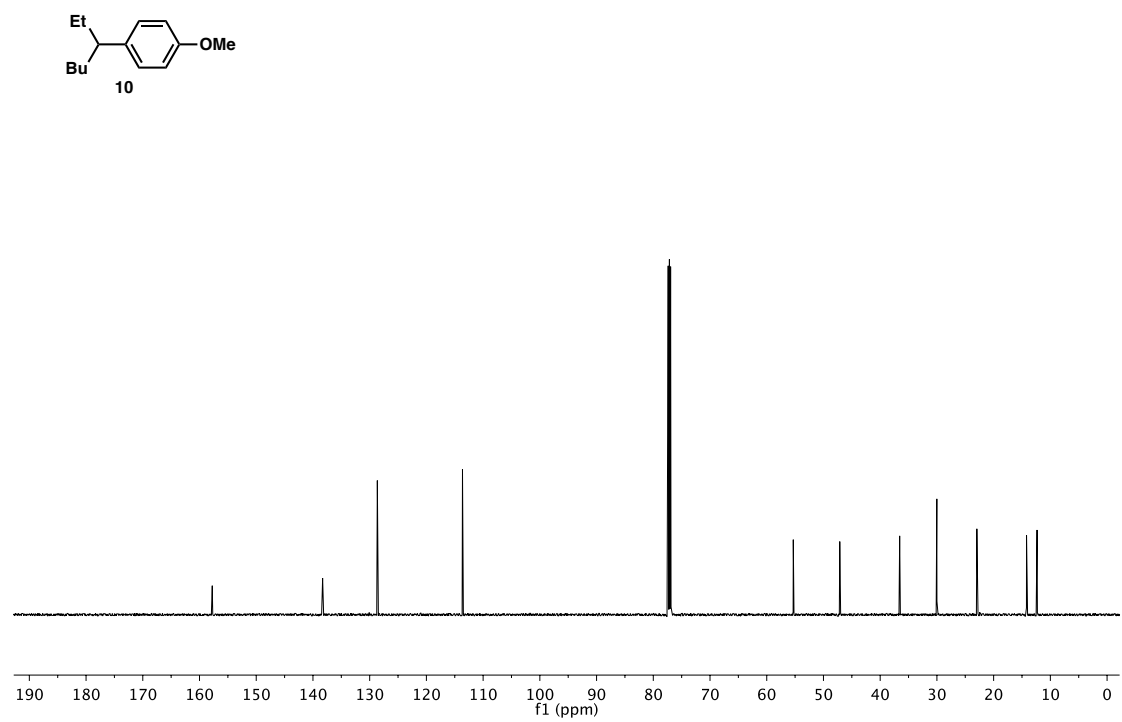
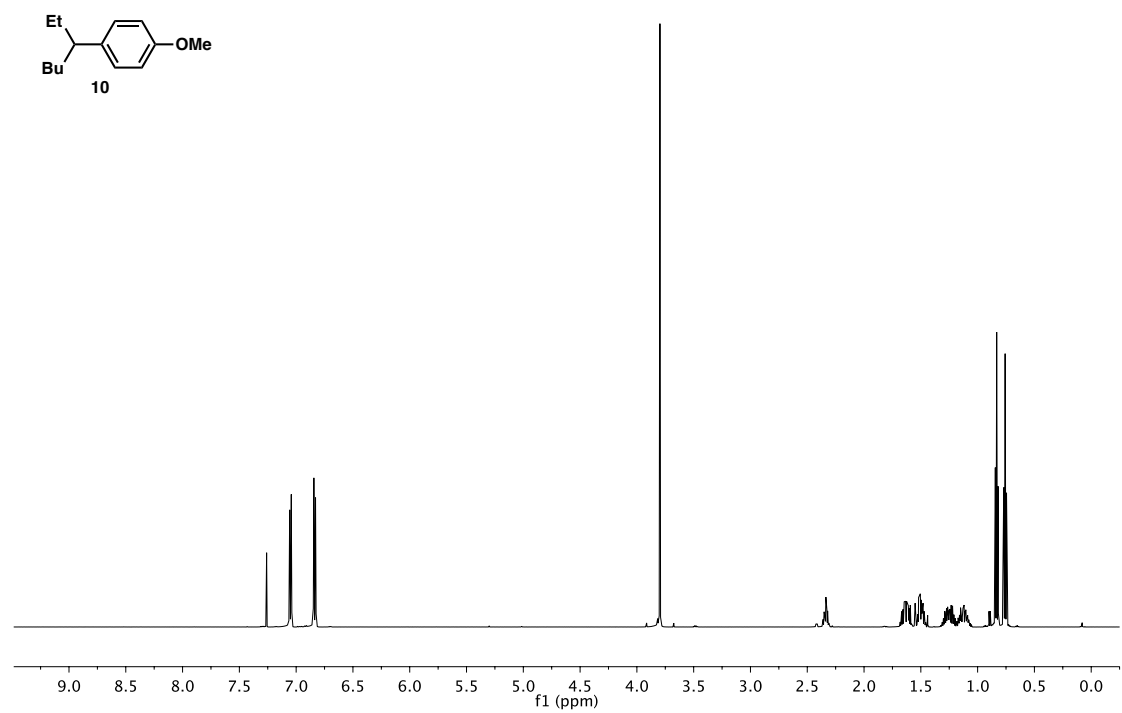


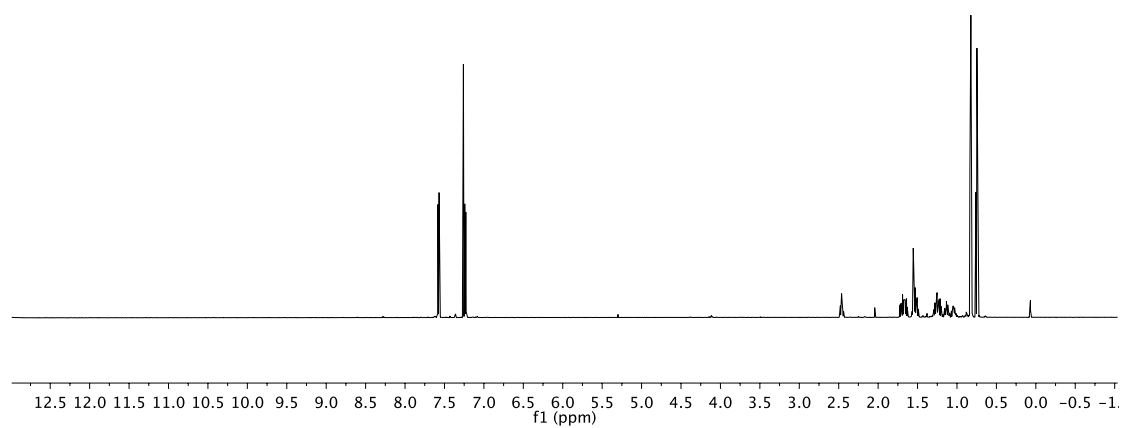
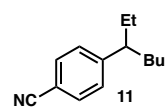
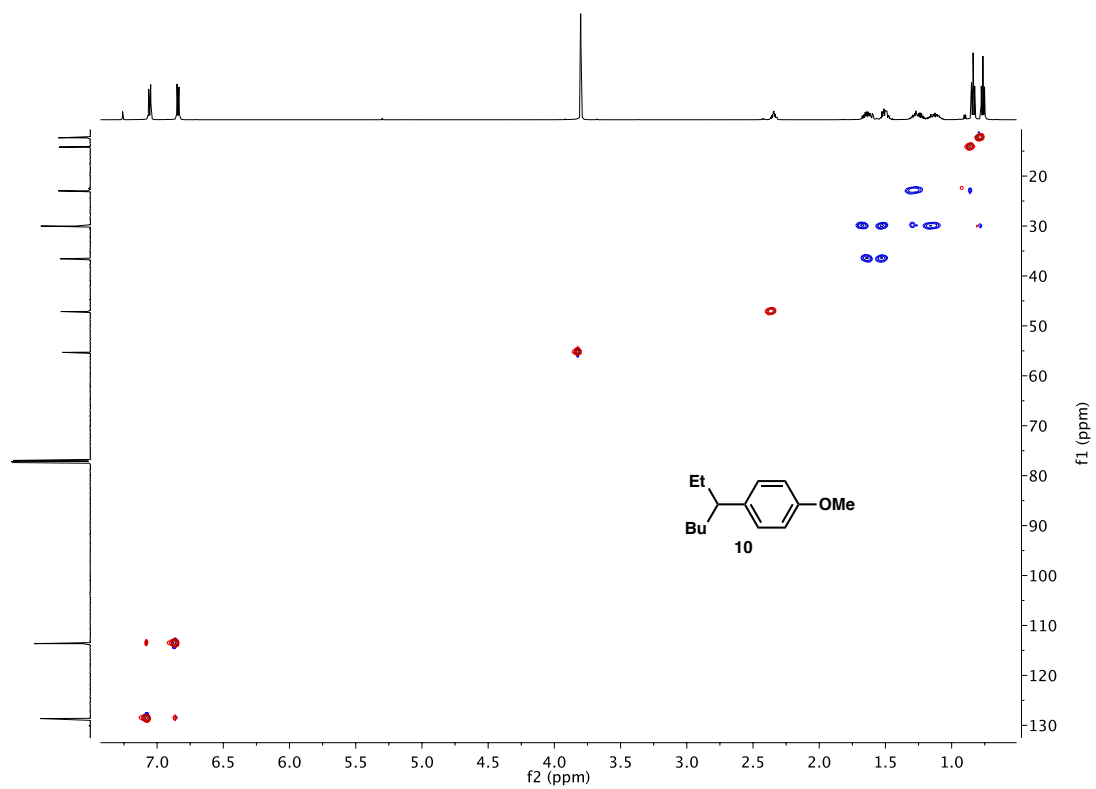


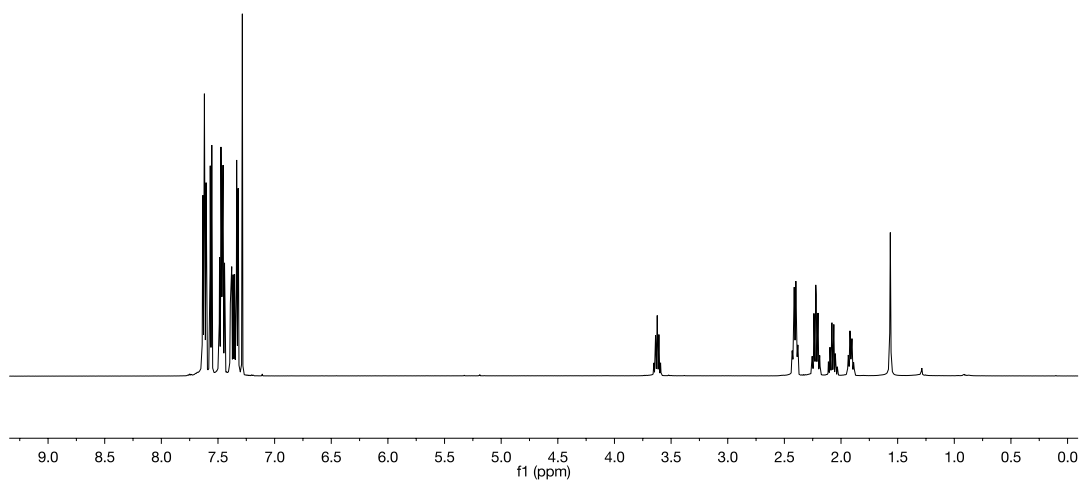
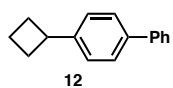
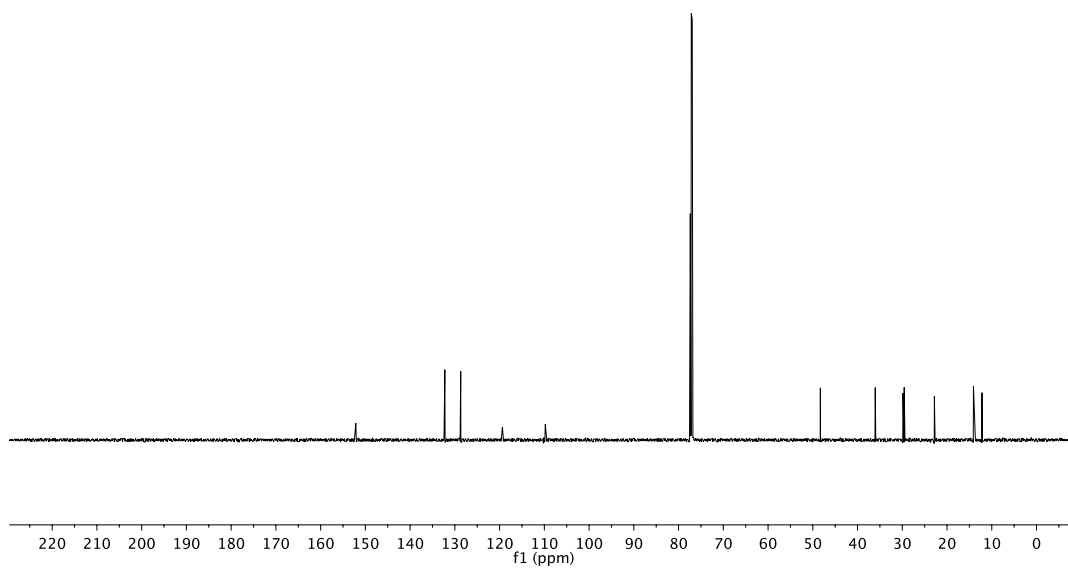
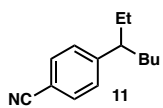


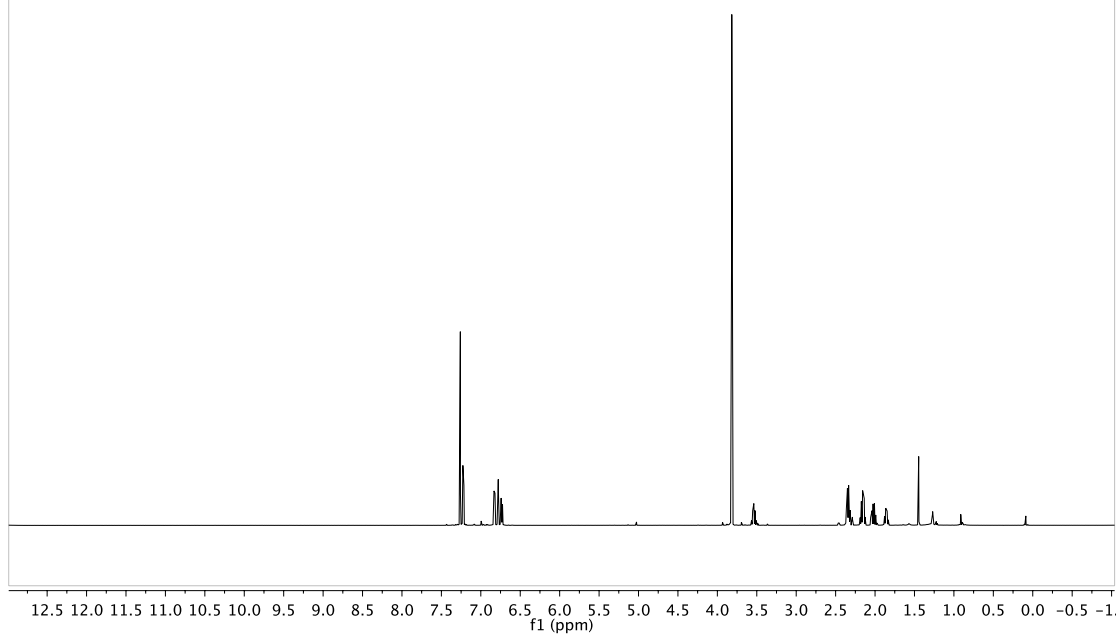
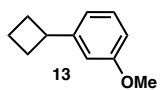
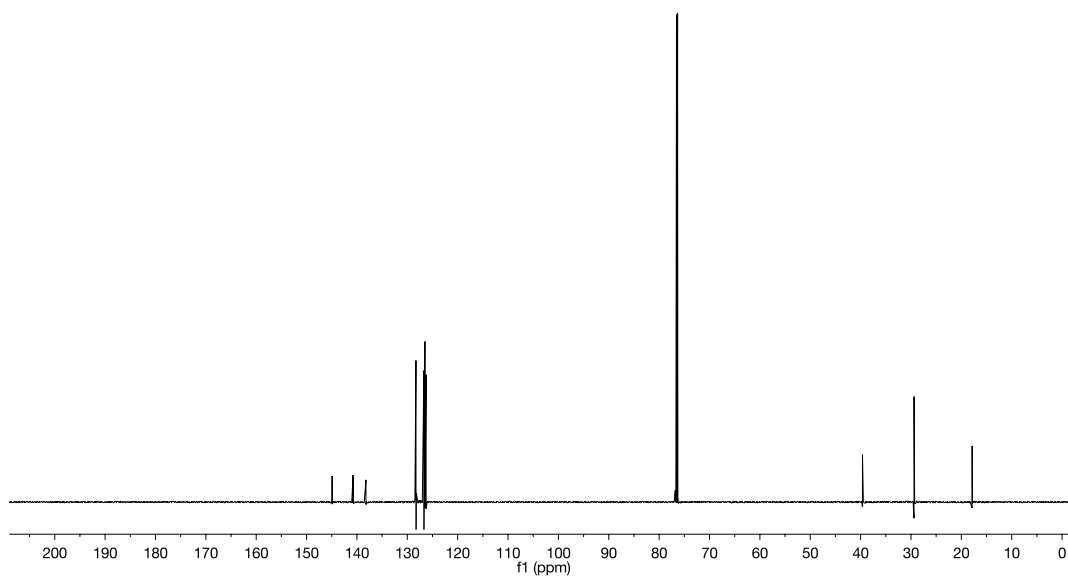
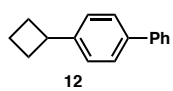


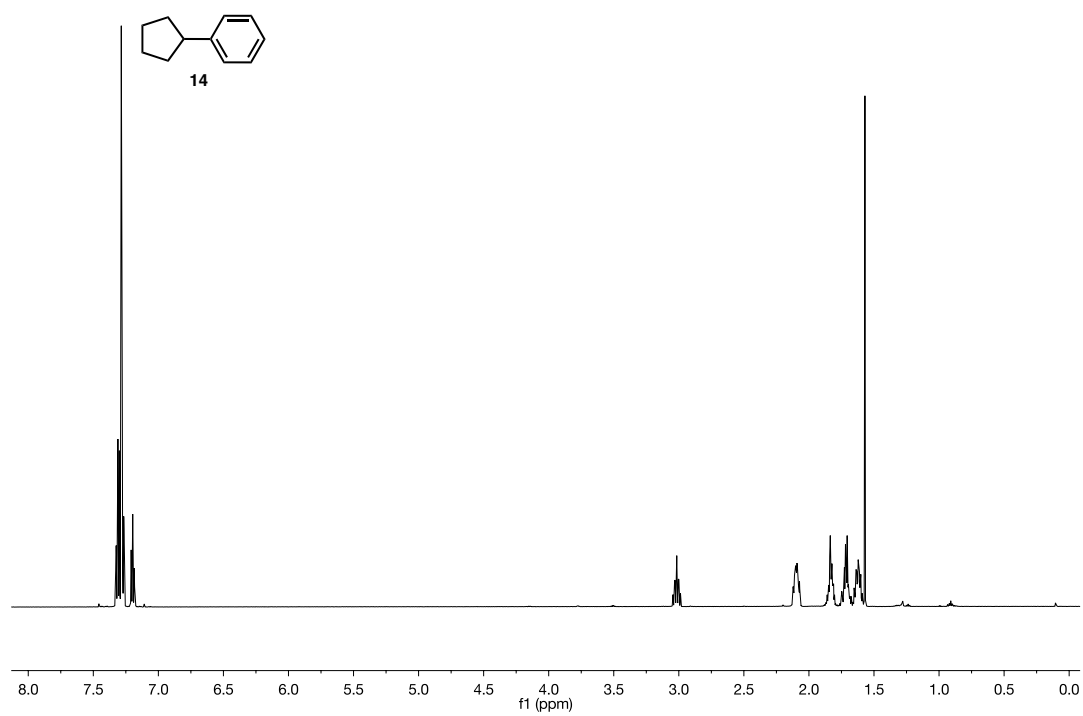
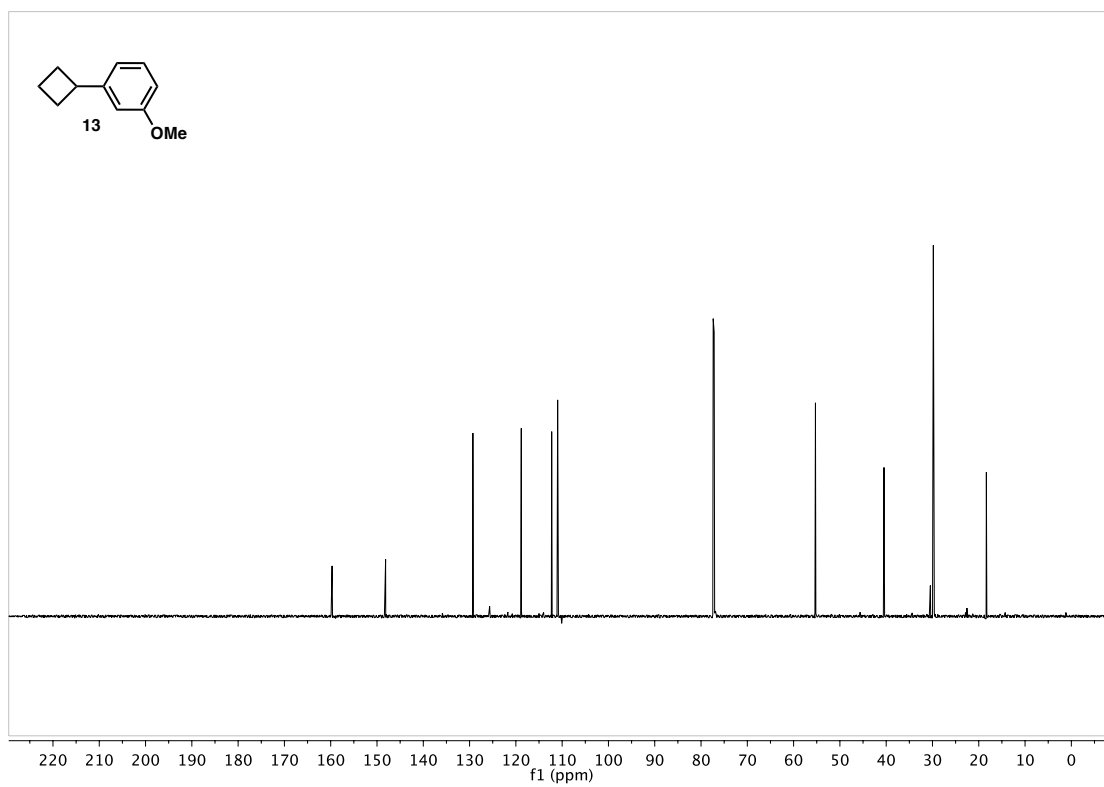


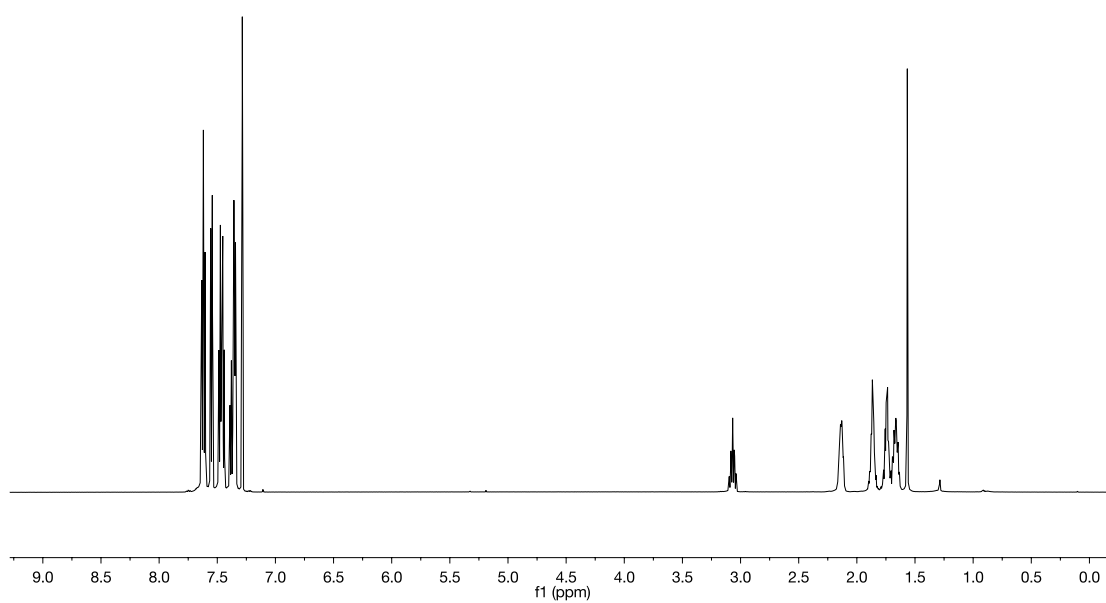
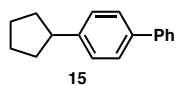
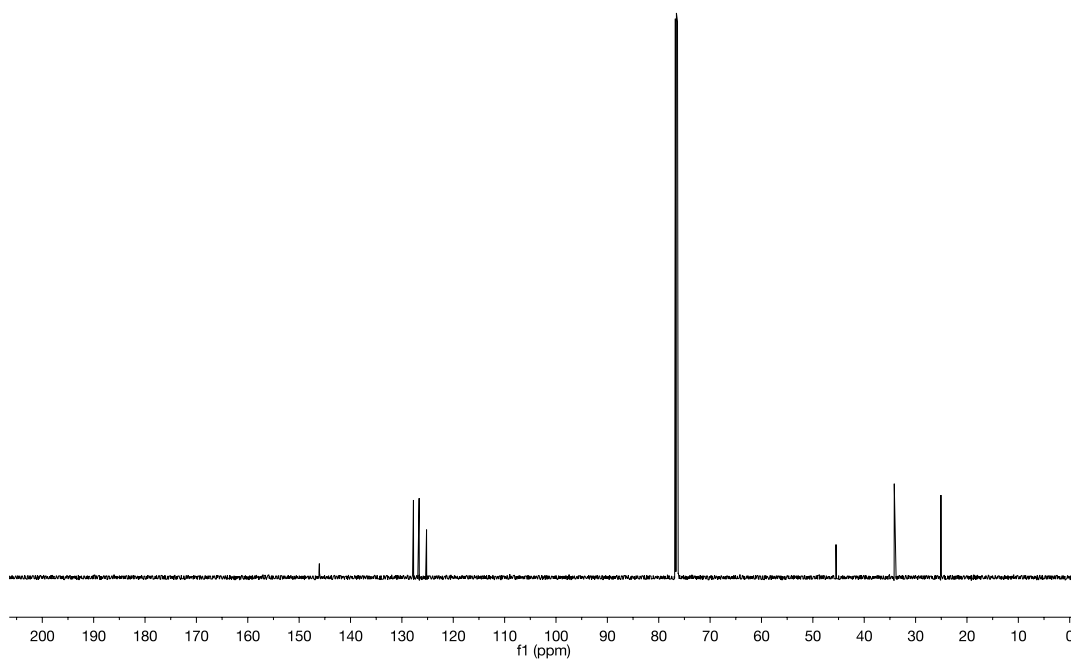
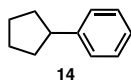


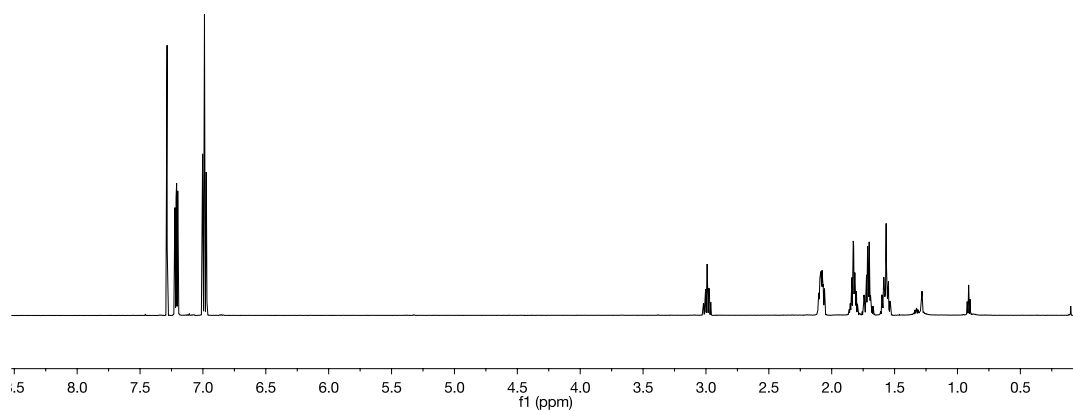
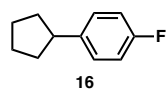
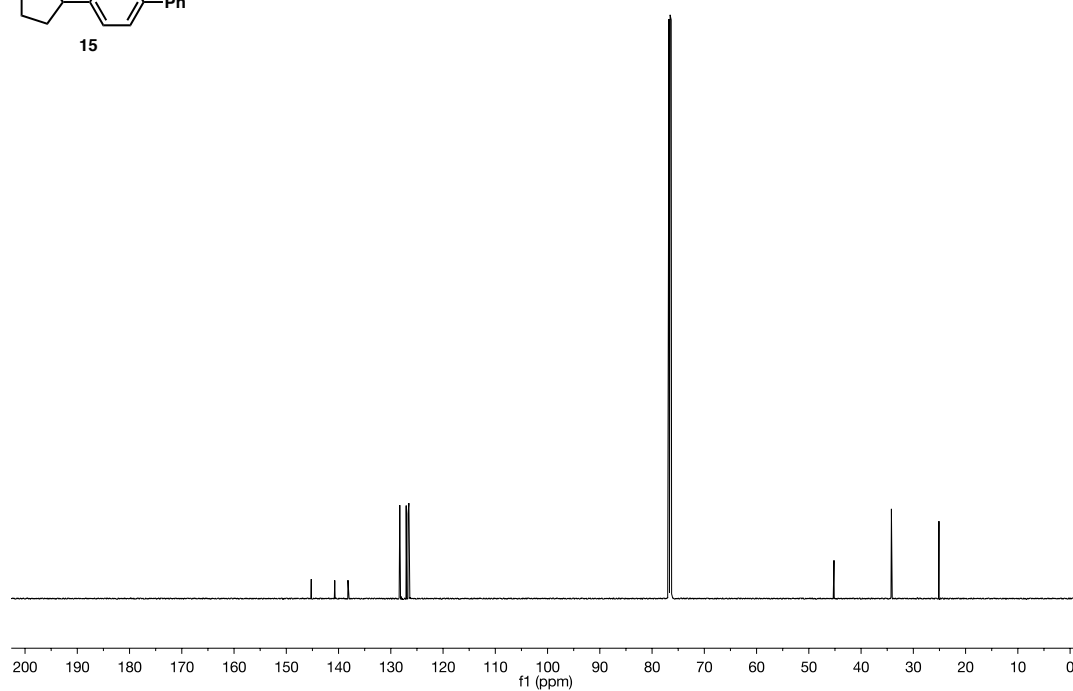
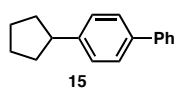


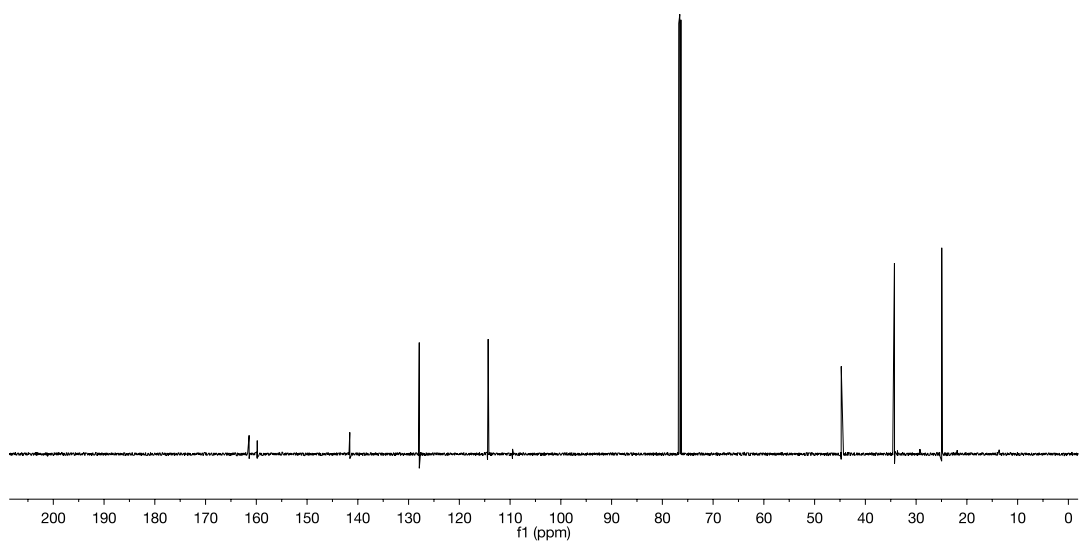
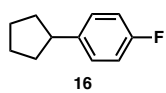
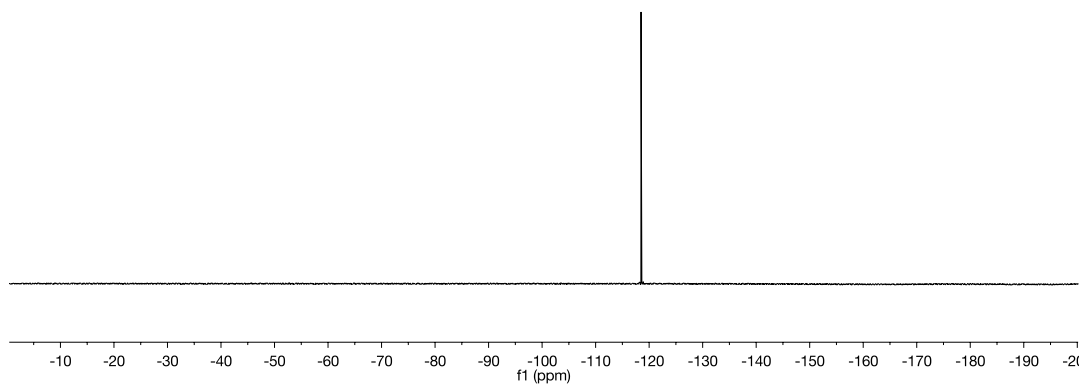
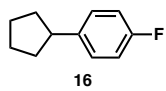


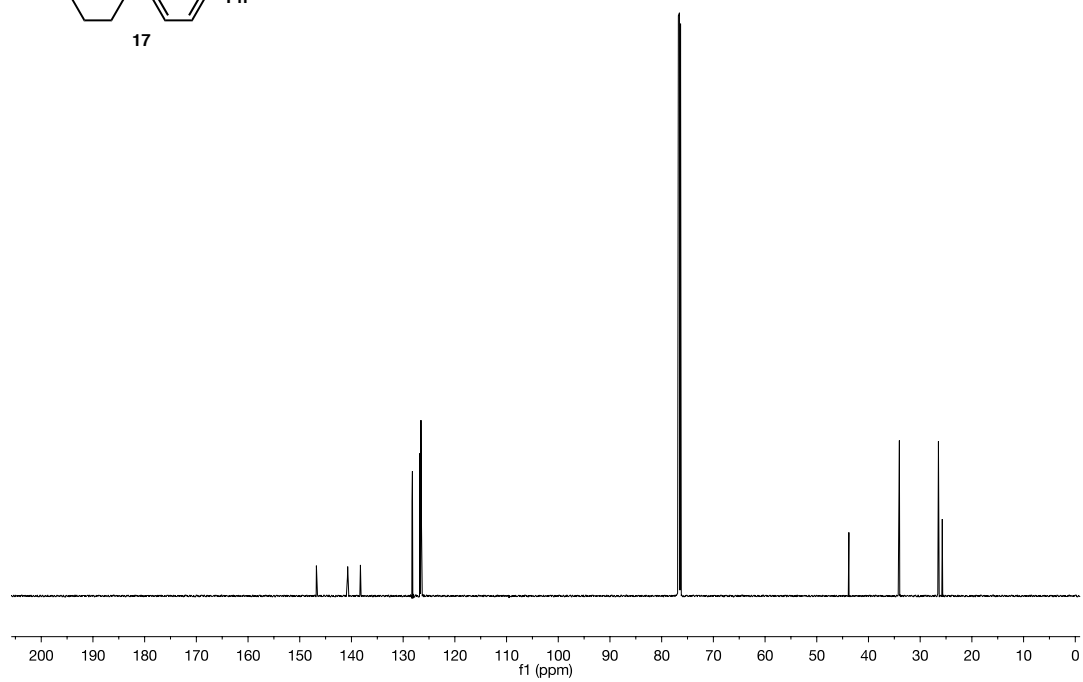
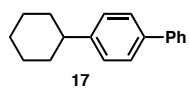
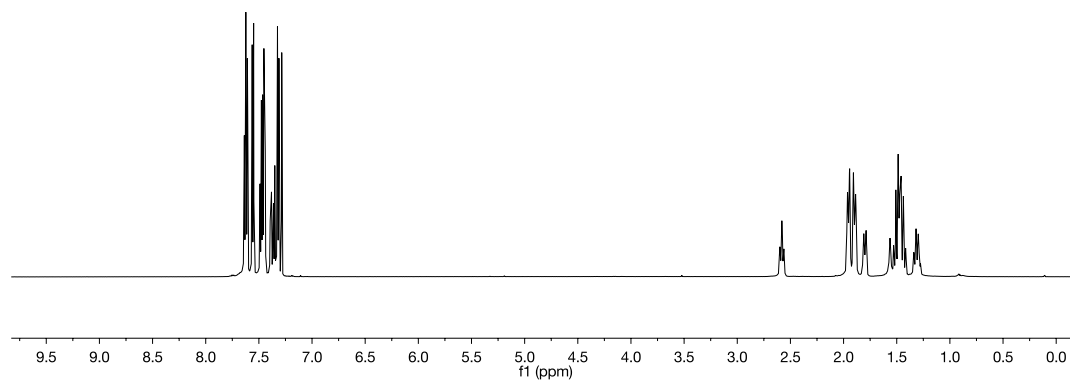
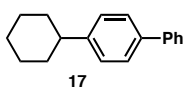


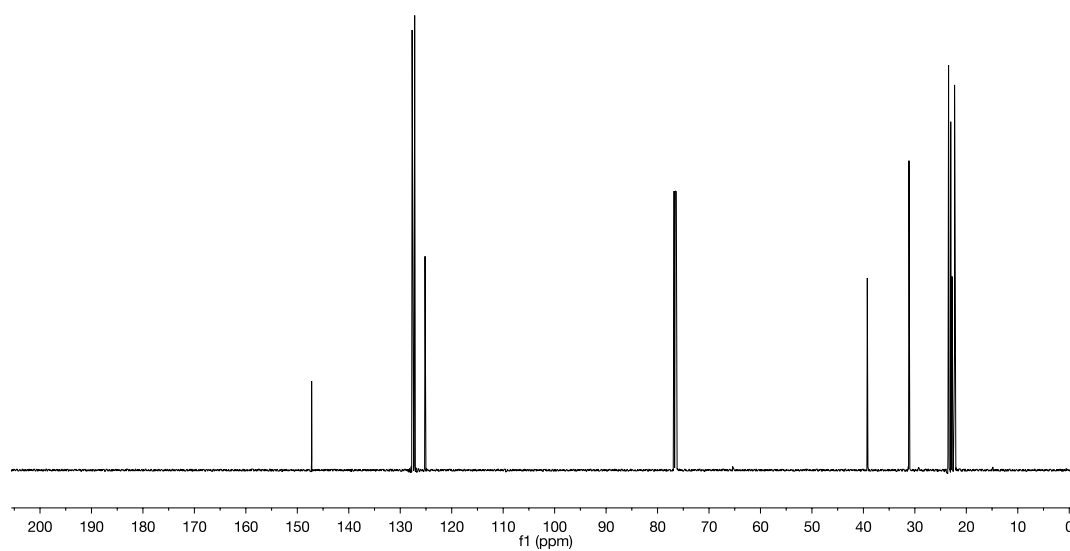
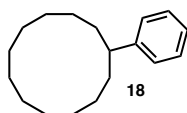
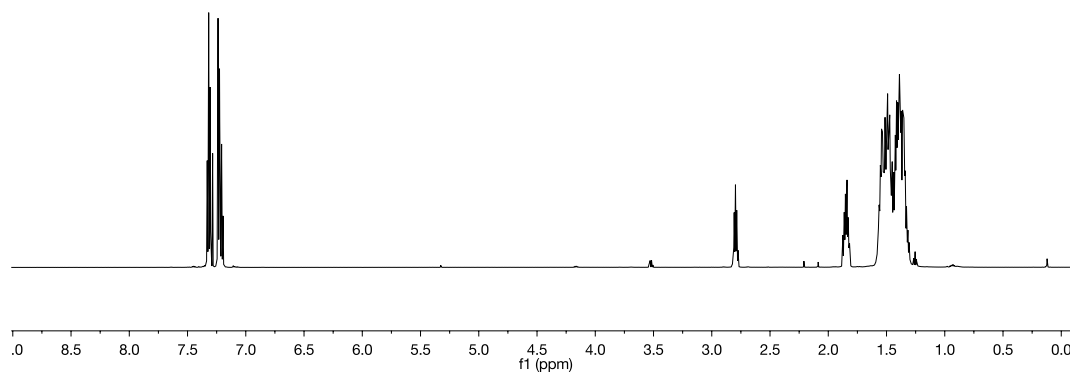
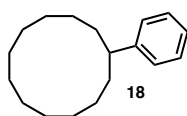


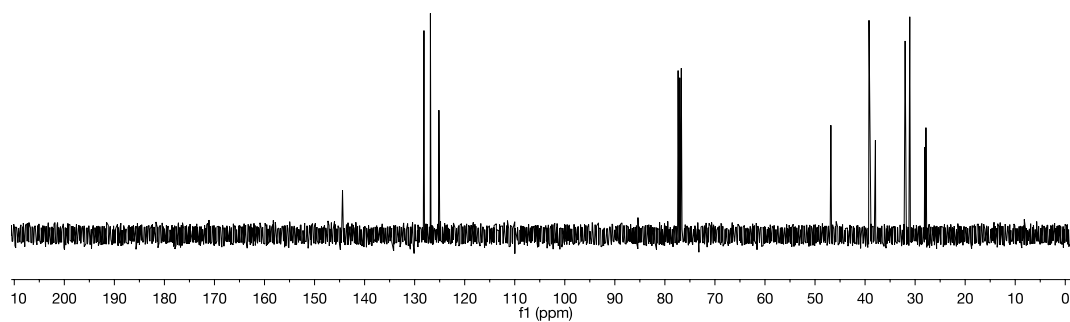
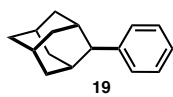
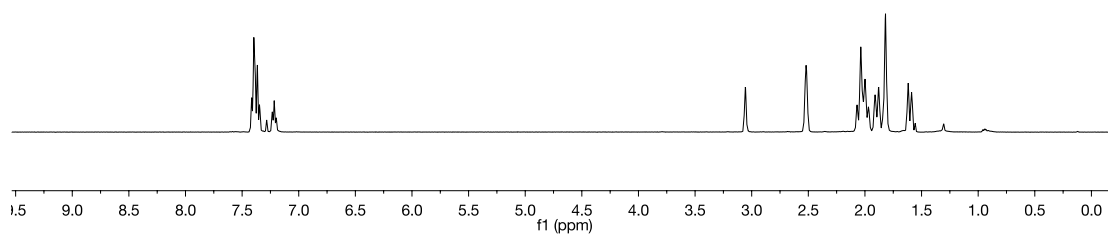
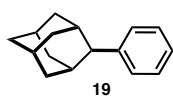


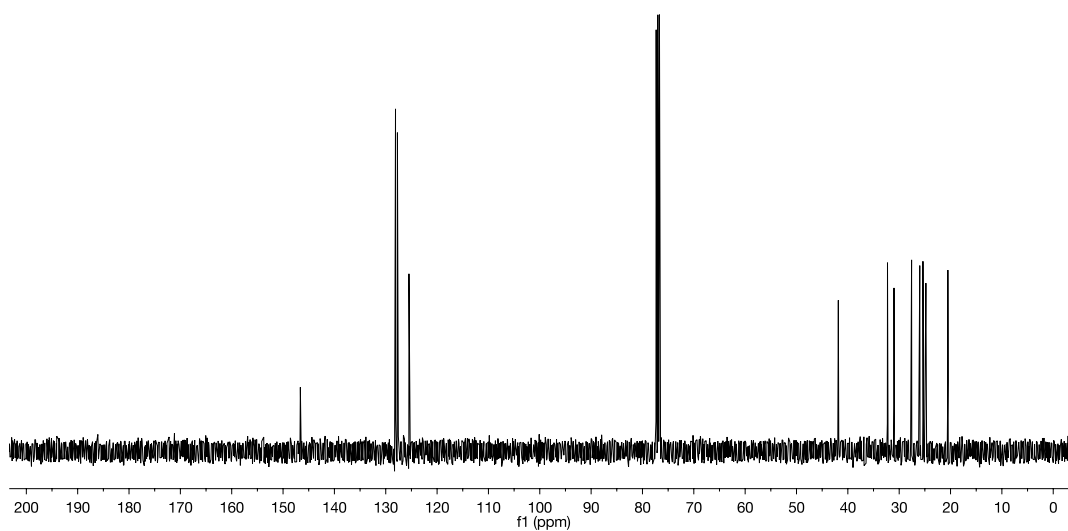
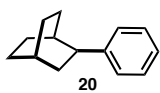
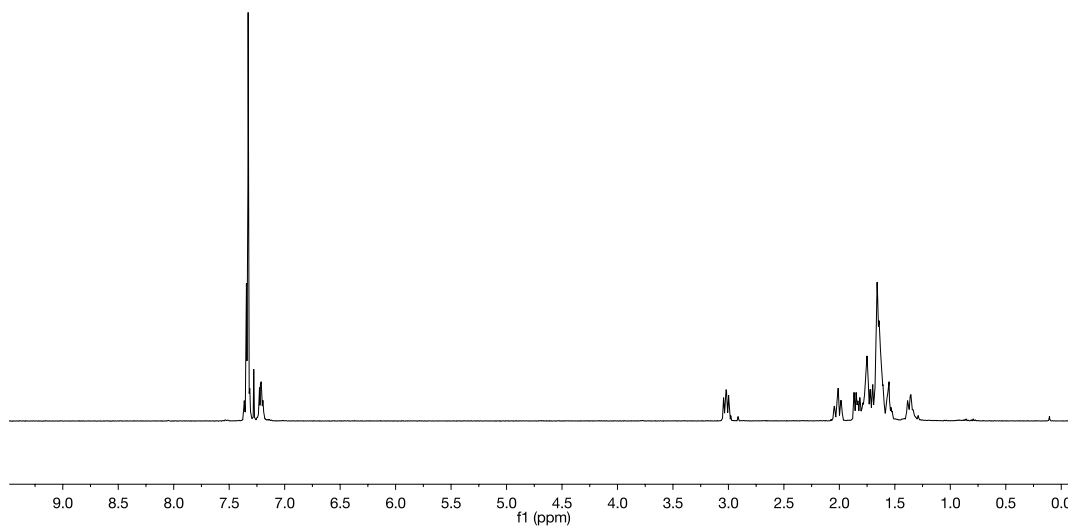
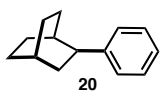


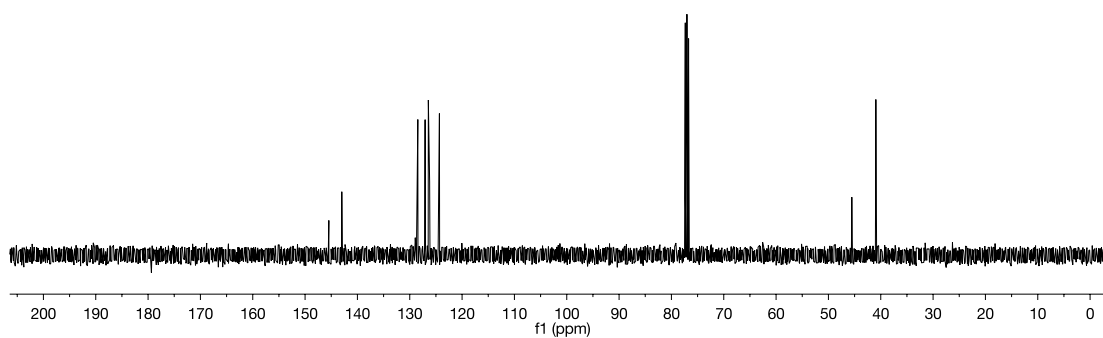
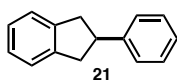
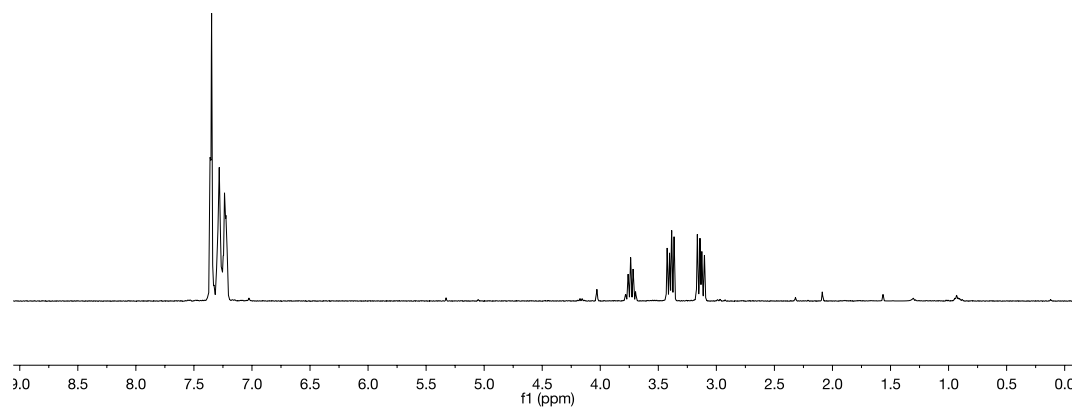
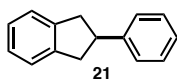


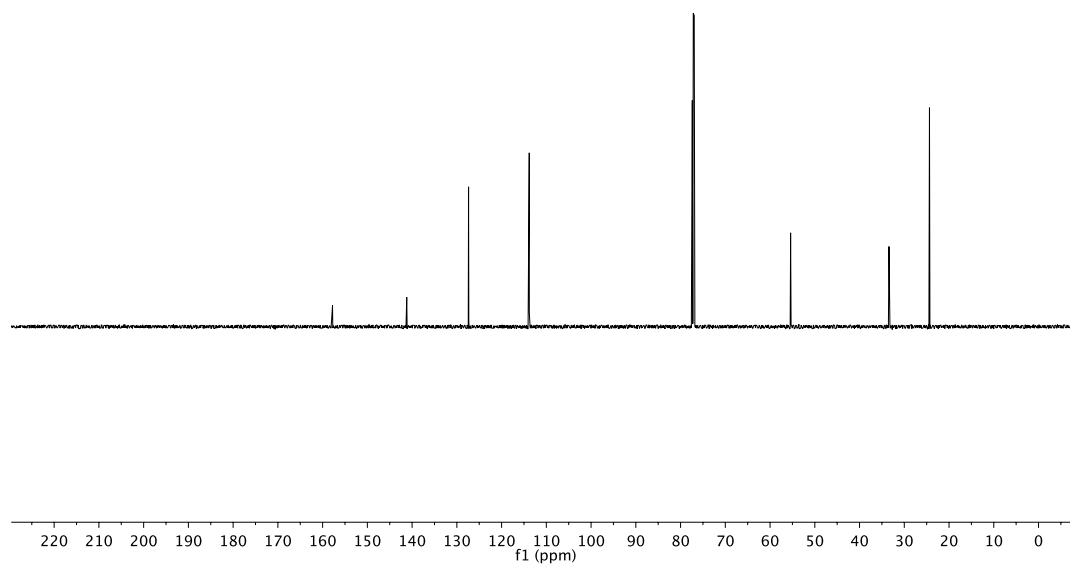
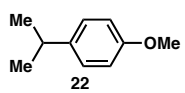
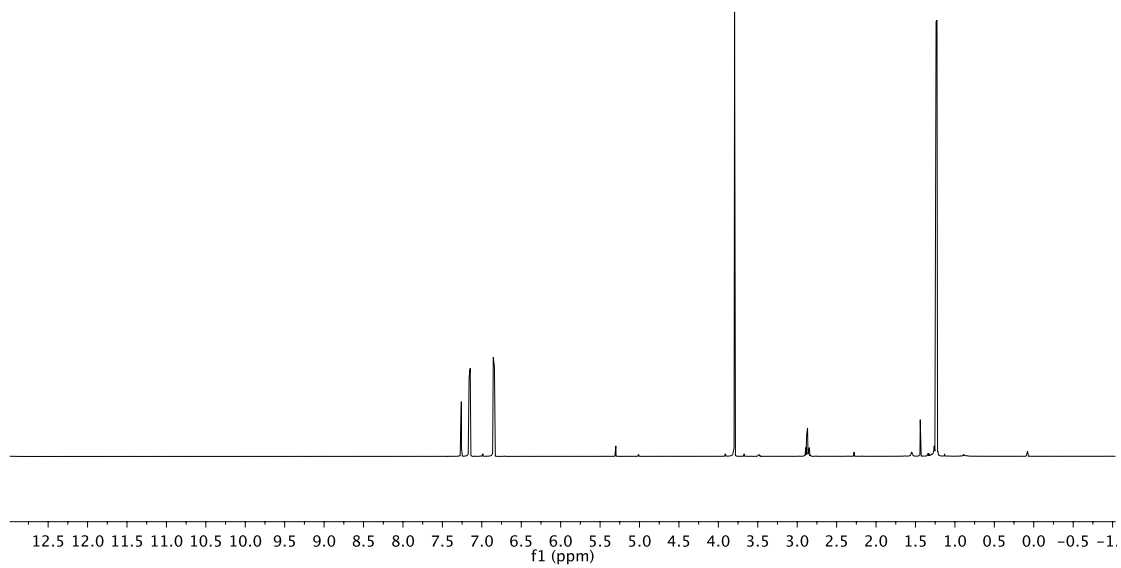
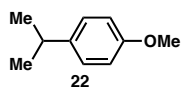


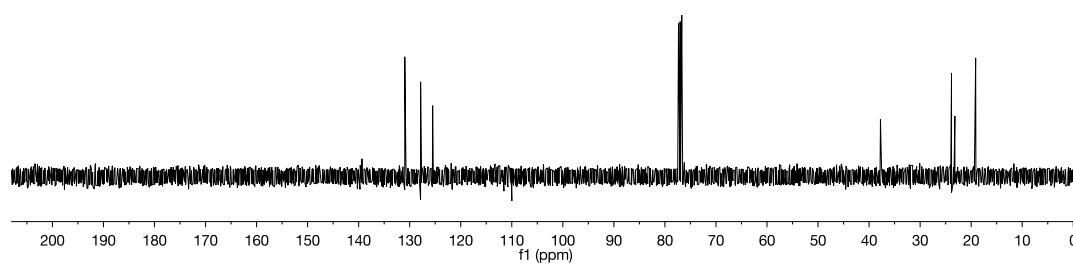
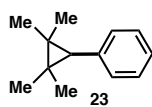
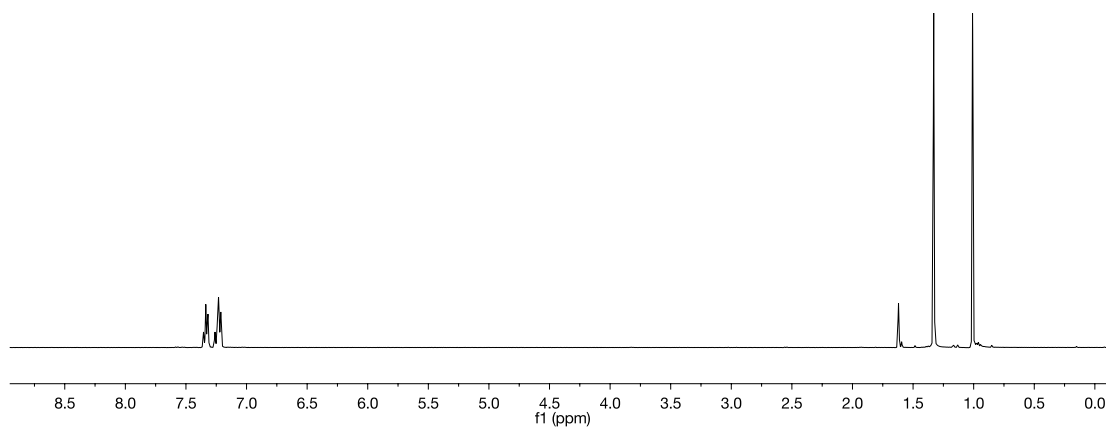
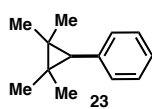


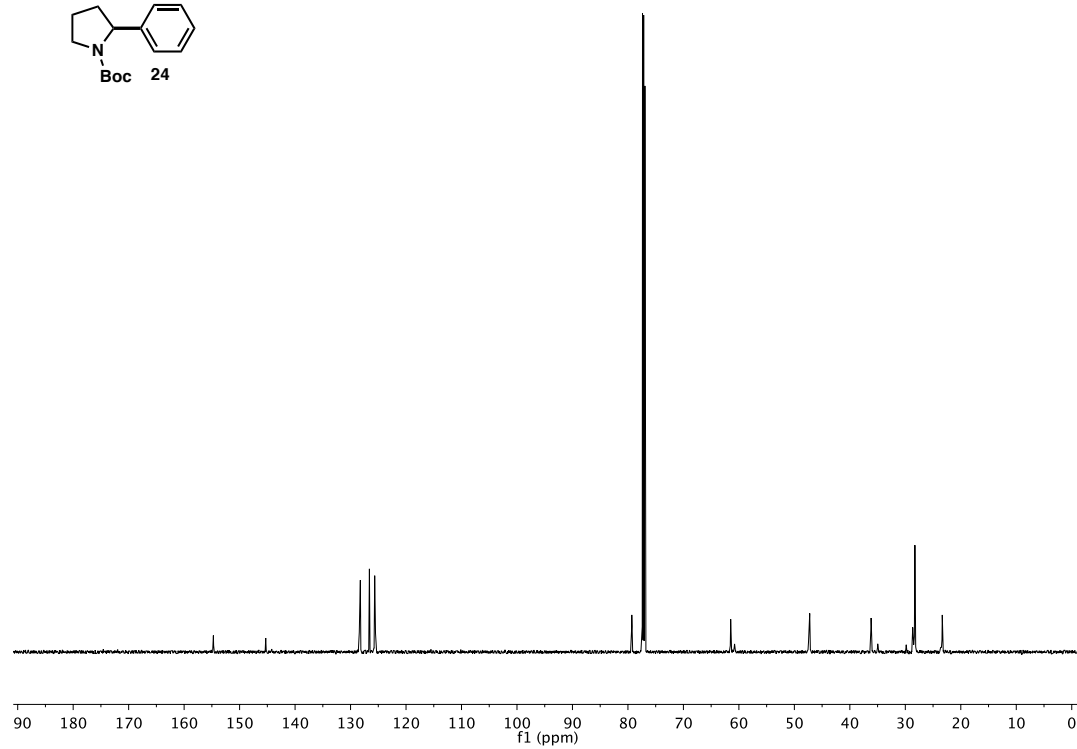
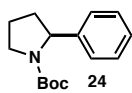
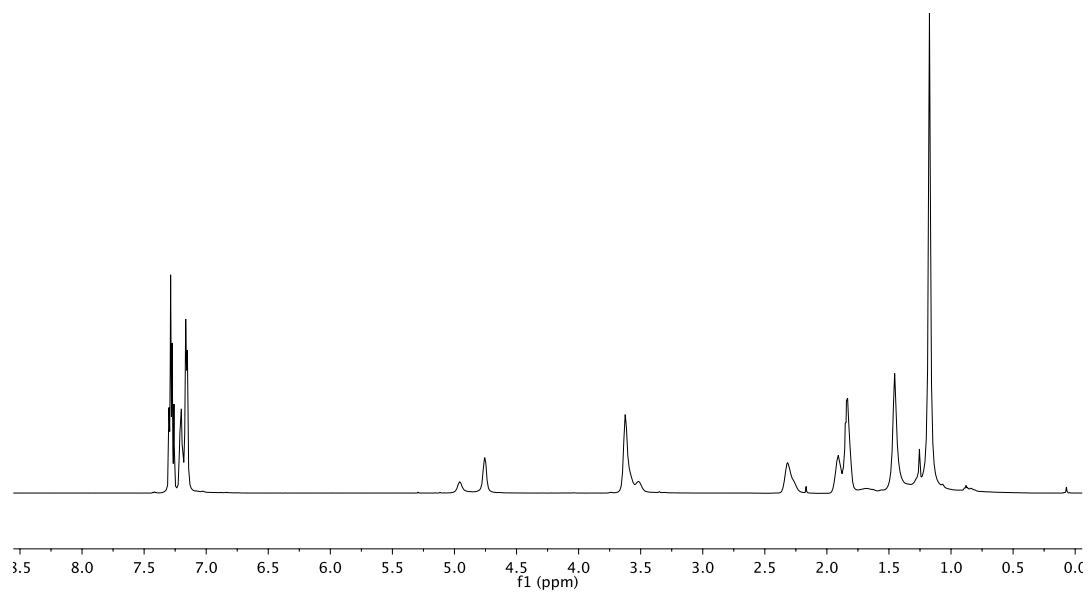
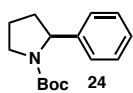


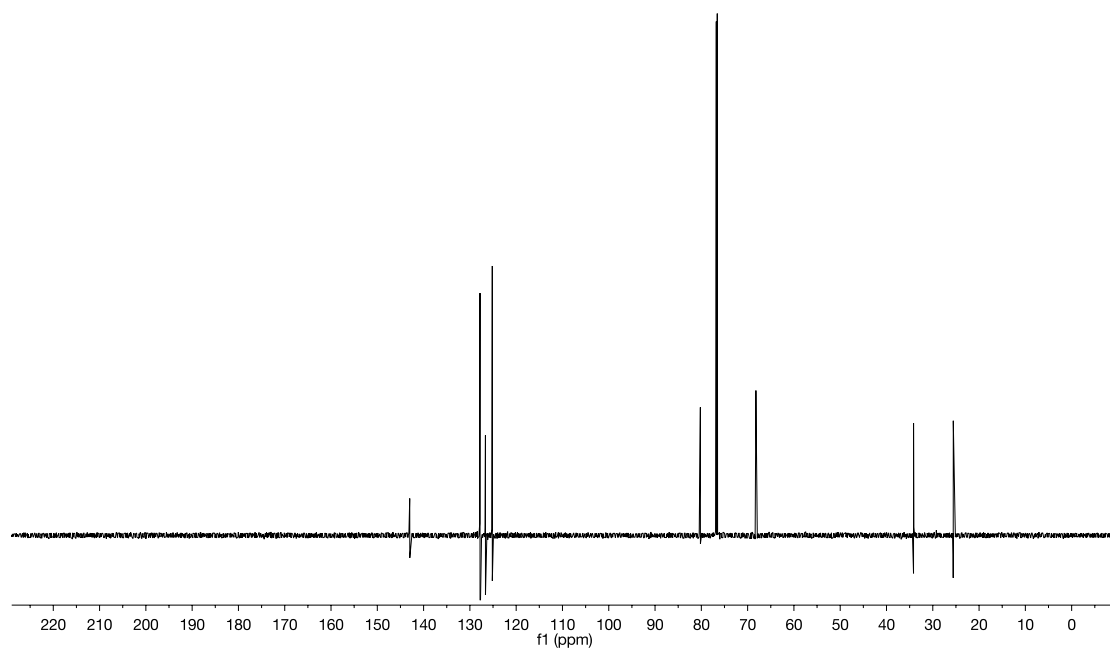
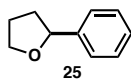
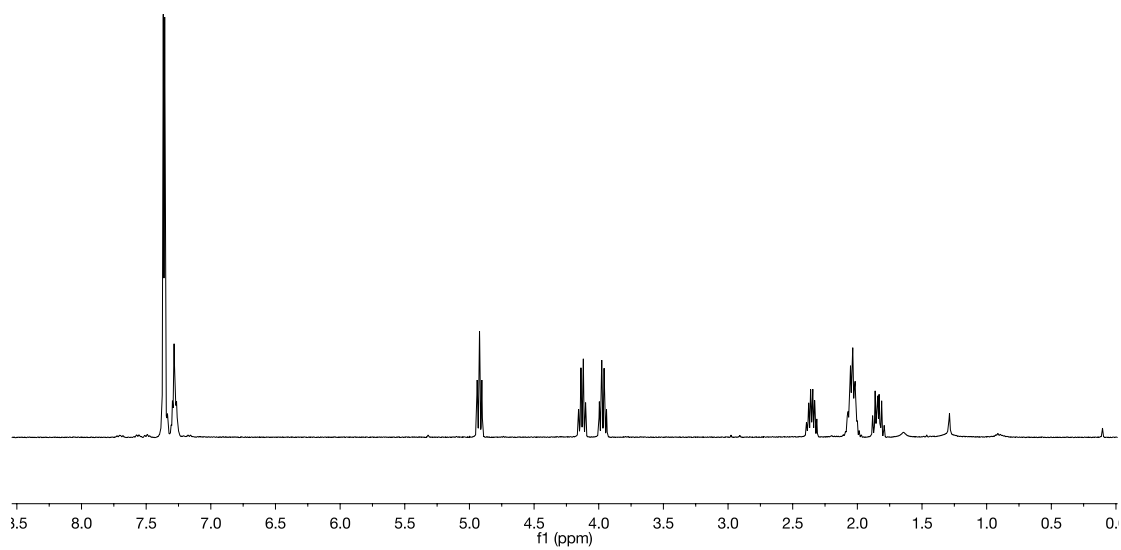
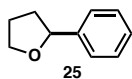


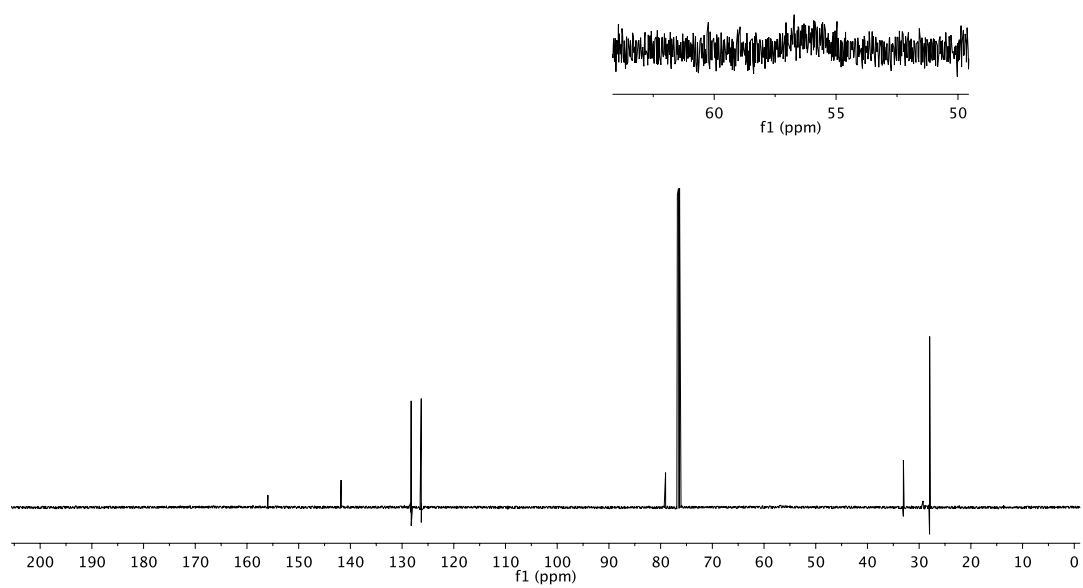
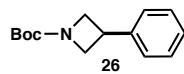
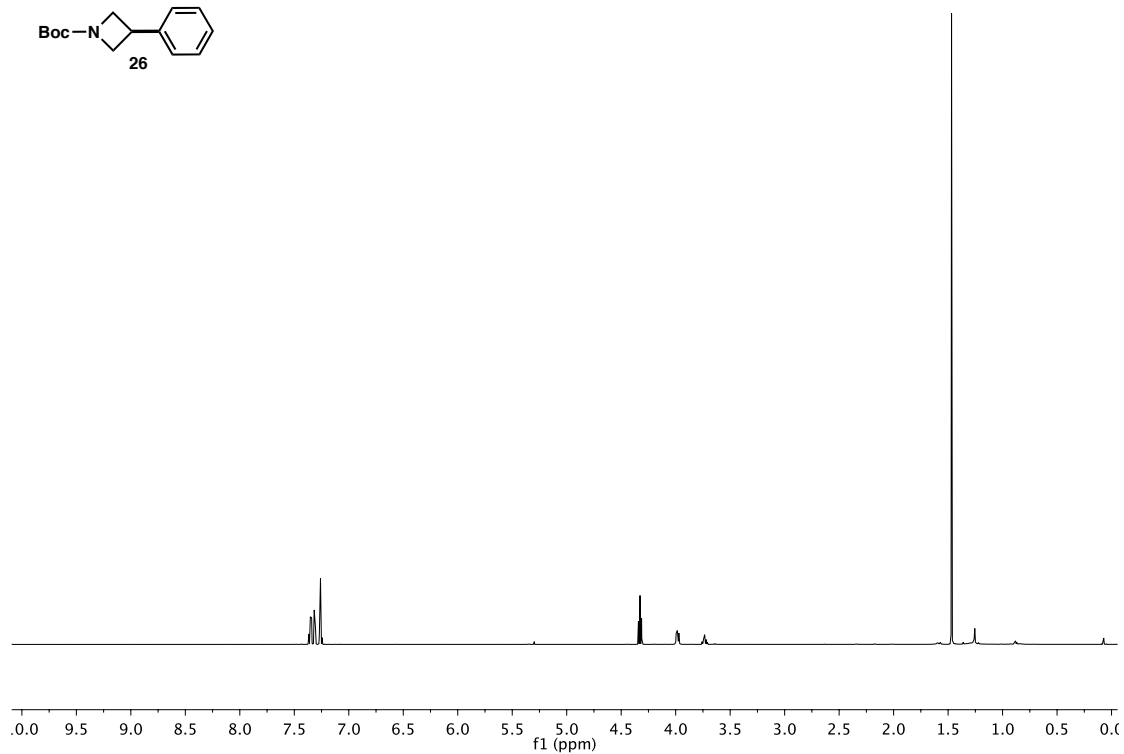
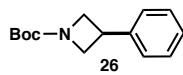


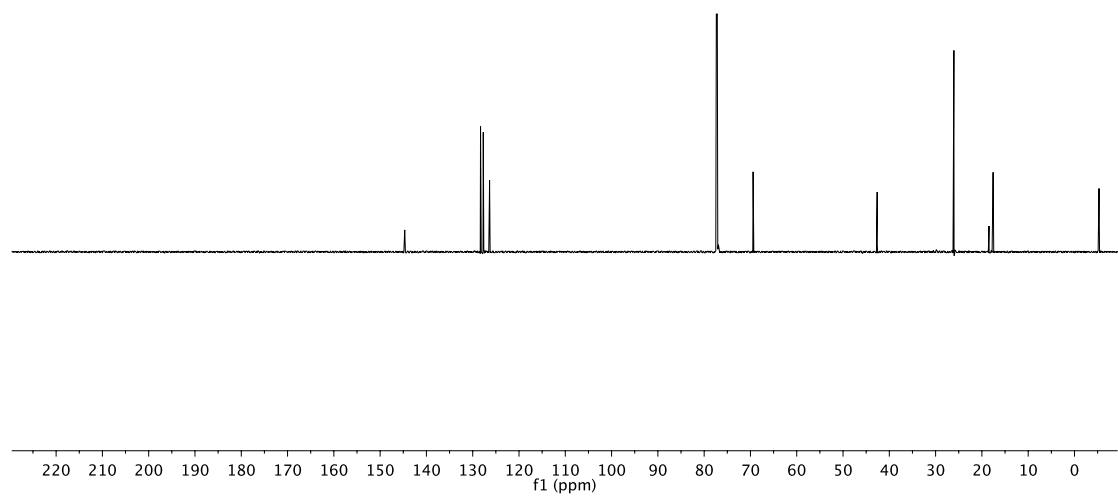
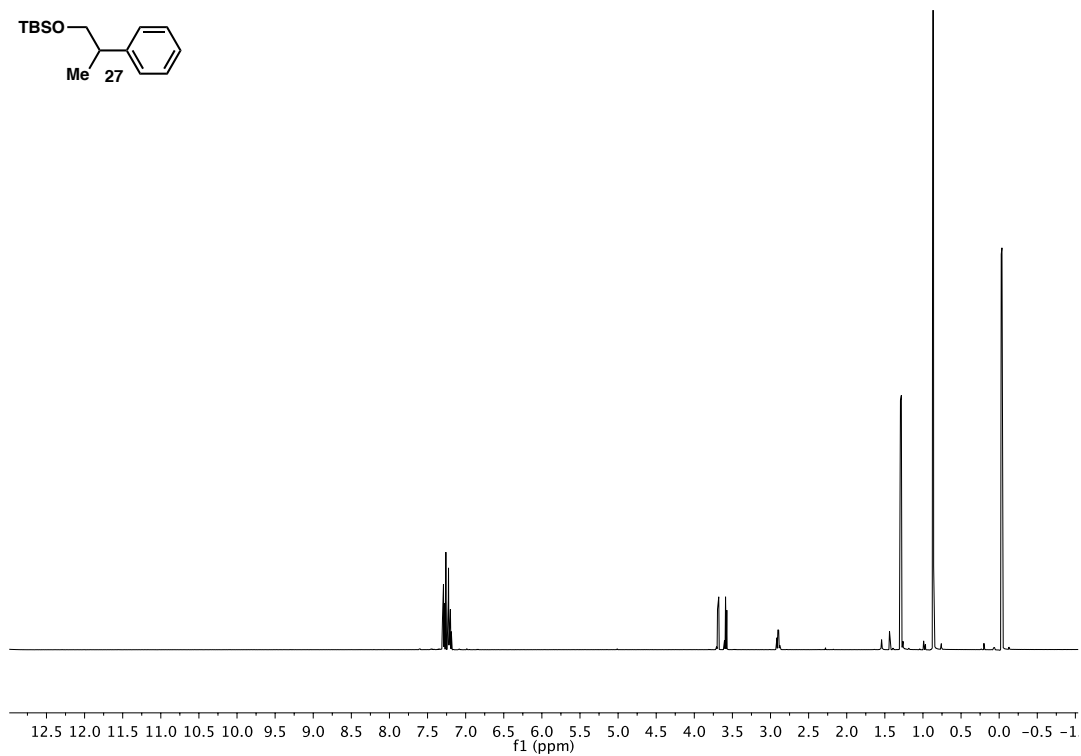


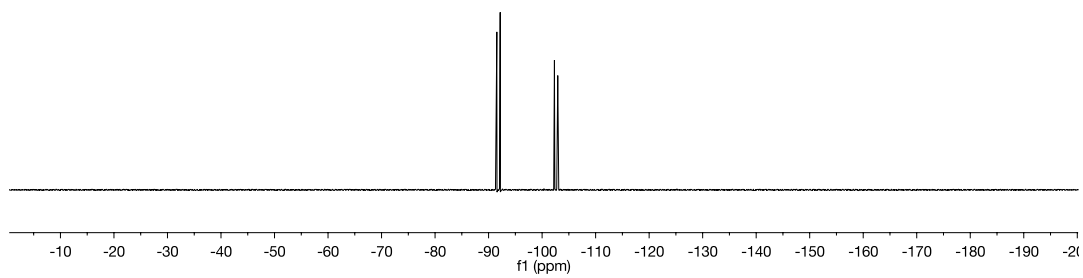
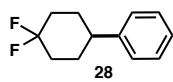
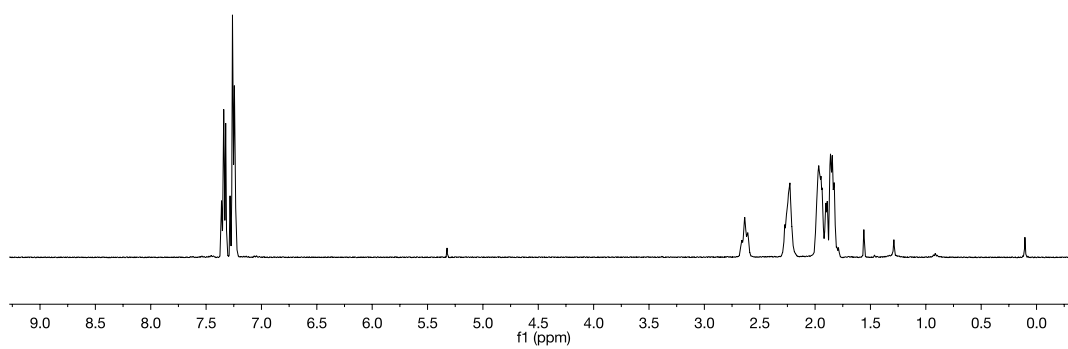
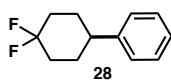


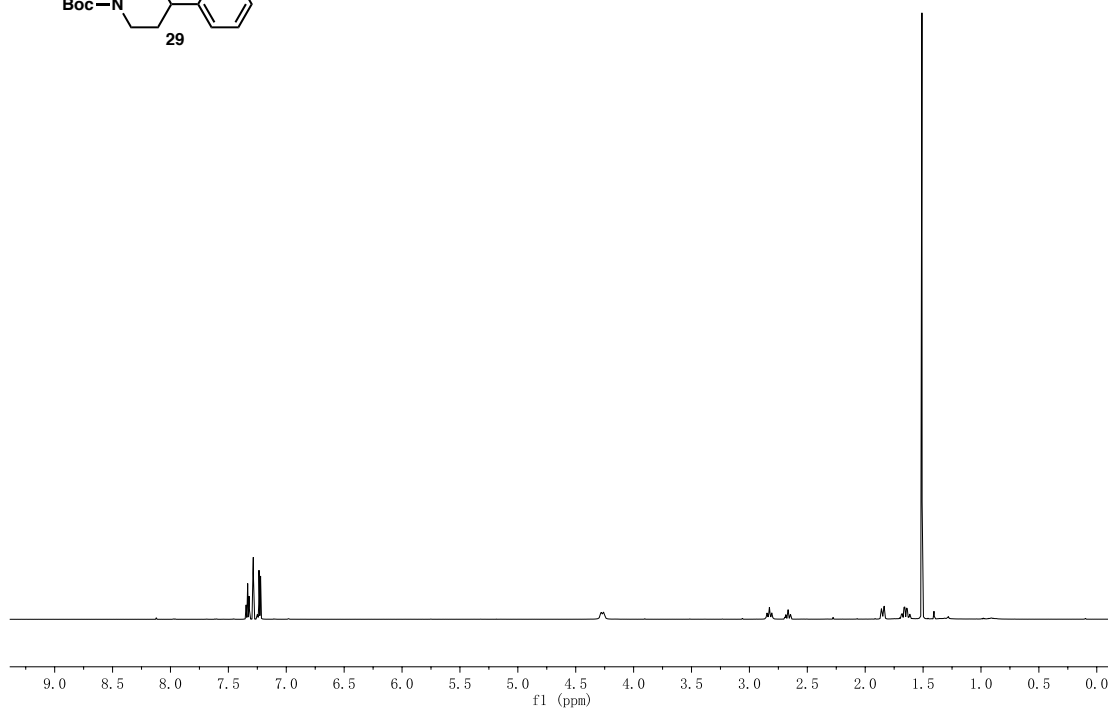
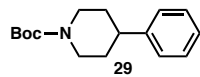
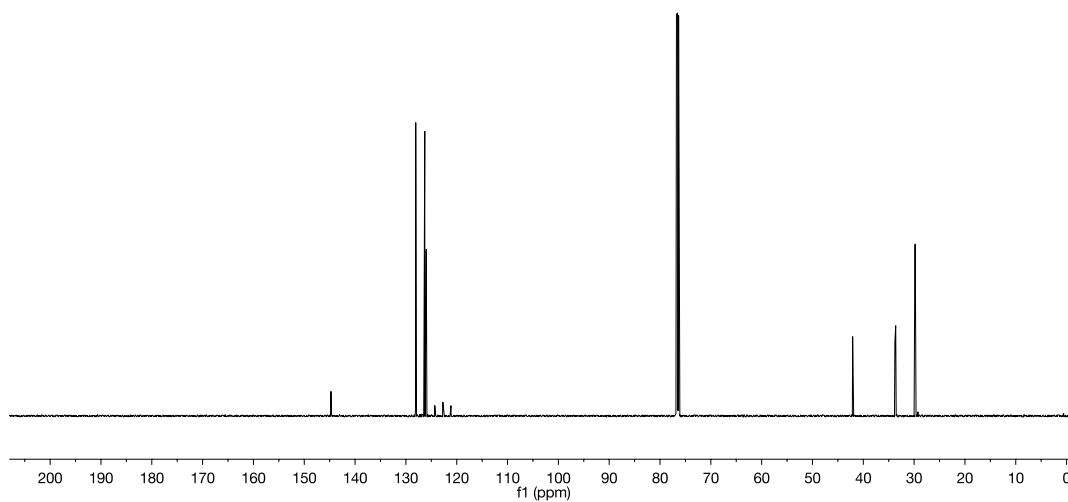
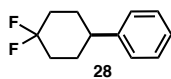


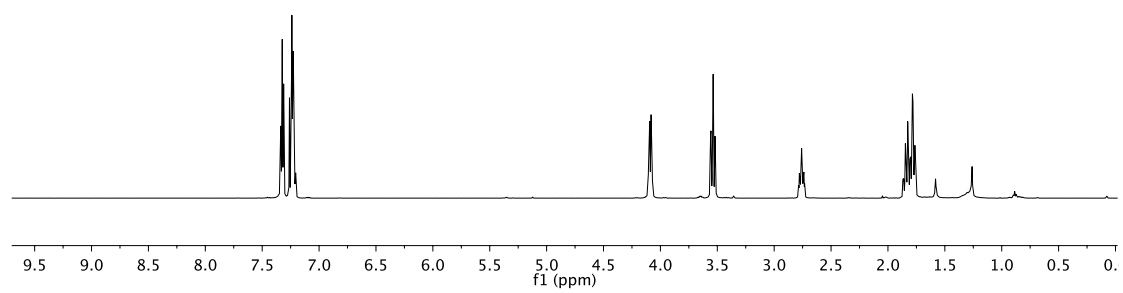
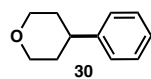
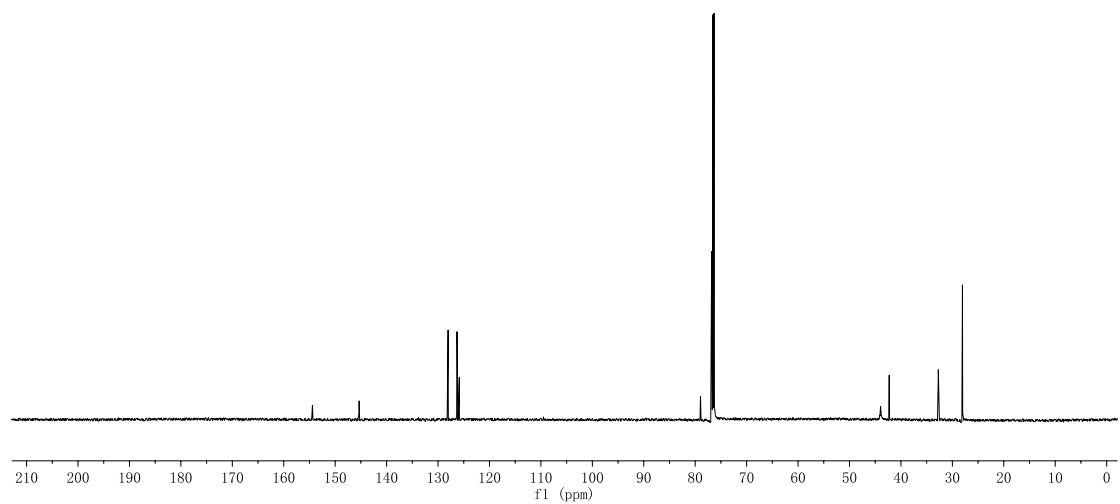
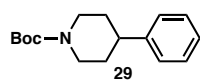


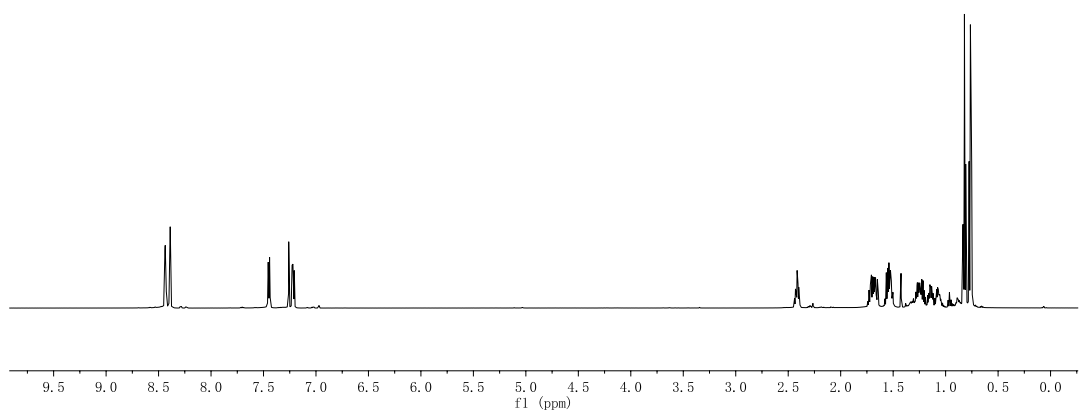
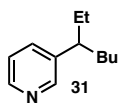
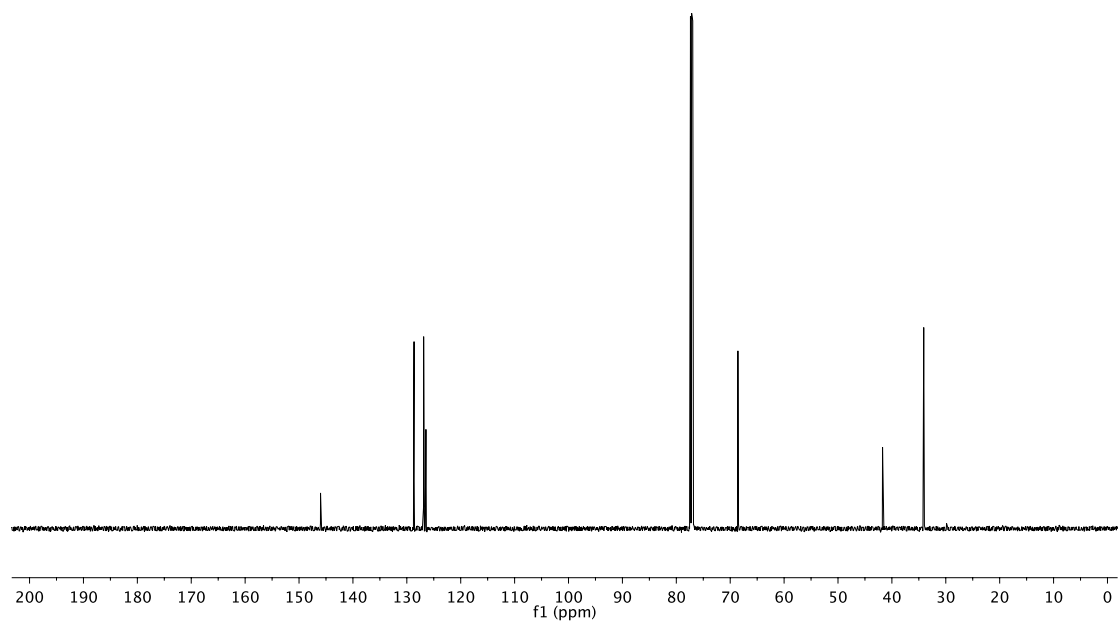
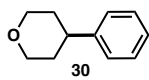


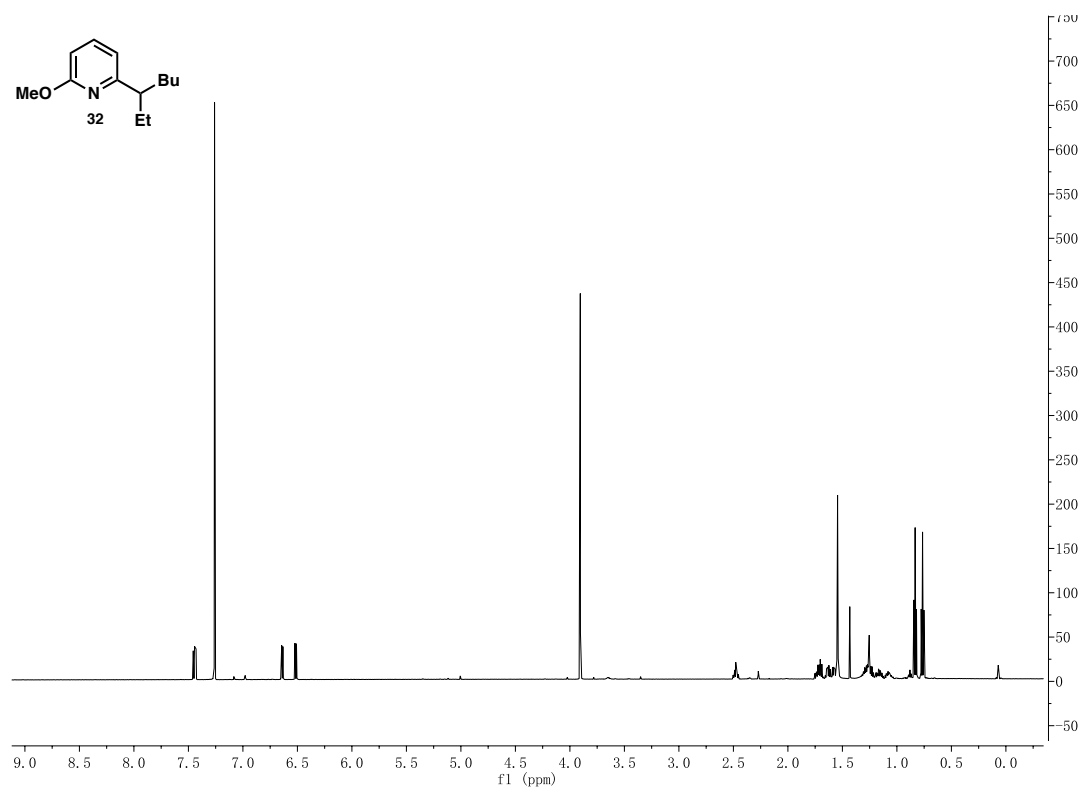
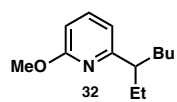
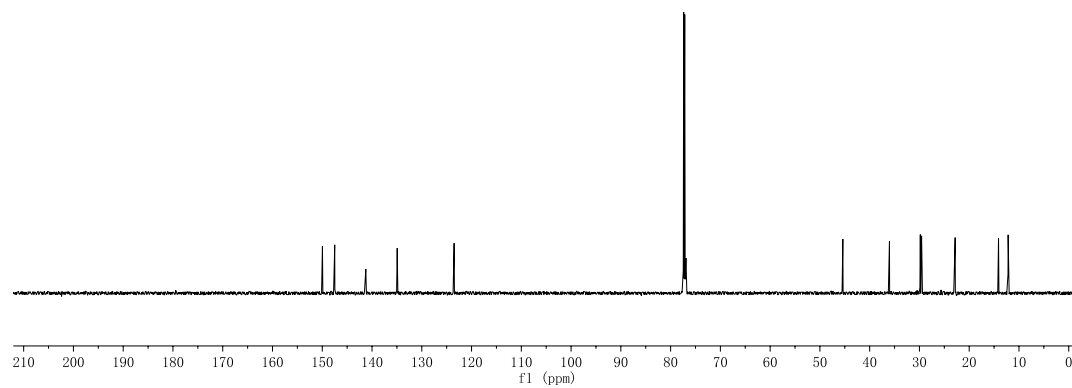
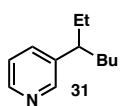


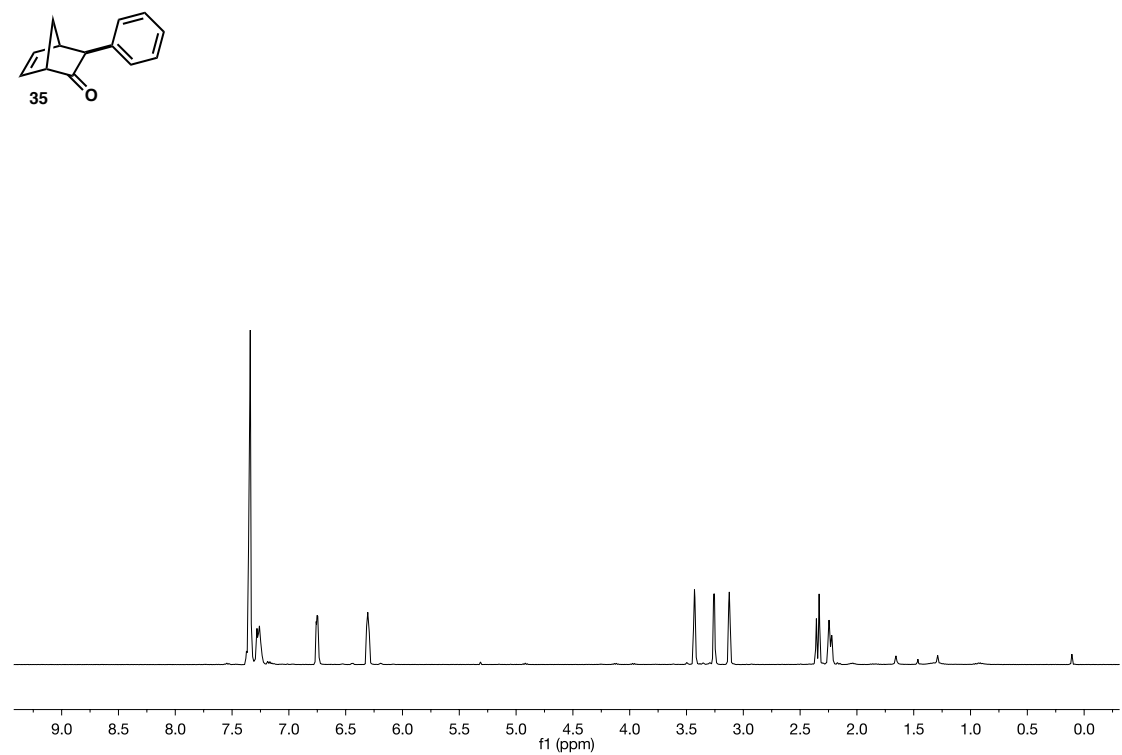
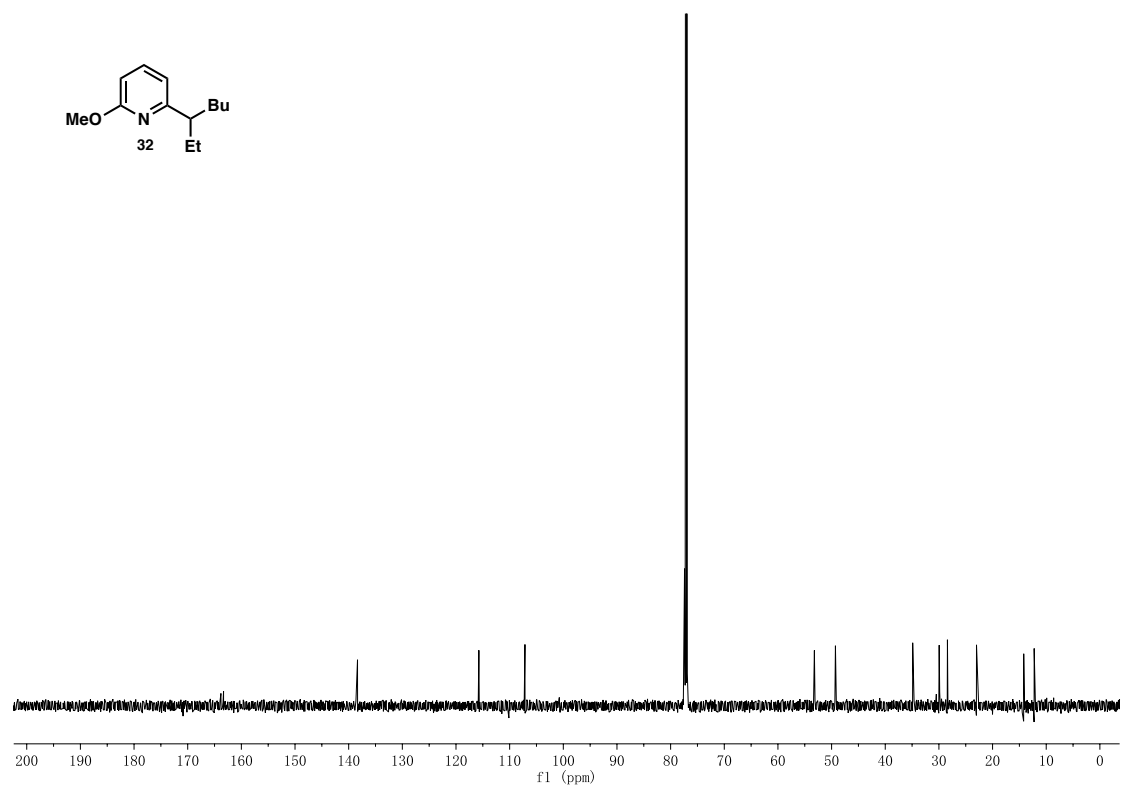


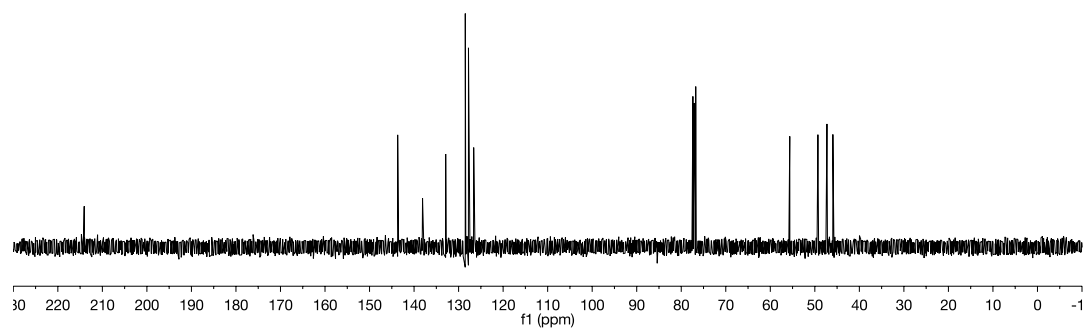
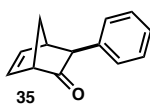












Crystallographic data (X-Ray)

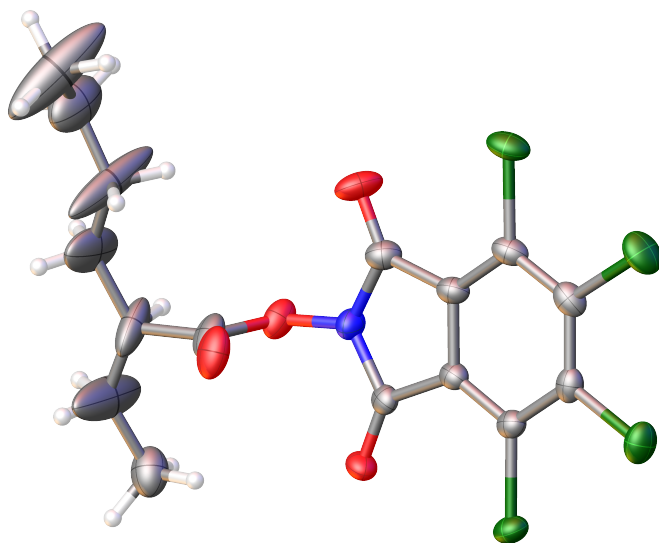


Table 1. Crystal data and structure refinement for **1f**.

Identification code	baran544
Empirical formula	C ₁₆ H ₁₅ Cl ₄ N O ₄
Formula weight	427.09

Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8700(7) Å	$\alpha = 104.489(3)^\circ$.
	b = 9.1094(8) Å	$\beta = 90.358(3)^\circ$.
	c = 12.6095(10) Å	$\gamma = 111.767(3)^\circ$.
Volume	910.54(13) Å ³	
Z	2	
Density (calculated)	1.558 Mg/m ³	
Absorption coefficient	0.671 mm ⁻¹	
F(000)	436	
Crystal size	0.29 x 0.2 x 0.08 mm ³	
Theta range for data collection	2.488 to 26.358°.	
Index ranges	-10 ≤ h ≤ 11, -11 ≤ k ≤ 7, -15 ≤ l ≤ 15	
Reflections collected	11540	
Independent reflections	3701 [R(int) = 0.0324]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2602 and 0.2261	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3701 / 0 / 228	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2sigma(I)]	R1 = 0.0544, wR2 = 0.1273	
R indices (all data)	R1 = 0.0755, wR2 = 0.1400	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.901 and -0.837 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for baran544. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Cl(1)	9086(1)	222(1)	-1466(1)	44(1)
Cl(2)	5403(1)	-893(1)	-2179(1)	38(1)
Cl(3)	10837(1)	3258(1)	538(1)	36(1)
Cl(4)	3434(1)	1166(1)	-994(1)	31(1)
O(1)	6968(3)	6648(3)	2571(2)	35(1)
O(2)	4321(3)	4334(3)	1022(2)	31(1)
O(3)	9720(3)	5834(3)	2153(2)	43(1)
N(1)	7043(3)	5419(4)	1697(2)	29(1)
C(1)	8021(4)	1334(4)	-794(3)	29(1)
C(2)	8810(4)	2697(4)	104(3)	28(1)
C(3)	7922(4)	3566(4)	623(3)	25(1)
C(4)	8446(4)	5060(4)	1585(3)	30(1)
C(5)	6345(5)	6042(5)	3462(3)	41(1)
C(6)	6322(7)	7428(7)	4402(3)	65(2)
C(7)	7670(7)	7904(7)	5249(5)	89(2)
C(8)	8981(11)	7544(9)	5301(6)	160(5)
C(9)	10384(8)	8132(8)	6066(5)	90(2)
C(10)	10864(15)	7225(8)	6502(8)	196(7)
C(11)	6361(4)	846(4)	-1126(3)	26(1)
C(12)	6275(4)	3113(4)	277(3)	23(1)
C(13)	5657(4)	4287(4)	1001(3)	24(1)
C(14)	4911(8)	7661(10)	4430(6)	144(4)
C(15)	3642(6)	7289(6)	3570(4)	54(1)
O(16)	5931(4)	4635(4)	3423(2)	49(1)
C(17)	5473(4)	1756(4)	-592(3)	24(1)

Table 3. Bond lengths [Å] and angles [°] for baran544.

Cl(1)-C(1)	1.712(3)
Cl(2)-C(11)	1.712(3)
Cl(3)-C(2)	1.720(3)
Cl(4)-C(17)	1.717(3)
O(1)-N(1)	1.383(4)
O(1)-C(5)	1.401(5)
O(2)-C(13)	1.202(4)
O(3)-C(4)	1.197(4)
N(1)-C(4)	1.398(4)
N(1)-C(13)	1.392(4)
C(1)-C(2)	1.398(5)
C(1)-C(11)	1.398(5)
C(2)-C(3)	1.373(5)
C(3)-C(4)	1.496(5)
C(3)-C(12)	1.396(4)
C(5)-C(6)	1.507(5)
C(5)-O(16)	1.183(5)
C(6)-H(6)	0.9800
C(6)-C(7)	1.458(7)
C(6)-C(14)	1.344(7)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-C(8)	1.326(8)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(8)-C(9)	1.414(8)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(9)-C(10)	1.284(8)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(17)	1.405(5)
C(12)-C(13)	1.493(5)
C(12)-C(17)	1.376(5)
C(14)-H(14A)	0.9700

C(14)-H(14B)	0.9700
C(14)-C(15)	1.441(8)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
N(1)-O(1)-C(5)	111.7(3)
O(1)-N(1)-C(4)	121.4(3)
O(1)-N(1)-C(13)	121.9(3)
C(13)-N(1)-C(4)	115.7(3)
C(2)-C(1)-Cl(1)	119.5(3)
C(11)-C(1)-Cl(1)	119.8(3)
C(11)-C(1)-C(2)	120.6(3)
C(1)-C(2)-Cl(3)	120.6(3)
C(3)-C(2)-Cl(3)	121.4(3)
C(3)-C(2)-C(1)	118.1(3)
C(2)-C(3)-C(4)	129.5(3)
C(2)-C(3)-C(12)	121.6(3)
C(12)-C(3)-C(4)	108.9(3)
O(3)-C(4)-N(1)	125.2(3)
O(3)-C(4)-C(3)	131.8(3)
N(1)-C(4)-C(3)	103.0(3)
O(1)-C(5)-C(6)	109.8(4)
O(16)-C(5)-O(1)	121.8(3)
O(16)-C(5)-C(6)	128.4(4)
C(5)-C(6)-H(6)	95.4
C(7)-C(6)-C(5)	110.2(4)
C(7)-C(6)-H(6)	95.4
C(14)-C(6)-C(5)	115.1(4)
C(14)-C(6)-H(6)	95.4
C(14)-C(6)-C(7)	132.0(5)
C(6)-C(7)-H(7A)	103.6
C(6)-C(7)-H(7B)	103.6
H(7A)-C(7)-H(7B)	105.3
C(8)-C(7)-C(6)	134.3(5)
C(8)-C(7)-H(7A)	103.6
C(8)-C(7)-H(7B)	103.6
C(7)-C(8)-H(8A)	103.5

C(7)-C(8)-H(8B)	103.5
C(7)-C(8)-C(9)	134.7(5)
H(8A)-C(8)-H(8B)	105.3
C(9)-C(8)-H(8A)	103.5
C(9)-C(8)-H(8B)	103.5
C(8)-C(9)-H(9A)	106.2
C(8)-C(9)-H(9B)	106.2
H(9A)-C(9)-H(9B)	106.3
C(10)-C(9)-C(8)	124.7(7)
C(10)-C(9)-H(9A)	106.2
C(10)-C(9)-H(9B)	106.2
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(1)-C(11)-Cl(2)	119.5(3)
C(1)-C(11)-C(17)	120.5(3)
C(17)-C(11)-Cl(2)	119.9(3)
C(3)-C(12)-C(13)	108.9(3)
C(17)-C(12)-C(3)	121.0(3)
C(17)-C(12)-C(13)	130.1(3)
O(2)-C(13)-N(1)	125.2(3)
O(2)-C(13)-C(12)	131.5(3)
N(1)-C(13)-C(12)	103.3(3)
C(6)-C(14)-H(14A)	104.4
C(6)-C(14)-H(14B)	104.4
C(6)-C(14)-C(15)	131.4(6)
H(14A)-C(14)-H(14B)	105.6
C(15)-C(14)-H(14A)	104.4
C(15)-C(14)-H(14B)	104.4
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

C(11)-C(17)-Cl(4)	120.8(3)
C(12)-C(17)-Cl(4)	121.0(3)
C(12)-C(17)-C(11)	118.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for baran544. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	50(1)	42(1)	54(1)	16(1)	19(1)	32(1)
Cl(2)	52(1)	28(1)	31(1)	4(1)	4(1)	14(1)
Cl(3)	23(1)	39(1)	57(1)	24(1)	7(1)	16(1)
Cl(4)	25(1)	35(1)	31(1)	10(1)	-4(1)	9(1)
O(1)	51(2)	28(1)	29(1)	2(1)	-3(1)	22(1)
O(2)	25(1)	43(1)	30(1)	11(1)	5(1)	19(1)
O(3)	31(1)	31(1)	57(2)	5(1)	-17(1)	7(1)
N(1)	30(2)	32(2)	25(2)	2(1)	1(1)	15(1)
C(1)	34(2)	27(2)	36(2)	17(2)	12(2)	17(2)
C(2)	23(2)	28(2)	40(2)	19(2)	6(2)	12(1)
C(3)	22(2)	25(2)	31(2)	14(2)	2(1)	9(1)
C(4)	27(2)	27(2)	37(2)	12(2)	-1(2)	10(2)
C(5)	64(3)	47(2)	23(2)	6(2)	-5(2)	36(2)
C(6)	116(4)	73(3)	25(2)	-7(2)	-11(2)	70(3)
C(7)	71(4)	78(4)	83(4)	-54(3)	-22(3)	38(3)
C(8)	218(9)	119(6)	137(6)	-99(5)	-141(6)	145(6)
C(9)	107(5)	84(4)	76(4)	-24(3)	-18(4)	64(4)
C(10)	348(15)	63(4)	155(8)	-41(5)	-173(10)	103(7)
C(11)	37(2)	22(2)	23(2)	10(1)	6(1)	12(1)
C(12)	23(2)	27(2)	24(2)	13(1)	4(1)	12(1)
C(13)	27(2)	29(2)	21(2)	12(1)	4(1)	13(1)
C(14)	86(5)	162(7)	136(6)	-109(6)	-51(4)	91(5)
C(15)	76(3)	59(3)	42(3)	18(2)	12(2)	40(3)
O(16)	83(2)	45(2)	28(2)	14(1)	6(1)	31(2)
C(17)	25(2)	27(2)	24(2)	12(1)	2(1)	9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for baran544.

	x	y	z	U(eq)
H(6)	6879	8299	4050	78
H(7A)	8112	9094	5441	107
H(7B)	7129	7618	5877	107
H(8A)	9428	7667	4614	192
H(8B)	8530	6371	5220	192
H(9A)	11294	8717	5711	108
H(9B)	10249	8951	6674	108
H(10A)	11149	6478	5937	294
H(10B)	10001	6614	6865	294
H(10C)	11801	7906	7029	294
H(14A)	5233	8826	4778	173
H(14B)	4347	7111	4964	173
H(15A)	3575	6332	3005	80
H(15B)	3890	8203	3260	80
H(15C)	2616	7086	3871	80

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