

Supporting Information

Ketone Synthesis from Benzyldiboronates and Esters: Leveraging α -Borylcarbanions for Carbon-Carbon Bond Formation

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I. General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. All glassware was stored in a pre-heated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.¹ Cyclopentylmethyl ether (CPME, Acros Organics) was dried and deoxygenated with sodium-benzophenone ketyl, distilled under reduced pressure, and stored over 4 Å molecular sieves prior to use. Benzene-*d*₆ (Cambridge Isotope Laboratories) and tetrahydrofuran-*d*₈ (thf-*d*₈, Cambridge Isotope Laboratories) were dried over sodium metal, distilled under reduced pressure, and stored over 4 Å molecular sieves prior to use. Chloroform-*d* (Cambridge Isotope Laboratories) and pinacolborane (HBPin, Oakwood Chemical) were used without further purification. Bis(pinacolato)diboron (B₂Pin₂, Allychem) and solid substrates were dried under reduced pressure prior to use. Liquid substrates were dried over CaH₂ and distilled under reduced pressure prior to use. Methylaluminoxane (MAO, 10 wt. % in toluene, Sigma Aldrich) was concentrated *in vacuo* to a white solid. Cobalt(II) 2-ethylhexanote solution (65 wt. % in mineral spirits) was purchased from Sigma-Aldrich and deoxygenated by several freeze-pump-thaw cycles prior to use. Lithium 2,2,6,6-tetramethylpiperidide (LiTMP, salt, Sigma Aldrich) and lithium *tert*-butoxide (LiO^tBu, Alfa Aesar) were received, brought into the glovebox, and used without further purification. Methyl phenylacetate (Sigma Aldrich), *N*-fluorosobzenesulfonimide (NFSI, Sigma Aldrich), iodomethane (MeI, Sigma Aldrich), propargyl bromide (80 wt. % in toluene, Sigma Aldrich), allyl bromide (Sigma Aldrich), and *N,N*-dimethylmethyleniminium iodide (Eschenmoser's salt, Sigma Aldrich), *N*-(*tert*-Butoxycarbonyl)-*L*-proline methyl ester (Boc-*L*-Pro-OMe, Sigma Aldrich) were used without further purification. *N*-Bromosuccinimide (NBS, Sigma Aldrich) was recrystallized from water and dried *in vacuo* for 24 hours. The following compounds were prepared according to literature procedures: ^cyADI,²

^{(*Cy*)ADI}Co(O₂C₈H₁₅)₂,² (^{(*Cy*)ADI}Co(OPiv)₂,² ^{(*ipc*)ADI},³ [(NEt₃)Ni(OPiv)]₂,³ (^{(*ipc*)ADI}Ni(OPiv)₂,³ benzylmonoboronate,² and 2-(*tert*-butoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.⁴

¹H NMR spectra were recorded on either Bruker ADVANCE 300 or 500 spectrophotometers operating at 300.13 MHz, and 500.46 MHz, respectively. ¹³C NMR spectra were recorded on either Bruker ADVANCE 300 or 500 spectrometer operating at 75.48 MHz and 125.85 MHz, respectively. ¹¹B NMR spectra were recorded on Bruker ADVANCE 300 operating at 96 MHz. ¹⁹F NMR spectra were recorded on Bruker ADVANCE 300 operating at 282 MHz. All ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ using the ¹H (chloroform-*d*: 7.26 ppm; benzene-*d*₆: 7.16 ppm; thf-*d*₈: 3.58 ppm) and ¹³C (chloroform-*d*: 77.16 ppm; benzene-*d*₆: 128.06 ppm; thf-*d*₈: 67.21 ppm) chemical shifts of the solvent as a standard. ¹H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, dd = doublet of doublet, td = triplet of doublet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration, assignment. ¹H NMR data for paramagnetic compounds are reported as follows: chemical shift, integration, peak width at half height (Hz). ¹³C NMR data for diamagnetic compounds are reported as follows: chemical shift, number of protons attached to carbon (e.g. CH₂), assignment. Carbons that are directly attached to boron atoms were not observed due to quadrupolar relaxation.⁵ ¹¹B NMR data and ¹⁹F NMR data were also reported for boron-, and fluorine-containing compounds, respectively.

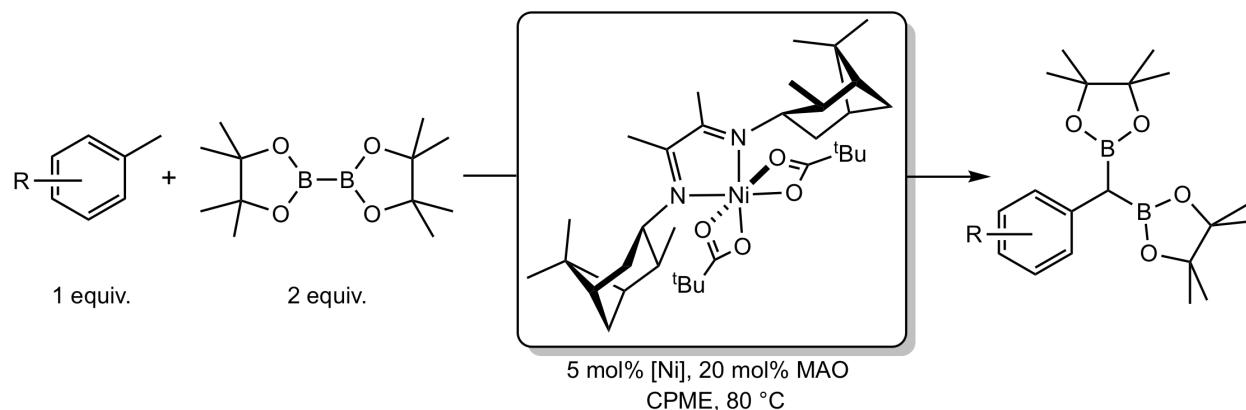
GC analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Shimadzu SHRXI-5MS capillary column (15m x 250μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 20:1, and inlet and detector temperatures of 250 °C and 275 °C, respectively. UHP-grade S3 helium was used as carrier gas with a flow rate of 1.82 mL/min. Two temperature programs were used for GC analyses depending on the components of the reaction mixtures. For mixtures containing products with relatively low molecular weight, the temperature program used was as follows: 60

°C, isothermal 1 min; 15 °C/min to 250 °C, isothermal 2 min. For mixtures containing products with relatively high molecular weight, the temperature program used was as follows: 60 °C, isothermal 1 min; 15 °C /min to 250 °C, isothermal 15 min.

High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard.

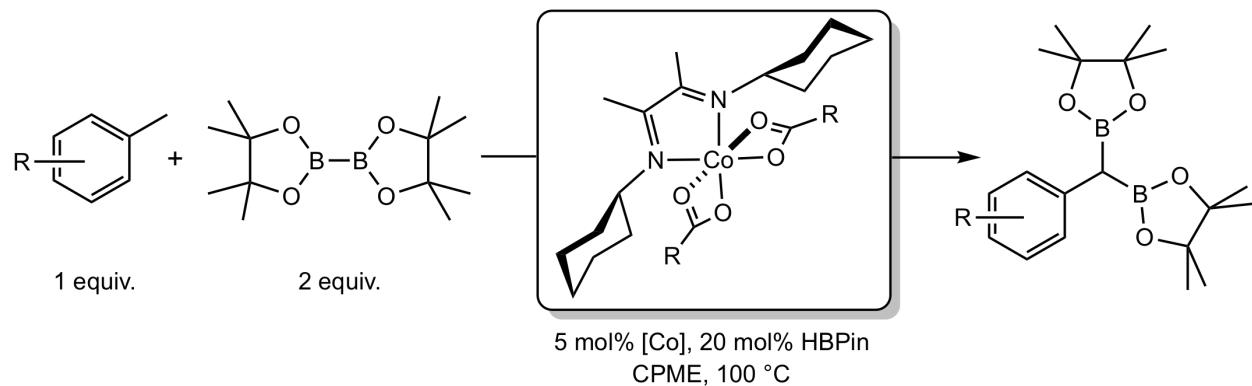
II. Preparation of *gem*-Diboronates.

General Procedure A: Catalytic Benzylic Diborylation of Methylarenes with (^{iPC}ADI)Ni(OPiv)₂.



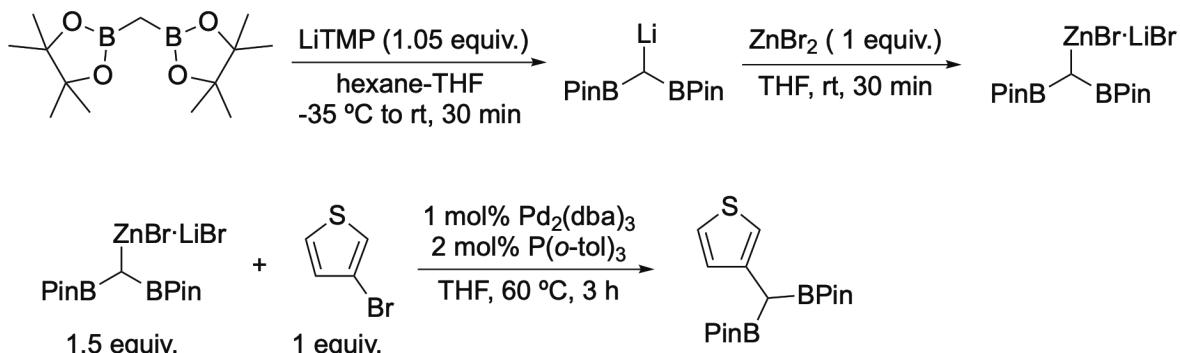
Benzylidiboronates were prepared according to modified literature procedures.³ To a scintillation vial charged with a magnetic stir bar was added the specified amount of (^{iPC}ADI)Ni(OPiv)₂ and B₂Pi_n₂ as solids in the glovebox. CPME was then added *via* syringe, followed by the methylarene substrate. The resulting mixture was treated with MAO and it turned dark purple immediately. The vial was capped and sealed, brought out of the glovebox, and the mixture was stirred at 80 °C for the specified time, during which time a color change from deep purple to brown was observed. In order to check the reaction progress, the vial was brought into the glove box and the GC aliquot was made in the glove box. After the full consumption of B₂Pi_n₂ was observed by GC, the reaction was quenched by exposure to air, concentrated *in vacuo*. Then the resulting crude residue was loaded onto a silica gel column for the purification of products. The isolated diboronate was analyzed by ¹H NMR, ¹³C NMR, ¹¹B NMR and HRMS to verify the identity and purity of the products.

General Procedure B: Catalytic Benzylic Diborylation of Methylarenes with $(^{cy}ADI)Co(OPiv)_2$ or $(^{cy}ADI)Co(O_2C_8H_{15})_2$.



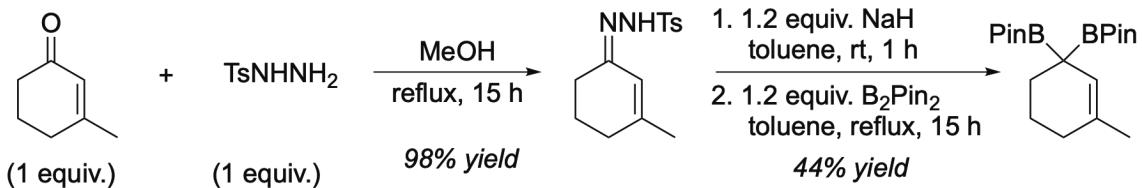
Benzylidiboronates were prepared according to the literature procedures.² To a scintillation vial charged with a magnetic stir bar was added the specified amount of cobalt catalyst and B_2Pin_2 as solids in the glovebox. CPME was then added *via* syringe, followed by the methylarene substrate. The resulting mixture was treated with HBPin. The vial was capped and sealed, brought out of the glovebox, and the mixture was stirred at 100 °C for the specified time. In order to check the reaction progress, the vial was brought into the glove box and the GC aliquot was made in the glove box. After the full consumption of B_2Pin_2 was observed by GC, the reaction was quenched by exposure to air, concentrated *in vacuo*. Then the resulting crude residue was loaded onto a silica gel column for the purification of products. The isolated diborionate was analyzed by 1H NMR, ^{13}C NMR, ^{11}B NMR and HRMS to verify the identity and purity of the products.

Preparation of 2,2'-(Thiophen-3-ylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).



This compound was made according to literature procedure.⁶ The resulting white solid was dried under vacuum for 2 hours prior to use.

Preparation of 2,2'-(3-Methylcyclohex-2-en-1-yl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).

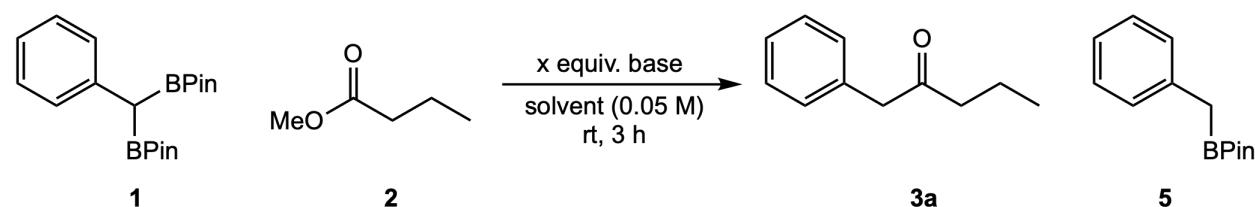


This compound was made according to literature procedure.⁷ The product was dried under vacuum for 13 hours prior to use.

III. Screening of Bases and Solvents.

Stock solutions of benzylidiboronate **1** (688 mg/10 mL THF, 0.20 M) and methyl butyrate **2** (227 μ L/10 mL THF, 0.20 M) were prepared. A scintillation vial with a magnetic stir bar was then charged in the glove box with the specified amount of base, and then 0.5 mL of each stock solution was added, followed by 1 mL of THF. For the solvent screening, a scintillation vial was charged with **1** (34 mg, 0.1 mmol) and LiO^tBu (12 mg, 0.15 mmol) as solids and then 2 mL of the specified solvent and **2** (11 μ L, 0.1 mmol) were added. The vial was capped and sealed, brought out of the glovebox, and the mixture was allowed to stir at room temperature for 3 hours. The mixture was quenched by adding water and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated. 1-chloro-4-nitrobenzene (12 μ L, 0.1 mmol) was added as an internal standard, and the residue was dissolved in CDCl₃ for NMR analysis. Yields were determined by integration of diagnostic peaks (**3a**: singlet at 3.68 ppm, benzylic CH / **11**: singlet at 2.29 ppm, benzylic CH) in the ¹H NMR spectrum.

Table S1. Screening of various bases and solvents.



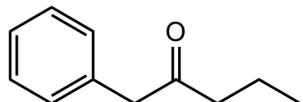
Base	Equiv.	Solvent	%yield 3a ^a	%yield 5 ^a
LiO ^t Bu	1	THF	83	15
LiO ^t Bu	1.5	THF	86 ^b	9 ^b
LiO ^t Bu	2	THF	85	9
LiOMe	1	THF	53	37
NaOMe	1	THF	80	17
NaOMe	1.5	THF	81	17
NaOMe	2	THF	81	13
NaOEt	1	THF	62	24

NaO ^t Bu	1	THF	66	21
KO ^t Bu	1	THF	60	39
LiO ^t Bu	1.5	Et ₂ O	53	36
LiO ^t Bu	1.5	CPME	50	39
LiO ^t Bu	1.5	TBME	36	39
LiO ^t Bu	1.5	2-MeTHF	17	52
LiO ^t Bu	1.5	Hexanes	46	44
LiO ^t Bu	1.5	Toluene	61	36

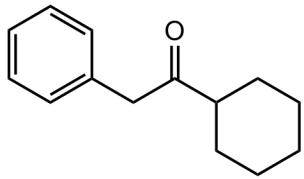
^aNMR yields. ^bIsolated yields.

IV. General Procedure for Deborylative Coupling of Benzyldiboronates with Esters and Carbonyl Derivatives. (Table 1, Table 2, and Scheme 3)

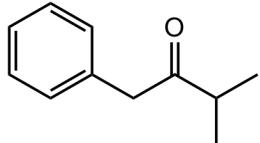
In a typical experiment, a scintillation vial with a magnetic stir bar was charged with the specified amount of diboronates, esters, and THF in the glovebox. LiO^tBu was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. The reaction progress was monitored by GC, and typically starting materials were fully consumed within 2 hours. After 3 hours, the reaction mixture was brought out of the glovebox, quenched by exposure to air, diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography. The resulting product was then analyzed by ¹H NMR, ¹³C NMR, and HRMS to verify the identity and purity. ¹¹B NMR and ¹⁹F NMR were also reported in the case compounds have boron and fluorine atom(s).



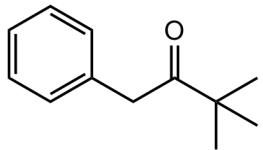
1-Phenylpentan-2-one 3a. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzyldiboronate **1**, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; 2% ethyl acetate in hexanes) yielded 14 mg (0.086 mmol, 86% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-d, 23 °C): δ 7.33 (t, *J*_{HH} = 7.3 Hz, 2H), 7.29–7.24 (m, 1H), 7.20 (d, *J*_{HH} = 7.3 Hz, 1H), 3.68 (s, 2H), 2.43 (t, *J*_{HH} = 7.3 Hz, 2H), 1.63–1.52 (m, 2H), 0.87 (t, *J*_{HH} = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 208.7, 134.5, 129.5, 128.8, 127.1, 50.3, 44.0, 17.3, 13.8. ¹H and ¹³C NMR data agree with previously reported data.⁸



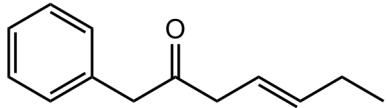
1-Cyclohexyl-2-phenylethan-1-one 3b. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 28 mg (0.20 mmol, 1 equiv.) of methyl cyclohexanecarboxylate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 2% to 2.5% to 3% to 4% ethyl acetate in hexanes) yielded 36 mg (0.18 mmol, 89% yield) of product as pale-yellow oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.32 (t, *J*_{HH} = 7.3 Hz, 2H), 7.25 (t, *J*_{HH} = 7.3 Hz, 1H), 7.19 (d, *J*_{HH} = 7.3 Hz, 2H), 3.73 (s, 2H), 2.46 (tt, *J*_{HH} = 11.5, 3.4, 1H), 1.89–1.72 (m, 4H), 1.69–1.63 (m, 1H), 1.44–1.31 (m, 2H), 1.31–1.14 (m, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 211.4, 134.6, 129.6, 128.7, 126.9, 50.2, 48.0, 28.7, 25.9, 25.7. ¹H and ¹³C NMR data agree with previously reported data.⁹



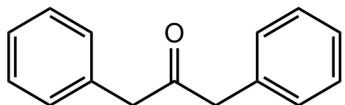
3-Methyl-1-phenylbutan-2-one 3c. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 20 mg (0.20 mmol, 1 equiv.) of methyl isobutyrate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 3% to 4% ethyl acetate in hexanes) yielded 28 mg (0.17 mmol, 86% yield) of product as colorless oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.32 (t, *J*_{HH} = 7.3 Hz, 2H), 7.25 (t, *J*_{HH} = 7.3 Hz, 1H), 7.20 (d, *J*_{HH} = 7.0 Hz, 2H), 3.75 (s, 2H), 2.73 (sep, *J*_{HH} = 6.9 Hz, 1H), 1.10 (d, *J*_{HH} = 6.9 Hz, 6H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 212.1, 134.6, 129.6, 128.8, 127.0, 47.8, 40.2, 18.5. ¹H and ¹³C NMR data agree with previously reported data.¹⁰



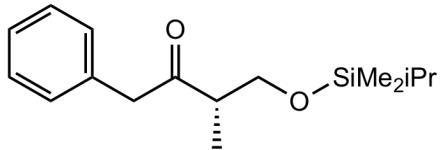
3,3-Dimethyl-1-phenylbutan-2-one 3d. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 23 mg (0.20 mmol, 1 equiv.) of methyl pivalate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 3% to 4% to 5% ethyl acetate in hexanes) yielded 32 mg (0.18 mmol, 91% yield) of product as colorless oil. ¹H NMR (300 MHz, chloroform-*d*, 23 °C): δ 7.35–7.14 (m, 5H), 3.80 (s, 2H), 1.21 (s, 9H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 213.0, 135.1, 129.7, 128.5, 126.8, 77.4, 77.2, 76.9, 44.8, 43.4, 26.6. ¹H and ¹³C NMR data agree with previously reported data.¹¹



(E)-1-Phenylhept-4-en-2-one 3e. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 26 mg (0.20 mmol, 1 equiv.) of methyl (*E*)-hex-3-enoate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 1% to 1.5% to 2% ethyl acetate in hexanes) yielded 31 mg (0.16 mmol, 82% yield) of product as pale-yellow oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.33 (t, *J*_{HH} = 7.4 Hz, 2H), 7.27 (t, *J*_{HH} = 7.4 Hz, 1H), 7.20 (d, *J*_{HH} = 7.4 Hz, 2H), 5.59–5.45 (m, 2H), 3.71 (s, 2H), 3.14 (d, *J*_{HH} = 6.5 Hz, 2H), 2.05 (quin, *J*_{HH} = 7.3 Hz, 2H), 0.98 (t, *J*_{HH} = 7.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 207.1, 137.1, 134.3, 129.6, 128.8, 127.1, 120.8, 49.5, 46.1, 25.8, 13.6. HRMS (ESI+) *m/z* calculated for C₁₃H₁₆O ([M+H]⁺) 189.1274, found *m/z* 189.1273.

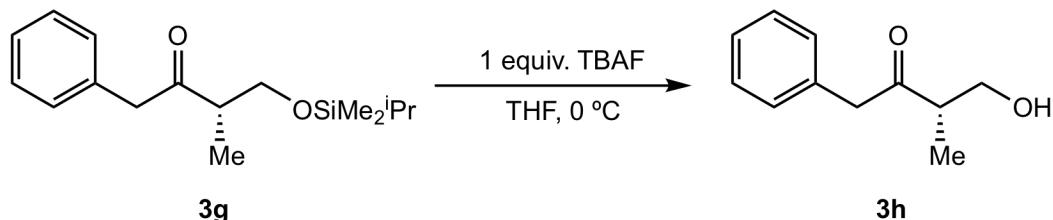


1,3-Diphenylpropan-2-one 3f. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzyldiboronate **1**, 15 mg (0.10 mmol, 1 equiv.) of methyl 2-phenylacetate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; eluent: 4% ethyl acetate in hexanes) yielded 17 mg (0.081 mmol, 81% yield) of product as light-yellow oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.32 (t, *J*_{HH} = 7.3 Hz, 4H), 7.27 (t, *J*_{HH} = 7.3 Hz, 2H), 7.15 (d, *J*_{HH} = 7.3 Hz, 4H), 3.72 (s, 4H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 205.8, 134.1, 129.7, 128.9, 127.2, 49.2. ¹H and ¹³C NMR data agree with previously reported data.¹²



(S)-4-((Isopropyldimethylsilyl)oxy)-3-methyl-1-phenylbutan-2-one 3g. Methyl (S)-3-((isopropyldimethylsilyl)oxy)-2-methylpropanoate was prepared according to the literature.¹³ Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 44 mg (0.20 mmol, 1 equiv.) of methyl (S)-3-((isopropyldimethylsilyl)oxy)-2-methylpropanoate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 1% to 1.5% to 2% ethyl acetate in hexanes) yielded 47 mg (0.17 mmol, 84% yield) of product as colorless oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.32 (t, *J*_{HH} = 7.4 Hz, 2H), 7.25 (t, *J*_{HH} = 7.3 Hz, 1H), 7.18 (d, *J*_{HH} = 7.3 Hz, 2H), 3.84–3.66 (m, 3H), 3.59 (dd, *J*_{HH} = 9.8, 5.6 Hz, 1H), 2.97–2.83 (m, 1H), 1.00 (d, *J*_{HH} = 7.1 Hz, 3H), 0.94 (dd, *J*_{HH} = 7.1, 1.9 Hz, 6H), 0.88–0.72 (m, 1H), 0.03 (d, *J*_{HH} = 3.1 Hz, 6H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 211.2, 134.3,

129.8, 128.7, 127.0, 65.5, 50.3, 47.8, 17.0, 14.5, 13.4, -4.5. **HRMS** (ESI+) m/z calculated for $C_{16}H_{26}O_2Si$ ($[M+H]^+$) 279.1775, found m/z 279.1772.



Deprotection of 3g to 3h(BL-II-051). A 20 mL scintillation vial was charged with 36 mg (0.20 mmol, 1 equiv.) of **3g** and a magnetic stir bar. To the vial was added 0.2 mL of TBAF solution (1M solution in THF, 0.2 mmol, 1 equiv.) at 0 °C. The resulting mixture was stirred at 0 °C for an hour, after which the starting material was fully consumed (monitored by TLC). The mixture was diluted with saturated aqueous NH₄Cl solution and transferred to a separatory funnel. The crude mixture was extracted with EtOAc twice and the combined organic layers were dried over MgSO₄, filtered, concentrated, and directly injected into a pre-packed silica column for purification. **3h** was afforded as colorless oil after flash column chromatography (silica gel packed with hexanes; loaded with DCM; gradient: 30% to 40% to 50% to 60% EtOAc in hexanes). **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.33 (t, J_{HH} = 7.3 Hz, 2H), 7.27 (t, J_{HH} = 7.3 Hz, 1H), 7.20 (d, J_{HH} = 7.0 Hz, 2H), 3.79 (s, 2H), 3.73 (dd, J_{HH} = 11.1, 7.3 Hz, 1H), 3.65 (dd, J_{HH} = 11.1, 4.2 Hz, 1H), 2.91–2.84 (m, 1H), 2.11 (s, br, 1H), 1.14 (d, J_{HH} = 7.3 Hz, 3H). **¹³C{¹H NMR}** (126 MHz, chloroform-*d*, 23 °C): δ 212.4, 133.8, 129.6, 128.8, 127.2, 64.5, 49.0, 47.4, 13.5. **HRMS** (ESI+) m/z calculated for $C_{11}H_{14}O_2$ ($[M+H]^+$) 179.1067, found 179.1071.

SFC traces for racemic and enantiopure Methyl (S)-3-((isopropyldimethylsilyl)oxy)-2-methylpropanoate:

Conditions: AD-H (25 x 0.46 cm), 5% methanol (DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

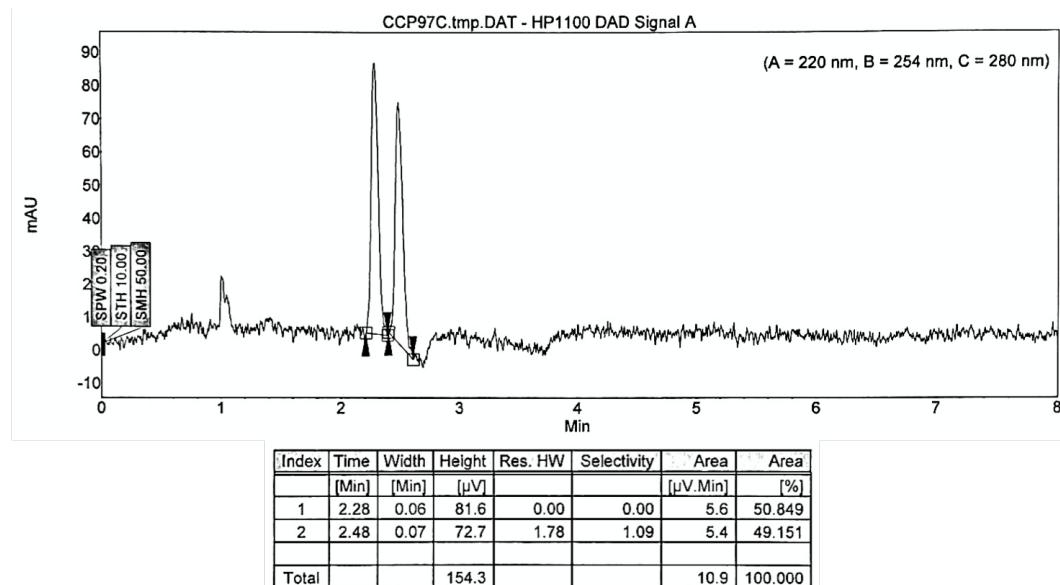


Figure S1. SFC trace of racemic Methyl 3-((isopropyldimethylsilyl)oxy)-2-methylpropanoate.

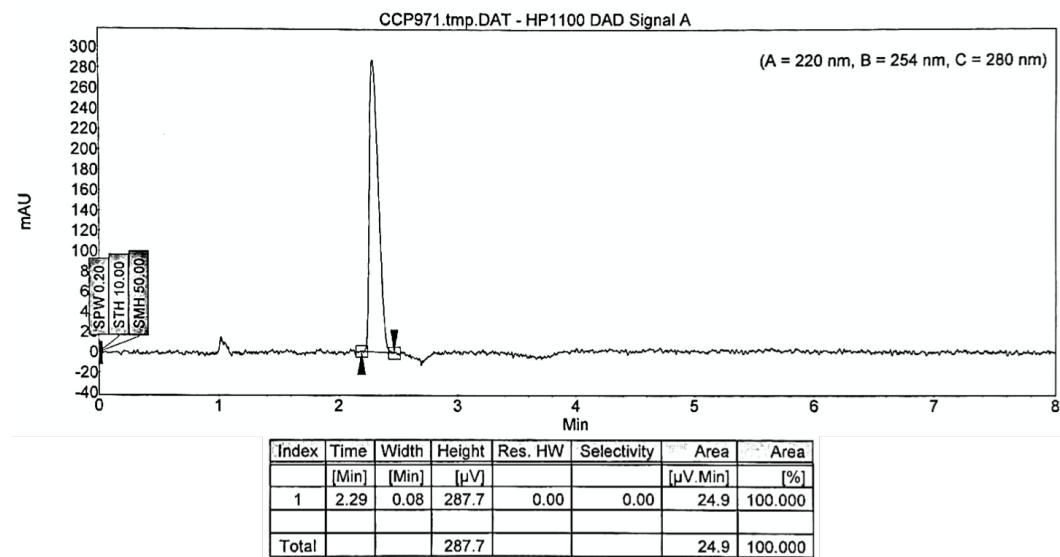


Figure S2. SFC trace of enantiopure Methyl (S)-3-((isopropyldimethylsilyl)oxy)-2-methylpropanoate.

SFC traces for racemic and enantiopure **3h**:

Conditions: OJ-H (25 x 0.46 cm), 20% methanol (0.1% DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

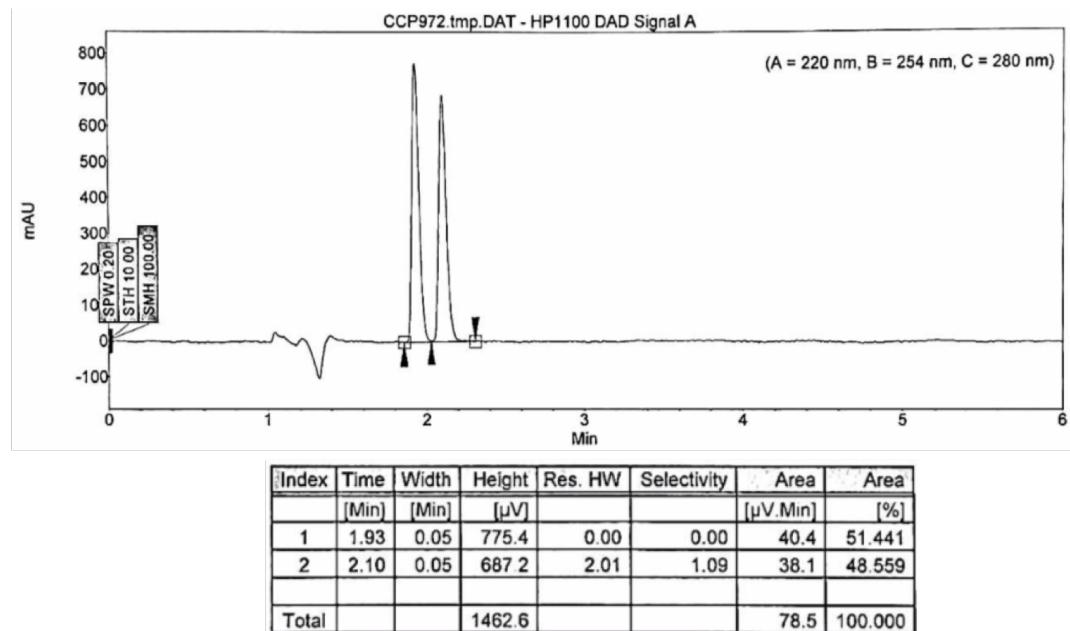


Figure S3. SFC trace of racemic **3h**.

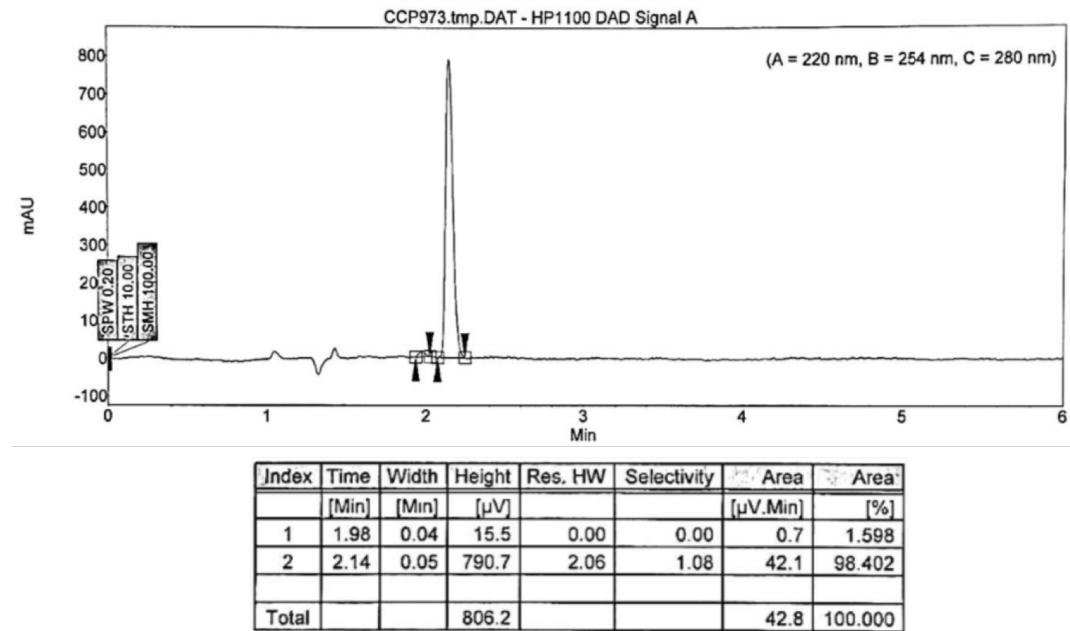
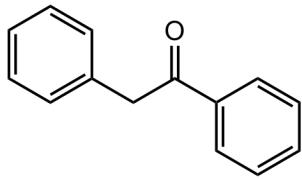
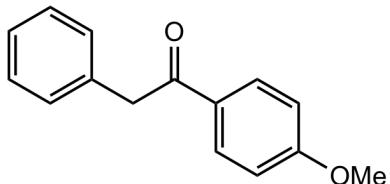


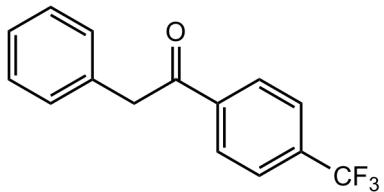
Figure S4. SFC trace of enantiopure **3h**.



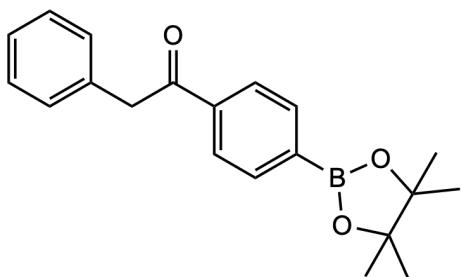
1,2-Diphenylethan-1-one 3i. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 27 mg (0.20 mmol, 1 equiv.) of methyl benzoate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 2% to 3% to 4% ethyl acetate in hexanes) yielded 36 mg (0.18 mmol, 92% yield) of product as a white solid. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 8.08–7.98 (m, 2H), 7.61–7.52 (m, 1H), 7.46(dd, *J*_{HH} = 8.3, 6.7 Hz, 2H), 7.38–7.18 (m, 5H), 4.29 (s, 1H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 197.7, 136.7, 134.7, 133.3, 129.6, 128.8, 128.8, 128.7, 127.0, 45.6. ¹H and ¹³C NMR data agree with previously reported data.¹⁴



1-(4-Methoxyphenyl)-2-phenylethan-1-one 3j. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 33 mg (0.20 mmol, 1 equiv.) of methyl 4-methoxybenzoate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; gradient: 1% to 3% to 5% to 7% ethyl acetate in hexanes) yielded 43 mg (0.19 mmol, 95% yield) of product as a white solid. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.98 (d, *J*_{HH} = 8.9 Hz, 2H), 7.30 (t, *J*_{HH} = 7.4 Hz, 2H), 7.24 (m, 3H), 6.91 (d, *J*_{HH} = 8.9 Hz, 2H), 4.22 (s, 2H), 3.84 (s, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 196.4, 163.6, 135.1, 131.0, 129.7, 129.5, 128.8, 126.9, 113.9, 55.6, 45.4. ¹H and ¹³C NMR data agree with previously reported data.¹⁴

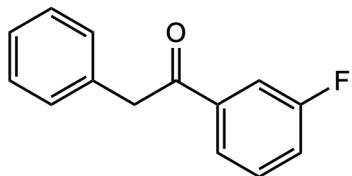


2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3k. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 41 mg (0.20 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; eluent: 5% ethyl acetate in hexanes) yielded 51 mg (0.19 mmol, 96% yield) of product as a white solid. ¹H NMR (500 MHz, chloroform-d, 23 °C): δ 8.11 (d, *J*_{HH} = 8.3 Hz, 2H), 7.72 (d, *J*_{HH} = 8.3 Hz, 2H), 7.35 (t, *J*_{HH} = 7.3 Hz, 2H), 7.31–7.24 (m, 3H), 4.31 (s, 2H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 196.8, 139.3, 134.6 (q, ²J_{CF} = 32.7 Hz), 133.9, 129.5, 129.1, 129.0, 127.3, 125.9 (q, ³J_{CF} = 3.7 Hz), 123.7 (q, ¹J_{CF} = 272.7 Hz), 46.0. ¹⁹F NMR (282 MHz, chloroform-d, 23 °C): δ -63.15. ¹H, ¹³C, and ¹⁹F NMR data agree with previously reported data.¹⁵

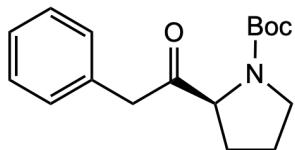


2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one 3l. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzyldiboronate **1**, 26 mg (0.10 mmol, 1 equiv.) of methyl 4-(BPin)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel

packed with hexanes; loaded with dichloromethane; eluent: 8% ethyl acetate in hexanes) yielded 24 mg (0.075 mmol, 74% yield) of product as a white solid. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.98 (d, *J_{HH}* = 8.2 Hz, 2H), 7.88 (d, *J_{HH}* = 8.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 4.30 (s, 2H), 1.35 (s, 11H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 198.1, 138.6, 135.1, 134.6, 131.4, 129.6, 128.8, 127.7, 127.0, 84.4, 45.8, 25.0. **¹¹B NMR** (96 MHz, chloroform-*d*, 23 °C): δ 30.40. **HRMS** (ESI+) *m/z* calculated for C₂₀H₂₃BO₃ ([M+H]⁺) 323.1813, found 323.1819.



1-(3-fluorophenyl)-2-phenylethan-1-one 3m. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzylboronate **1**, 15 mg (0.10 mmol, 1 equiv.) of methyl 3-fluorobenzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; eluent: 5% ethyl acetate in hexanes) yielded 20 mg (0.093 mmol, 93% yield) of product as a white solid. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.80–7.76 (m, 1H), 7.69 (dt, *J_{HH}* = 9.5, 2.0 Hz, 1H), 7.46–7.42 (m, 1H), 7.36–7.33 (m, 2H), 7.29–7.22 (m, 4H), 4.27 (s, 2H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 196.5, 163.0 (d, ¹*J_{CF}* = 248.0 Hz), 138.8 (d, ³*J_{CF}* = 6.1 Hz), 134.2, 130.4 (d, ³*J_{CF}* = 7.6 Hz), 129.6, 128.9, 127.2, 124.5 (d, ⁴*J_{CF}* = 3.0 Hz), 120.3 (d, ²*J_{CF}* = 21.5 Hz), 115.5 (d, ²*J_{CF}* = 22.3 Hz), 45.8. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -111.7. ¹H and ¹³C NMR data agree with previously reported data.¹⁶



tert-butyl (S)-2-(2-phenylacetyl)pyrrolidine-1-carboxylate 3n. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzylboronate **1**, 23 mg (0.10 mmol, 1 equiv.) of Boc-L-Pro-OMe, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; eluent: 15% ethyl acetate in hexanes to 18 % to 20%) yielded 25 mg (0.086 mmol, 86% yield) of product as colorless oil which was slowly converted to white solid. Rotamers ratio = 60:40. Major: ¹H NMR (500 MHz, chloroform-d, 23 °C): δ 7.33–7.20 (m, 5H), 4.34 (dd, *J*_{HH} = 8.5, 4.8 Hz, 1H), 3.75 (s, 2H), 3.59–3.35 (m, 2H), 2.14–2.09 (m, 1H), 1.82–1.75 (m, 3H), 1.39 (s, 9H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 207.5, 154.1, 133.7, 129.7, 128.8, 127.2, 80.4, 65.2, 46.9, 46.0, 30.4, 28.5, 23.8. Minor: ¹H NMR (500 MHz, chloroform-d, 23 °C): δ 7.32–7.21 (m, 5H), 4.44 (dd, *J*_{HH} = 8.4, 3.9 Hz, 1H), 3.83 (s, 2H), 3.59–3.35 (m, 2H), 1.97–1.93 (m, 1H), 1.82–1.75 (m, 3H), 1.48 (s, 9H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 208.0, 154.8, 134.0, 129.9, 128.7, 127.0, 80.0, 64.7, 47.1, 47.0, 29.4, 28.6, 24.6. ¹H and ¹³C NMR data agree with previously reported data.¹⁷

SFC traces for racemic and enantiopure Boc-Pro-OMe:

Conditions: IC (25 x 0.46 cm), 10% ethanol (DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

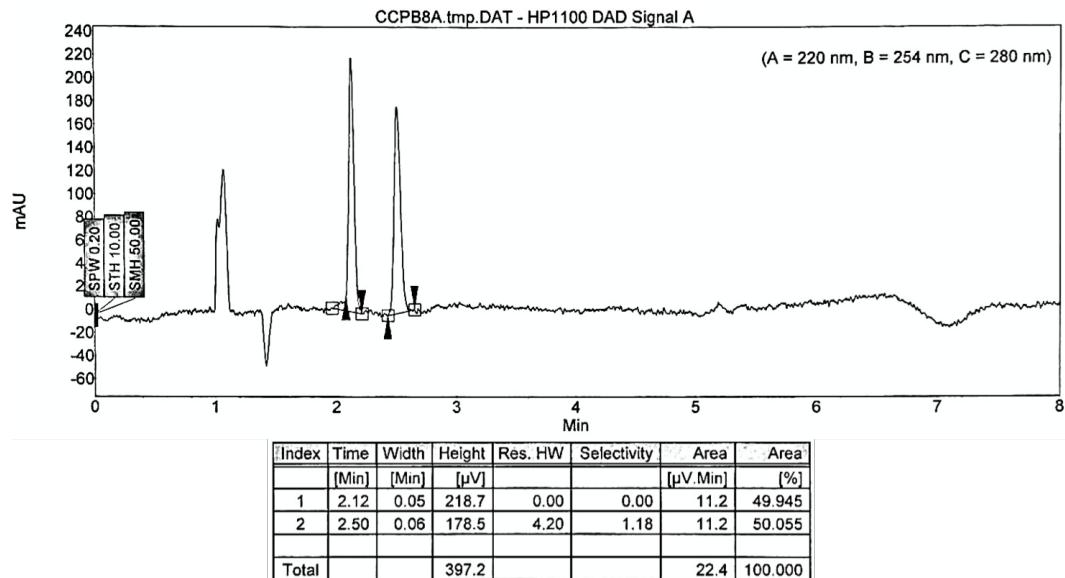


Figure S5. SFC trace of Boc-rac-Pro-OMe.

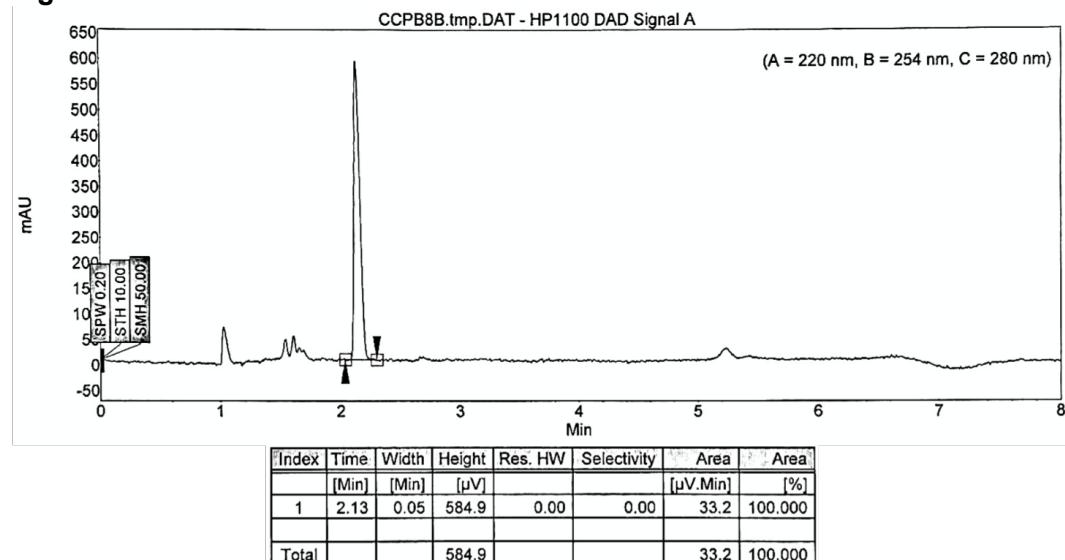


Figure S6. SFC trace of Boc-L-Pro-OMe.

SFC traces for racemic and enantiopure **3n**:

Conditions: IG (25 x 0.46 cm), 20% methanol (0.1% DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

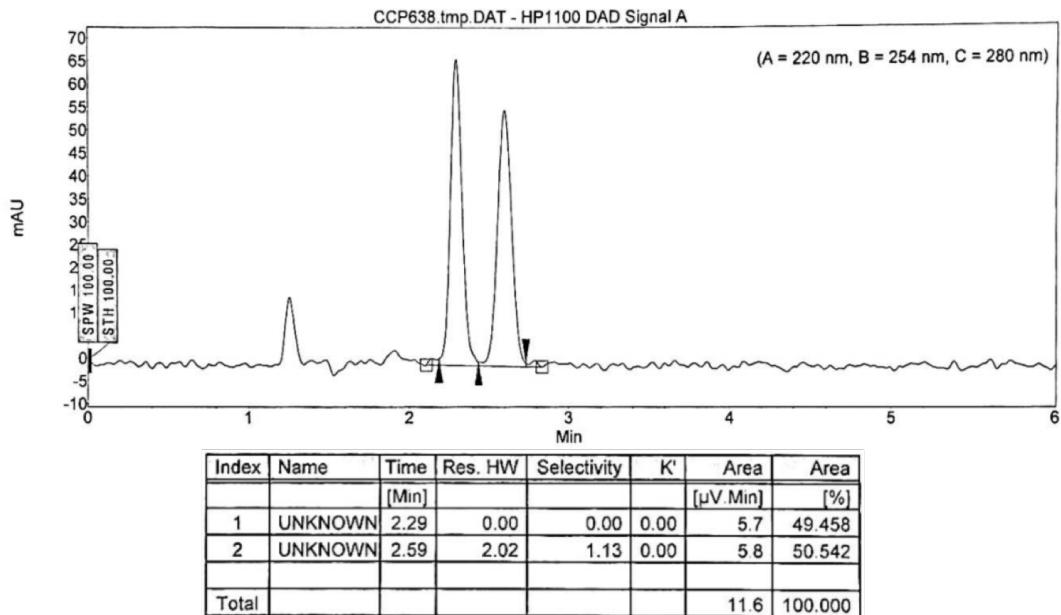


Figure S7. SFC trace of racemic **3n**.

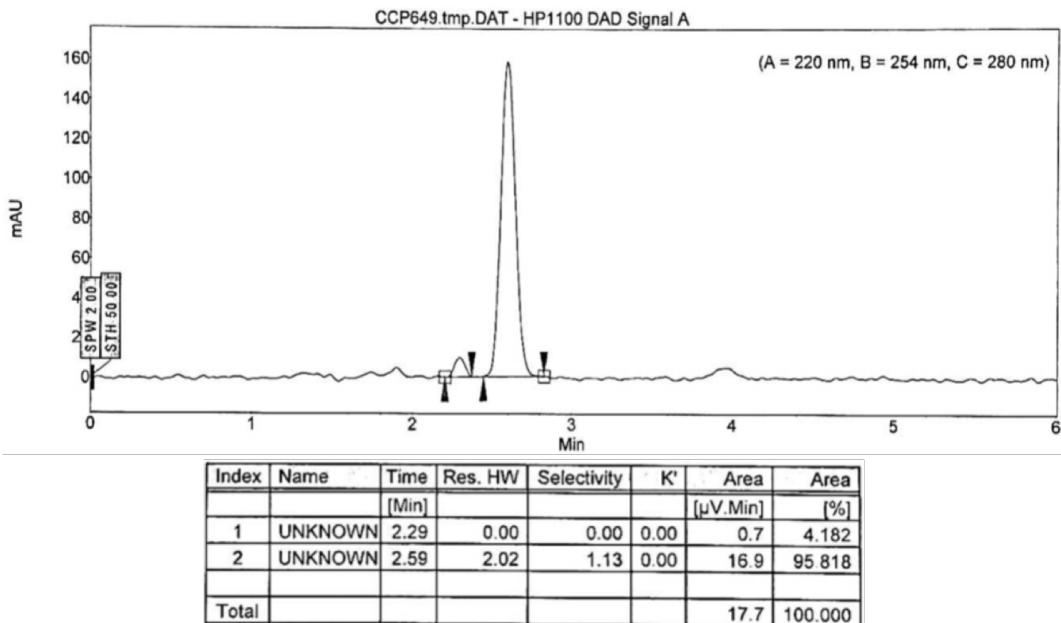
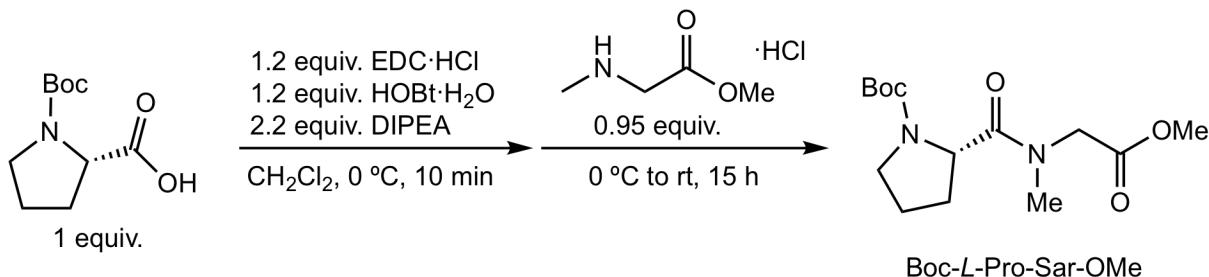


Figure S8. SFC trace of enantiopure **3n**.



Preparation of dipeptide Boc-Pro-Sar-OMe (*tert*-butyl (*R*)-2-((2-methoxy-2-oxoethyl)(methyl)carbamoyl)pyrrolidine-1-carboxylate). Prepared according to the modified literature procedure.¹⁸ An oven-dried 50 mL Schlenk tube was charged with 453 mg (2.1 mmol, 1 equiv.) of Boc-*L*-Pro-OH, 483 mg (2.5 mmol, 1.2 equiv.) of EDC·HCl, and 426 mg (2.5 mmol, 1.2 equiv. wetted, not less than 20 wt%) of HOBr·H₂O. The flask was evacuated and backfilled with Ar. This evacuation/refill cycle was repeated three times. To the mixture was added 10 mL of DCM. After cooled to 0 °C, 0.8 mL (4.6 mmol, 2.2 equiv.) of DIPEA was dropwise added. After stirred at 0 °C for 5 min, 279 mg (2 mmol, 0.95 equiv.) of Sarcosine methyl ester-HCl salt was added all at once as solids. The mixture was stirred at 0 °C for additional 5 min and then allowed to warm to rt. After 15h, the reaction mixture was quenched with aq. 0.1 M HCl solution. The layers were separated and the aqueous layer was extracted with DCM three times. The combined organic layers were washed with aq. 1 M NaHCO₃ solution, brine, and water and then dried over MgSO₄, filtered, concentrated *in vacuo*. The desired product was purified by flash column chromatography on SiO₂ (packed with EtOAc; loaded with EtOAc; eluent: EtOAc; stained with KMnO₄ solution) as colorless oil (367 mg, 1.2 mmol, 61% yield).

Rotamers ratio = 54:46. Major: **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 4.77 (d, *J*_{HH} = 17.3 Hz, 1H), 4.71 (d, *J*_{HH} = 8.6 Hz, 1H), 3.71 (s, 3H), 3.55 (m, 1H), 3.47 (d, *J*_{HH} = 17.3 Hz, 1H), 3.42–3.37 (m, 1H), 3.14 (s, 3H), 2.19–2.11 (m, 1H), 2.08–1.97 (m, 1H), 2.05–1.96 (m, 1H), 1.89–1.86 (m, 1H), 1.44 (s, 9H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 173.1, 170.0, 154.7, 79.7, 56.6, 52.2, 49.9, 46.9, 36.4, 29.2, 28.6, 24.2. Minor: **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 4.62 (dd, *J*_{HH} = 8.5, 3.0 Hz, 1H), 4.31 (d, *J* = 17.3 Hz, 1H), 3.94 (d, *J* = 17.3 Hz, 1H),

3.72 (s, 3H), 3.63–3.57 (m, 1H), 3.50 – 3.45 (m, 1H), 3.12 (s, 3H), 2.25–2.18 (m, 1H), 1.98–1.90 (m, 2H), 1.84–1.77 (m, 1H), 1.41 (s, 9H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C): δ 173.5, 169.8, 154.0, 79.7, 56.6, 52.2, 49.7, 46.6, 36.3, 30.3, 28.4, 23.5. HRMS (ESI+) *m/z* calculated for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_4$ ([M+H]⁺) 301.1758, found 301.1757.

SFC traces for racemic and enantiopure Boc-Pro-Sar-OMe:

Conditions: IG (25 x 0.46 cm), 20% methanol (DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

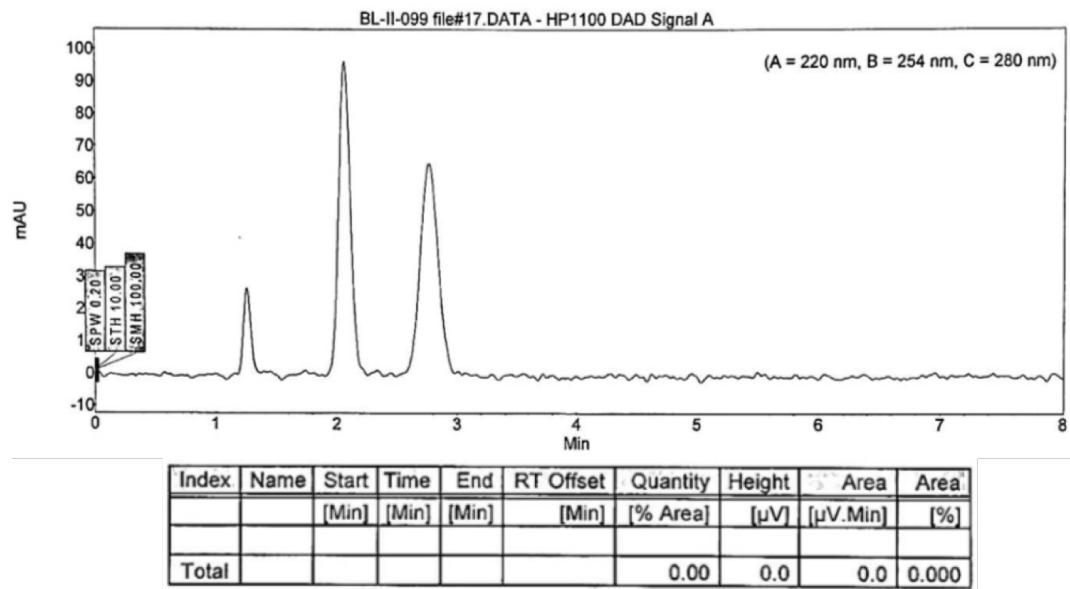


Figure S9. SFC trace of racemic Boc-Pro-Sar-OMe.

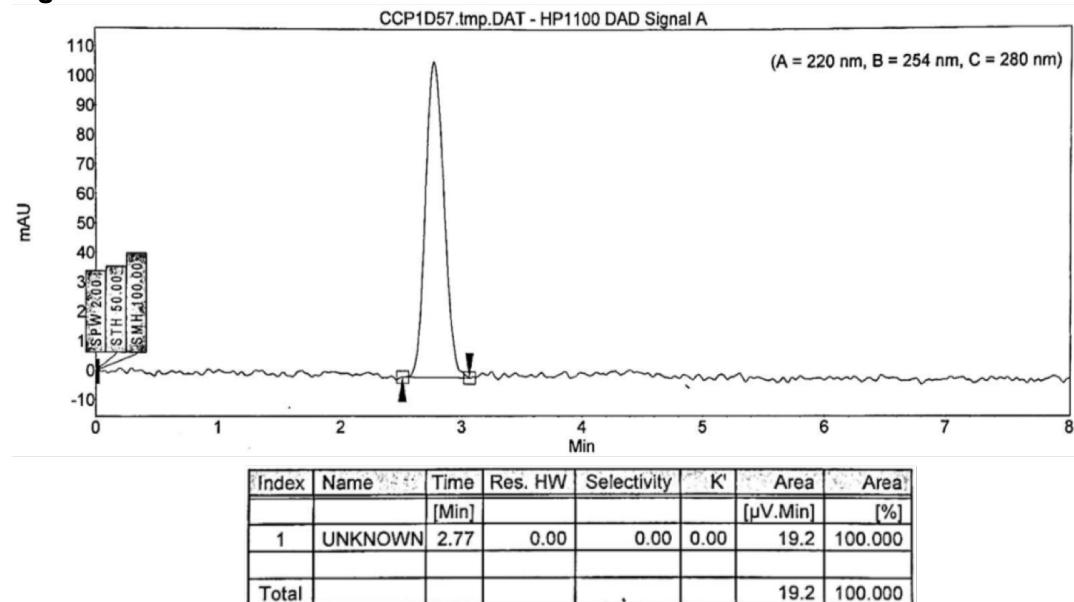
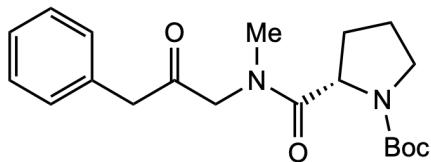


Figure S10. SFC trace of enantiopure Boc-Pro-Sar-OMe.



tert-butyl (R)-2-(methyl(2-oxo-3-phenylpropyl)carbamoyl)pyrrolidine-1-carboxylate 3o.

Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzylidboronate **1**, 30 mg (0.10 mmol, 1 equiv.) of Boc-L-Pro-Sar-OMe, 8 mg (0.10 mmol, 1 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; eluent: 15% ethyl acetate in hexanes to 20 % to 30%) yielded 29 mg (0.080 mmol, 80% yield) of product as colorless oil.

Rotamers ratio = 56:44. Major: **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.31 (t, J_{HH} = 7.3 Hz, 2H), 7.26 (t, J_{HH} = 7.7 Hz, 1H), 7.21–7.18 (m, 2H), 4.73 (d, J_{HH} = 17.6 Hz, 1H), 4.68 (dd, J_{HH} = 8.6, 2.7 Hz, 1H), 3.71 (s, 2H), 3.61 (d, J_{HH} = 17.6 Hz, 1H), 3.57–3.51 (m, 1H), 3.40–3.35 (m, 1H), 3.02 (s, 3H), 2.23–2.10 (m, 1H), 2.05–1.90 (m, 2H), 1.89–1.78 (m, 1H), 1.43 (s, 9H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 203.6, 173.1, 154.7, 133.4, 129.6, 128.8, 127.2, 79.6, 57.4, 56.5, 47.2, 46.9, 36.5, 29.3, 28.6, 24.2. Minor: **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): 7.31 (t, J_{HH} = 7.3 Hz, 2H), 7.26 (t, J_{HH} = 7.7 Hz, 1H), 7.21–7.18 (m, 2H), 4.59 (dd, J_{HH} = 8.6, 3.2 Hz, 1H), 4.39 (d, J_{HH} = 17.6 Hz, 1H), 3.98 (d, J_{HH} = 17.6 Hz, 1H), 3.72 (s, 2H), 3.58–3.52 (m, 1H), 3.47–3.43 (m, 1H), 3.00 (s, 3H), 2.23–2.09 (m, 1H), 2.05–1.89 (m, 2H), 1.89–1.78 (m, 1H), 1.39 (s, 9H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 202.9, 173.4, 153.9, 133.4, 129.5, 128.9, 127.3, 79.7, 56.9, 56.6, 47.6, 46.6, 36.4, 30.3, 28.4, 23.4. **HRMS** (ESI+) *m/z* calculated for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_4$ ([M+H]⁺) 361.2122, found 361.2120.

SFC traces for racemic and enantiopure **3o**:

Conditions: IG (25 x 0.46 cm), 30% methanol (DEA)/CO₂, 100 bar, 3 mL/min.

SFC analyses were performed by Lotus Separations, LLC, Princeton, NJ 08544.

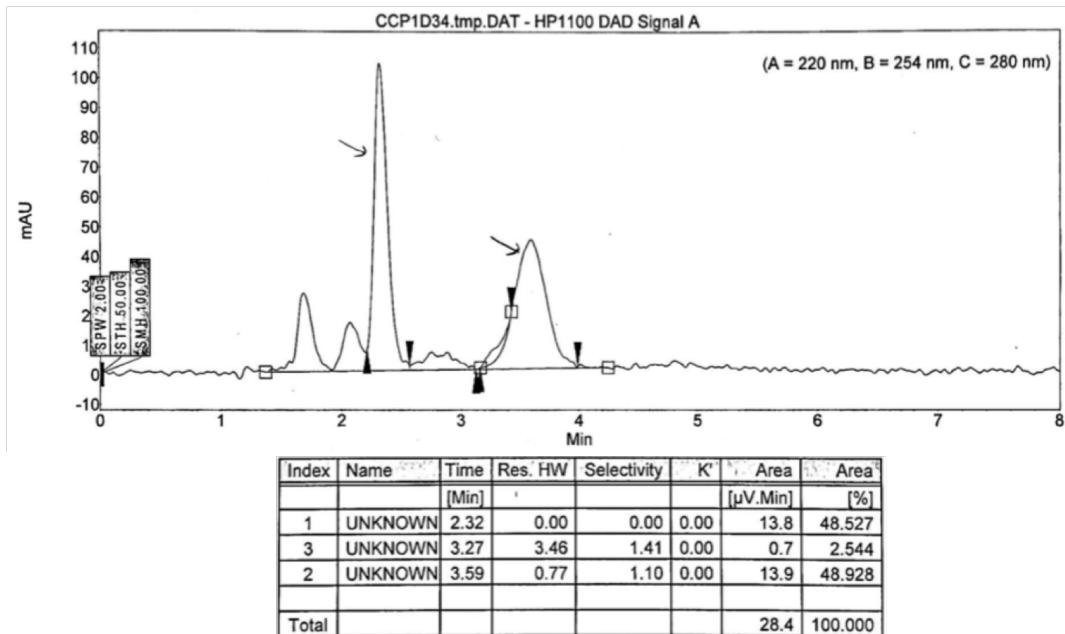


Figure S11. SFC trace of racemic **3o**.

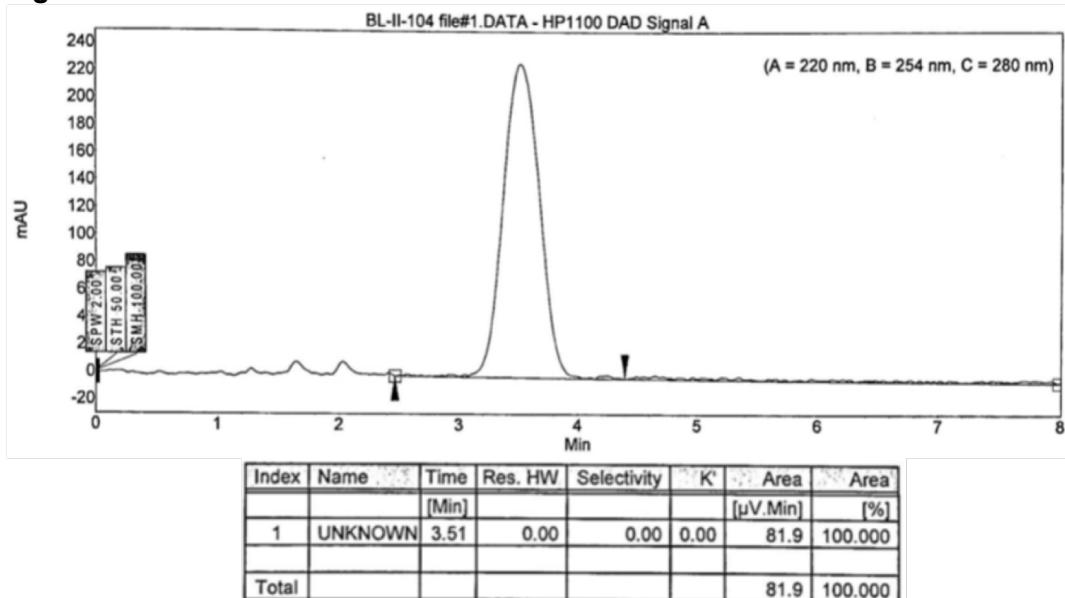
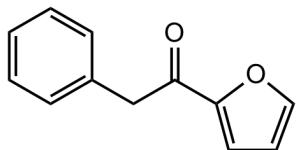
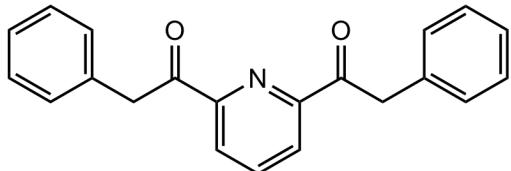


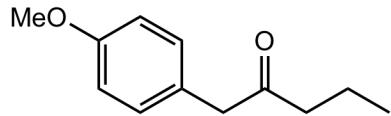
Figure S12. SFC trace of enantiopure **3o**.



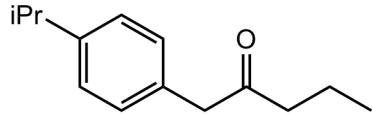
1-(Furan-2-yl)-2-phenylethan-1-one 3p. Prepared according to the general procedure using 69 mg (0.20 mmol, 1 equiv.) of benzyldiboronate **1**, 25 mg (0.20 mmol, 1 equiv.) of methyl furan-2-carboxylate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 4 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 2% ethyl acetate in hexanes; gradient: 3% to 5% to 7% to 10% ethyl acetate in hexanes) yielded 35 mg (0.19 mmol, 94% yield) of product as yellow oil. ¹H NMR (300 MHz, chloroform-d, 23 °C): δ 7.58–7.49 (m, 1H), 7.32–7.13 (m, 6H), 6.48 (dd, *J*_{HH} = 3.6, 1.7 Hz, 1H), 4.07 (s, 2H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 186.7, 152.5, 146.7, 134.2, 129.6, 128.8, 127.1, 118.0, 112.5, 45.5. ¹H and ¹³C NMR data agree with previously reported data.¹⁹



1,1'-(Pyridine-2,6-diyl)bis(2-phenylethan-1-one) 3q. Prepared according to the general procedure using 138 mg (0.40 mmol, 2 equiv.) of benzyldiboronate **1**, 39 mg (0.20 mmol, 1 equiv.) of dimethyl pyridine-2,6-dicarboxylate, 32 mg (0.40 mmol, 2 equiv.) of LiO^tBu, and 8 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; gradient: 12.5% to 15% to 20% ethyl acetate in hexanes) yielded 49 mg (0.16 mmol, 78% yield) of product as a pale yellow solid. ¹H NMR (300 MHz, chloroform-d, 23 °C): δ 8.24 (d, *J*_{HH} = 7.7 Hz, 2H), 7.99 (t, *J*_{HH} = 7.7 Hz, 1H), 7.37–7.23 (m, 10H), 4.62 (s, 4H). ¹³C{¹H} NMR (126 MHz, chloroform-d, 23 °C): δ 198.4, 152.3, 138.4, 134.5, 129.9, 128.8, 127.1, 125.9, 44.4. HRMS (ESI+) *m/z* calculated for C₂₁H₁₇NO₂ ([M+H]⁺) 316.1332, found *m/z* 316.1332.

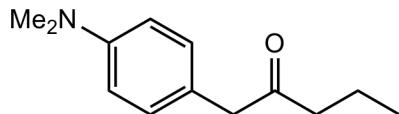


1-(4-Methoxyphenyl)pentan-2-one 3r. Prepared according to the general procedure using 37 mg (0.10 mmol, 1 equiv.) of (*p*-methoxy)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 5% ethyl acetate in hexanes) yielded 17 mg (0.088 mmol, 88% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.11 (d, *J*_{HH} = 8.6 Hz, 2H), 6.86 (d, *J*_{HH} = 8.6 Hz, 2H), 3.80 (s, 3H), 3.61 (s, 2H), 2.41 (t, *J*_{HH} = 7.3 Hz, 2H), 1.57 (sex, *J*_{HH} = 7.3 Hz, 2H), 0.86 (t, *J*_{HH} = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 209.1, 158.7, 130.5, 126.5, 114.2, 55.4, 49.4, 43.9, 17.3, 13.8. HRMS (ESI+) *m/z* calculated for C₁₂H₁₆O₂ ([M+H]⁺) 193.1223, found *m/z* 193.1225.

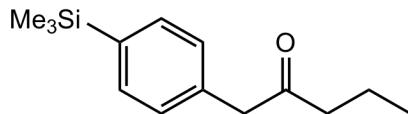


1-(4-Isopropylphenyl)pentan-2-one 3s. Prepared according to the general procedure using 39 mg (0.10 mmol, 1 equiv.) of (*p*-isopropyl)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; eluent: 3% ethyl acetate in hexanes) yielded 18 mg (0.088 mmol, 88% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): 7.19 (d, *J*_{HH} = 7.9 Hz, 2H), 7.12 (d, *J*_{HH} = 7.8 Hz, 2H), 3.64 (s, 2H), 2.89 (hept, *J*_{HH} = 6.9 Hz, 1H), 2.43 (t, *J*_{HH} = 7.3 Hz, 2H), 1.58 (m, 2H), 1.24 (d, *J*_{HH} = 6.9 Hz, 6H), 0.87 (td, *J*_{HH} = 7.4, 1.1 Hz, 3H). ¹³C{¹H} NMR (126

MHz, chloroform-*d*, 23 °C): δ 209.0, 147.7, 131.8, 129.4, 126.9, 49.9, 44.0, 33.9, 24.1, 17.3, 13.8. **HRMS** (ESI+) *m/z* calculated for C₁₄H₂₀O ([M+H]⁺) 205.1517, found *m/z* 205.1517.

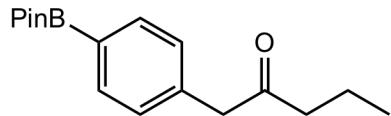


1-(4-(Dimethylamino)phenyl)pentan-2-one 3t. Prepared according to the general procedure using 39 mg (0.10 mmol, 1 equiv.) of (*p*-dimethylamino)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiOBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 7% ethyl acetate in hexanes; gradient: 7% to 10% ethyl acetate in hexanes) yielded 18 mg (0.088 mmol, 88% yield) of product as yellow oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): 7.07 (d, *J*_{HH} = 8.5 Hz, 2H), 6.70 (d, *J*_{HH} = 8.6 Hz, 2H), 3.56 (s, 2H), 2.93 (s, 6H), 2.40 (t, *J*_{HH} = 7.3 Hz, 2H), 1.60–1.52 (m, 2H), 0.86 (t, *J*_{HH} = 7.4 Hz, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 209.7, 149.8, 130.1, 122.3, 113.0, 49.5, 43.6, 40.8, 29.9, 17.4, 13.8. **HRMS** (ESI+) *m/z* calculated for C₁₃H₁₉NO ([M+H]⁺) 206.1539, found *m/z* 206.1536.

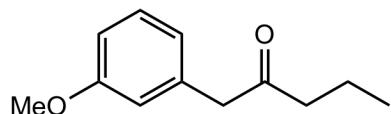


1-(4-(Trimethylsilyl)phenyl)pentan-2-one 3u. Prepared according to the general procedure using 42 mg (0.10 mmol, 1 equiv.) of (*p*-trimethylsilyl)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiOBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; eluent: 3% ethyl acetate in hexanes) yielded 18 mg (0.077 mmol, 77% yield) of product as colorless oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): 7.48 (d, *J*_{HH} = 7.9 Hz, 2H), 7.19 (d, *J*_{HH} = 7.9 Hz, 2H), 3.67 (s, 2H), 2.43 (t, *J*_{HH} = 7.3 Hz, 2H), 1.65–1.53 (m, 2H), 0.88

(t, $J_{HH} = 7.4$ Hz, 3H), 0.26 (s, 9H). **$^{13}\text{C}\{\text{H}\}$ NMR** (126 MHz, chloroform-d, 23 °C): δ 208.6, 139.0, 135.0, 133.9, 128.9, 50.2, 44.1, 17.3, 13.8, -1.0. **HRMS** (ESI+) m/z calculated for $\text{C}_{14}\text{H}_{22}\text{OSi}$ ($[\text{M}+\text{H}]^+$) 235.1513, found m/z 235.1511.

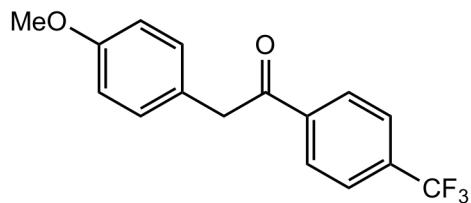


1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentan-2-one 3v. Prepared according to the general procedure using 47 mg (0.10 mmol, 1 equiv.) of (*p*-trimethylsilyl)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 7% ethyl acetate in hexanes; gradient: 7% to 10% ethyl acetate in hexanes) yielded 24 mg (0.083 mmol, 83% yield) of product as a white solid. **^1H NMR** (300 MHz, chloroform-d, 23 °C): 7.77 (d, $J_{HH} = 7.9$ Hz, 2H), 7.21 (d, $J_{HH} = 7.9$ Hz, 2H), 3.68 (s, 2H), 2.40 (t, $J_{HH} = 7.3$ Hz, 2H), 1.56 (sep, $J_{HH} = 7.3$ Hz, 2H), 1.34 (s, 12H), 0.85 (t, $J_{HH} = 7.4$ Hz, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** (126 MHz, chloroform-d, 23 °C): δ 208.4, 137.7, 135.3, 128.9, 83.9, 50.6, 44.0, 25.0, 17.3, 13.8. **^{11}B NMR** (96 MHz, chloroform-d, 23 °C) δ 29.37 (br). **HRMS** (ESI+) m/z calculated for $\text{C}_{17}\text{H}_{25}\text{BO}_3$ ($[\text{M}+\text{H}]^+$) 289.1970, found m/z 289.1975.

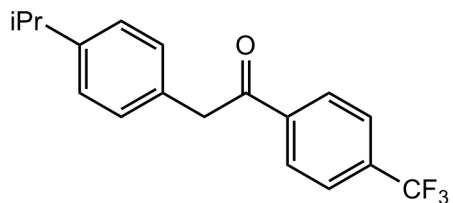


1-(3-Methoxyphenyl)pentan-2-one 3w. Prepared according to the general procedure using 37 mg (0.10 mmol, 1 equiv.) of (*m*-methoxy)benzyldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 5% ethyl acetate in hexanes) yielded 17 mg (0.088 mmol, 88% yield) of

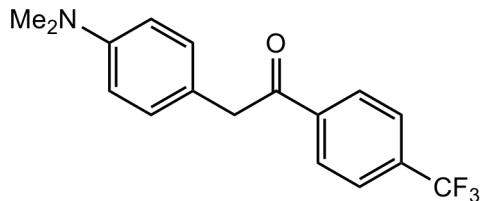
product as colorless oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.28–7.21 (m, 1H), 6.84–6.76 (m, 2H), 6.74 (s, 1H), 3.80 (s, 3H), 3.64 (s, 2H), 2.42 (t, *J_{HH}* = 7.3 Hz, 2H), 1.62–1.53 (m, 2H), 0.87 (t, *J_{HH}* = 7.4 Hz, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 208.6, 159.9, 136.0, 129.8, 121.9, 115.1, 112.6, 55.3, 50.4, 43.9, 17.3, 13.8. **HRMS** (ESI+) *m/z* calculated for C₁₂H₁₆O₂ ([M+H]⁺) 193.1223, found *m/z* 193.1223.



2-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3x. Prepared according to the general procedure using 37 mg (0.10 mmol, 1 equiv.) of (*p*-methoxy)boryldiboronate, 10 mg (0.10 mmol, 1 equiv.) of methyl butyrate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; gradient: 5% to 7% ethyl acetate in hexanes) yielded 27 mg (0.092 mmol, 92% yield) of product as a pale yellow solid. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 8.10 (d, *J_{HH}* = 8.1 Hz, 2H), 7.72 (d, *J_{HH}* = 8.2 Hz, 2H), 7.17 (d, *J_{HH}* = 8.7 Hz, 2H), 6.87 (d, *J_{HH}* = 8.7 Hz, 2H), 4.25 (s, 2H), 3.79 (s, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 197.1, 158.9, 139.3, 134.5 (q, ²*J_{CF}* = 32.7 Hz), 130.5, 129.1, 125.9 (q, ³*J_{CF}* = 3.6 Hz), 123.7 (q, ¹*J_{CF}* = 272.7 Hz), 114.4, 55.4, 45.1. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.14. **HRMS** (ESI+) *m/z* calculated for C₁₆H₁₃F₃O₂ ([M+H]⁺) 294.0868, found *m/z* 294.0872.

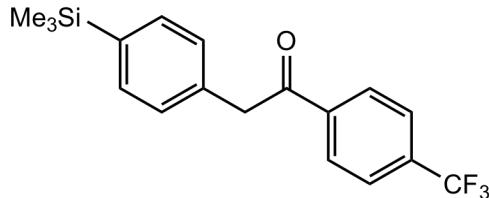


2-(4-Isopropylphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3y. Prepared according to the general procedure using 39 mg (0.10 mmol, 1 equiv.) of (*p*-isopropyl)benzyldiboronate, 20 mg (0.10 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; gradient: 3% to 5% ethyl acetate in hexanes) yielded 26 mg (0.085 mmol, 85% yield) of product as a white solid. **¹H NMR** (300 MHz, chloroform-*d*, 23 °C): 8.11 (d, J_{HH} = 8.1 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.22–7.16 (m, 4H), 4.27 (s, 2H), 2.89 (sep, J = 6.9 Hz, 1H), 1.23 (d, J_{HH} = 6.9 Hz, 6H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 197.0, 147.9, 139.4, 134.5 (q, $^2J_{CF}$ = 32.7 Hz), 131.1, 129.4, 129.1, 127.1, 125.9 (q, $^3J_{CF}$ = 3.8 Hz), 123.7 (q, $^1J_{CF}$ = 272.7 Hz), 45.6, 33.9, 24.1. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.13. **HRMS** (ESI+) *m/z* calculated for C₁₈H₁₇F₃O ([M+H]⁺) 307.1304, found *m/z* 307.1303.

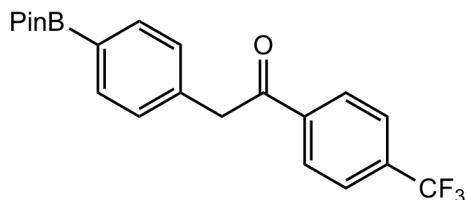


2-(4-(Dimethylamino)phenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3z. Prepared according to the general procedure using 39 mg (0.10 mmol, 1 equiv.) of (*p*-dimethylamino)benzyldiboronate, 20 mg (0.10 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with dichloromethane; eluent: 10% ethyl acetate in hexanes) yielded 26 mg (0.085 mmol, 85% yield) of product as a white solid. **¹H NMR** (300 MHz, chloroform-*d*, 23 °C): 8.09 (d, J_{HH} = 8.1 Hz, 2H), 7.69 (d, J_{HH} = 8.2 Hz, 2H), 7.12 (d, J_{HH} = 8.7 Hz, 2H), 6.70 (d, J_{HH} = 8.7 Hz, 2H), 4.20 (s, 2H), 2.92 (s, 6H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 197.4, 149.8, 139.5, 134.3 (q, $^2J_{CF}$

= 32.6 Hz), 130.1, 129.2, 123.8 (q, $^1J_{CF}$ = 272.7 Hz), 125.8 (q, $^3J_{CF}$ = 3.7 Hz), 121.3, 113.1, 45.2, 40.7. ^{19}F NMR (282 MHz, chloroform-*d*, 23 °C): δ -63.13. HRMS (ESI+) *m/z* calculated for C₁₇H₁₆F₃NO ([M+H]⁺) 308.1257, found *m/z* 308.1256.

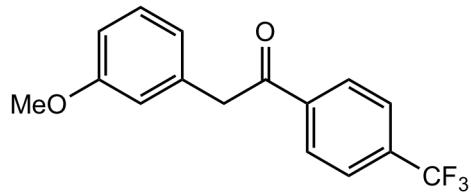


2-(4-(Trimethylsilyl)phenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3aa. Prepared according to the general procedure using 42 mg (0.10 mmol, 1 equiv.) of (*p*-trimethylsilyl)benzylidboronate, 20 mg (0.10 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with hexanes; gradient: 1% to 2% to 3% ethyl acetate in hexanes) yielded 26 mg (0.077 mmol, 77% yield) of product as a white solid. 1H NMR (500 MHz, chloroform-*d*, 23 °C): 8.11 (d, J_{HH} = 8.2 Hz, 2H), 7.72 (d, J_{HH} = 8.2 Hz, 2H), 7.49 (d, J_{HH} = 7.9 Hz, 2H), 7.25 (d, J_{HH} = 9.6 Hz, 2H), 4.30 (s, 2H), 0.25 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, chloroform-*d*, 23 °C): δ 196.7, 139.4, 139.3, 134.6 (q, $^2J_{CF}$ = 32.7 Hz), 134.4, 134.0, 129.1, 128.9, 125.9 (q, $^3J_{CF}$ = 3.7 Hz), 123.7 (q, $^1J_{CF}$ = 272.8 Hz), 45.9, -1.0. ^{19}F NMR (282 MHz, chloroform-*d*, 23 °C): δ -63.14. HRMS (ESI+) *m/z* calculated for C₁₈H₁₉F₃OSi ([M+H]⁺) 337.1230, found *m/z* 337.1228.



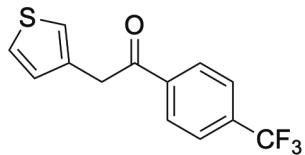
2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3ab. Prepared according to the general procedure using

47 mg (0.10 mmol, 1 equiv.) of (*p*-trimethylsilyl)benzyldiboronate, 20 mg (0.10 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 8% ethyl acetate in hexanes; eluent: 8% ethyl acetate in hexanes) yielded 33 mg (0.085 mmol, 85% yield) of product as a white solid. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 8.08 (d, *J*_{HH} = 8.2 Hz, 2H), 7.78 (d, *J*_{HH} = 7.9 Hz, 2H), 7.70 (d, *J*_{HH} = 8.2 Hz, 2H), 7.27 (d, *J*_{HH} = 7.3 Hz, 2H), 4.31 (s, 2H), 1.33 (s, 12H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 196.5, 139.2, 137.0, 135.5, 134.5 (q, ²*J*_{CF} = 32.7 Hz), 129.1, 128.9, 125.9 (q, ³*J*_{CF} = 3.7 Hz), 123.7 (q, ¹*J*_{CF} = 272.8 Hz), 84.0, 46.3, 25.0. **¹¹B NMR** (96 MHz, chloroform-*d*, 23 °C) δ 30.52 (br). **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.17. **HRMS** (ESI+) *m/z* calculated for C₂₁H₂₂BF₃O₃ ([M+H]⁺) 391.1687, found *m/z* 391.1685.

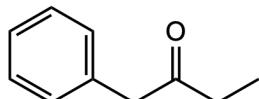


2-(3-Methoxyphenyl)pentan-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3ac. Prepared according to the general procedure using 37 mg (0.10 mmol, 1 equiv.) of (*m*-methoxy)benzyldiboronate, 20 mg (0.10 mmol, 1 equiv.) of methyl 4-(trifluoromethyl)benzoate, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 7% ethyl acetate in hexanes; eluent: 7% ethyl acetate in hexanes) yielded 27 mg (0.092 mmol, 92% yield) of product as a white solid. **¹H NMR** (300 MHz, chloroform-*d*, 23 °C): δ 8.10 (d, *J*_{HH} = 8.1 Hz, 2H), 7.72 (d, *J*_{HH} = 8.2 Hz, 2H), 7.30–7.20 (m, 1H), 6.83 (dd, *J*_{HH} = 9.2, 7.3 Hz, 3H), 4.27 (s, 2H), 3.79 (s, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 196.7, 160.0, 139.3, 135.4, 134.6 (q, ²*J*_{CF} = 32.6 Hz), 130.0, 129.1, 125.9 (q, ³*J*_{CF} = 3.7 Hz), 123.8 (q, ¹*J*_{CF} = 272.7 Hz), 121.8, 115.2, 112.7,

55.4, 46.0. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.15. **HRMS** (ESI+) *m/z* calculated for C₁₆H₁₃F₃O₂ ([M+H]⁺) 295.0940, found *m/z* 295.0939.

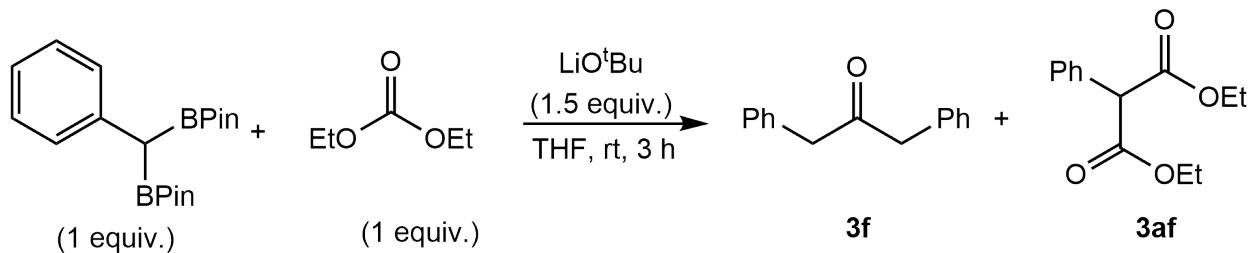


2-(Thiophen-3-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 3ad. Prepared according to the general procedure using (3-thienyl)-substituted diboronate (70 mg, 0.20 mmol), methyl (*p*-trifluoromethyl)benzoate (41 mg, 0.20 mmol), LiO^tBu (24 mg, 0.30 mmol) and THF (4 mL). After work-up, the resulting white solid was washed with cold pentane (~5 mL) to afford pure **3ad** (52 mg, 0.19 mmol, 96% yield). **¹H NMR** (500 MHz, chloroform-*d*, 23 °C) δ 8.10 (d, *J_{HH}* = 8.1 Hz, 2H), 7.73 (d, *J_{HH}* = 8.2 Hz, 2H), 7.32 (dd, *J_{HH}* = 5.0, 2.9 Hz, 1H), 7.16–7.11 (m, 1H), 7.02 (dd, *J_{HH}* = 5.0, 1.3 Hz, 1H), 4.34 (s, 2H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C) δ 196.2, 139.2, 134.6 (q, ²*J_{CF}* = 32.7 Hz), 133.5, 129.0, 128.6, 126.3, 125.9 (q, ³*J_{CF}* = 3.7 Hz), 123.2, 123.7 (q, ¹*J_{CF}* = 272.7 Hz), 40.5. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.17. **HRMS** (ESI+) *m/z* calculated for C₁₃H₉F₃OS ([M+H]⁺) 270.0326, found 270.0330.



1-Phenylbutan-2-one 3ae. Prepared according to the general procedure using 34 mg (0.10 mmol, 1 equiv.) of benzyldiboronate **1**, 10 mg (0.10 mmol, 1 equiv.) of *N,N*-dimethylpropionamide, 12 mg (0.15 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 5% ethyl acetate in hexanes) yielded 14 mg (0.094 mmol, 94% yield) of product as colorless oil. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.33 (t, *J_{HH}* = 7.3 Hz, 2H), 7.26 (t, *J_{HH}* = 7.3 Hz, 1H), 7.21 (d, *J_{HH}* = 7.1 Hz, 2H), 3.69 (s, 2H), 2.48 (q, *J_{HH}* = 7.3 Hz, 2H),

1.03 (t, $J_{HH} = 7.3$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C): δ 209.2, 134.6, 129.5, 128.8, 127.1, 50.0, 35.4, 7.9. ^1H and ^{13}C NMR data agree with previously reported data.²⁰



Diethyl 2-phenylmalonate 3af. Prepared according to the general procedure using 68 mg (0.20 mmol, 1 equiv.) of benzylidboronate **1**, 24 mg (0.20 mmol, 1 equiv.) of diethyl carbonate, 24 mg (0.30 mmol, 1.5 equiv.) of LiO^tBu, and 2 mL of THF. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 5% ethyl acetate in hexanes) yielded 14 mg (0.067 mmol, 33% yield) of **3f** and 10 mg (0.042 mmol, 21% yield) of **3af**. **3af:** ^1H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.43–7.32 (m, 5H), 4.61 (s, 1H), 4.29–4.11 (m, 4H), 1.26 (t, $J_{HH} = 7.1$ Hz, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C): δ 168.3, 132.9, 129.4, 128.7, 128.3, 62.0, 58.1, 14.2. ^1H and ^{13}C NMR data agree with previously reported data.²¹

Ineffective Substrates

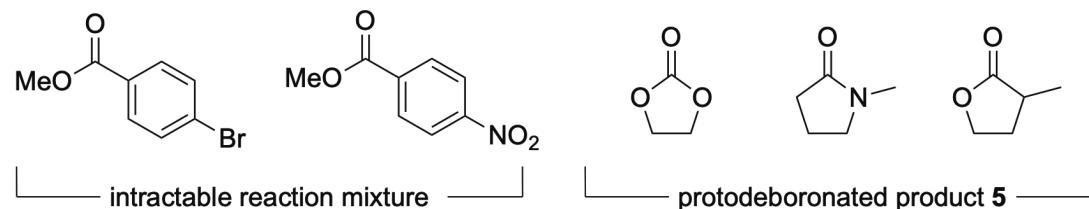
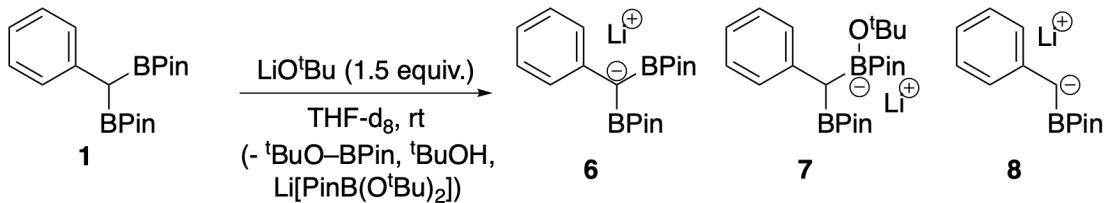


Figure S13. Substrates for which no desired ketone product was observed.

V. NMR Experiments

Activation of **1** by LiO^tBu



In a N₂ filled glove box, a J-Young tube was charged with LiO^tBu (6 mg, 0.08 mmol, 1.5 equiv).

To the J-Young tube was added a solution of **1** (17 mg, 0.05 mmol in 0.8 mL thf-*d*₈). The tube was sealed and brought out of the box, and ¹H, ¹¹B, ¹³C, g-CO SY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR spectra of the mixture were recorded.

With *N,N*-dimethyl-*p*-toluidine as an internal standard: this experiment was repeated with 16 mg of **1** (0.05 mmol, 1 equiv.), 6 mg of LiO^tBu (0.07 mmol, 1.5 equiv.), and 6.7 μ L of *N,N*-dimethyl-*p*-toluidine (0.05 mmol, 1 equiv.). ¹H NMR was recorded after 5 min, 15 min, 60 min, and 24 h (Figure S20).

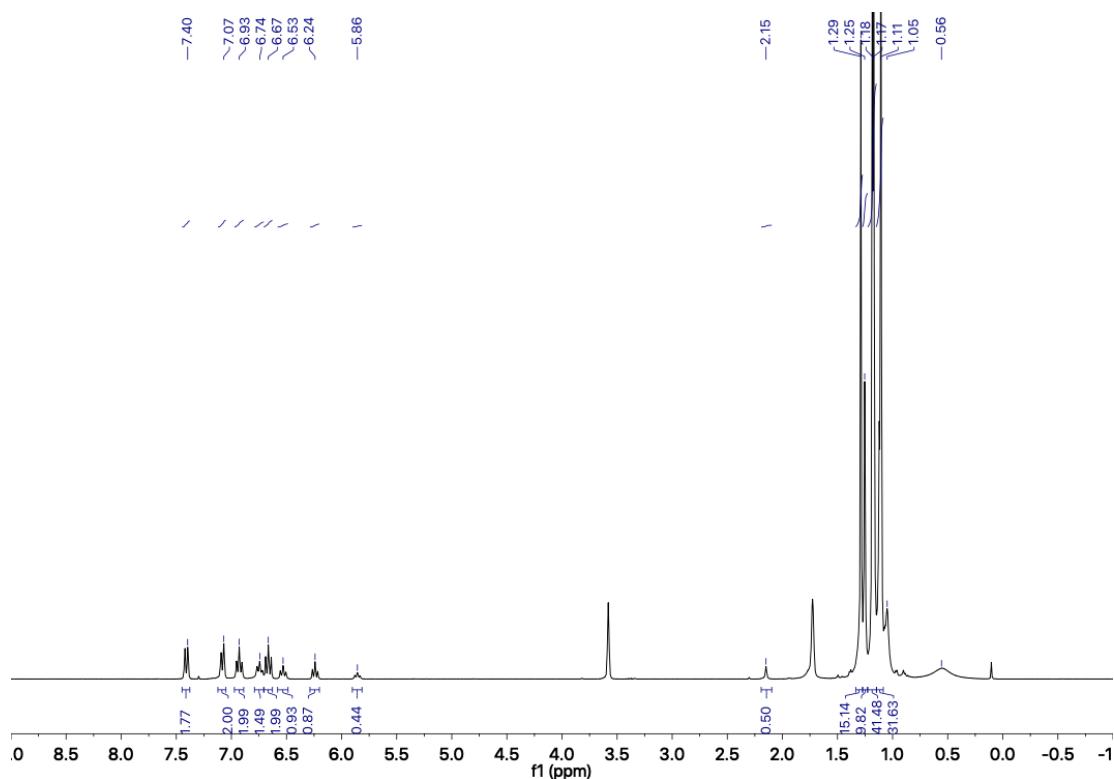


Figure S14. ¹H NMR spectrum (500 MHz, THF-*d*₈, 23 °C).

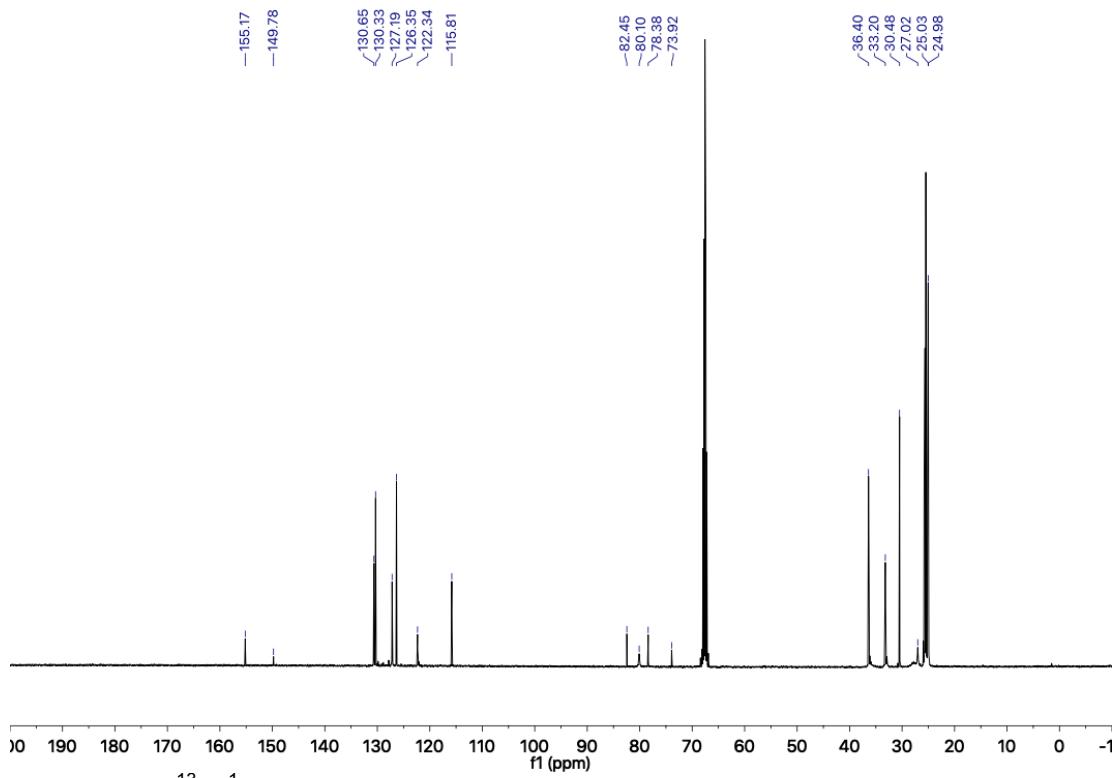


Figure S15. $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, $\text{THF}-d_8$, 23°C).

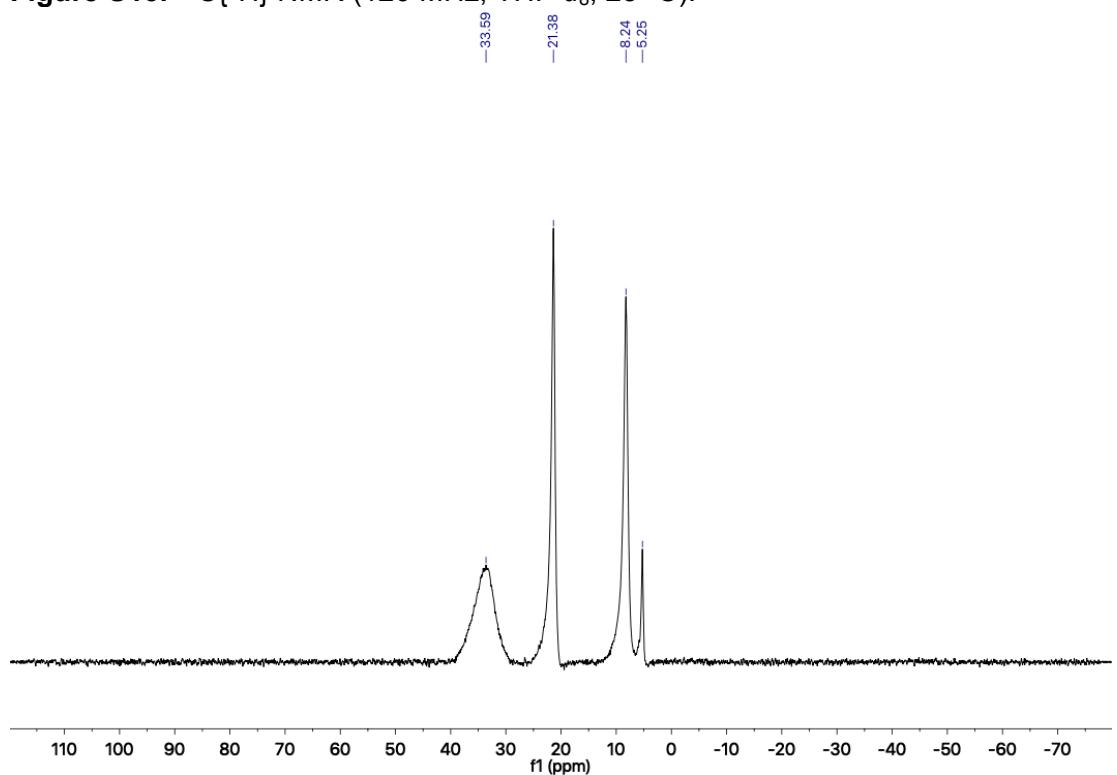


Figure S16. ^{11}B NMR spectrum (96 MHz, $\text{THF}-d_8$, 23°C).

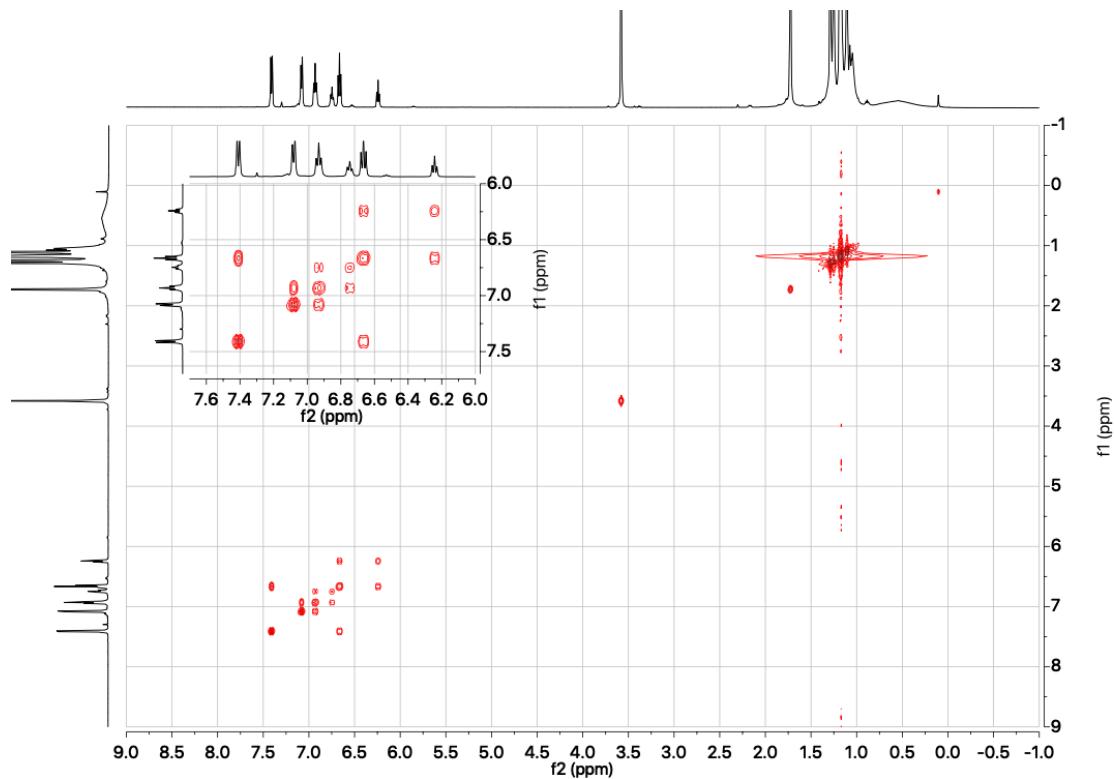


Figure S17. g-COSY spectrum.

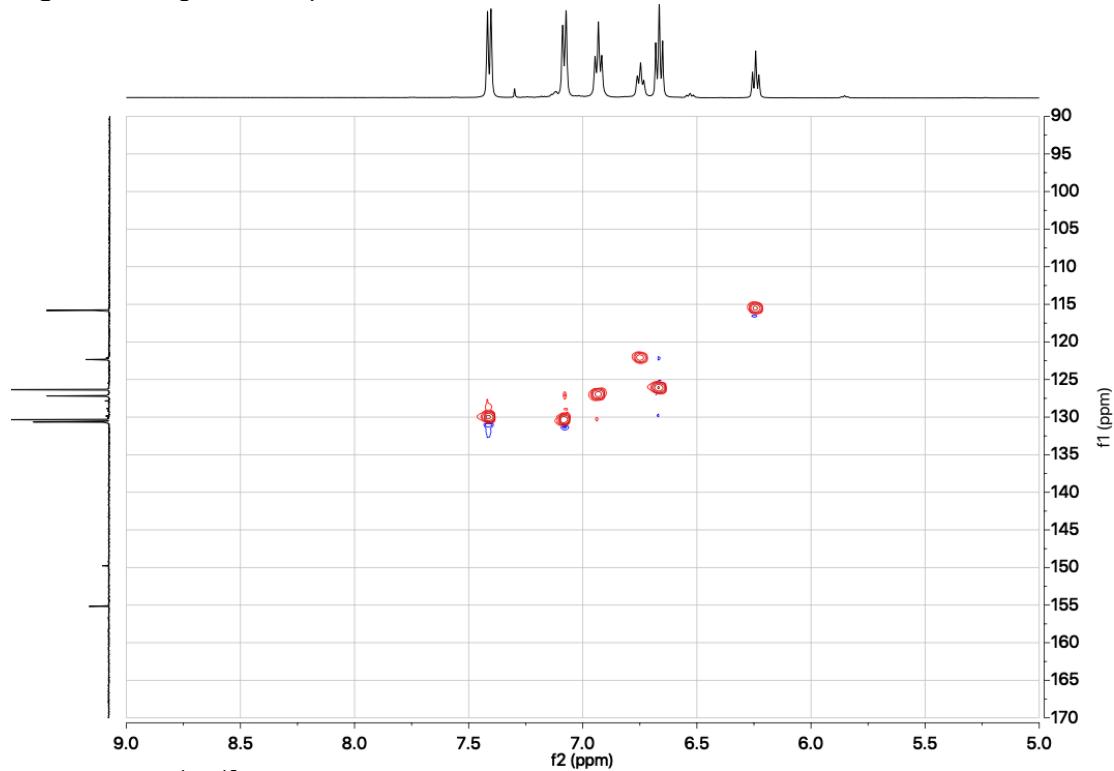


Figure S18. ^1H - ^{13}C HSQC spectrum (aromatic region).

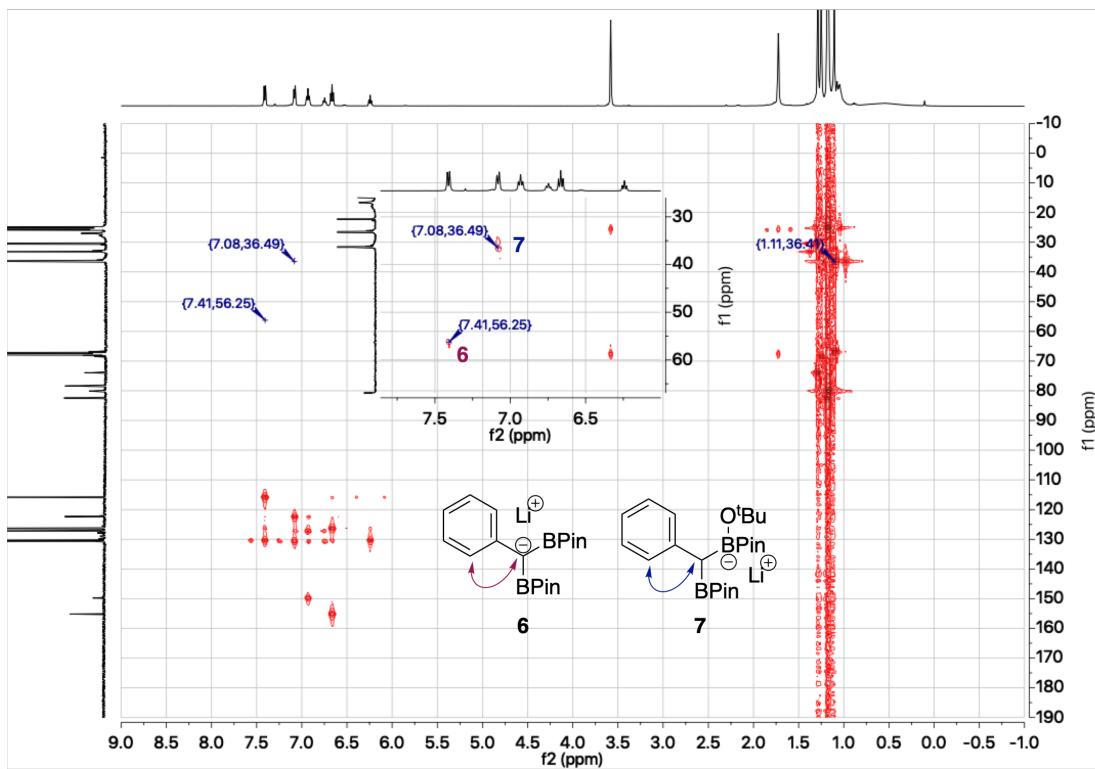


Figure S19. ^1H - ^{13}C HMBC spectrum.

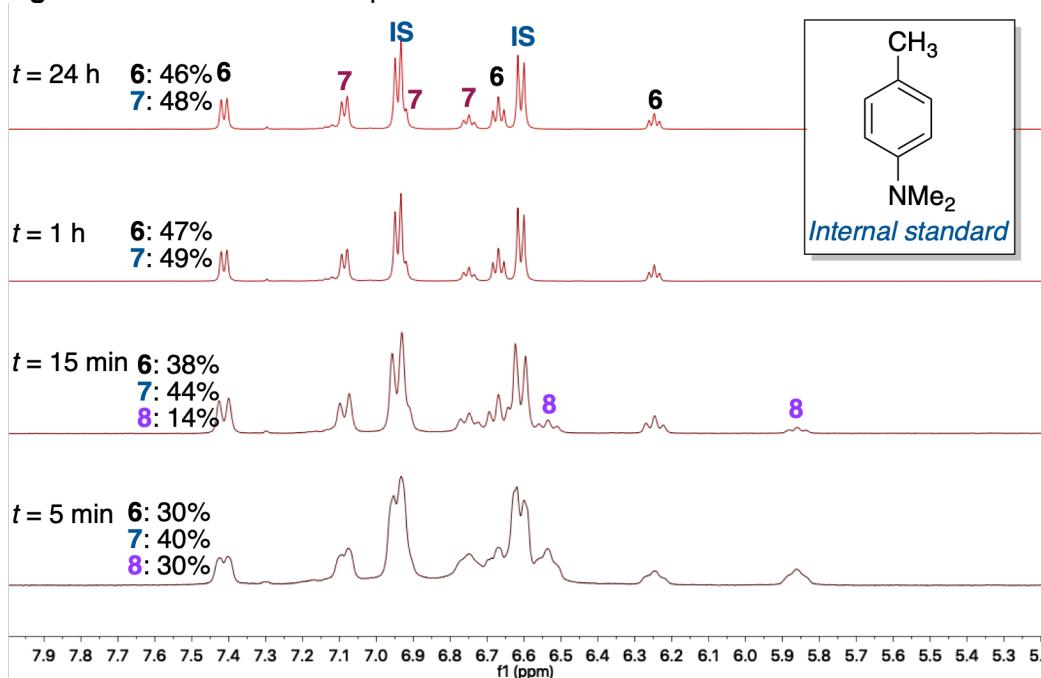
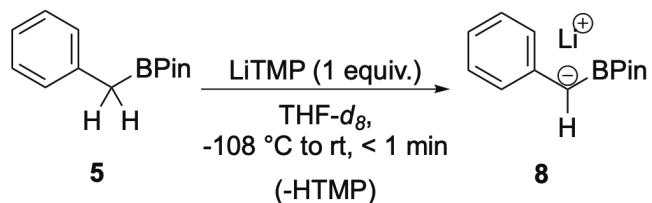


Figure S20. Monitoring of the treatment of **1** with $\text{LiO}^{\text{t}}\text{Bu}$ in the presence of internal standard by ^1H NMR spectroscopy

Deprotonation of 5 using LiTMP.



A vial was charged with 5 (9 mg, 0.04 mmol) and $\text{thf}-d_8$ (0.6 mL) and placed in a cold well filled with liquid nitrogen until the solution froze. To the frozen solution was added LiTMP (6 mg, 0.04 mmol) as solid. The resulting solution was stirred for 15 seconds and transferred to a J-Young tube. The J-Young tube was then sealed, brought out of the glove box. The resulting solution was analyzed by ^1H , ^{11}B , ^{13}C , $^1\text{H}-^{13}\text{C}$ HSQC and $^1\text{H}-^{13}\text{C}$ HMBC NMR spectroscopies. ^1H NMR (500 MHz, $\text{THF}-d_8$, 23 °C) δ 6.81–6.66 (br, m, 2H), 6.54 (dd, $J_{HH} = 8.5, 7.0$ Hz, 2H), 5.87 (t, $J_{HH} = 7.0$ Hz, 1H), 2.16 (s, 1H), 1.12 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{THF}-d_8$, 23 °C): δ 156.7, 127.8, 122.1, 110.5, 79.6 (br), 47.6 (br), 25.7. ^{11}B NMR (96 MHz, $\text{THF}-d_8$, 23 °C) δ 31.23.

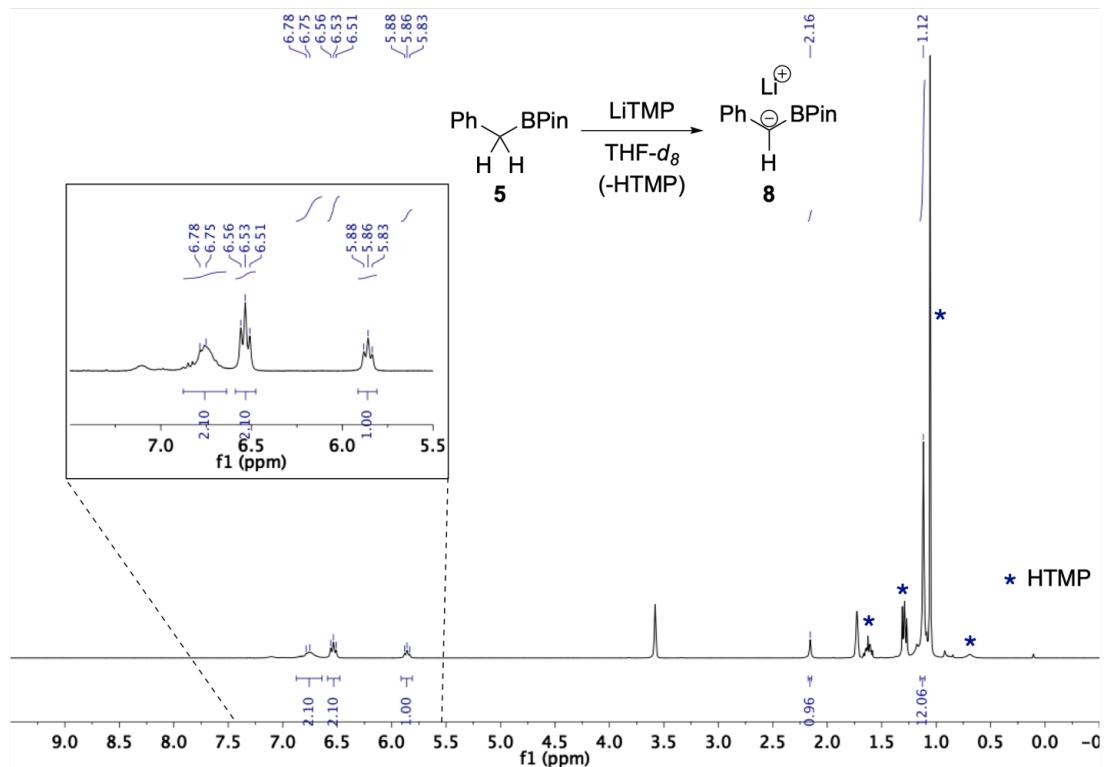


Figure S21. ^1H NMR spectrum (400 MHz, $\text{THF}-d_8$, 23 °C) of 8.

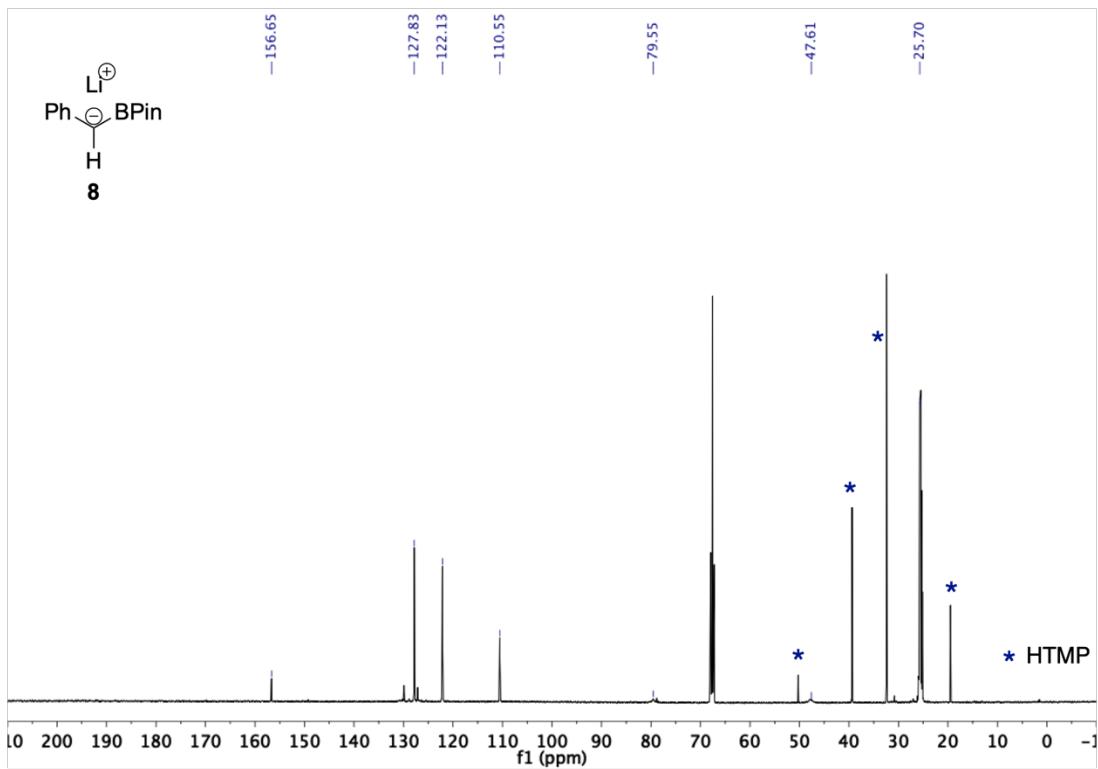


Figure S22. ¹³C{¹H} NMR (126 MHz, THF-*d*₈, 23 °C) of **8**.

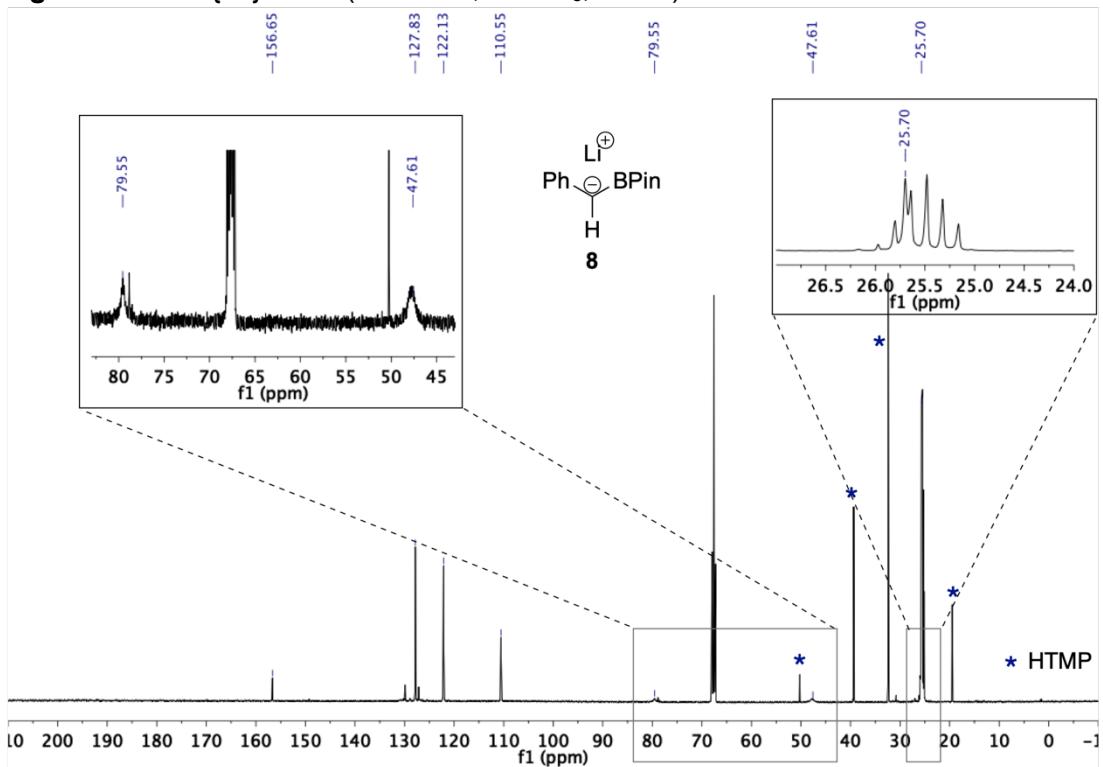


Figure S23. ¹³C{¹H} NMR (126 MHz, THF-*d*₈, 23 °C) of **8** with zoom-in spectrum in the inset.

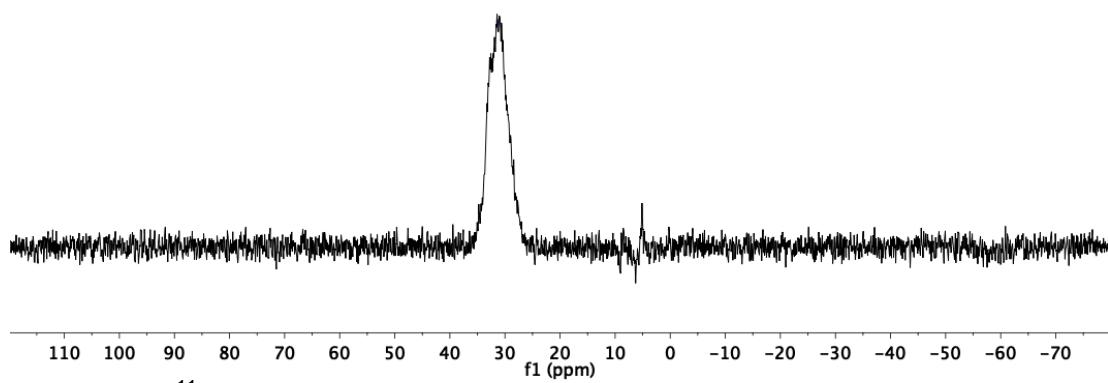
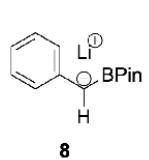


Figure S24. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of **8**.

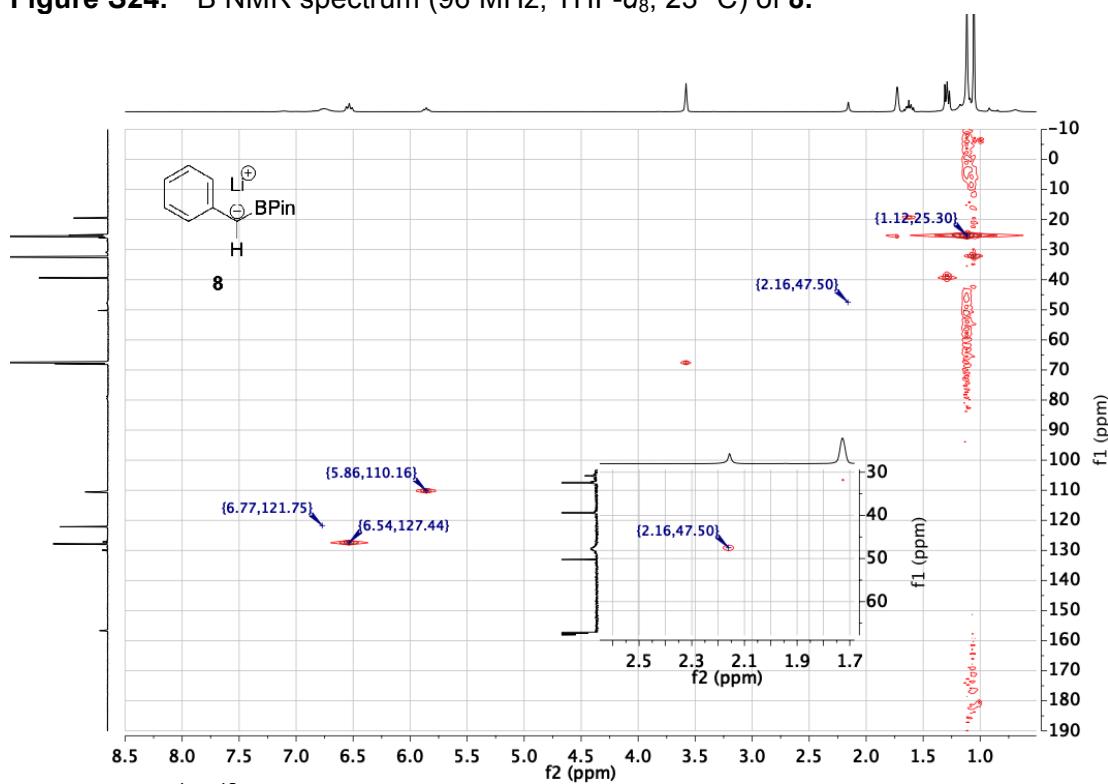


Figure S25. ^1H - ^{13}C HSQC spectrum. The inset shows the key correlation.

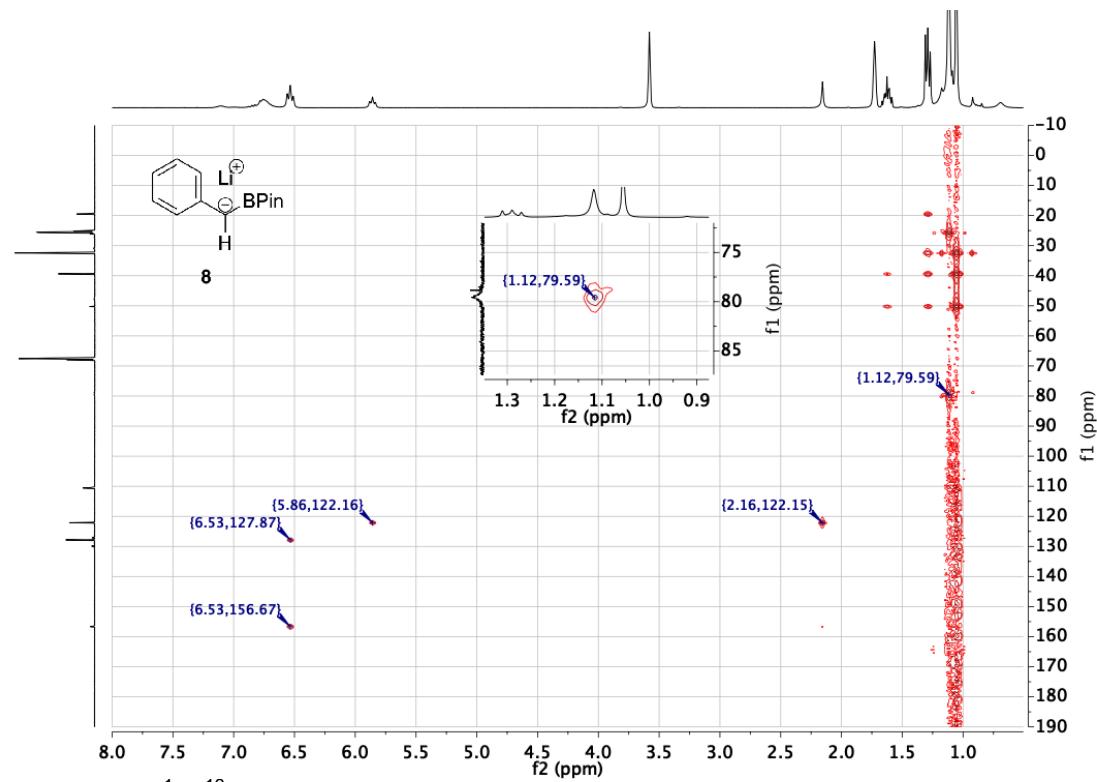


Figure S26. ^1H - ^{13}C HMBC spectrum. The inset shows the key correlation.

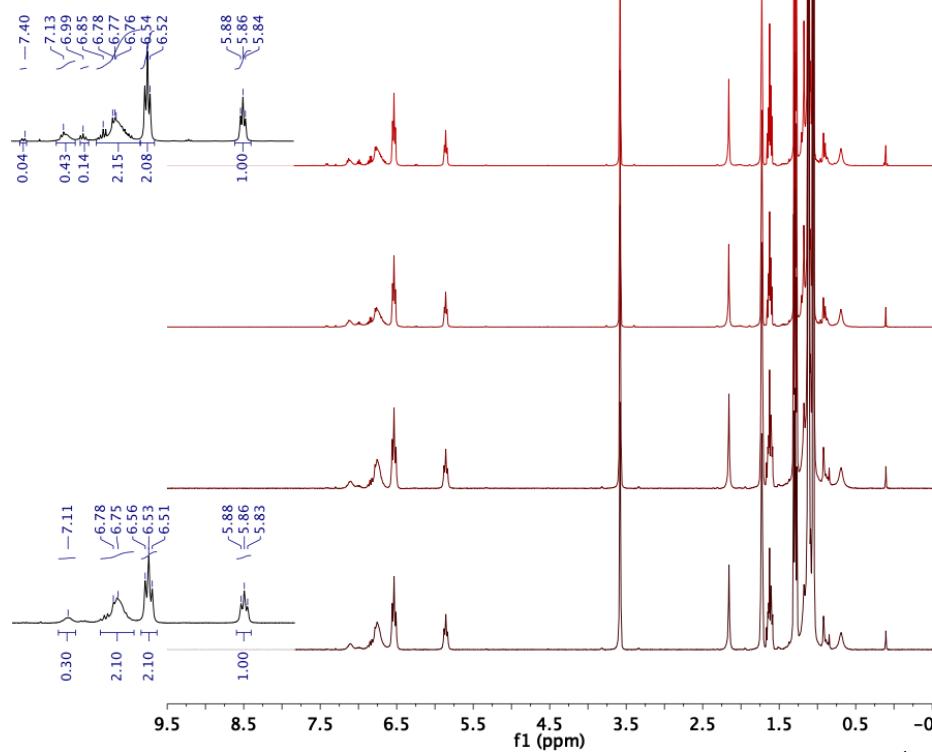
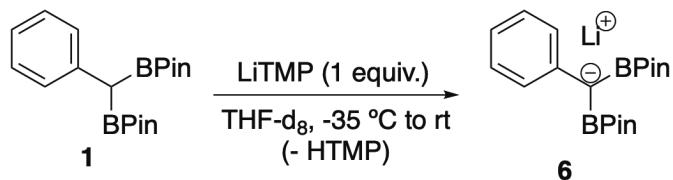
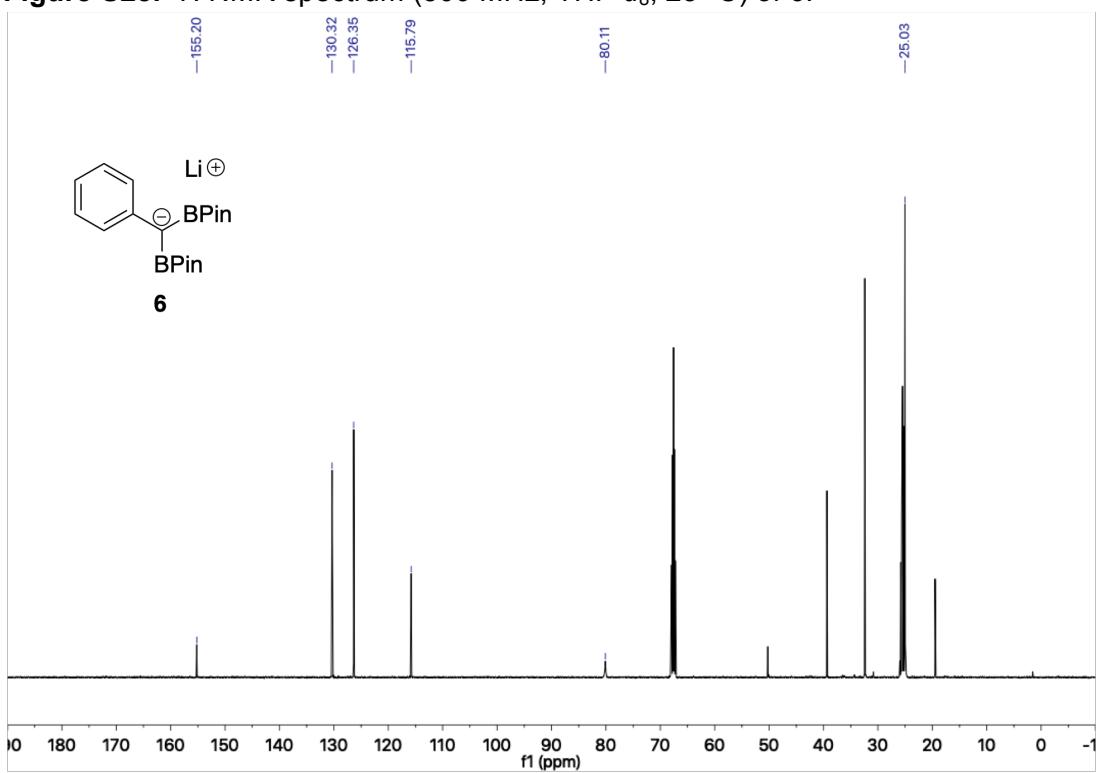
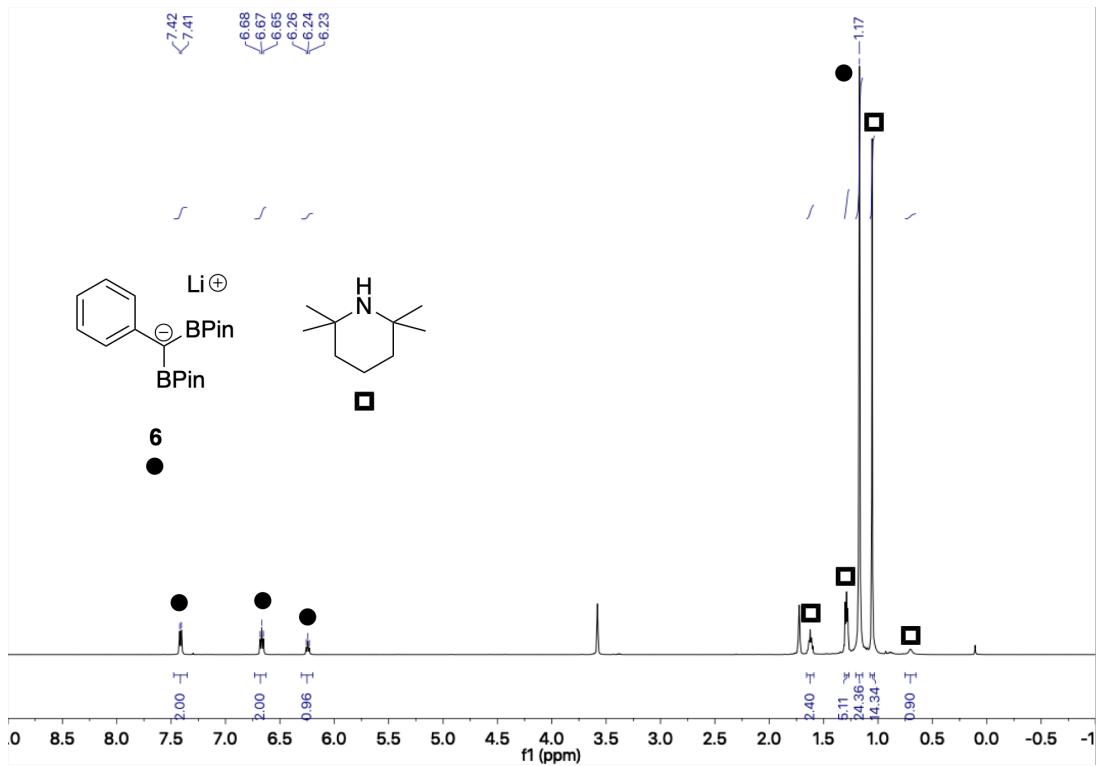


Figure S27. In situ monitoring of the treatment of **5** with LiTMP by ^1H NMR spectroscopy (300 MHz, THF- d_8 , 23 °C).

Deprotonation of 1 by LiTMP



In a N₂ filled glove box, a J-Young tube was charged with LiTMP (7 mg, 0.05 mmol). A solution of benzyldiboroante **1** (17 mg, 0.05 mmol in 0.8 mL thf-d₈) was prepared in a scintillation vial and chilled to -35 °C. The chilled solution was transferred to the J-Young tube and the vial was washed again with 0.1 mL of thf- d₈. The J-Young tube was placed in the cold well for 10 minutes and brought out of the box. ¹H, ¹¹B, ¹³C, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR spectra were obtained. **¹H NMR** (500 MHz, THF-d₈) δ 7.41 (d, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.6 Hz, 2H), 6.24 (t, *J* = 7.1 Hz, 1H), 1.17 (s, 24H). **¹³C{¹H} NMR** (126 MHz, THF-d₈, 23 °C): δ 155.2, 130.3, 126.4, 115.8, 80.1, 25.0; benzylic carbon (attached to boron) resonance not observed by ¹³C NMR; ¹H-¹³C HMBC correlation observed at 56.3 ppm. **¹¹B NMR** (96 MHz, THF-d₈, 23 °C) δ 33.08.



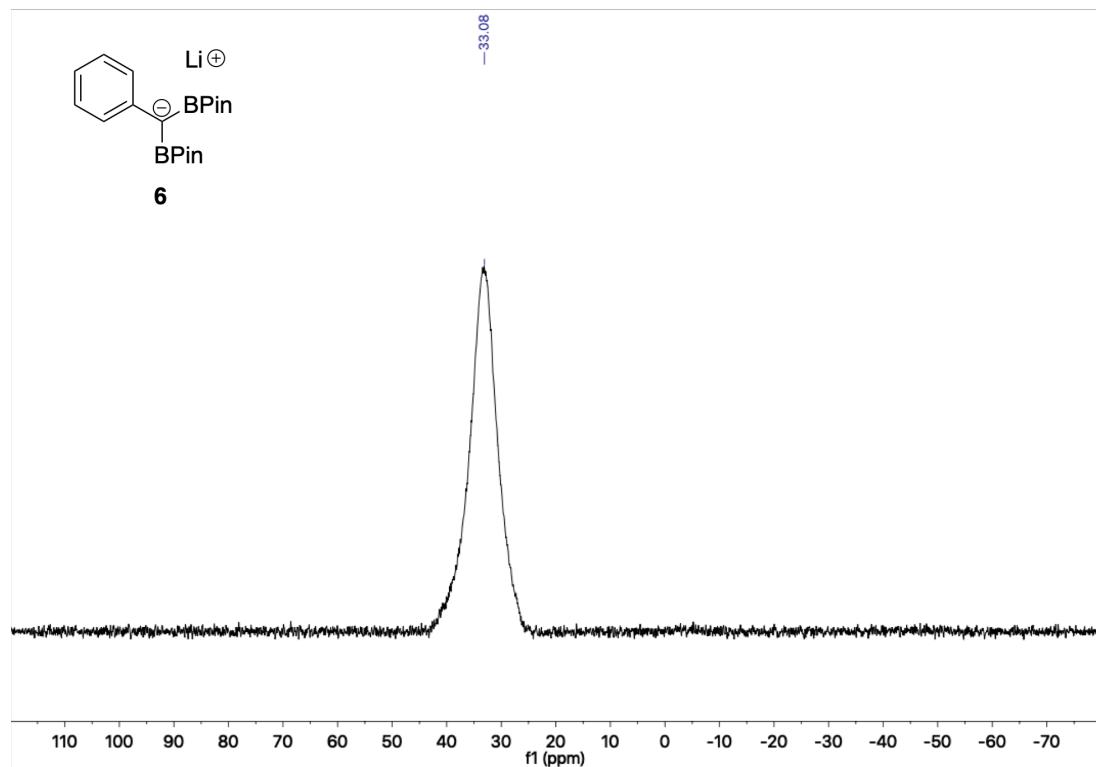


Figure S30. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of **6**.

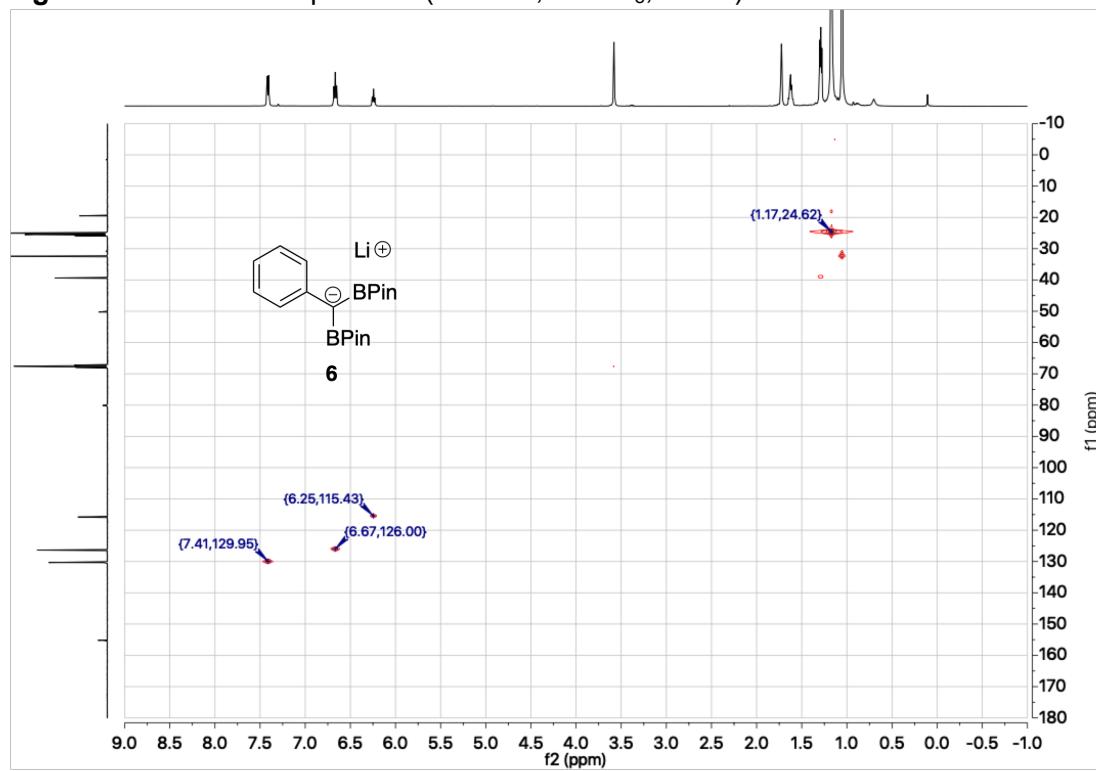


Figure S31. ^1H - ^{13}C HSQC spectrum.

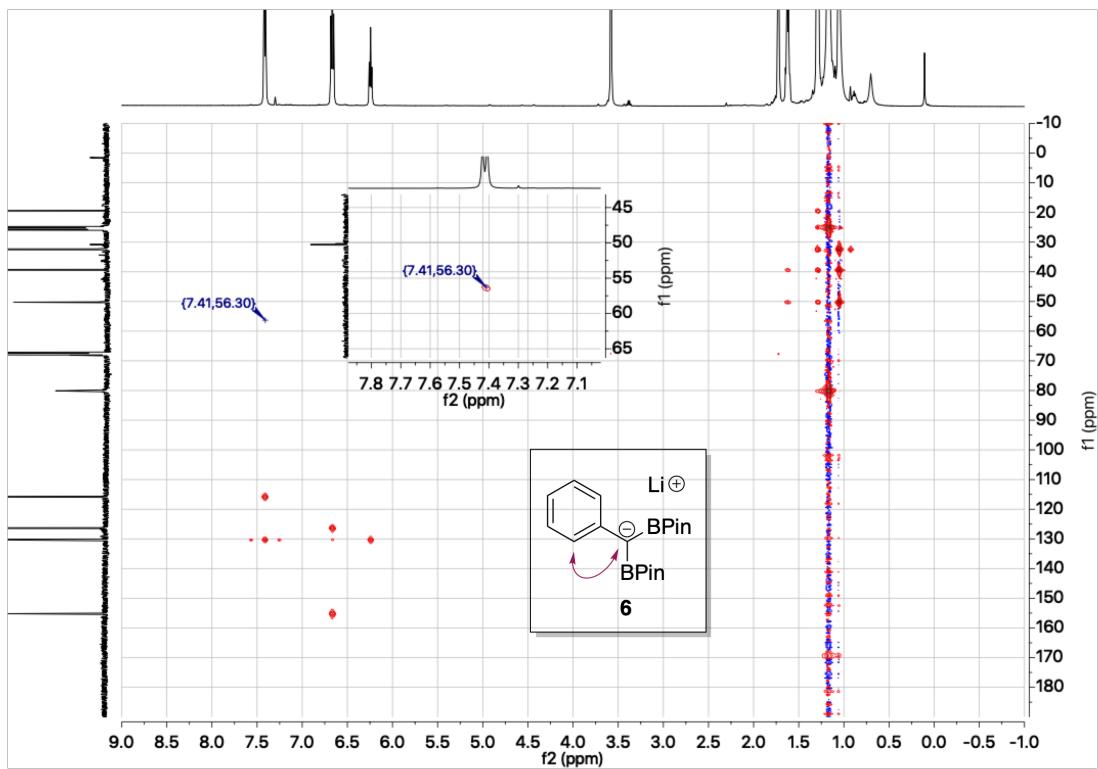
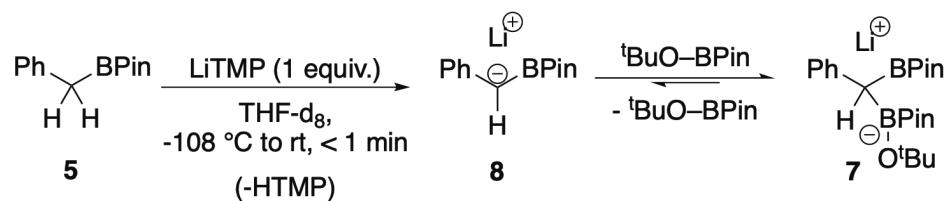


Figure S32. ^1H - ^{13}C HMBC spectrum.

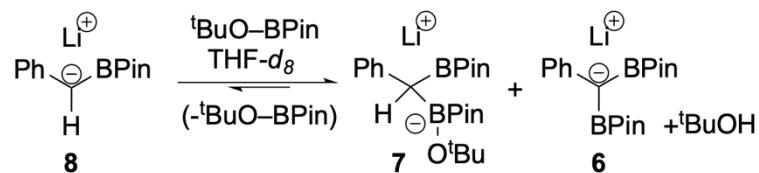
Addition of $^t\text{BuO-BPin}$ to 8.



To confirm the equilibrium between **8** and **7**, **8** was independently prepared by deprotonation of **5** by LiTMP and then treated with ^tBuO–BPin.

Procedure: A vial was charged with **5** (9 mg, 0.04 mmol) and $\text{thf-}d_8$ (0.6 mL) and placed in a cold well filled with liquid nitrogen until the solution froze. To the frozen solution was added LiTMP (6 mg, 0.04 mmol) as solid. The resulting solution was stirred for 1 min, followed by the addition of $^t\text{BuO-BPin}$ (8 mg, 0.04 mmol). The resulting mixture was then transferred to a J-Young tube. The J-Young tube was then sealed, brought out of the glove box. ^1H and ^{11}B NMR spectra were recorded after 5, 15, 30, and 60 minutes.

Observation:



Interestingly, addition of ^tBuO-BPin to **8** yielded **6** as well as **7** and other unidentified compound(s) (see Figure SX). Most of **8** was converted in 5 minutes and no **8** was observed in the reaction mixture after 30 minutes. This implies the “ate” complex **7** is the dominant compound in the equilibrium between **8** and **7** in the presence of ^tBuO-BPin and **7** is also in equilibrium with stabilized carbanion **6** due to resonance delocalization into empty p-orbitals of two boron atoms and empty pi*-orbitals of the phenyl substituent. To demonstrate the equilibrium between **6** and **7**, an additional experiment was carried out and the details are described in the later section (see SX). Despite of the formation of **6**, resonance of ^tBuOH was not observed in the ¹H NMR spectrum, presumably due to the interaction between ^tBuOH and

boron atom. The ratio of **6** : **7** : **8** changed from 1.0 : 0.8 : 0.8 (after 5 minutes) to 1.0 : 0.7 : 0.06 (after 15 minutes), and 1.0 : 0.7 : trace (after 30, 60 minutes).

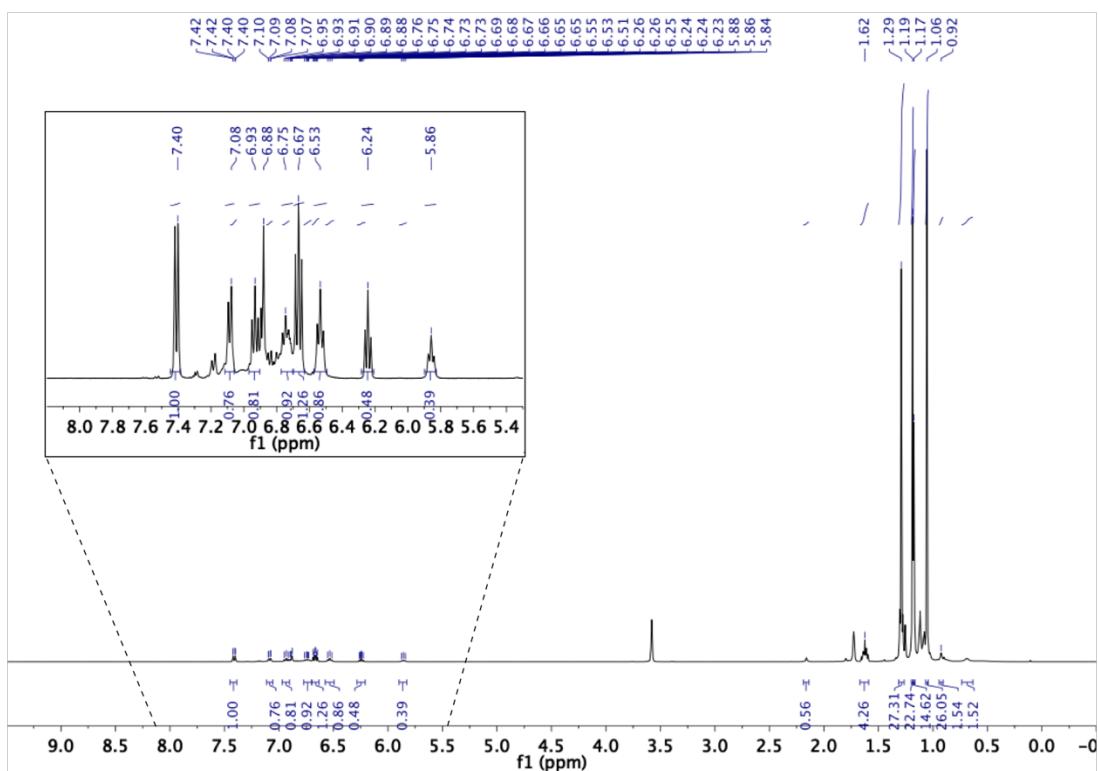


Figure S33. ^1H NMR spectrum (400 MHz, $\text{THF}-d_8$, 23 °C) of the mixture after 5 minutes. Inset: zoom-in from 8.2 to 5.3 ppm.

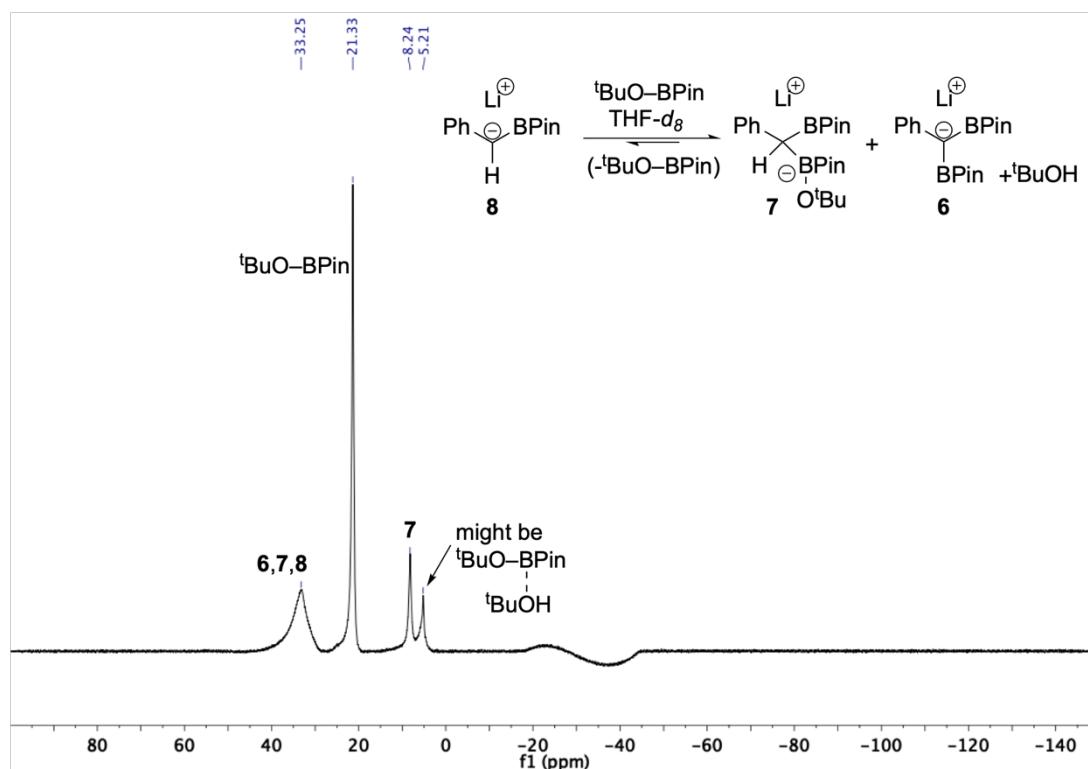


Figure S34. ^{11}B NMR spectrum (96 MHz, $\text{THF}-d_8$, 23 °C) of the mixture after 5 minutes.

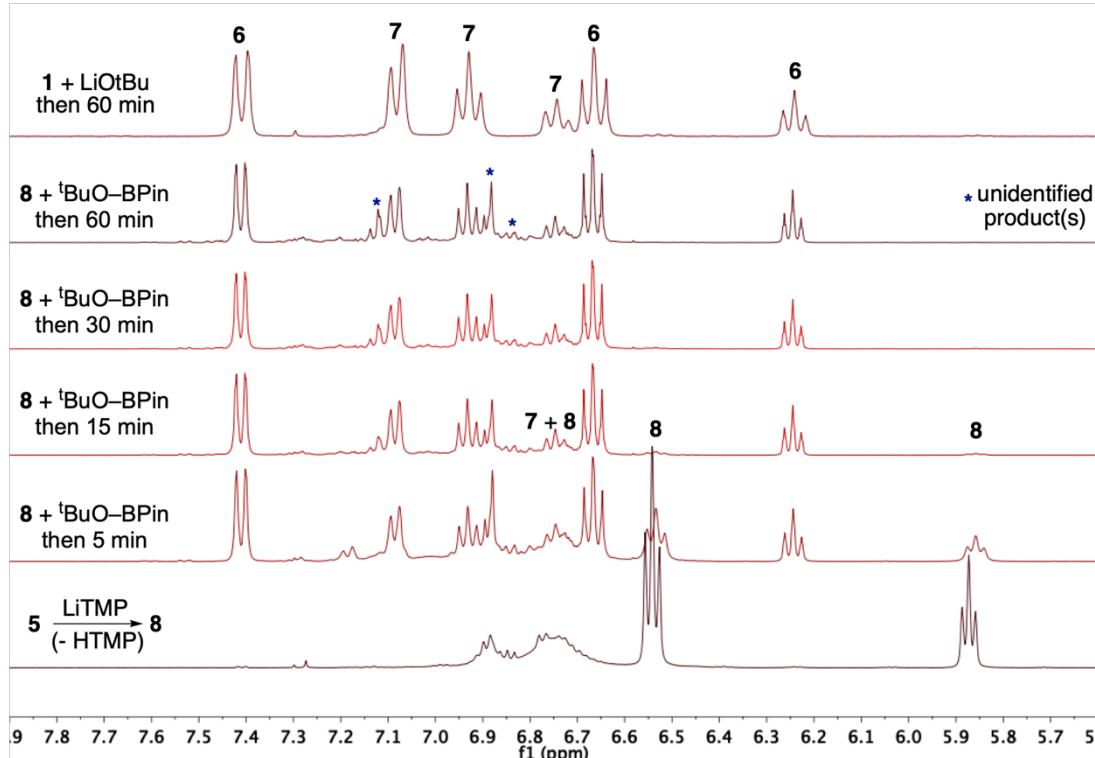
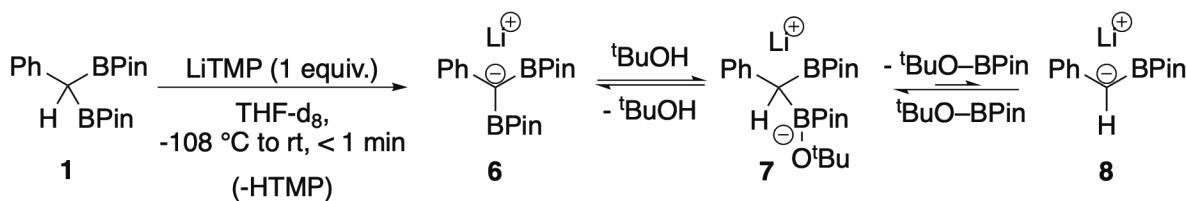


Figure S35. In situ monitoring of the treatment of **8** with $(^t\text{BuO})\text{BPin}$ by ^1H NMR spectroscopy (400 MHz, $\text{THF}-d_8$, 23 °C). Top: mixture of **6** and **7** prepared by mixing **1** and LiO^tBu . Bottom: **8** prepared by deprotonation of **5** with LiTMP .

Addition of ^tBuOH to **6.**



To demonstrate the equilibrium between **6** and **7**, **6** was independently prepared by deprotonation of **1** by LiTMP and then treated with 1 equivalent of ^tBuOH.

Procedure: *tert*-BuOH was dried over CaH₂ for 2 days and then distilled before brought in to the glove box. A vial was charged with **1** (12 mg, 0.035 mmol) and thf-d₈ (0.55 mL) and placed in a cold well filled with liquid nitrogen until the solution froze. To the frozen solution was added LiTMP (5 mg, 0.035 mmol) as solid. The resulting solution was stirred for 1 min and transferred to a J-Young tube. Then ^tBuOH (3.3 μL, 0.035 mmol) was added to the mixture via microsyringe. Then the ¹H and ¹¹B spectra of the mixture were recorded after 5, 15, 30, and 60 minutes.

The ratio of **6** : **7** : **8** changed from 1.0 : 7.0 : 0.2 (after 5 minutes) to 1.0 : 6.3 : 0.1 (after 15 minutes), and 1.0 : 6.0 : trace (after 30, 60 minutes).

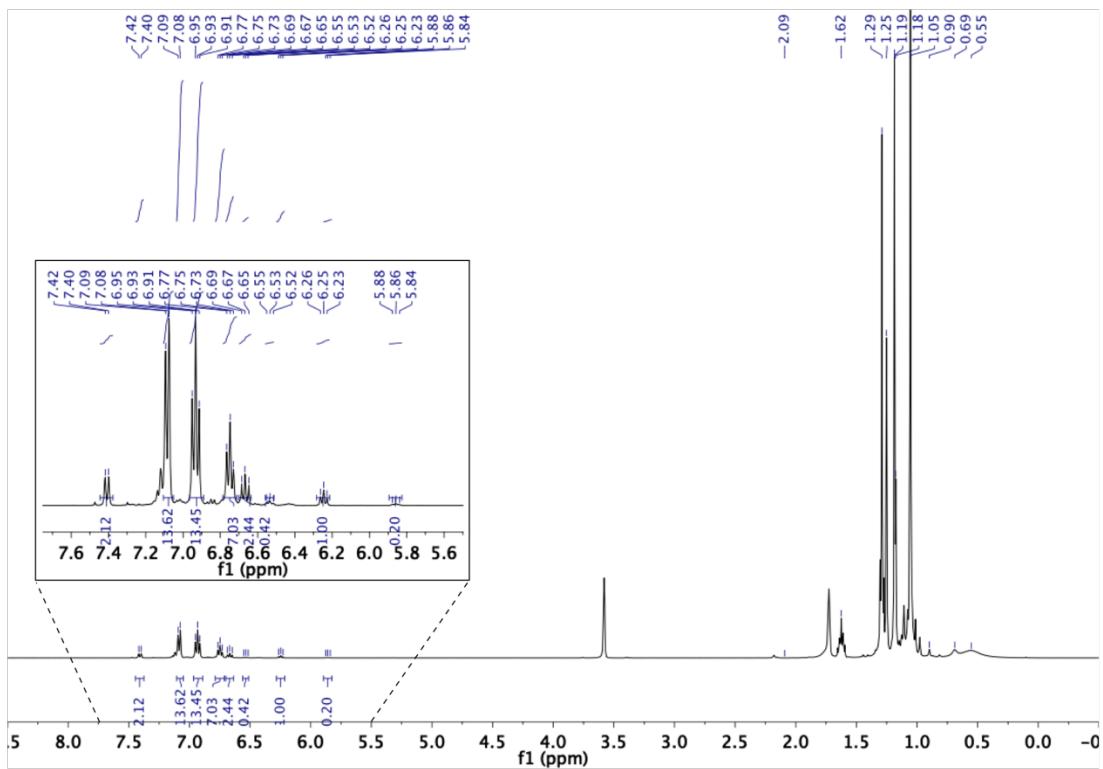


Figure S36. ^1H NMR spectrum (400 MHz, THF- d_8 , 23 °C) of the mixture after 5 minutes. Inset: zoom-in from 7.7 to 5.5 ppm.

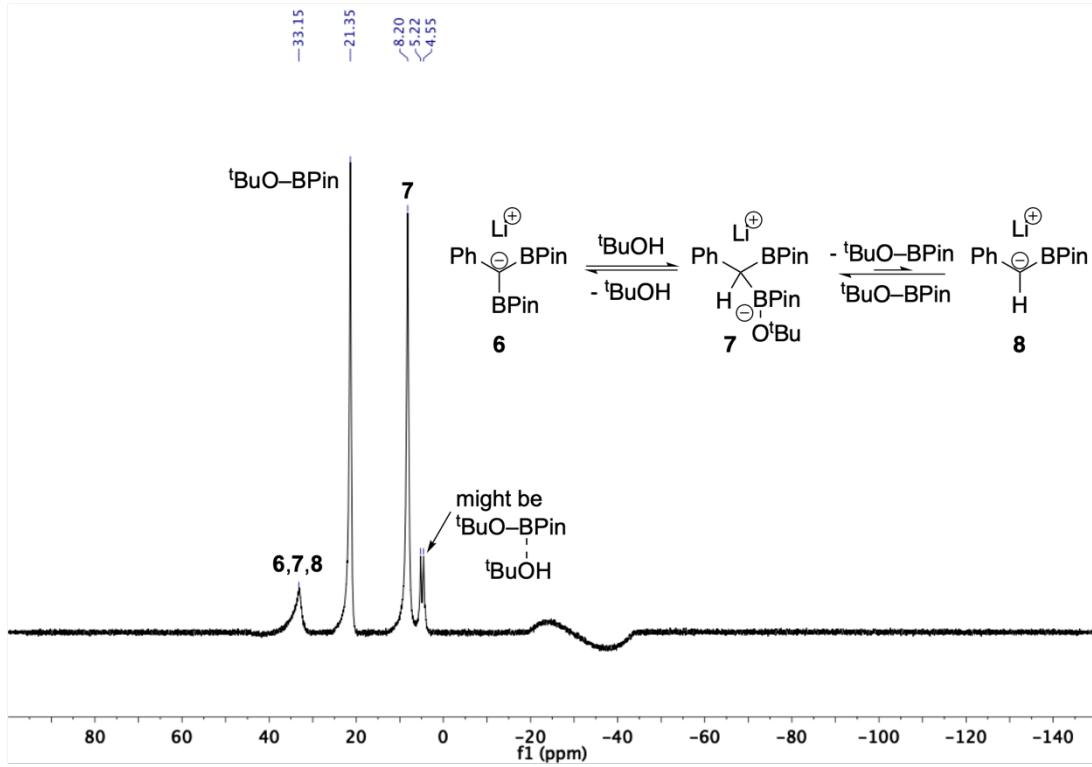


Figure S37. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of the mixture after 5 minutes.

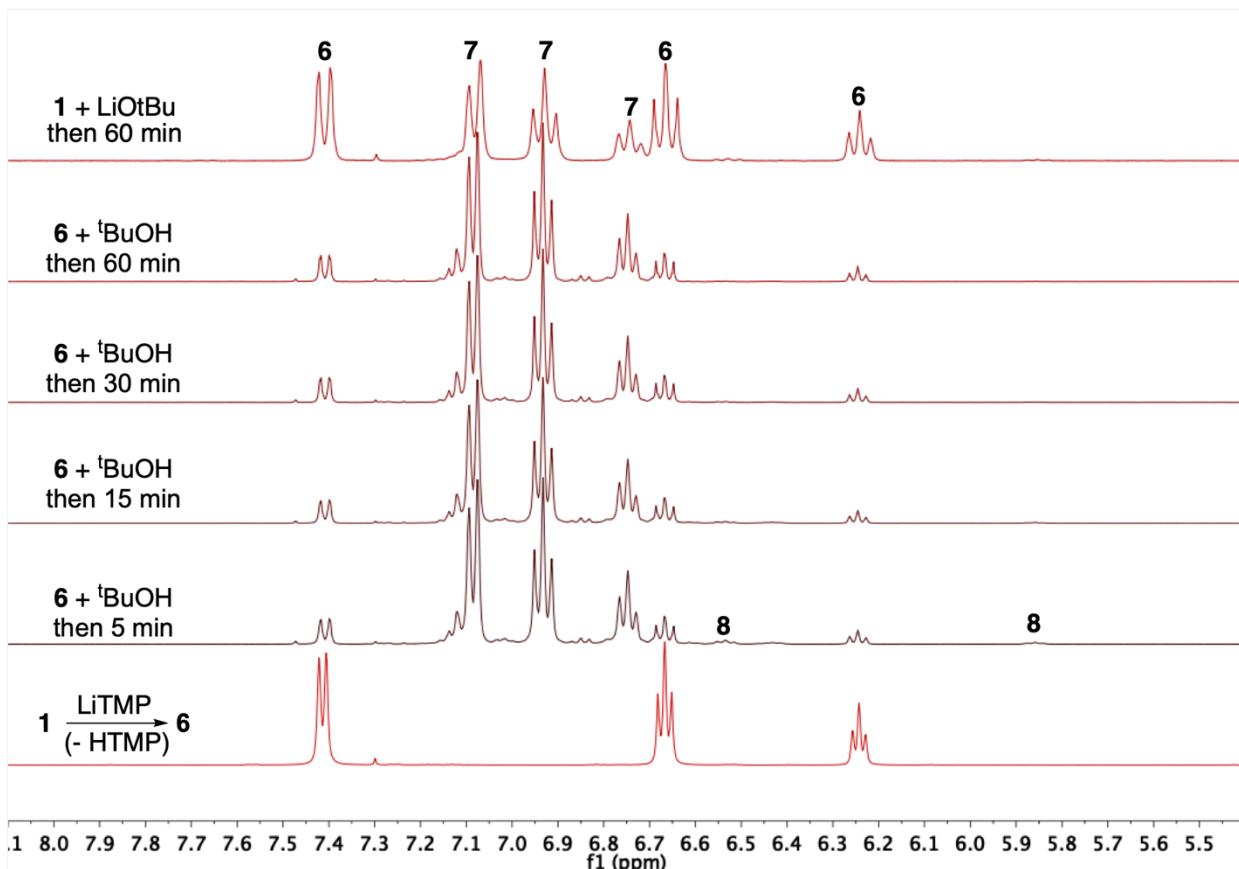
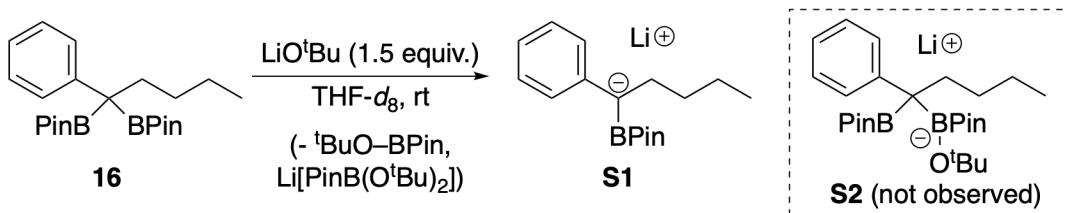


Figure S38. In situ monitoring of the treatment of the treatment of **6** with ^tBuOH by ¹H NMR spectroscopy (500 MHz, THF-*d*₈, 23 °C). Top: mixture of **6** and **7** prepared by mixing **1** and LiOtBu. Bottom: **8** prepared by deprotonation of **1** with LiTMP.

Deborylation of **16** by LiOtBu



In a N₂ filled glove box, a J-Young tube was charged with LiOtBu (4 mg, 0.05 mmol, 1.5 equiv). To the J-Young tube was added a solution of **16** (12 mg, 0.03 mmol in 0.5 mL thf-*d*₈). The tube was sealed and brought out of the box, and ¹H, ¹¹B, ¹³C, g-COSY, ¹H-¹³C HSQC, and ¹H-¹³C

HMBC NMR spectra of the mixture were recorded. ¹H and ¹¹B NMR spectra were recorded after 15 minutes and 1 hour. 84% conversion was observed.

Compound **16**. **¹H NMR** (300 MHz, THF-*d*₈, 23 °C) δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.21 (d, *J* = 2.1 Hz, 26H), 0.82 (t, *J* = 7.1 Hz, 3H). **¹¹B NMR** (96 MHz, THF-*d*₈, 23 °C) δ 33.65.

Compound **S1**. **¹H NMR** (300 MHz, THF-*d*₈, 23 °C) δ 6.85 (br, s, 2H), 6.58 (t, *J* = 7.7 Hz, 2H), 5.77 (t, *J* = 6.9 Hz, 1H), 2.13 (t, *J* = 6.5 Hz, 2H), 1.29 (s, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); Resonances of two aliphatic C–Hs are buried in the BPin & ^tBu region (1.35–1.05 ppm). **¹¹B NMR** (96 MHz, THF-*d*₈, 23 °C) δ 30.71.

The absence of ¹¹B resonance at 8.24 ppm supports the formation of **S1**, not **S2**. The resonances at 21.38 ppm and 5.25 ppm correspond to the PinB–O^tBu and tetravalente boron of “ate” complex, respectively. As shown in Figure S20, aromatic protons of **S1** are upfield shifted compared to those of **16** and the resonance of *ortho*-C–Hs is broadened (top two spectra). **1** shows a similar behavior upon the deborylation promoted by LiO^tBu.

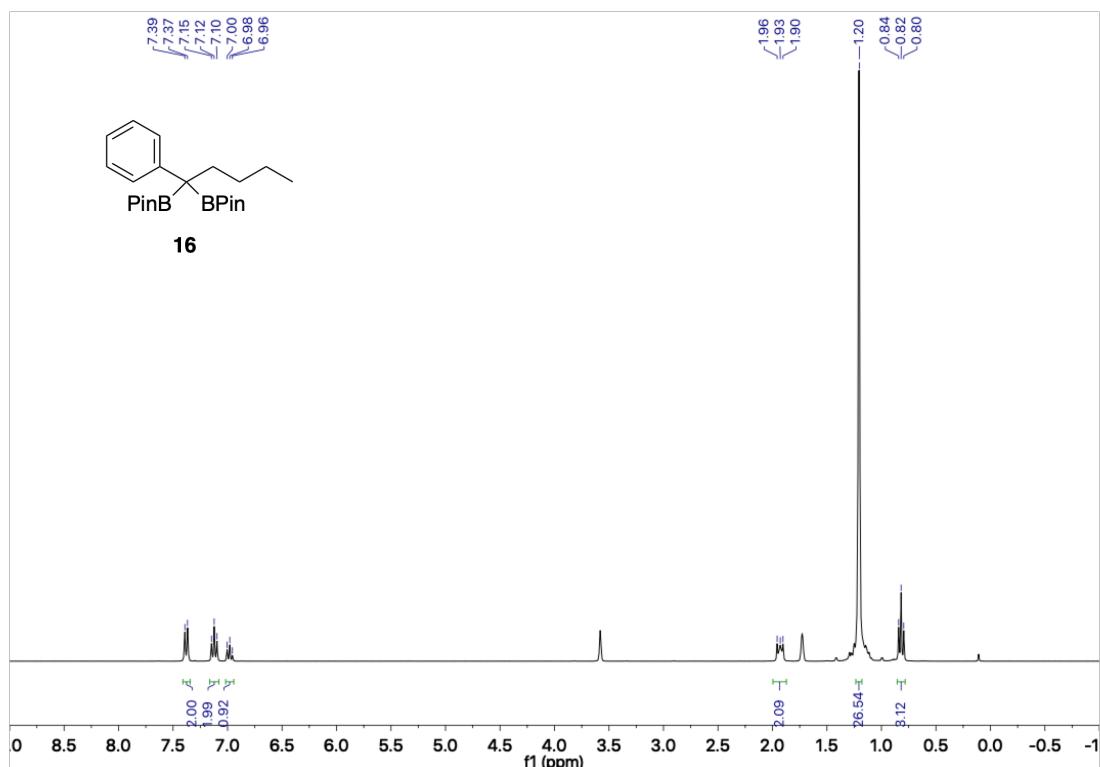


Figure S39. ^1H NMR spectrum (500 MHz, THF- d_8 , 23 °C) of **16**.

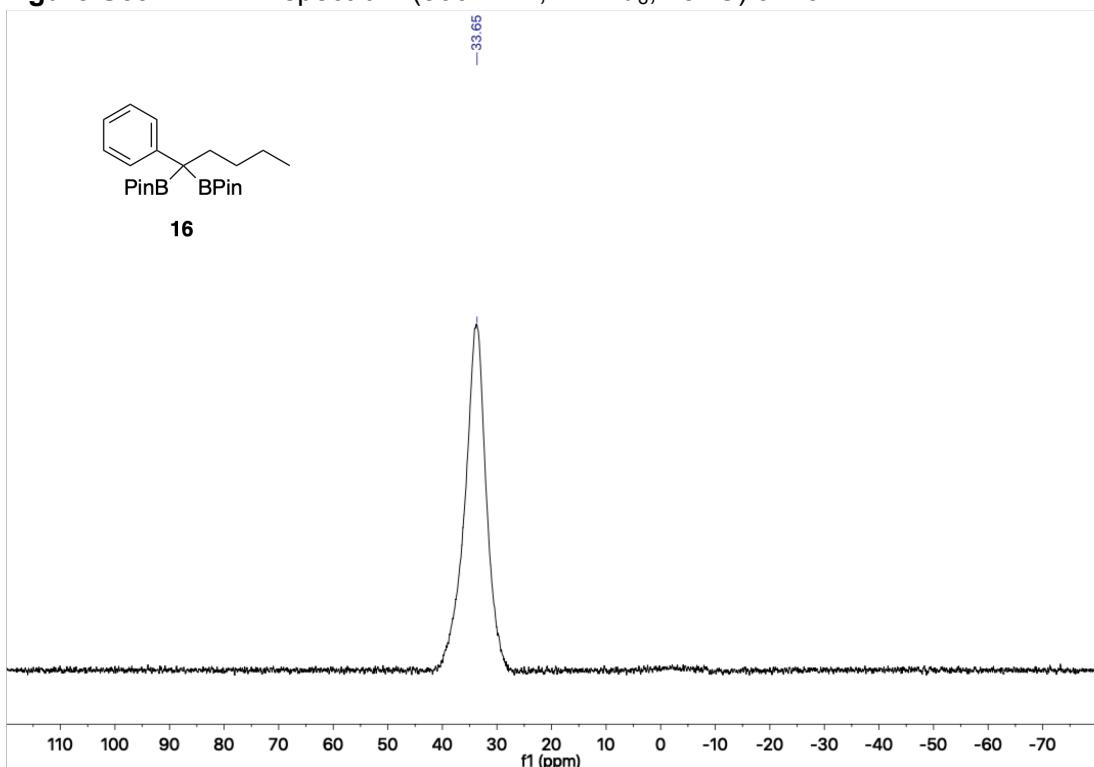


Figure S40. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of **16**.

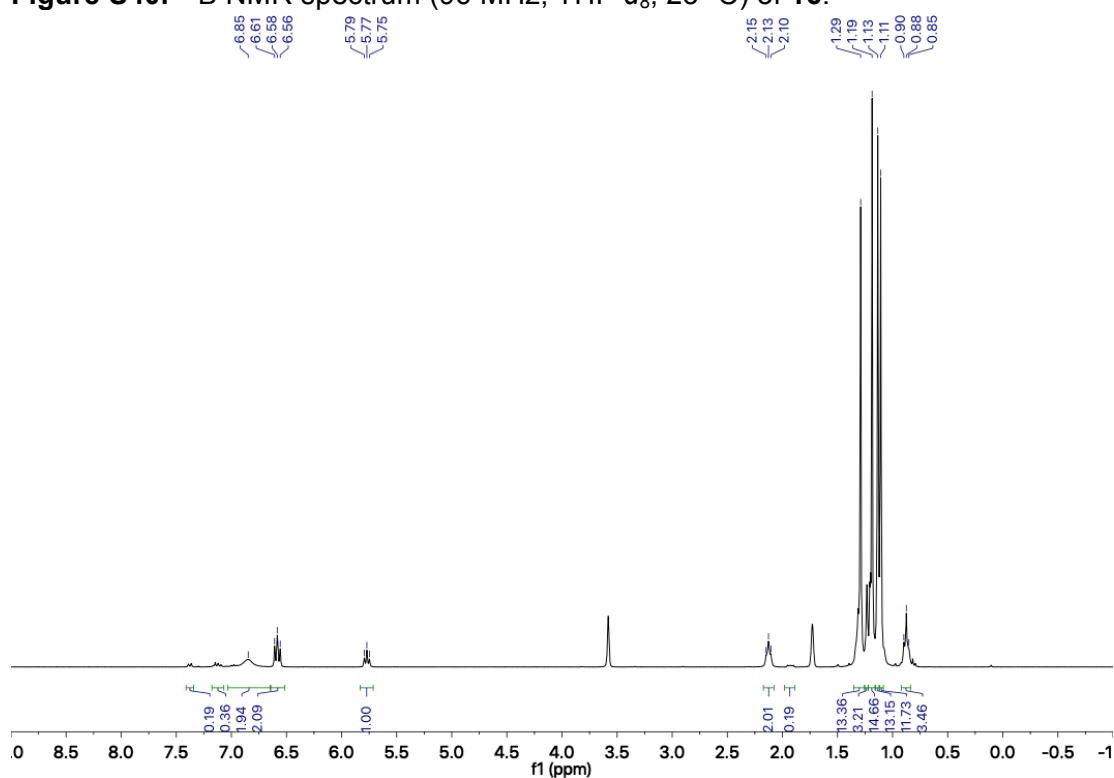


Figure S41. ^1H NMR spectrum (500 MHz, THF- d_8 , 23 °C) of the mixture.

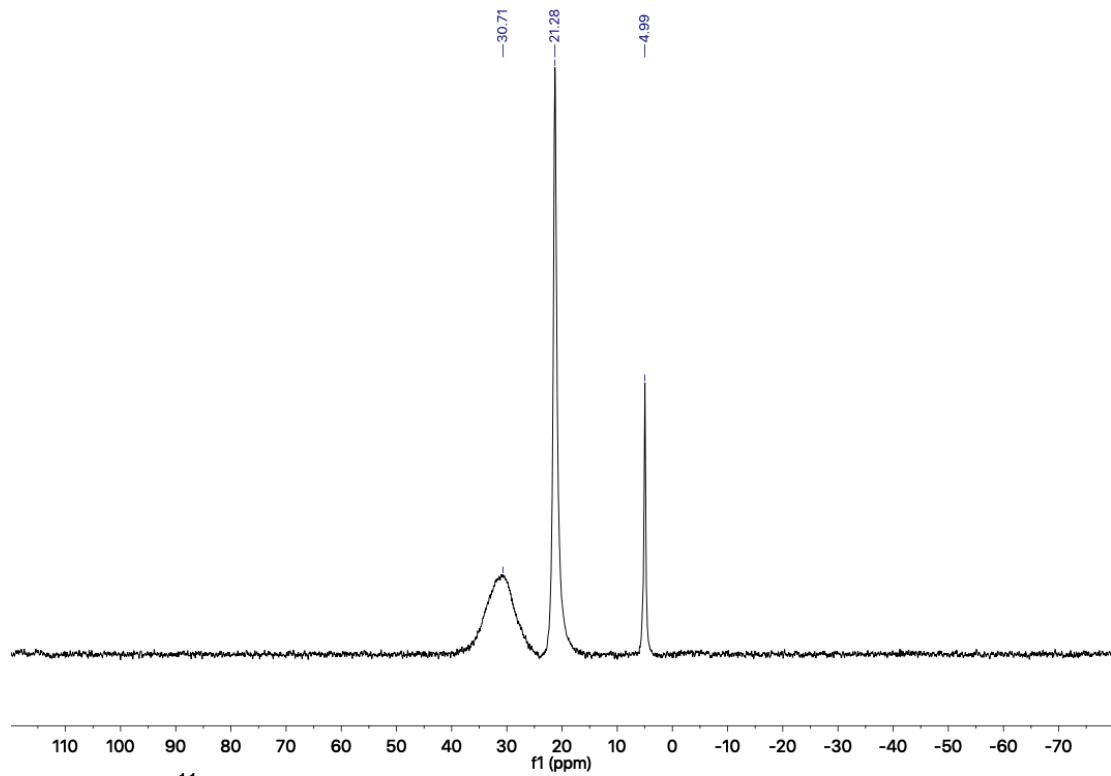


Figure S42. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of the mixture.

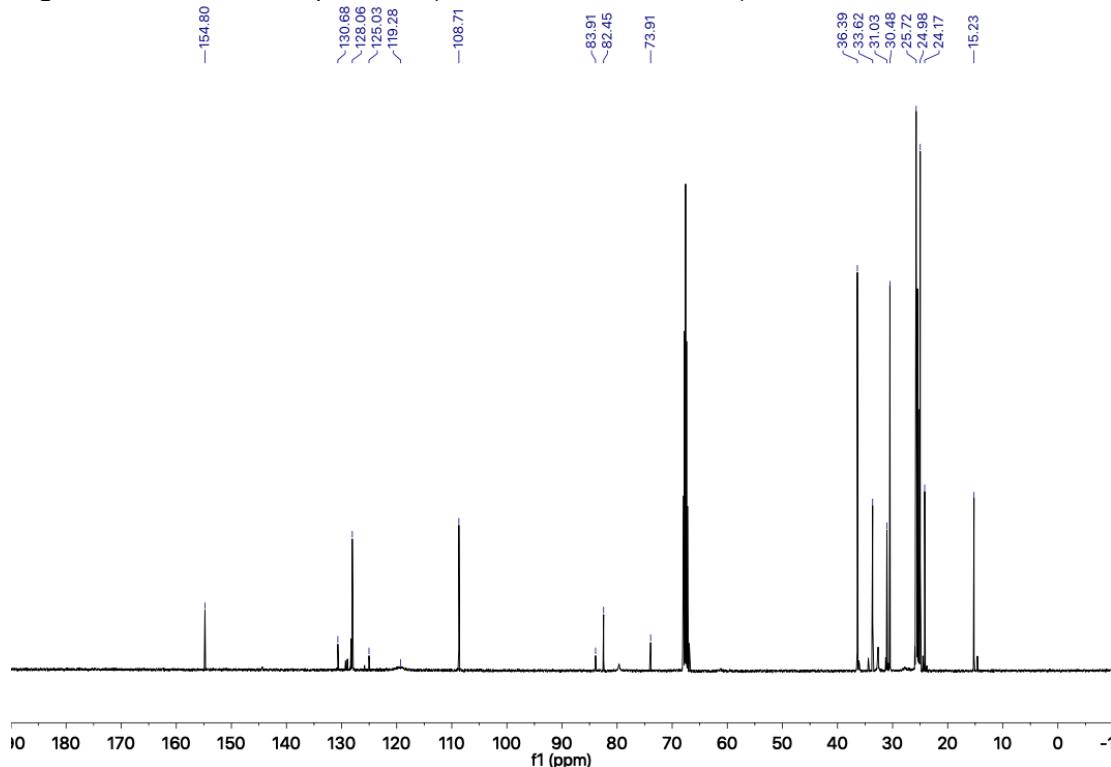


Figure S43. $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, THF- d_8 , 23 °C) of the mixture.

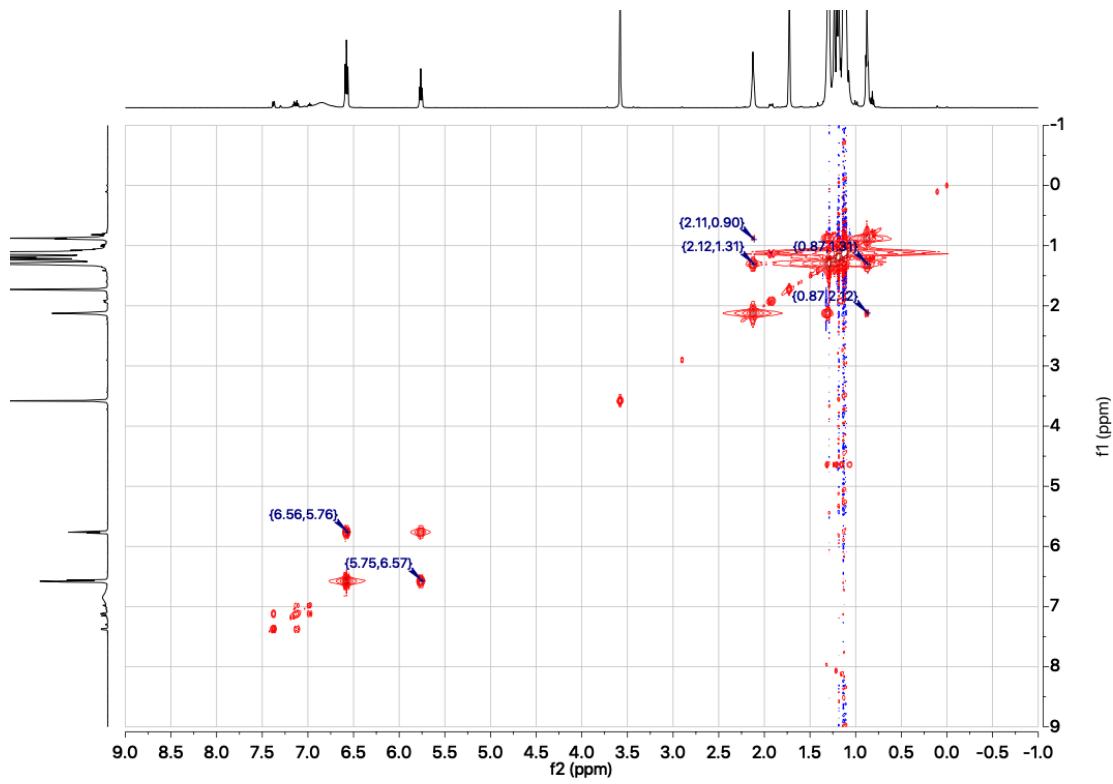


Figure S44. g-COSY spectrum of the mixture.

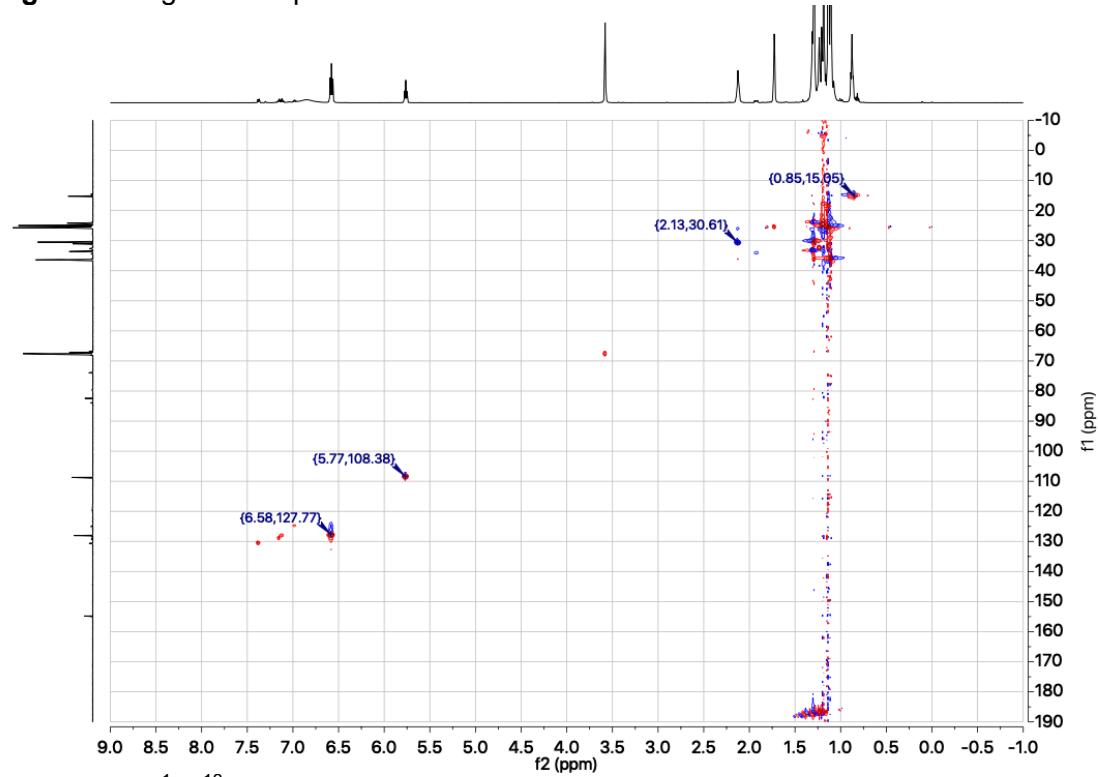


Figure S45. ^1H - ^{13}C HSQC spectrum of the mixture.

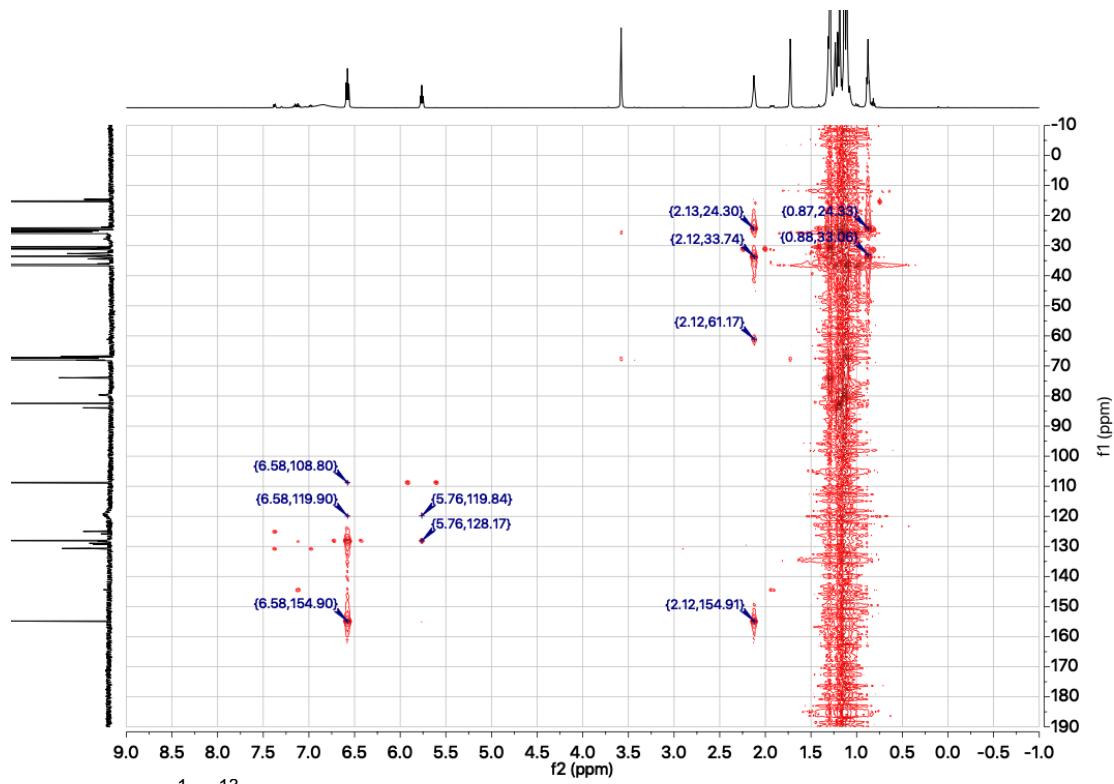


Figure S46. ¹H-¹³C HMBC spectrum of the mixture.

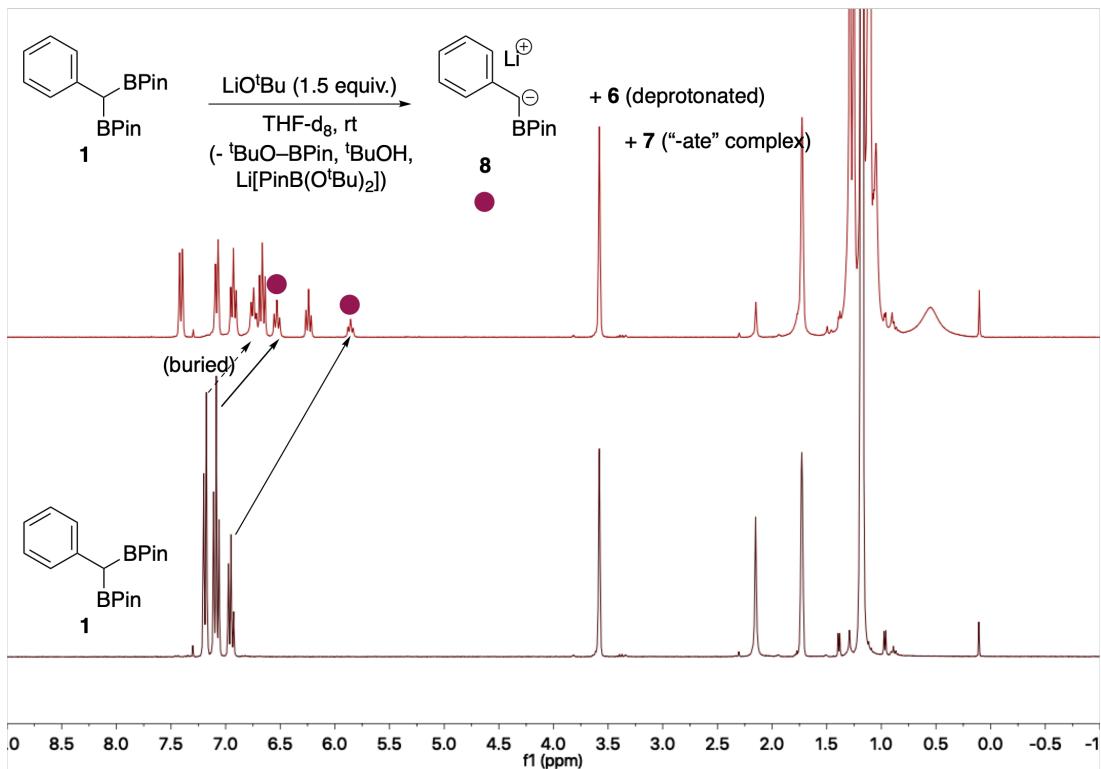
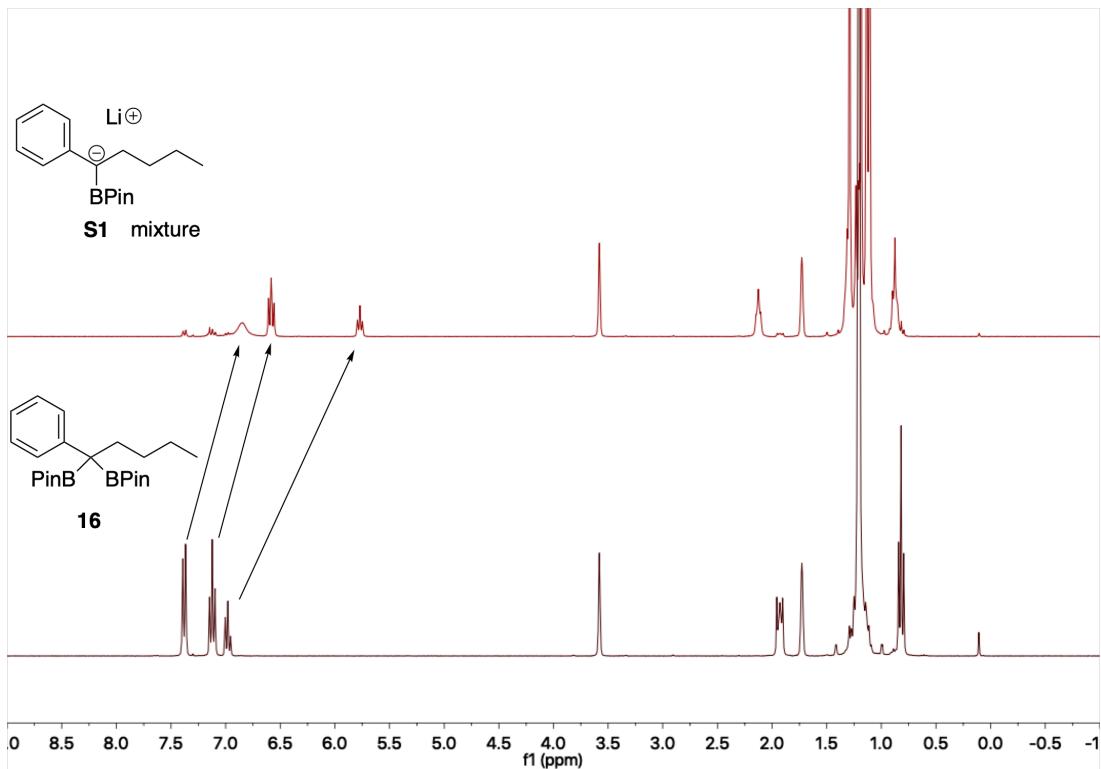
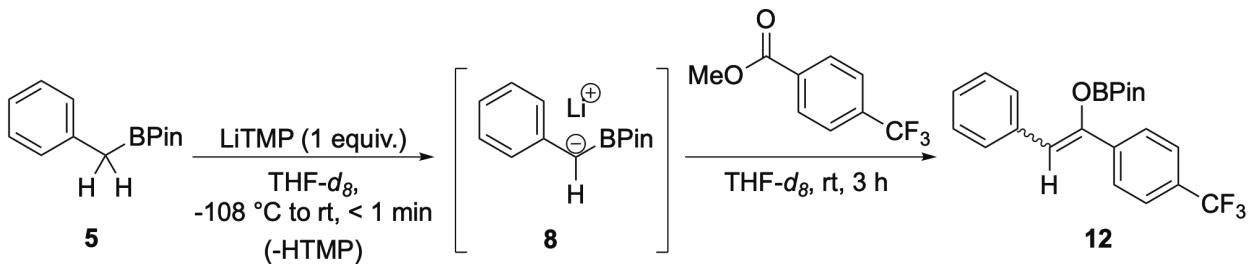


Figure S47. Comparison between **16** (top two) and **1** (bottom two) upon the addition of LiO^tBu .

Coupling between 8 and ester



In an N₂ filled glove box, a scintillation vial was charged with benzylmonoboroante **5** (8 mg, 0.035 mmol) and thf-*d*₈ (0.55 mL) and placed in the cold well filled with liquid nitrogen until the solution froze. To the frozen solution was added LiTMP (5 mg, 0.035 mmol) was added all at once. The resulting solution was stirred and all solid was dissolved in the solution while thawing. After the solution became homogeneous, methyl (*p*-trifluoromethyl)benzoate (5.6 μ L, 0.035 mmol) was added via microsyringe. The resulting yellow solution was transferred to a J-Young tube, and the solution was analyzed by ¹H, ¹¹B, ¹³C, gCOSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR spectroscopies after 3 hours.

Compound **12**. **¹H NMR** (400 MHz, THF-*d*₈, 23 °C) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.83 (tt, *J* = 7.3, 1.3 Hz, 1H), 5.81 (br, s, 1 H), 1.20 (s, 12H). **¹¹B NMR** (96 MHz, THF-*d*₈, 23 °C) δ 22.26, 6.16, 5.26. **¹³C NMR** (126 MHz, THF-*d*₈, 23 °C) δ 163.3, 151.6, 143.5, 128.3, 127.2, 125.5 (br), 125.0 (q, ³*J*_{CF}=3.8 Hz), 122.5, 98.3 (br), 83.2 (br), 25.1; Resonance of the carbon of CF₃ group is not found; Resonance of the carbon attached to CF₃ group shows no C–F coupling, but has broad shape.

The gCOSY and ¹H-¹³C HSQC spectra depict clear correlations between ¹H resonances at 5.81 ppm and 7.95 ppm (*ortho*-C–H at phenyl group), and ¹H resonance at 5.81 ppm and ¹³C resonance at 98.3 ppm, confirming existence of the vinylic proton. Several key ¹H-¹³C HSQC correlations are also found (Figure S53).

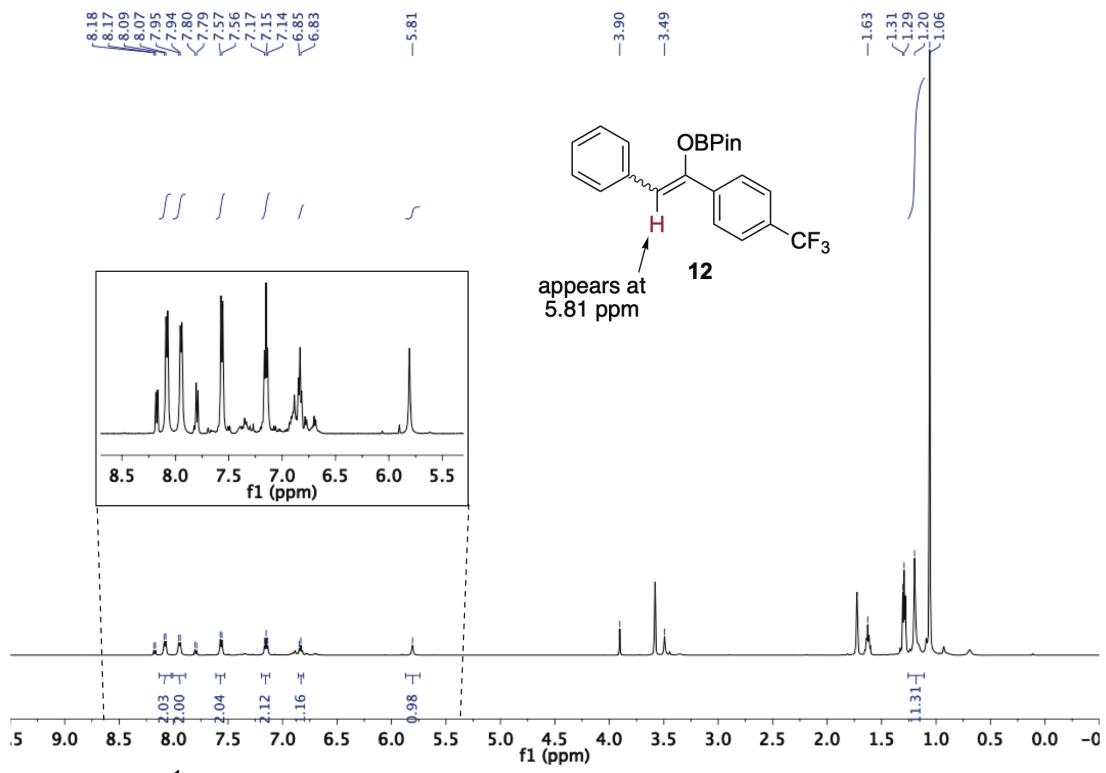


Figure S48. ^1H NMR spectrum (400 MHz, THF- d_8 , 23 °C) of the reaction mixture.

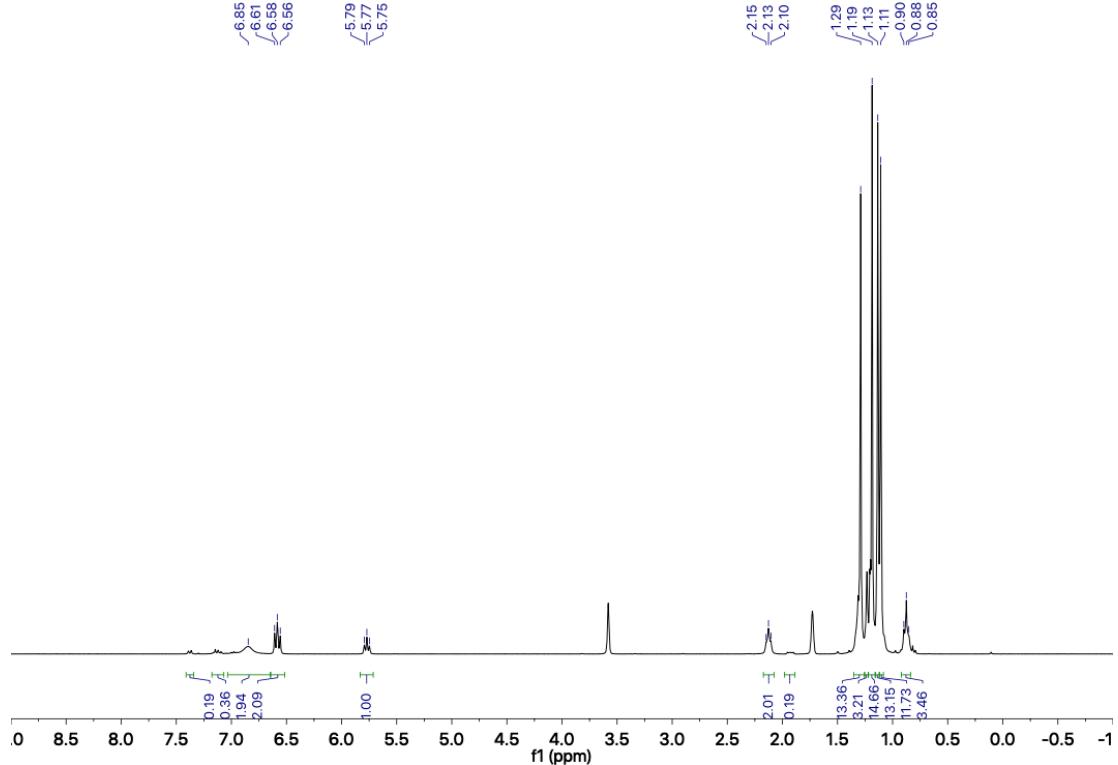


Figure S49. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of the reaction mixture.

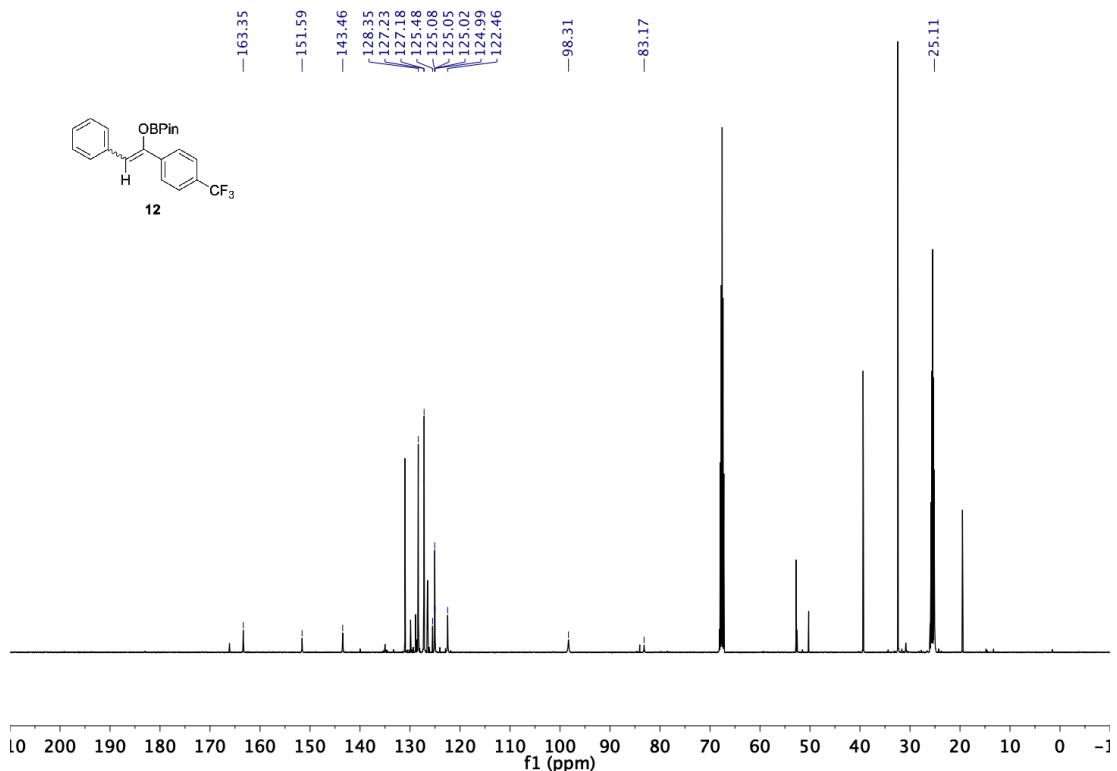


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF- d_8 , 23 °C) of the mixture.

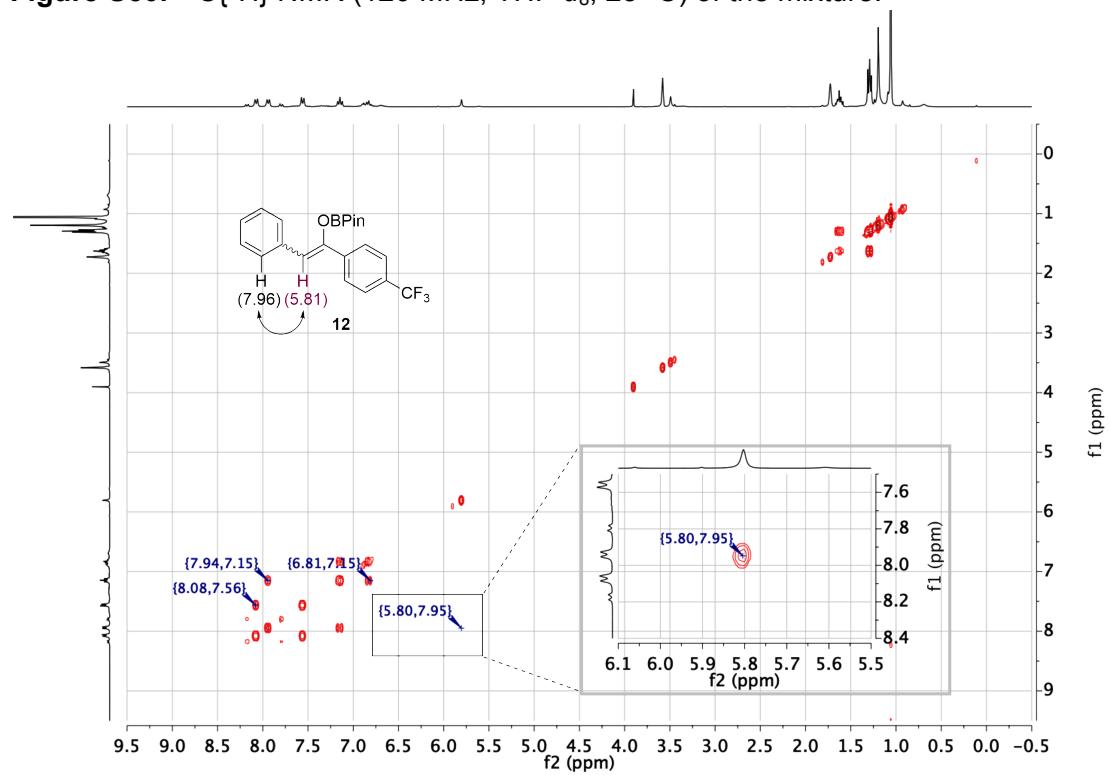


Figure S51. g-COSY spectrum of the mixture.

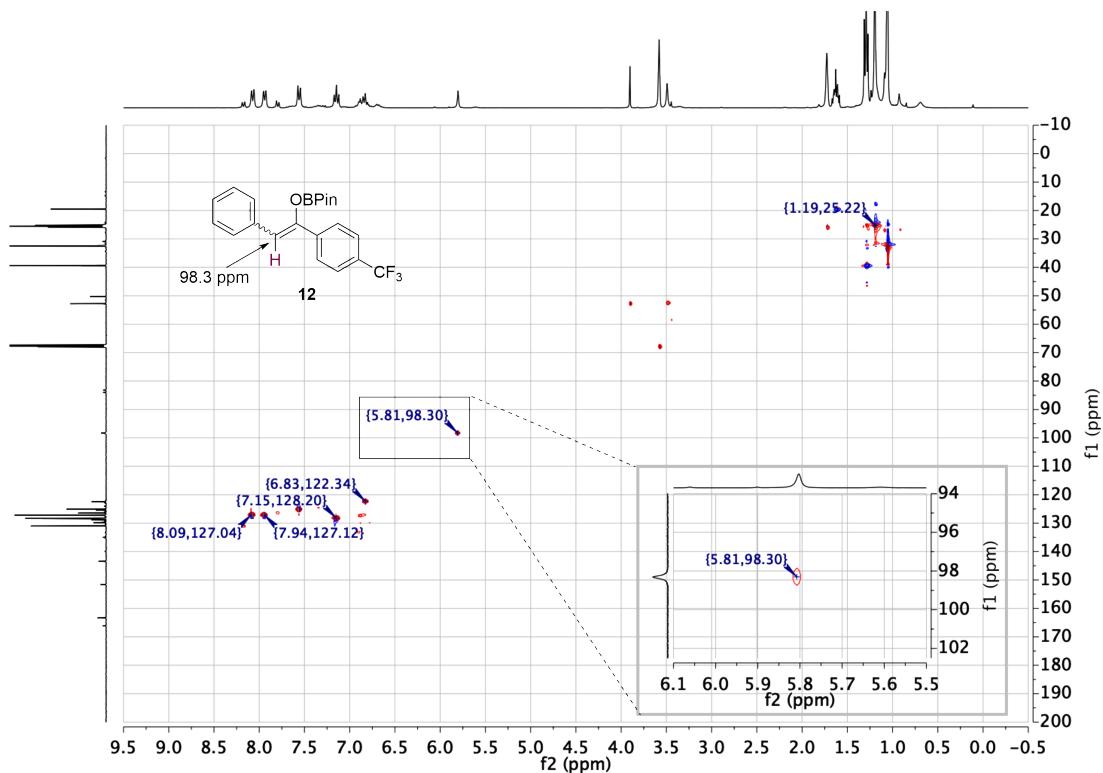


Figure S52. ^1H - ^{13}C HSQC spectrum of the mixture.

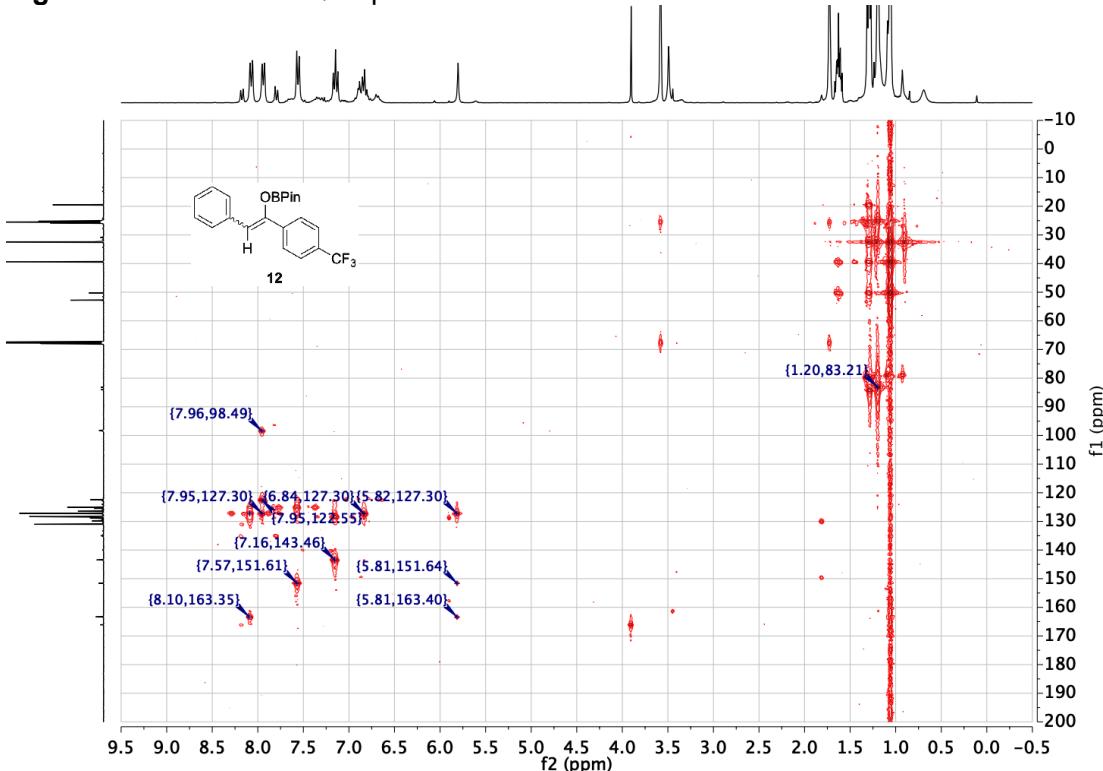
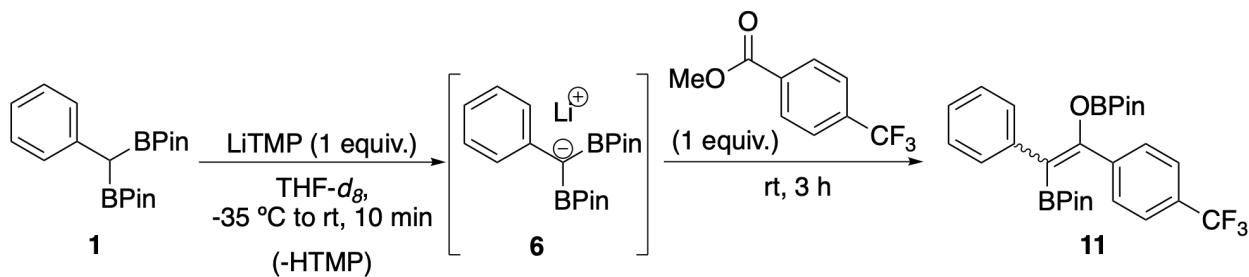
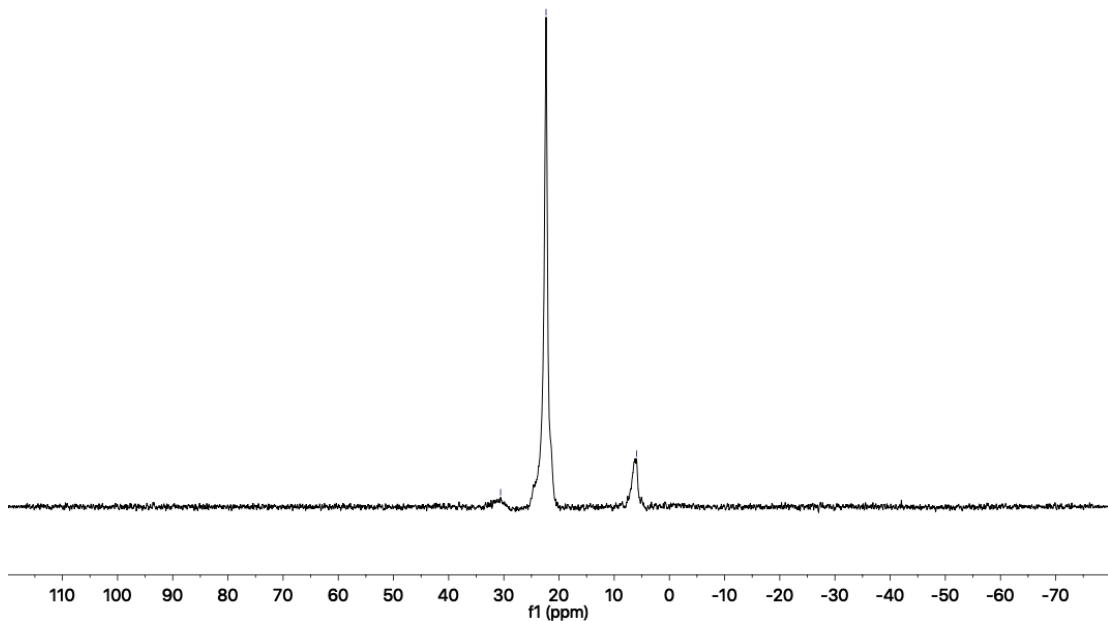
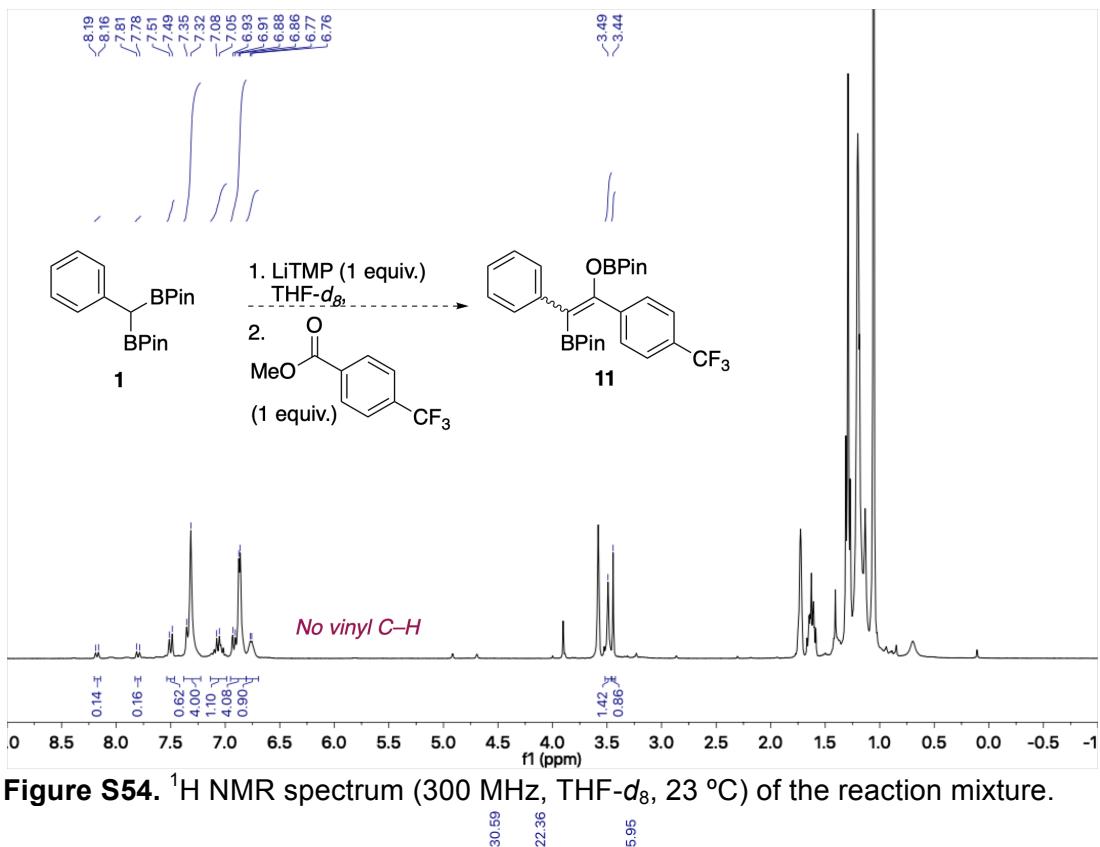


Figure S53. ^1H - ^{13}C HMBC spectrum of the mixture.

Deprotonative coupling of **1** with ester



In an N₂ filled glove box, a J-Young tube was charged with LiTMP (7 mg, 0.05 mmol). A solution of benzylidiboroante **1** (17 mg, 0.05 mmol in 0.8 mL thf-*d*₈) was prepared in a scintillation vial and chilled to -35 °C. The chilled solution was transferred to the J-Young tube and the vial was washed again with 0.1 mL of thf- *d*₈. The J-Young tube was placed in the cold well for 10 minutes and brought out of the box. ¹H, ¹¹B, ¹³C, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR spectra were obtained. Then in the glove box, LiO^tBu (4 mg, 0.05 mmol) was added to the reaction mixture. No change was observed in the ¹H NMR spectrum (Figure S56).



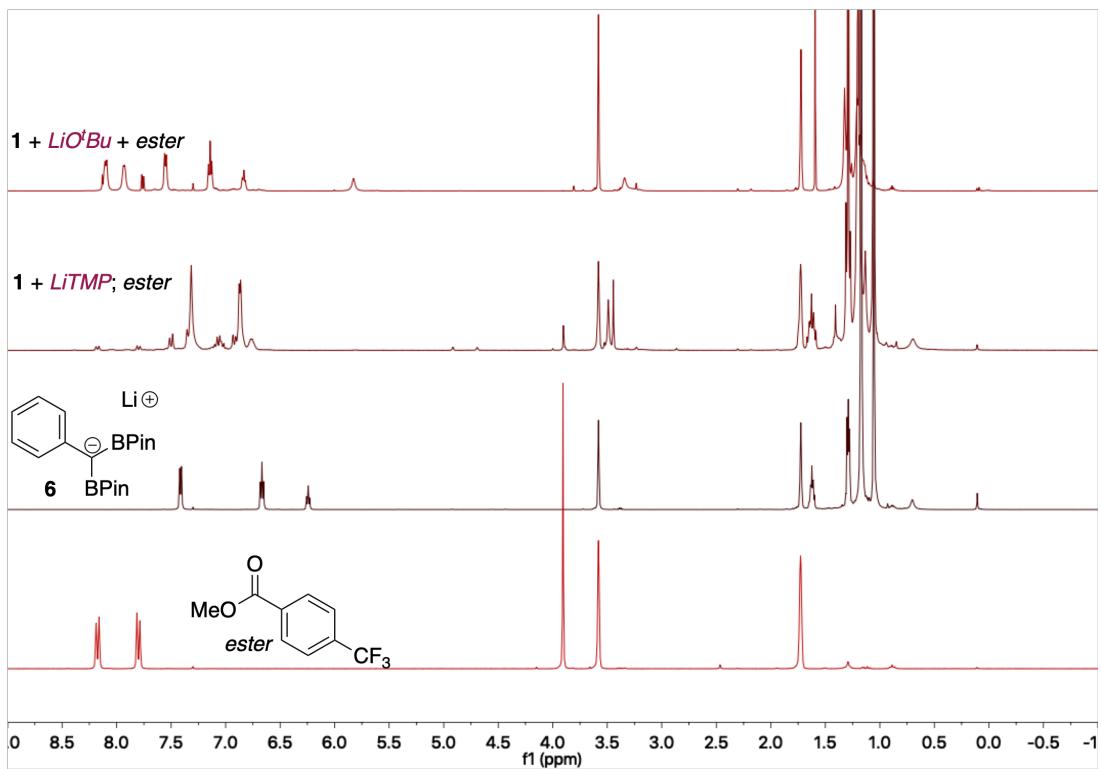
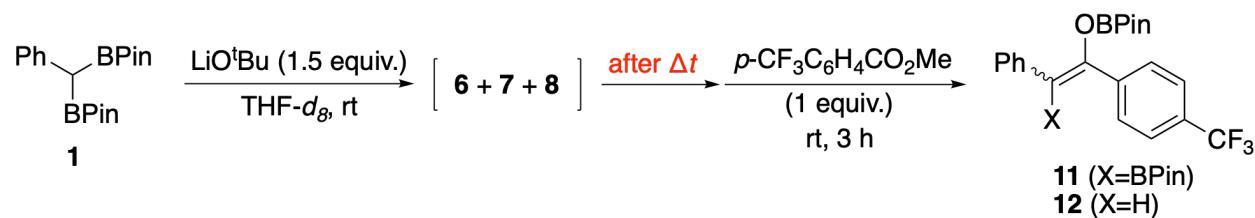


Figure S56. Stacked ¹H NMR spectra of ester, **6**, LiTMP-promoted reaction mixture, and LiOtBu-promoted reaction mixture (from bottom to top).

Coupling of **1 and ester in the presence of LiO^tBu with various time interval**



In N₂ filled glove box, a scintillation vial was charged with 6 mg of LiO^tBu (0.075 mmol, 1.5 equiv.), 17 mg of **1** (0.05 mmol, 1 equiv.), and 0.8 mL thf-*d*₈. After Δt , 8 μ L of methyl 4-(trifluoromethyl)benzoate (0.05 mmol, 1.5 equiv.) was added via microsyringe. The mixture was stirred for 3 hours at rt and then transferred to a J-Young tube. Then ¹H NMR spectroscopy of the mixture was recorded.

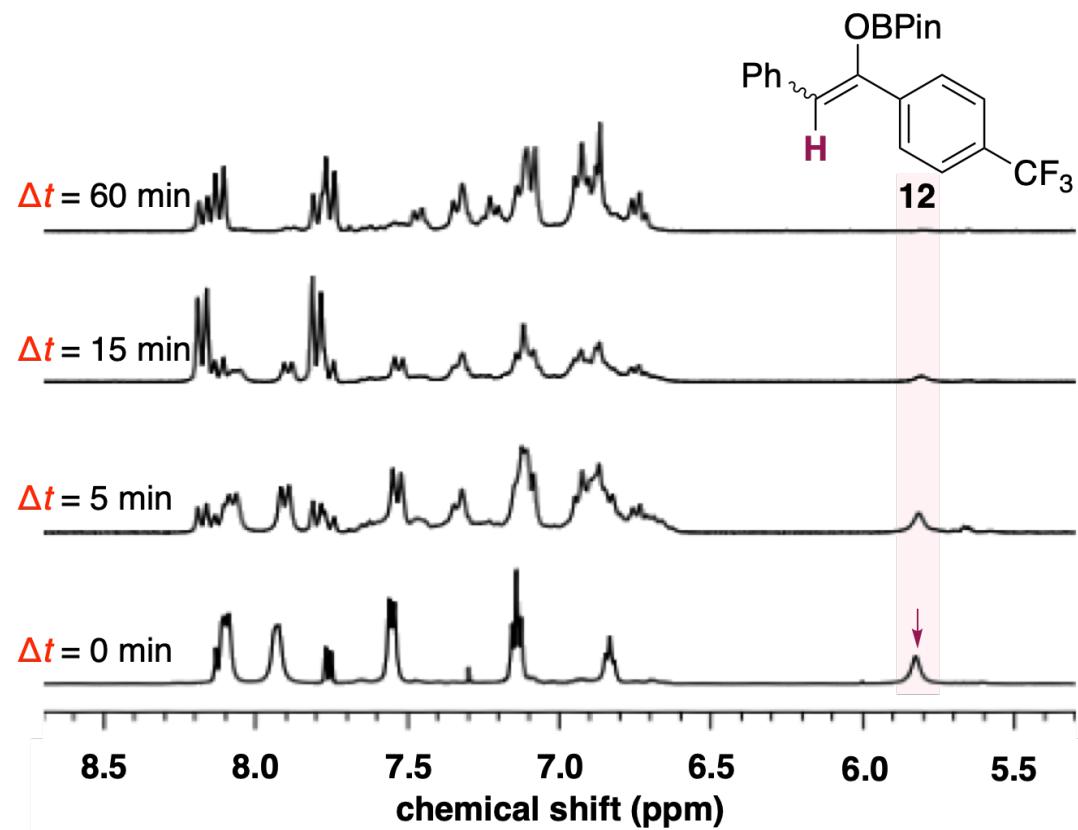
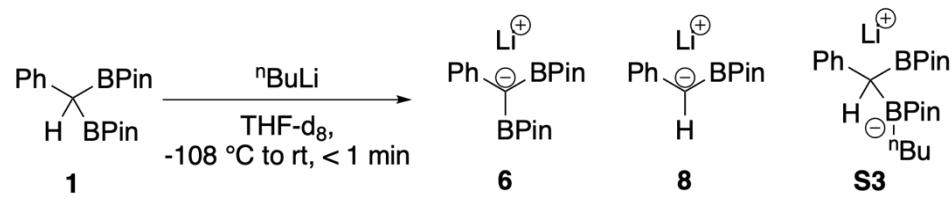


Figure S57. Characteristic signal of vinylic proton of **12** in ¹H NMR spectrum (300 MHz, THF-*d*₈, 23 °C).

Activation of **1** with $^n\text{BuLi}$



The concentration of $^n\text{BuLi}$ was determined by titration with diphenylacetic acid prior to use. A vial was charged with **1** (12 mg, 0.035 mmol) and $\text{thf-}d_8$ (0.55 mL) and placed in a cold well filled with liquid nitrogen until the solution froze. To the frozen solution was dropwise added $^n\text{BuLi}$ (2.65 M in hexanes, 13.2 μL , 0.035 mmol) via microsyringe. The resulting solution was stirred for 1 min and transferred to a J-Young tube. The J-Young tube was sealed, brought out of the box, and immediately placed in a Dewar flask filled with liquid nitrogen. Then the ^1H and ^{11}B spectra of the mixture were recorded.

Deborylated carbanion **8** was the major product along with deprotonated species **6** as a minor product. There still remained some unreacted **1** and an unidentified product (denoted as *) was also observed, the resonances of which were obscured by those of **1**. Given the small shift of the proton resonances from those of **1** and a broad ^{11}B resonance at 8.80 ppm in the ^{11}B NMR spectrum, the unidentified product was tentatively assigned as **S3**. Due to overlapping of ^1H resonances of **1** and **S3**, the ratio between four species could not be calculated but the ratio of **6** : (**S3 + 1**) : **8** was roughly 0.4 : 1 : 1.

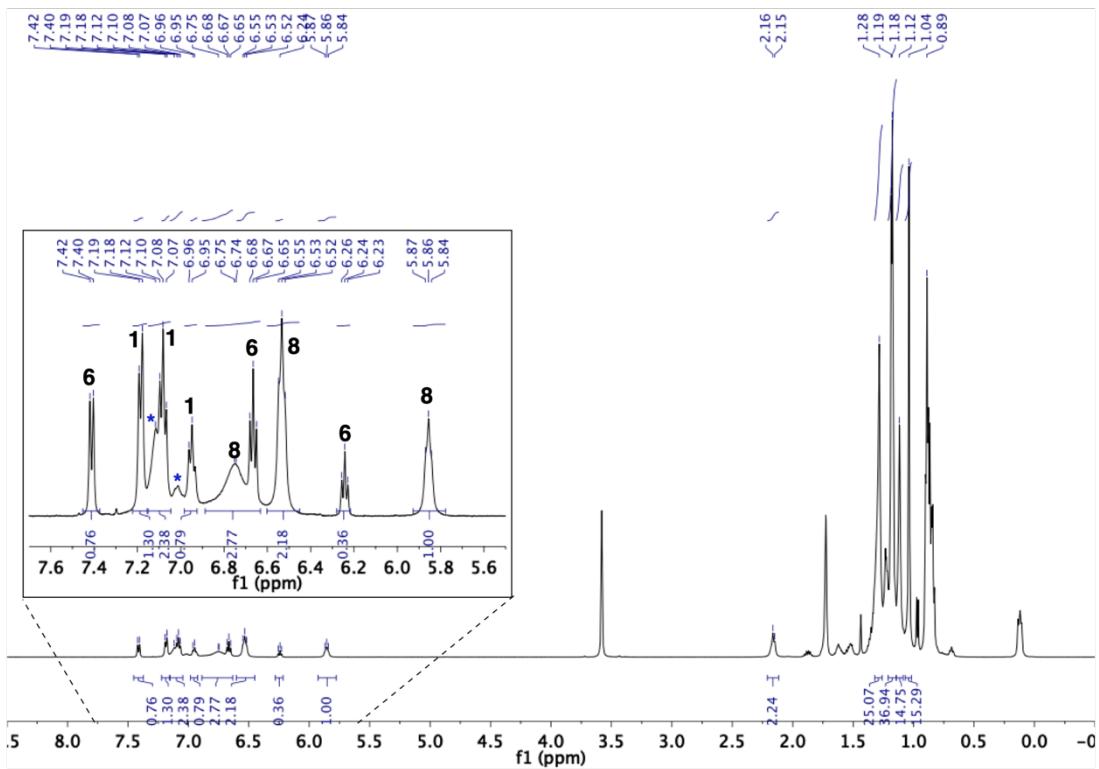


Figure S58. ^1H NMR spectrum (500 MHz, THF- d_8 , 23 °C) of the mixture. Inset: zoom-in from 7.7 to 5.5 ppm.

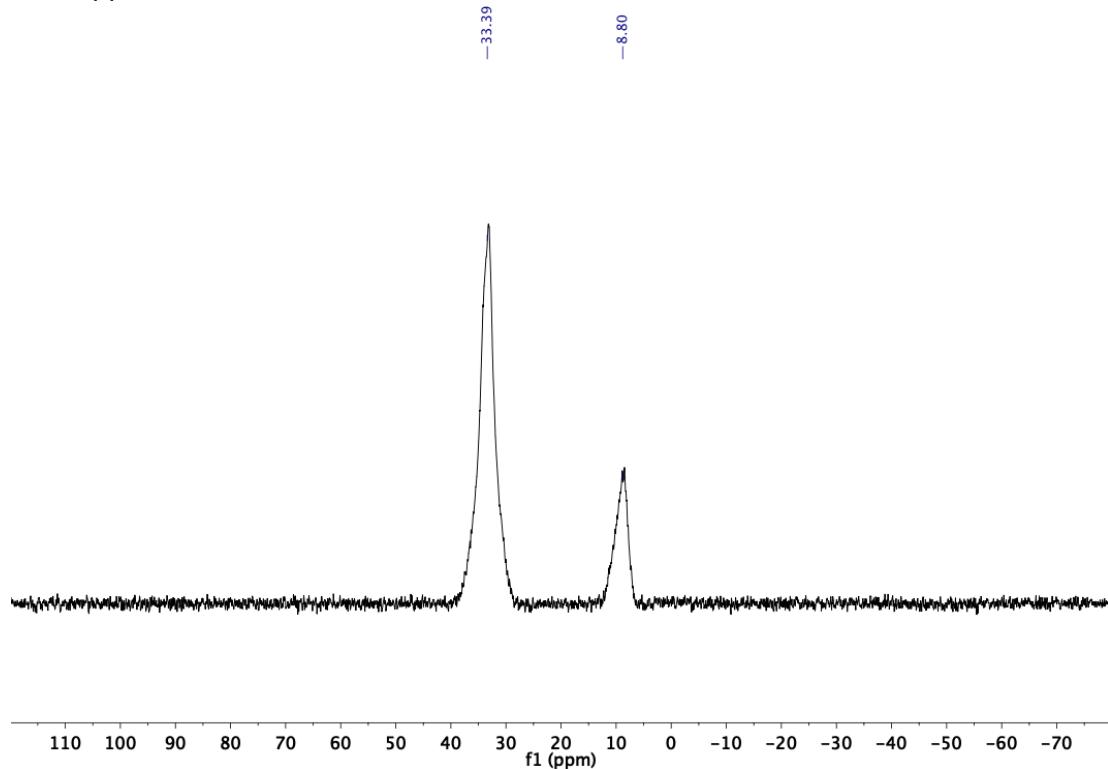
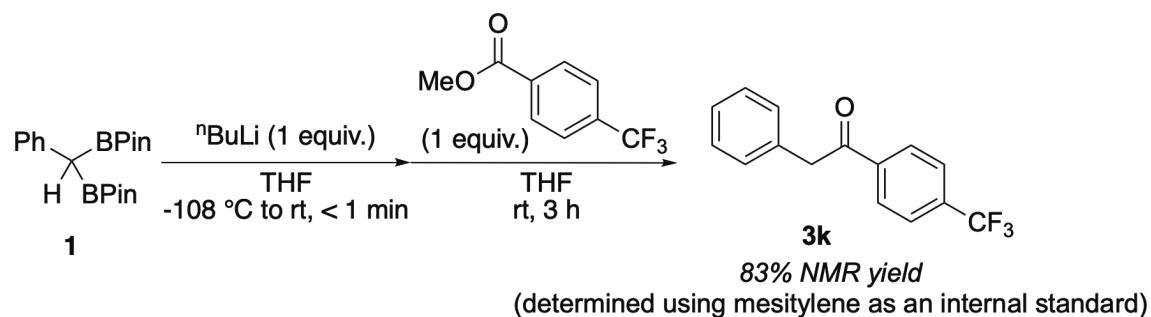


Figure S59. ^{11}B NMR spectrum (96 MHz, THF- d_8 , 23 °C) of the mixture.

Using $^n\text{BuLi}$ as an activator for the coupling of benzylboronate with an ester



The concentration of $^n\text{BuLi}$ was determined by titration with diphenylacetic acid prior to use. A vial was charged with **1** (34 mg, 0.10 mmol) and thf (2 mL) and placed in a cold well filled with liquid nitrogen until the solution froze. To the frozen solution was dropwise added $^n\text{BuLi}$ (2.65 M in hexanes, 38 μL , 0.10 mmol) via microsyringe. After 10 seconds, 16 μL of methyl (p-trifluoromethyl)benzoate was added. The resulting yellow solution was stirred at rt for 3 hours after which the reaction was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with Et_2O three times and the combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The resulting crude mixture was dissolved in 1 mL CDCl_3 and mesitylene (13.9 μL , 0.10 mmol) was added to the mixture. Then the crude mixture was analyzed by ^1H and ^{13}C spectroscopies. With the longer time interval (5 min) between the addition of $^n\text{BuLi}$ and ester, the yield of **3k** dropped to 52% along with the formation of protodeboronated product **5** with 39% yield.

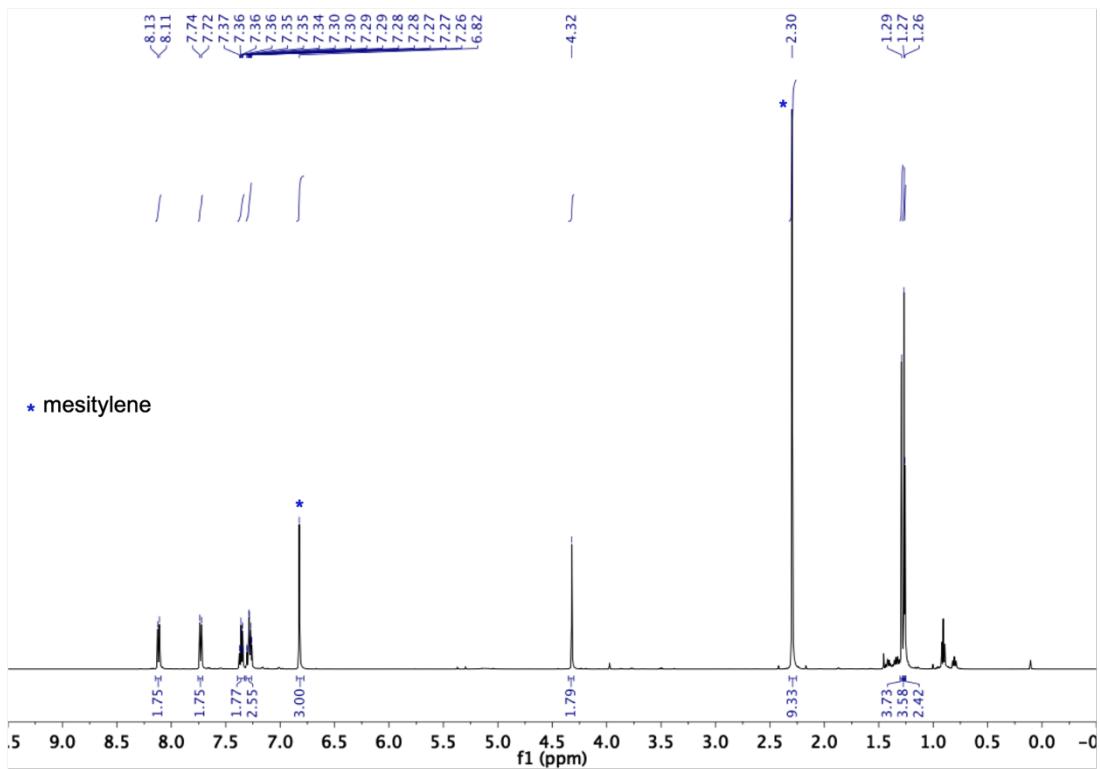


Figure S60. ^1H NMR spectrum (400 MHz, chloroform-*d*, 23 °C) of the mixture.

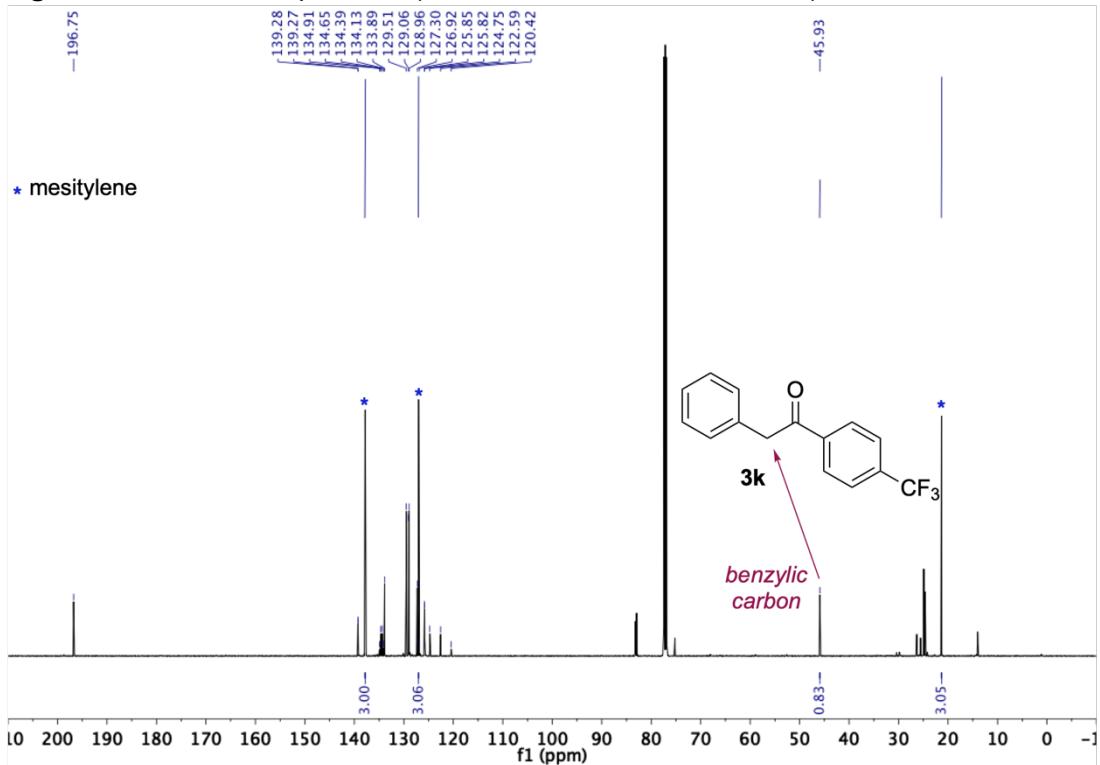
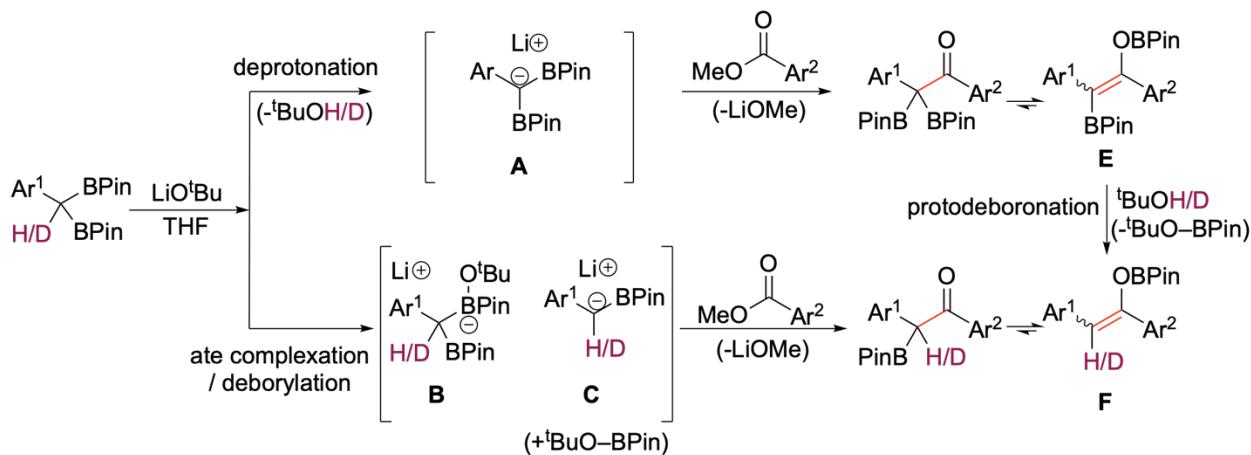


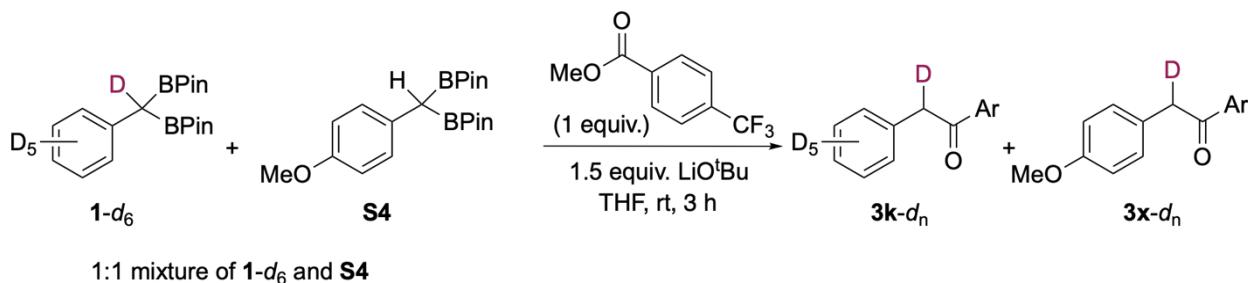
Figure S61. Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF-*d*₈, 23 °C) of the mixture.

VI. Crossover Experiment

H/D Crossover experiment using (*p*-methoxy)benzyldiboronate **S4** and deuterated benzyldiboronate **1-d₆**.



We have proposed the possible mechanism as shown above. Protodeboronation induced by excess amount of alkoxide bases was ruled out from the experiment where 1 equivalent of LiO^tBu was added to **E** but no change in ¹H NMR spectrum was observed (Figure S32). *tert*-Butyl alcohol, byproduct of the initial deprotonation to get **A**, might play an important role in the protodeboronation step. To test this hypothesis, the following experiment was carried out.



The coupling reaction was performed from 1:1 mixture of benzyldiboronates with and without benzylic C–D bonds. If the deborylative pathway (bottom) is operative, one can predict that the deuterium label heavily appears at **3k** and no deuterium is incorporated at the benzylic position of **3x**. However, if the deprotonative path (top) is operative, H/D scrambling would take place through protodeboronation by ^tBuOH/D.

To test this, deuterated benzylboronate **1-d₆** was prepared according to the general procedure A with toluene-*d*₈. After column chromatography, the white solid was recrystallized from hexane to afford **1-d₆** with high purity. The white crystals were dried under vacuum for 12 hours and brought into the N₂-filled glove box. The isotopic incorporation of the product was determined by ¹H and ²H NMR spectroscopies. (The isotopic incorporation cannot be calculated from quantitative ¹³C{¹H} NMR spectroscopy because the benzylic carbon is not observable in ¹³C spectrum.) The loss of deuterium at benzylic position is due to triborylation and the subsequent protodeboronation event.

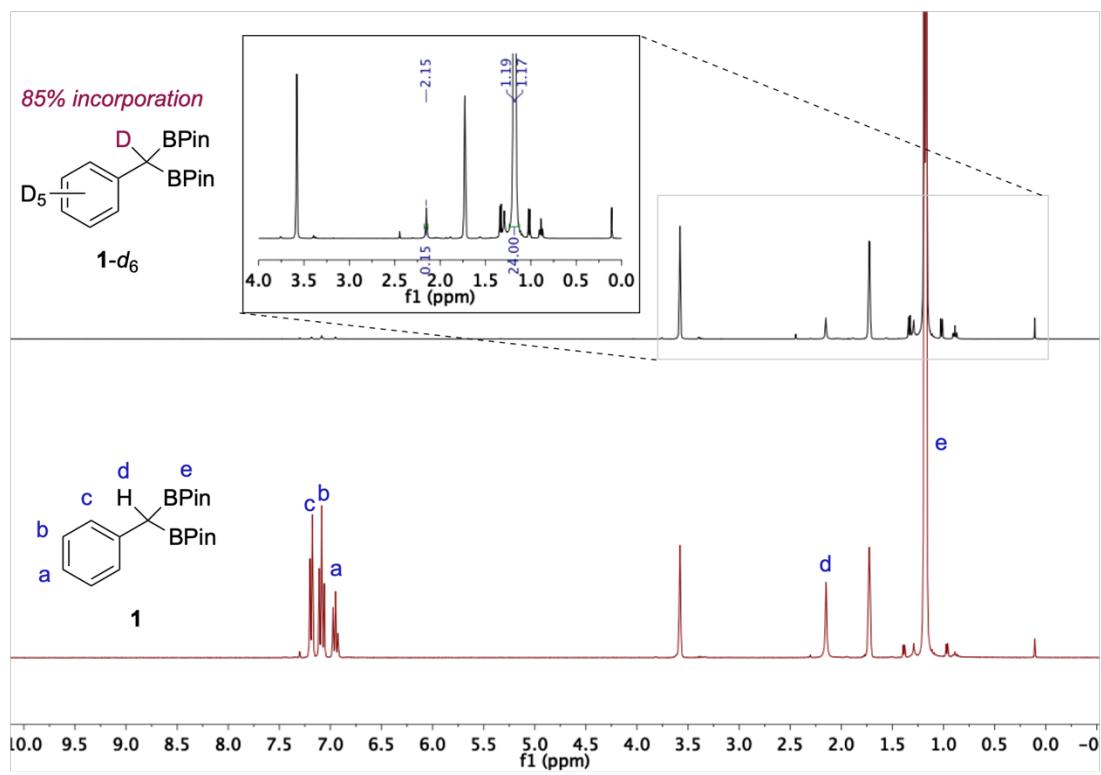


Figure S62. Stacked ¹H NMR spectra (400 MHz, thf-*d*₈, 23 °C) of **1-d₆** (top) and **1** (bottom). Inset: zoom-in from 4.0 to 0 ppm.

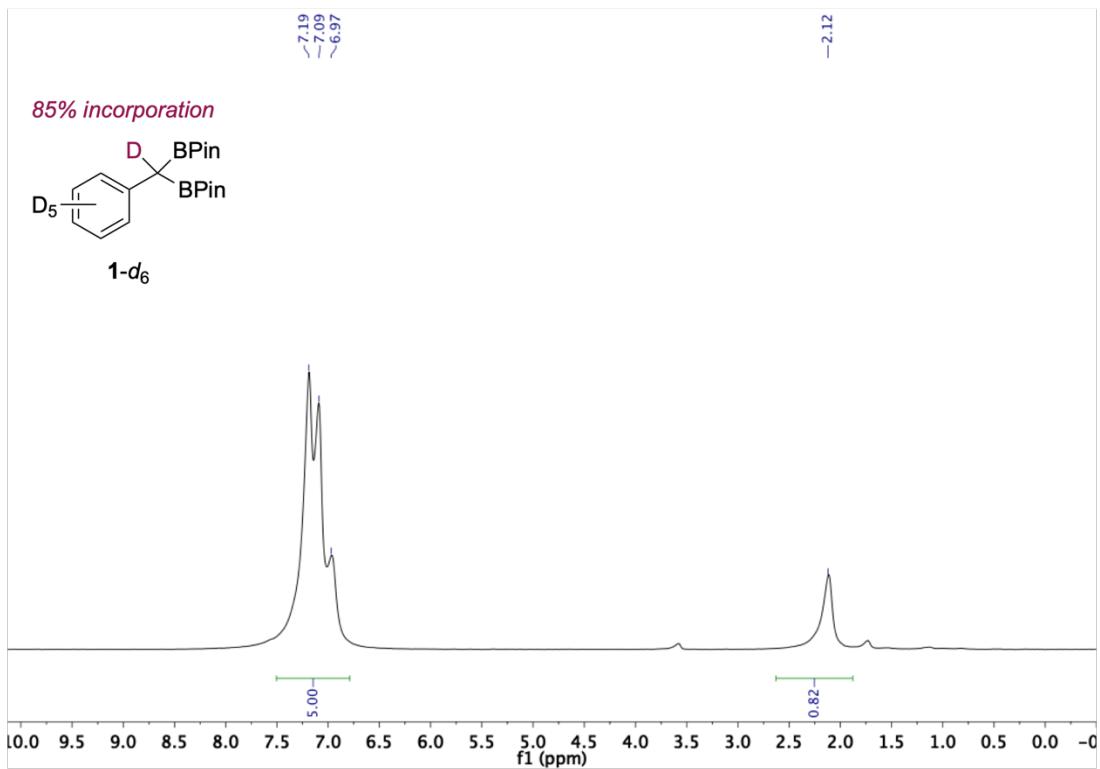
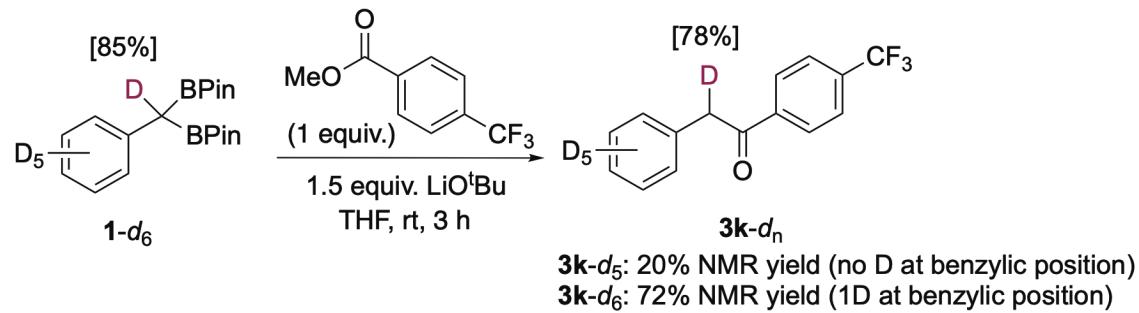


Figure S63. ²H NMR spectra (77 MHz, thf, 23 °C) of **1-d₆**.

With **1-d₆** in hand, coupling between **1-d₆** and methyl (*p*-trifluoromethyl)benzoate followed by quenching with water was carried out as a control experiment.



Procedure: A vial was charged with **1-d₆** (35 mg, 0.10 mmol), methyl (*p*-trifluoromethyl)benzoate (16 μ L, 0.10 mmol) and THF (2.0 mL). To the mixture was added LiO*t*Bu (12 mg, 0.15 mmol) as solid. The resulting yellow mixture was stirred at rt for 3 hours, after which water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with Et₂O twice. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated to afford white solid. The crude mixture was redissolved in 1 mL of CDCl₃, and

then mesitylene ($13.9 \mu\text{L}$, 0.10 mmol) was added to the mixture. The crude mixture was diluted with CDCl_3 , transferred to an NMR tube, and analyzed ^1H and quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies to measure the isotopic incorporation at the benzylic position of the product.

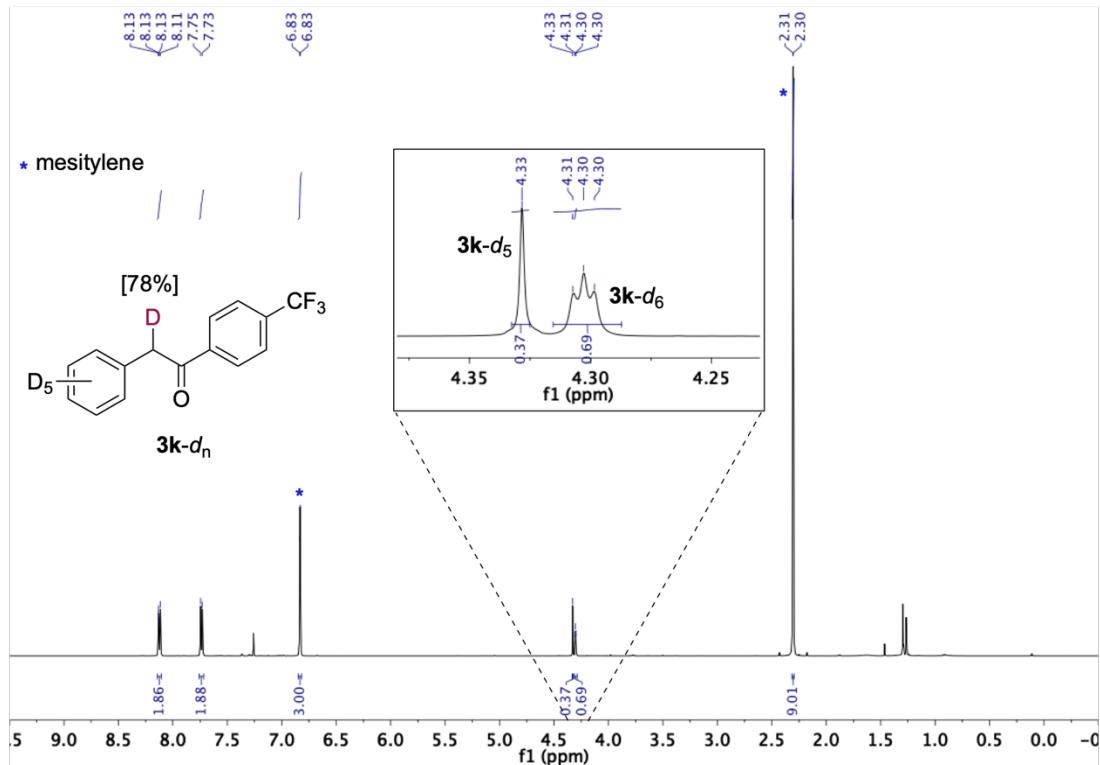


Figure S64. ^1H NMR spectrum (400 MHz, chloroform- d , 23°C) of the mixture. Inset: zoom-in from 4.38 to 4.23 ppm.

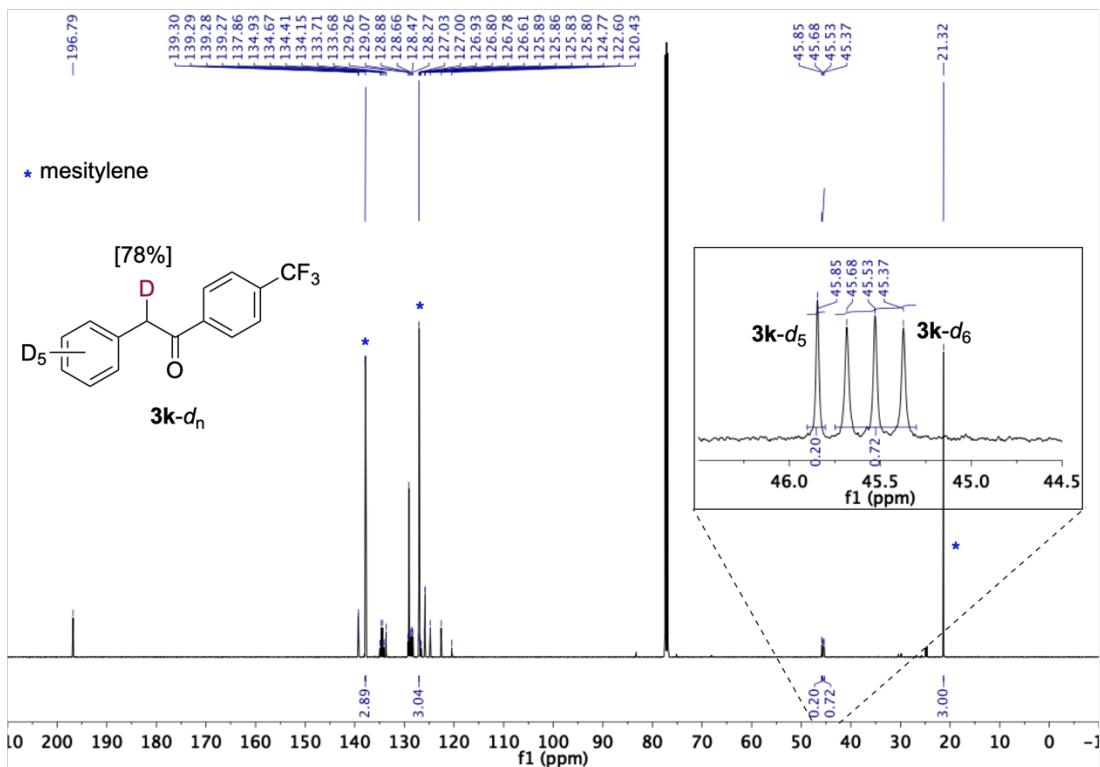
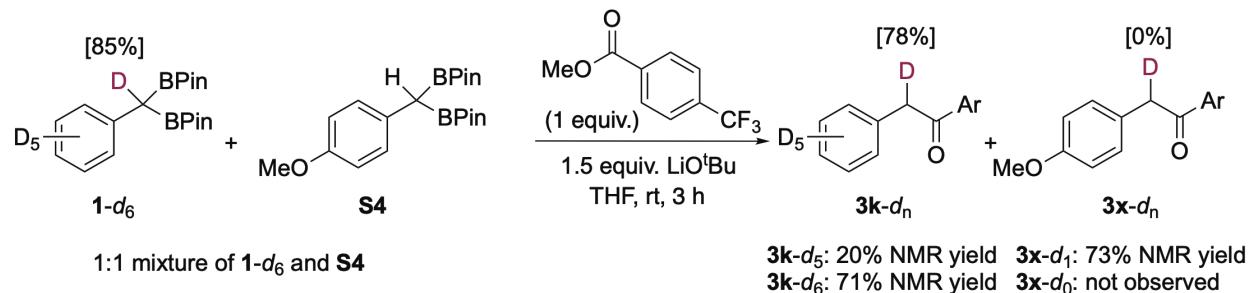


Figure S65. Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF- d_8 , 23 °C) of the mixture. Inset: zoom-in from 46.5 to 44.5 ppm.

The erosion of the deuterium incorporation at benzylic position (from 85% to 78%) is probably due to the partial deprotonation of the product by the alkoxide bases present in the reaction mixture.

Then the crossover experiment was conducted from the 1:1 mixture of **1-d₆** and **S4**.



Procedure: A vial was charged with **1-d₆** (35 mg, 0.10 mmol), **S4** (37 mg, 0.10 mmol), methyl (*p*-trifluoromethyl)benzoate (32 μL , 0.20 mmol) and THF (4.0 mL). To the mixture was added LiO^tBu (24 mg, 0.30 mmol) as solid. The resulting yellow mixture was stirred at rt for 3 hours, after which water was added to quench the reaction. The organic layer was separated, and the

aqueous layer was extracted with Et₂O twice. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated to afford white solid. The crude mixture was dissolved in 1 mL of CDCl₃, and then mesitylene (13.9 μ L, 0.10 mmol) was added to the mixture. The crude mixture was then transferred to an NMR tube and analyzed ¹H and quantitative ¹³C{¹H} NMR spectroscopies to determine the isotopic incorporation at the benzylic position of each product.

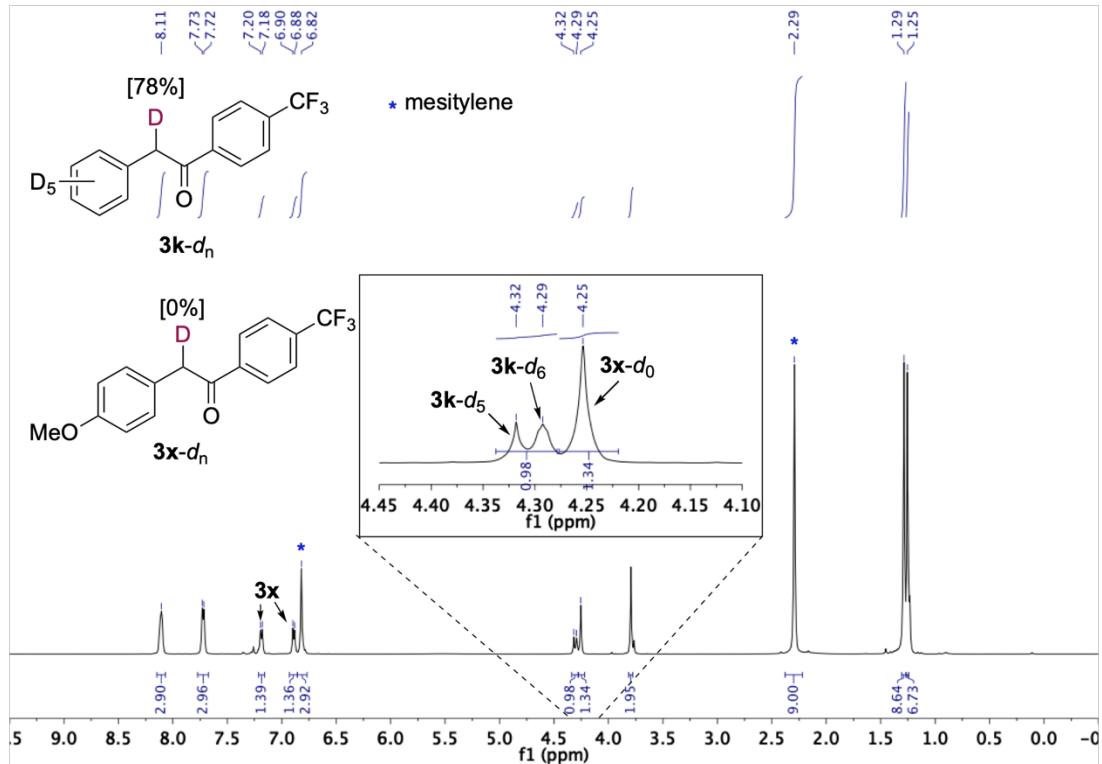


Figure S66. ¹H NMR spectrum (400 MHz, chloroform-*d*, 23 °C) of the mixture. Inset: zoom-in from 4.45 to 4.10 ppm.

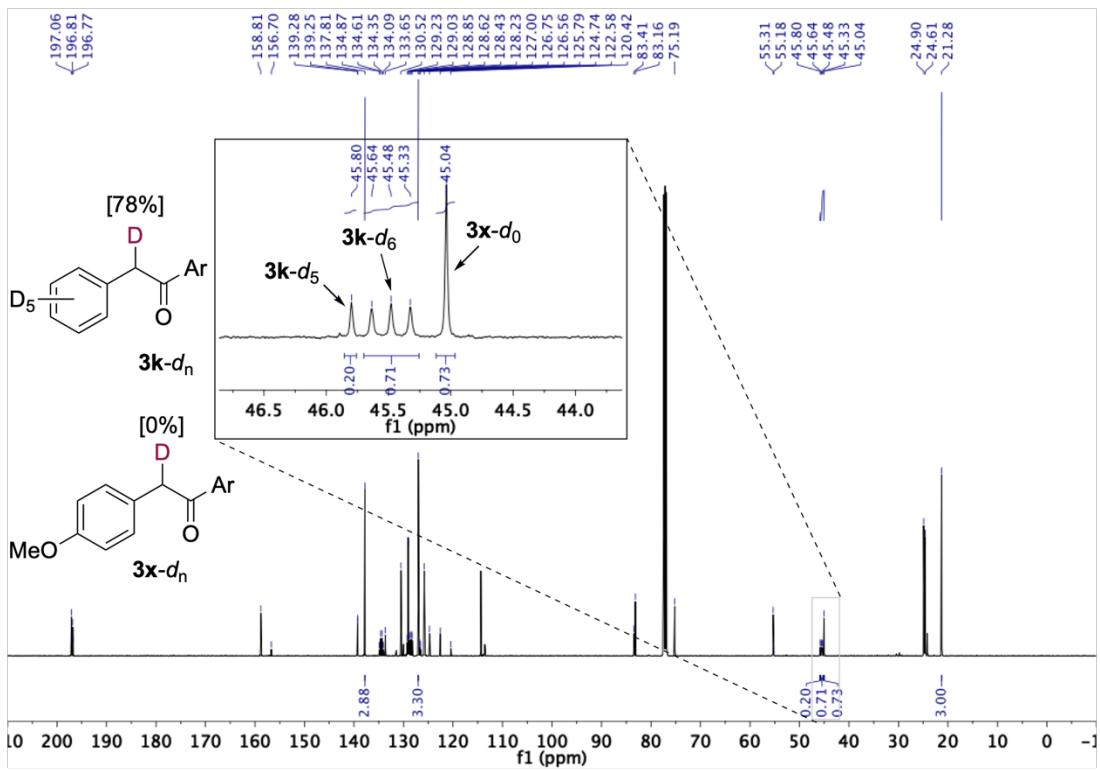
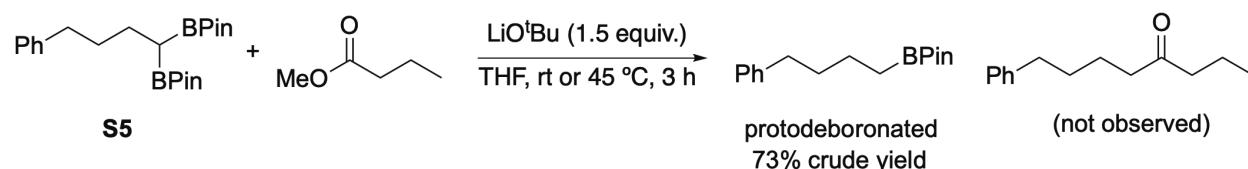


Figure S67. Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{THF}-d_8$, 23 °C) of the mixture. Inset: zoom-in from 46.8 to 44.6 ppm.

VII. Reaction with Alkyl- and Allylic-diboronates

Reaction from alkylboronate **S5**.



Alkyldiboronate **S5** was prepared according to the literature procedure.²² A vial was charged with **S5** (77 mg, 0.20 mmol), methyl butyrate (23 μL , 0.20 mmol), and THF (4.0 mL). To the mixture was added LiOtBu (24 mg, 0.30 mmol) as solid. The resulting mixture was stirred at rt for 3 hours, after which water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with Et₂O twice. The combined organic layers were dried over MgSO₄, filtered, and concentrated to afford the protodeboronated product as colorless oil (38 mg, 0.15 mmol, 73% crude yield). The reaction was also conducted in the same condition but at higher temperature, 45 °C. However, the coupling product was not observed. ¹H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.26 (t, J_{HH} = 7.4 Hz, 2H), 7.18–7.14 (m, 3H), 2.60 (t, J_{HH} = 7.8 Hz, 2H), 1.63 (p, J_{HH} = 7.6 Hz, 2H), 1.47 (p, J_{HH} = 7.6 Hz, 2H), 1.24 (s, 12H), 0.81 (t, J_{HH} = 7.8 Hz, 3H). The ¹H NMR spectrum agree with previously reported data.²³

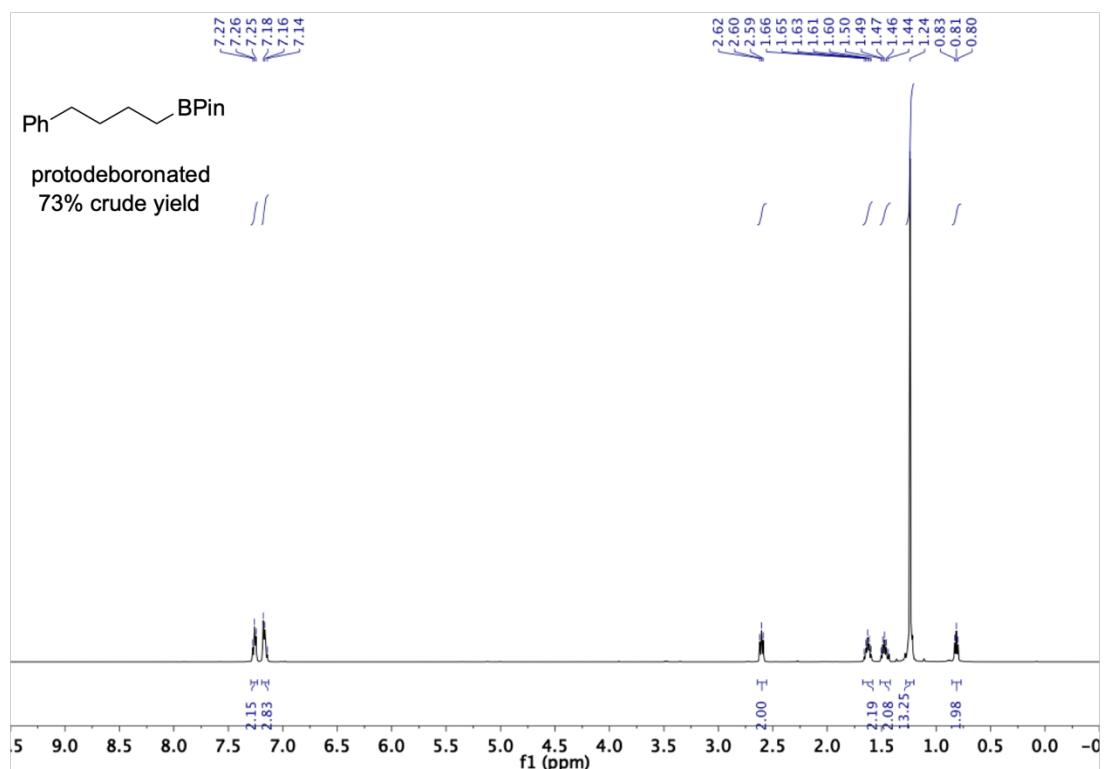
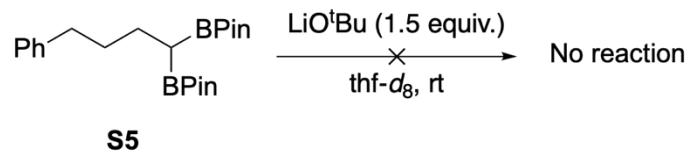


Figure S68. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of the crude mixture.

Activation of **S5** by LiO^tBu.

To elucidate the problematic step of the reaction from alkyldiboronate **S5**, the activation of **S5** with LiO^tBu was monitored by ^1H NMR spectroscopy.



A J-Young tube was charged with **S5** (13 mg, 0.035 mmol) and thf-*d*₈ (0.55 mL), and then LiO^tBu (4 mg, 0.53 mmol) was added as solid. The J-Young tube was sealed, brought out of the box, and the ^1H and ^{11}B NMR spectra of the mixture were recorded after 5, 15, 30, and 60 minutes.

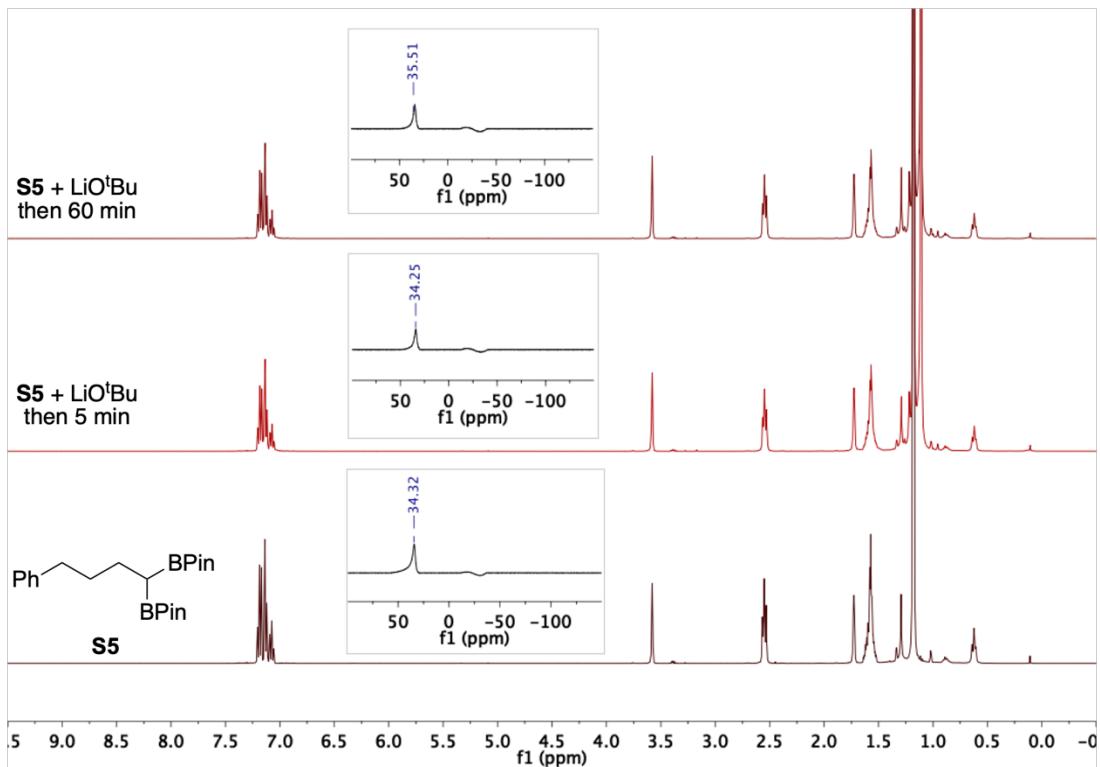
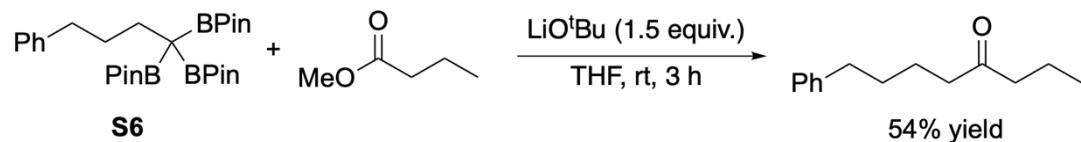


Figure S69. In situ monitoring of the treatment of **S5** with LiO^tBu by ¹H NMR spectroscopy (400 MHz, thf-*d*₈, 23 °C). Top: after 60 min. Middle: after 5 min. Bottom: **S5**. Insets: ¹¹B NMR spectra.

It clearly turned out that, contrary to benzylidiboronates, alkyldiboronate **S5** cannot be activated by 1.5 equivalents of LiO^tBu presumably due to the lack of stabilizing effect by phenyl group. This implies the presence of an additional substituent that contributes to stabilization of the anionic species might enable the deborylation, generating the reactive species towards coupling with esters. To test this, the following experiment was conducted where alkyltriborionate was used as the nucleophile precursor.

Reaction from alkyltriboronate **S6.**



A vial was charged with **S6** (48 mg, 0.10 mmol), methyl butyrate (11 μ L, 0.10 mmol), and THF (2.0 mL). To the mixture was added LiOtBu (12 mg, 0.15 mmol) as solid. The resulting mixture was stirred at rt for 3 hours, after which water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with Et₂O twice. The combined organic layers were dried over MgSO₄, filtered, and concentrated to afford the desired ketone product as colorless oil (11 mg, 0.054 mmol, 54% yield). **¹H NMR** (300 MHz, chloroform-d, 23 °C) δ 7.31–7.12 (m, 5H), 2.62 (t, J_{HH} = 7.0 Hz, 2H), 2.46–2.29 (m, 4H), 1.60 (ddd, J_{HH} = 12.5, 8.5, 4.7 Hz, 6H), 0.90 (t, J_{HH} = 7.4 Hz, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-d, 23 °C) δ 211.4, 142.4, 128.5, 128.4, 125.9, 44.9, 42.8, 35.9, 31.2, 23.6, 17.4, 13.9. **HRMS** (ESI+) *m/z* calculated for C₁₄H₂₀O ([M+H]⁺) 204.1514, found *m/z* 204.1511.

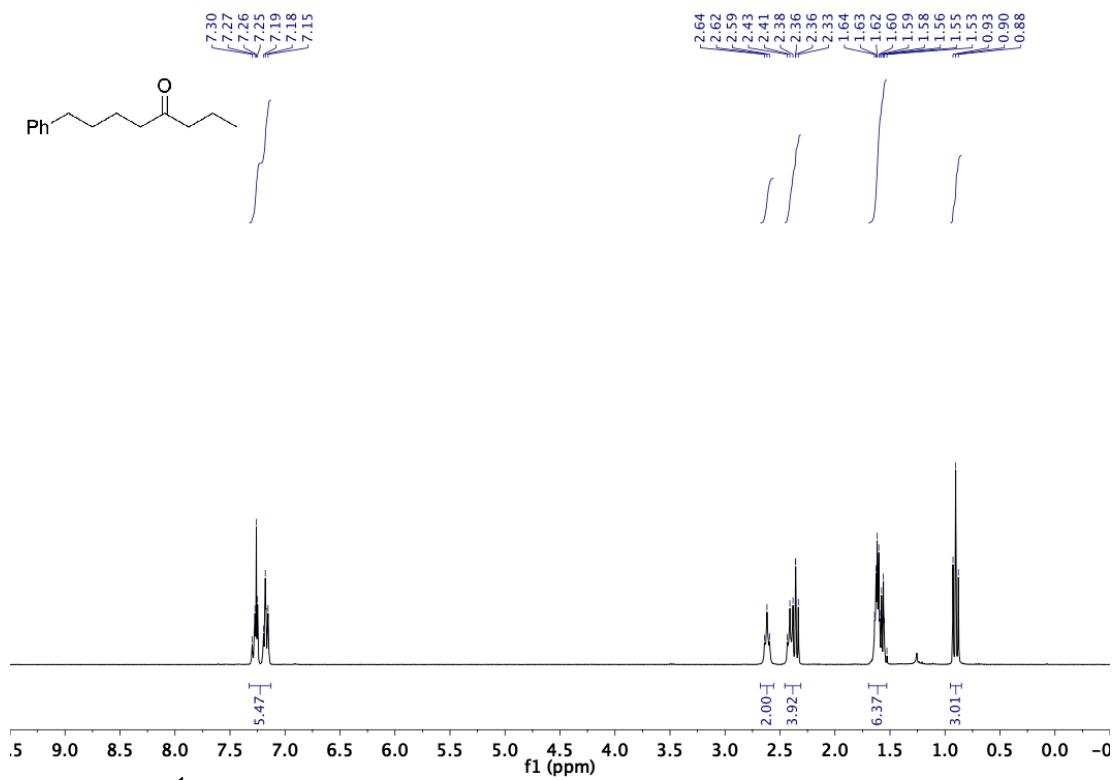


Figure S70. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of 4-phenylbutyl propyl ketone.

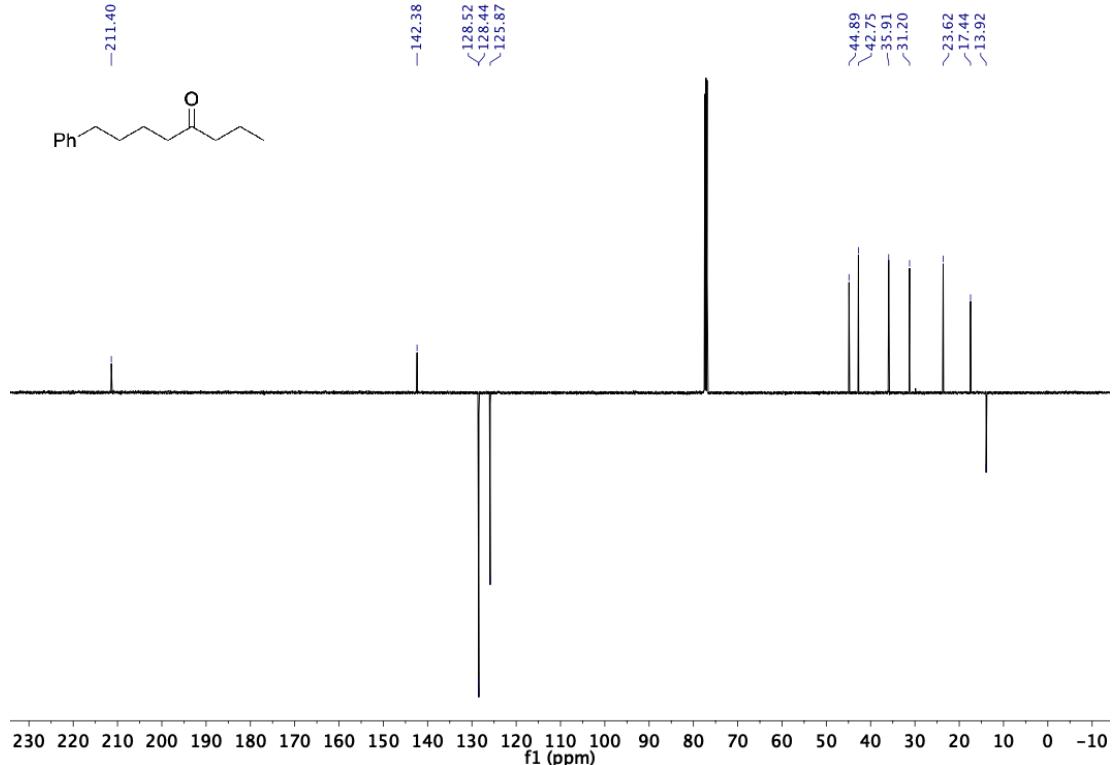
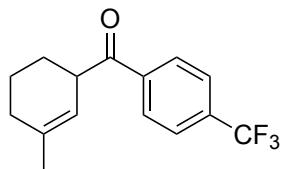
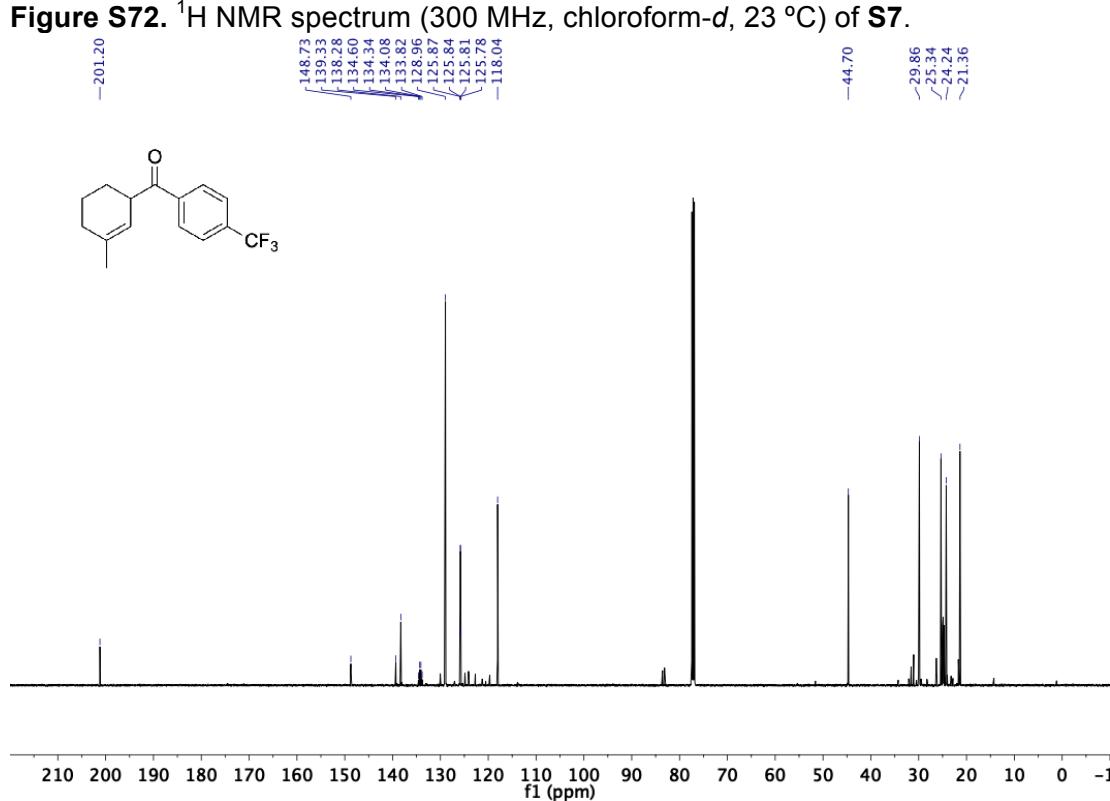
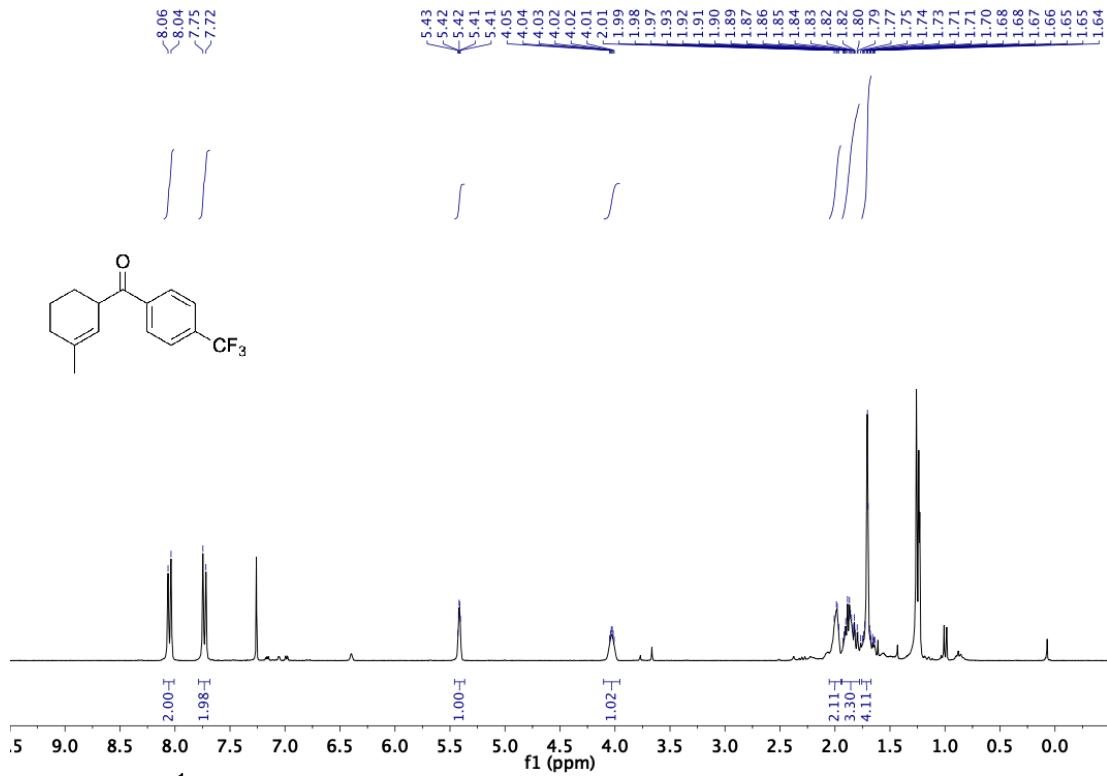


Figure S71. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C) of 4-phenylbutyl propyl ketone.

Reaction from Allyldiboronate



(3-methylcyclohex-2-en-1-yl)(4-(trifluoromethyl)phenyl)methanone S7. Prepared according to the general procedure using (alkenyl)substituted diboronate (79 mg, 0.23 mmol), methyl (*p*-trifluoromethyl)benzoate (46 mg, 0.23 mmol), LiO^tBu (27 mg, 0.34 mmol) and THF (4.5 mL). Purification by flash column chromatography (silica gel packed with hexanes; loaded with 1% ethyl acetate in hexanes; eluent: 1% ethyl acetate in hexane) yielded 29 mg (0.11 mmol, 48% crude yield) of product as colorless oil. In the ¹H NMR spectrum, there are resonances from some impurities around 1.2 ppm. NMR yield was determined as 41% using CH₂Br₂ as an internal standard. ¹H NMR (300 MHz, chloroform-*d*, 23 °C) δ ¹H NMR (300 MHz, Chloroform-*d*) δ 8.05 (d, *J_{HH}* = 8.1 Hz, 2H), 7.73 (d, *J_{HH}* = 8.2 Hz, 2H), 5.43–5.41 (m, 1H), 4.05–4.01 (m, 1H), 2.01–1.97 (m, 2H), 1.93–1.77 (m, 3H), 1.75–1.67 (m, 4H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 201.2, 148.7, 139.3, 138.3, 134.2 (q, ²J_{CF} = 32.6 Hz), 125.8 (q, ³J_{CF} = 3.7 Hz), 123.7 (q, ¹J_{CF} = 272.7 Hz), 118.0, 44.7, 29.9, 25.3, 24.2, 21.4. ¹⁹F NMR (282 MHz, chloroform-*d*, 23 °C): δ -63.09. HRMS (ESI+) *m/z* calculated for C₁₅H₁₅F₃O ([M+H]⁺) 268.1075, found 268.1073.



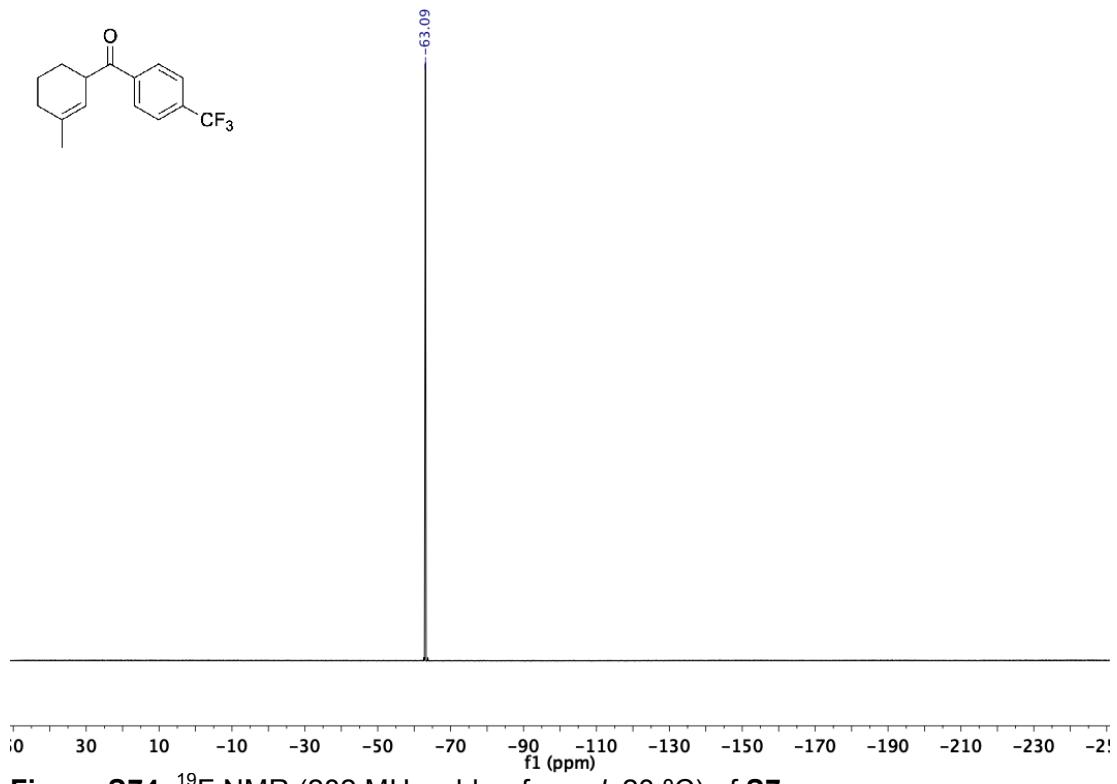
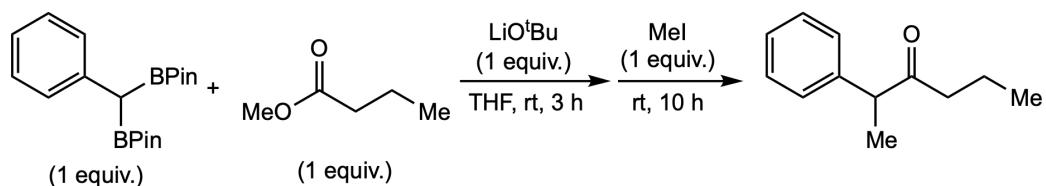


Figure S74. ^{19}F NMR (282 MHz, chloroform-*d*, 23 °C) of **S7**.

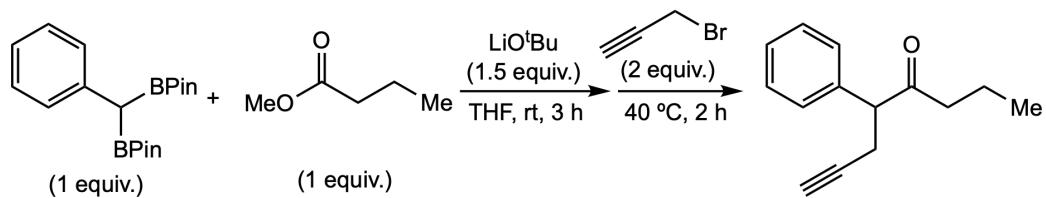
VIII. Trapping with Electrophiles (Scheme 6)

2-Phenylhexan-3-one 14a.



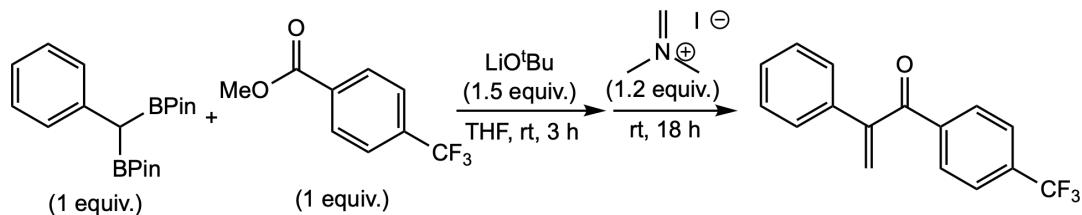
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 103 mg of benzyl diboronate (0.30 mmol, 1 equiv.), 31 mg of methyl butyrate (0.30 mmol, 1 equiv.), and 6 mL of THF. 24 mg of LiO^tBu (0.30 mmol, 1 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. The vial was capped with a rubber septum, sealed with electrical tape, and brought out of the glovebox. The vial was cooled to 0 °C and then 19 µL of MeI (0.30 mmol, 1 equiv.) was treated *via* a micro syringe. The reaction solution was stirred for additional 10 hours at 23 °C and then diluted with ethyl acetate and saturated aqueous ammonium chloride solution and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; gradient: 3% to 5% ethyl acetate in hexanes) yielded 36 mg (0.20 mmol, 68% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.33 (t, *J*_{HH} = 7.4 Hz, 2H), 7.28–7.23 (m, 1H), 7.23 –7.19 (m, 2H), 3.74 (q, *J*_{HH} = 7.0 Hz, 1H), 2.35–2.29 (m, 2H), 1.59–1.45 (m, 3H; should be 2H but contains water), 1.38 (d, *J*_{HH} = 7.0 Hz, 3H), 0.79 (t, *J*_{HH} = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 211.1, 140.9, 129.0, 128.0, 127.2, 53.1, 43.1, 17.6, 17.4, 13.7. ¹H and ¹³C NMR data agree with previously reported data.²⁴

5-Phenyl-7-yn-4-one 14b.



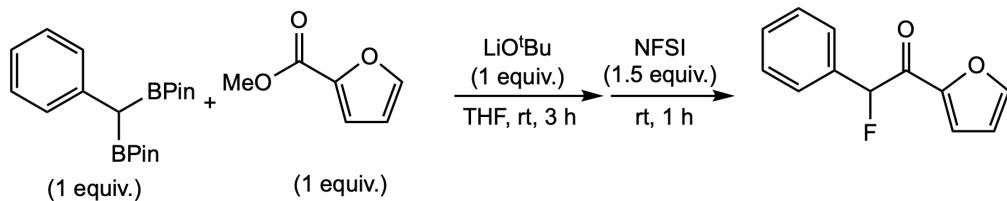
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 34 mg of benzylidiboronate (0.10 mmol, 1 equiv.), 10 mg of methyl butyrate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiO^tBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. The vial was capped with a rubber septum, sealed with electrical tape, and brought out of the glovebox. To the mixture was added 22 µL of propargyl bromide (80 wt. % in toluene, 0.20 mmol, 2 equiv.) *via* a micro syringe and the solution was allowed to stir at 45 °C for 2 hours. The reaction mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and then transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 1.5% ethyl acetate in hexanes; gradient: 1.5% to 3% ethyl acetate in hexanes) yielded 16 mg (0.80 mmol, 80% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.38–7.30 (m, 2H), 7.32–7.25 (m, 1H), 7.24–7.19 (m, 2H), 3.87 (t, *J*_{HH} = 7.4 Hz, 1H), 2.90 (ddd, *J*_{HH} = 16.9, 7.5, 2.6 Hz, 1H), 2.53 (ddd, *J*_{HH} = 16.9, 7.5, 2.7 Hz, 1H), 2.36 (t, *J*_{HH} = 7.3 Hz, 2H), 1.90 (t, *J*_{HH} = 2.6 Hz, 1H), 1.62–1.46 (m, 2H), 0.80 (t, *J*_{HH} = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 208.7, 137.6, 129.1, 128.3, 127.9, 82.3, 69.7, 57.7, 43.9, 22.0, 17.3, 13.7. HRMS (ESI+) *m/z* calculated for C₁₄H₁₆O ([M+H]⁺) 201.1274, found *m/z* 201.1269.

2-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one 14c.



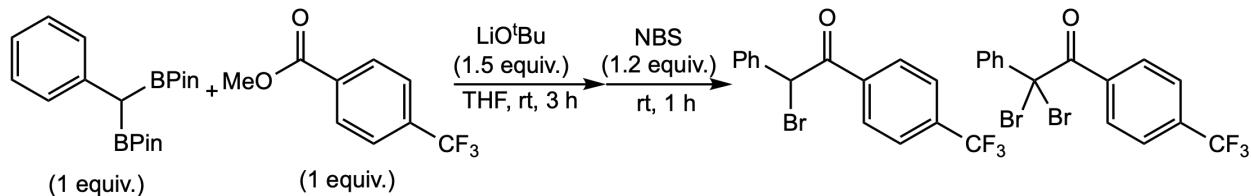
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 34 mg of benzylidenebis(pinacol boronate ester) (0.10 mmol, 1 equiv.), 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiO^tBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. To the mixture was then added 19 mg of Eschenmoser's salt (0.10 mmol, 1 equiv.) and the solution was allowed to stir at rt for 18 hours. The reaction mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and then transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 5% ethyl acetate in hexanes) yielded 13 mg (0.047 mmol, 47% yield) of product. ¹H NMR (500 MHz, chloroform-*d*, 23 °C): δ 7.98 (d, *J*_{HH} = 8.2 Hz, 1H), 7.70 (d, *J*_{HH} = 8.2 Hz, 1H), 7.43–7.34 (m, 5H), 6.14 (s, 1H), 5.71 (s, 1H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 196.5, 148.1, 140.2, 136.7, 134.4 (q, ²J_{CF} = 32.6 Hz), 130.3, 128.9, 128.9, 127.3, 125.6 (q, ³J_{CF} = 3.7 Hz), 123.7 (q, ¹J_{CF} = 272.8 Hz), 122.9. ¹H and ¹³C NMR data agree with previously reported data.²⁵

2-Fluoro-1-(furan-2-yl)-2-phenylethan-1-one 14d.



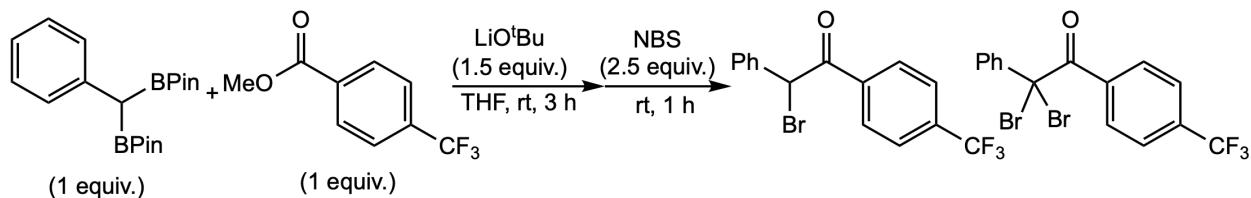
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 46 mg of benzylbiphenyl boronate (0.13 mmol, 1 equiv.), 17 mg of methyl 2-furanoate (0.13 mmol, 1 equiv.), and 2.6 mL of THF. 11 mg of LiO^tBu (0.13 mmol, 1 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. To the mixture was added 61 mg of NFSI (*N*-fluorobenzenesulfonimide, 0.25 mmol, 2.5 equiv.) as solid and the solution was allowed to stir at ambient temperature for 1 hour. The reaction mixture was then concentrated and loaded onto silica column with 5% ethyl acetate in hexanes. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 5% ethyl acetate in hexanes; eluent: 10% ethyl acetate in hexanes) yielded 22 mg (0.108 mmol, 83% yield) of **14d**. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.63 (d, *J*_{HH} = 1.6 Hz, 1H), 7.51 (dt, *J*_{HH} = 7.7, 1.6 Hz, 2H), 7.43–7.35 (m, 4H), 6.55 (dd, *J*_{HH} = 3.7, 1.6 Hz, 1H), 6.30 (d, *J*_{HF} = 47.9 Hz, 1H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 183.2 (d, ²*J*_{CF} = 24.1 Hz), 149.9, 147.7, 134.2 (d, ²*J*_{CF} = 20.3 Hz), 129.7 (d, ⁴*J*_{CF} = 2.4 Hz), 129.0, 127.2 (d, ³*J*_{CF} = 6.0 Hz), 120.7 (d, ³*J*_{CF} = 6.8 Hz), 112.7 (d, ⁴*J*_{CF} = 1.2 Hz), 93.8 (d, ¹*J*_{CF} = 186.3 Hz). **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -180.89 (d, *J*_{FH} = 48.0 Hz). **HRMS** (ESI+) *m/z* calculated for C₁₂H₉FO₂ ([M+H]⁺) 205.0659, found *m/z* 205.0660.

2-Bromo-2-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one 14e.



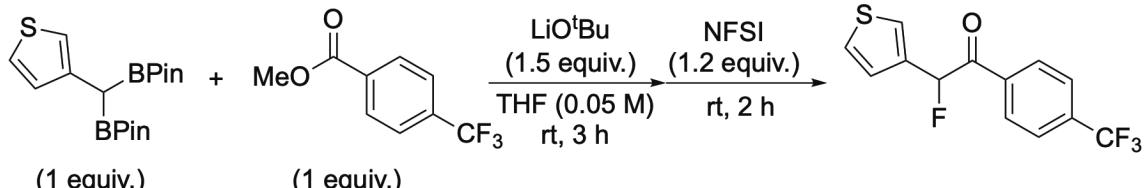
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 34 mg of benzylidiboronate (0.10 mmol, 1 equiv.), 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiO^tBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. To the mixture was added 21 mg of NBS (*N*-bromosuccinimide, 0.12 mmol, 1.2 equiv.) as solid and the solution was allowed to stir at ambient temperature for 1 hour. The reaction mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and then transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; gradient: 3% to 5% ethyl acetate in hexanes) yielded 17 mg (0.050 mmol, 50% yield) of **14e** and 12 mg (0.028 mmol, 28% yield) of **14e**. **¹H NMR** (300 MHz, chloroform-*d*, 23 °C): δ 8.09 (d, *J*_{HH} = 8.2 Hz, 2H), 7.72 (d, *J*_{HH} = 8.2 Hz, 2H), 7.56–7.48 (m, 2H), 7.42–7.35 (m, 3H), 6.32 (s, 1H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 190.2, 136.9, 135.2, 134.9 (q, ²*J*_{CF} = 32.6 Hz), 129.5, 129.4, 129.2, 129.1, 125.9 (q, ³*J*_{CF} = 3.6 Hz), 123.4 (q, ¹*J*_{CF} = 272.8 Hz), 50.8. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C) δ -63.30. **HRMS** (ESI+) *m/z* calculated for C₁₅H₁₀BrF₃O ([M+H]⁺) 342.9940, found *m/z* 342.9939.

2,2-Dibromo-2-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one 14f.



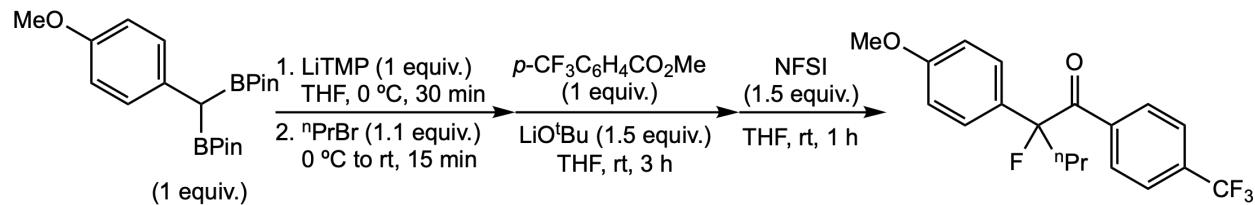
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 34 mg of benzylidiboronate (0.10 mmol, 1 equiv.), 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiO^tBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. To the mixture was added 44 mg of NBS (*N*-bromosuccinimide, 0.25 mmol, 2.5 equiv.) as solid and the solution was allowed to stir at ambient temperature for 1 hour. The reaction mixture was then concentrated and loaded onto silica column with 3% ethyl acetate in hexanes. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; eluent: 3% ethyl acetate in hexanes) yielded 25 mg (0.059 mmol, 59% yield) of **14f**. **¹H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.83 (d, *J*_{HH} = 8.3 Hz, 2H), 7.65–7.63 (m, 2H), 7.55 (d, *J*_{HH} = 8.3 Hz, 2H), 7.43–7.36 (m, 3H). **¹³C{¹H} NMR** (126 MHz, chloroform-*d*, 23 °C): δ 185.5, 140.3, 134.4 (q, ²*J*_{CF} = 32.8 Hz), 134.1, 131.8, 130.2, 129.4, 126.9, 125.2 (q, ³*J*_{CF} = 3.7 Hz), 123.4 (q, ¹*J*_{CF} = 273.0 Hz), 68.6. **¹⁹F NMR** (282 MHz, chloroform-*d*, 23 °C) δ -63.30. **HRMS** (ESI+) *m/z* calculated for C₁₅H₉Br₂F₃O ([M+H]⁺) 420.9045, found *m/z* 420.9047.

2-Fluoro-2-(thiophen-3-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one 14g.



In the glovebox, a scintillation vial with a magnetic stir bar was charged with (3-thienyl)-substituted diboronate (70 mg, 0.20 mmol), methyl (*p*-trifluoromethyl)benzoate (41 mg, 0.20 mmol), and THF (4 mL). LiO^tBu (24 mg, 0.30 mmol) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. To the mixture was added NFSI (76 mg, 0.24 mmol) was added as solid and the resulting mixture was stirred for additional 2 hours at 23 °C and then quenched by adding water. The crude mixture was diluted with Et₂O and saturated aqueous ammonium chloride solution, and then transferred to a separatory funnel. The aqueous layer was extracted with Et₂O twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 2% ethyl acetate in hexanes; gradient: 2% to 4% to 6% ethyl acetate in hexanes) yielded 48 mg (0.17 mmol, 83% yield) of product as colorless oil. ¹H NMR (500 MHz, chloroform-*d*, 23 °C) δ 8.06 (d, *J*_{HH} = 8.2 Hz, 2H), 7.71 (d, *J*_{HH} = 8.2 Hz, 2H), 7.48–7.46 (m, 1H), 7.38 (ddd, *J*_{HH} = 5.1, 3.0, 1.1 Hz, 1H), 7.14 (dt, *J*_{HH} = 5.1, 1.0 Hz, 1H), 6.55 (d, *J*_{HF} = 49.0 Hz, 1H). ¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 193.4 (d, ²J_{CF} = 22.3 Hz), 136.7, 135.1 (q, ²J_{CF} = 32.9 Hz), 134.6 (d, ²J_{CF} = 22.0 Hz), 129.6 (d, ³J_{CF} = 3.3 Hz), 127.8, 126.1 (d, ³J_{CF} = 3.1 Hz), 125.9 (q, ³J_{CF} = 3.8 Hz), 125.8 (d, ³J_{CF} = 7.0 Hz), 123.5 (q, ¹J_{CF} = 272.9 Hz), 90.4 (d, ¹J_{CF} = 186.3 Hz). ¹⁹F NMR (376 MHz, chloroform-*d*, 23 °C): δ -63.37, -173.09 (dd, *J*_{HF} = 49.0, 2.6 Hz). HRMS (ESI+) *m/z* calculated for C₁₃H₈F₄OS ([M+H]⁺) 288.0232, found 288.0236.

2-(4-Methoxyphenyl)-2-propyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one 15a.



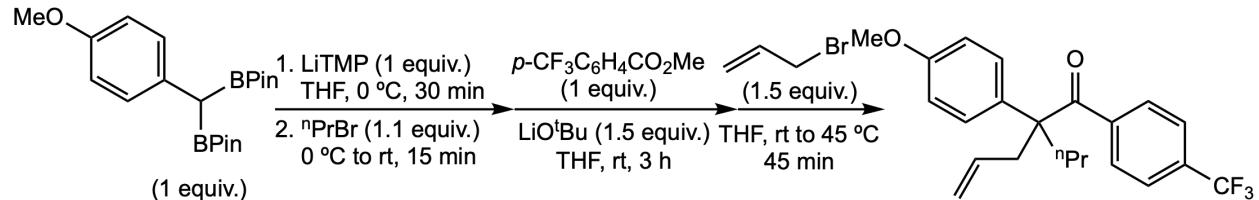
In the glovebox, a scintillation vial with a magnetic stir bar was charged with 37 mg of benzyldiboronate (0.10 mmol, 1 equiv.) and 0.1 mL of THF. The vial was sealed with septum and brought out of the box and then a N₂ balloon was equipped. The mixture was then cooled to 0 °C and treated with 1 M LiTMP solution (15 mg in 0.1 mL THF, 0.10 mmol, 1 equiv.) slowly. The resulting mixture was stirred at 0 °C for 30 min after which 1.8 M ⁿPrBr solution (10 µL in 0.6 mL THF, 0.11 mmol, 1.1 equiv.). After stirring at 0 °C for 15 min, the mixture was brought into the glove box. The mixture was diluted with 0.2 mL THF (0.05 M w.r.t. benzyldiboronate) and then treated with 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.) and 12 mg of LiOtBu (0.15 mmol, 1.5 equiv.). The mixture was stirred at rt for 3 h after which 47 mg of NFSI (*N*-fluorobenzenesulfonimide, 0.15 mmol, 1.5 equiv.) was added as solid and the mixture was allowed to stir at ambient temperature for 1 hour. The reaction mixture was then concentrated and loaded onto silica column with 4% ethyl acetate in hexanes. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 4% ethyl acetate in hexanes; eluent: 4% ethyl acetate in hexanes) yielded 29 mg (0.08 mmol, 83% yield) of **15a**.

¹H NMR (300 MHz, chloroform-*d*, 23 °C): δ 7.95 (d, *J*_{HH} = 8.2 Hz, 2H), 7.61 (d, *J*_{HH} = 8.2 Hz, 2H), 7.38 (d, *J*_{HH} = 8.7 Hz, 2H), 6.92 (d, *J*_{HH} = 8.7 Hz, 2H), 3.80 (s, 3H), 2.44–2.26 (m, 1H), 2.24–2.05 (m, 1H), 1.43–1.31 (m, 2H), 0.92 (t, *J*_{HH} = 7.4 Hz, 3H).

¹³C{¹H} NMR (126 MHz, chloroform-*d*, 23 °C): δ 198.2 (d, ²*J*_{CF} = 29.0 Hz), 159.7, 138.2, 134.1 (q, ²*J*_{CF} = 32.6 Hz), 130.5 (d, ²*J*_{CF} = 22.8 Hz), 130.3 (d, ³*J*_{CF} = 6.3 Hz), 125.6 (d, ³*J*_{CF} = 9.0 Hz), 125.3 (q, ³*J*_{CF} = 3.5 Hz), 123.7 (q, ¹*J*_{CF} = 272.7 Hz), 114.4 (d, ⁴*J*_{CF} = 1.4 Hz), 103.6 (d, ¹*J*_{CF} = 187.7 Hz), 55.4, 41.7 (d, ²*J*_{CF} = 23.1 Hz),

16.6 (d, $^3J_{CF} = 3.5$ Hz), 14.3. **^{19}F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.29, -161.17. **HRMS** (ESI+) *m/z* calculated for $C_{19}H_{18}F_4O_2$ ([M+H] $^+$) 355.1316, found *m/z* 355.1318.

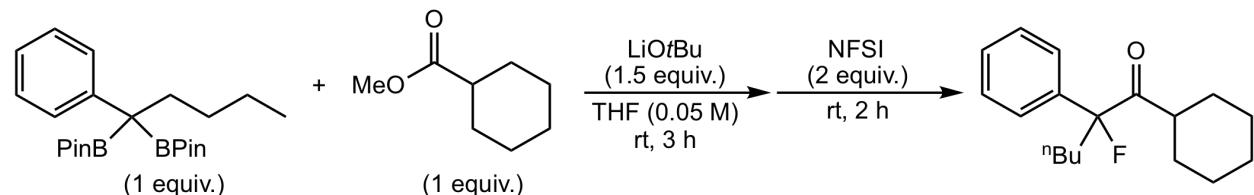
2-Fluoro-2-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)pentan-1-one 15b.



In the glovebox, a scintillation vial with a magnetic stir bar was charged with 37 mg of benzylidenebis(pinacol)boronate (0.10 mmol, 1 equiv.) and 0.1 mL of THF. The vial was sealed with septum and brought out of the box and then a N₂ balloon was equipped. The mixture was then cooled to 0 °C and treated with 1 M LiTMP solution (15 mg in 0.1 mL THF, 0.10 mmol, 1 equiv.) slowly. The resulting mixture was stirred at 0 °C for 30 min after which 1.8 M nPrBr solution (10 µL in 0.6 mL THF, 0.11 mmol, 1.1 equiv.). After stirring at 0 °C for 15 min, the mixture was brought into the glove box. The mixture was diluted with 0.2 mL THF (0.05 M w.r.t. benzylidenebis(pinacol)boronate) and then treated with 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.) and 12 mg of LiOtBu (0.15 mmol, 1.5 equiv.). The mixture was stirred at rt for 3 h after which 1 M of allyl bromide (13 µL in 0.15 mL THF, 0.15 mmol, 1.5 equiv.) was added via syringe and the mixture was stirred at 45 °C for 45 min. The reaction mixture was then concentrated and loaded onto silica column with 1% ethyl acetate in hexanes. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 1% ethyl acetate in hexanes; eluent: 1% to 2 % ethyl acetate in hexanes) yielded 28 mg (0.075 mmol, 75% yield) of **15b**. **1H NMR** (300 MHz, chloroform-*d*, 23 °C): δ 7.47 (s, 4H), 7.18 (d, $J_{HH} = 8.8$ Hz, 2H), 6.91 (d, $J_{HH} = 8.8$ Hz, 2H), 5.39 (ddt, $J_{HH} = 17.2, 9.9, 7.2$ Hz, 1H), 5.05–4.82 (m, 2H), 3.82 (s, 3H), 2.79 (d, $J_{HH} = 7.2$ Hz, 1H), 2.15–1.88 (m, 2H), 1.35–1.10 (m, 3H), 0.79 (t, $J_{HH} = 7.1$ Hz, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, chloroform-*d*, 23 °C): δ 202.7, 158.8, 140.5, 133.9, 133.4, 132.9 (q, $^2J_{CF} = 32.7$ Hz), 129.7,

128.0, 125.1 (q, $^3J_{CF} = 3.7$ Hz), 123.7 (q, $^1J_{CF} = 272.6$ Hz), 118.5, 114.6, 57.4, 55.4, 39.7, 36.3, 16.9, 14.8. **^{19}F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -63.15. **HRMS** (ESI+) *m/z* calculated for C₂₂H₂₃F₃O₂ ([M+H]⁺) 377.1723, found *m/z* 377.1724.

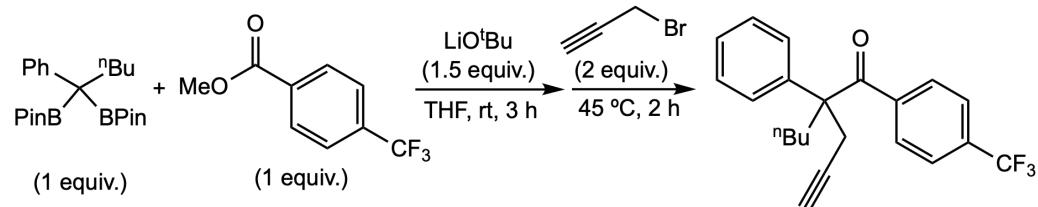
1-Cyclohexyl-2-fluoro-2-phenylhexan-1-one 17a.



In the glovebox, a scintillation vial with a magnetic stir bar was charged with 40 mg of *n*-pentylbenzene-benzylboronate (0.10 mmol, 1 equiv.), 14 mg of methyl cyclohexanecarboxylate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiOtBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. The vial was capped with a rubber septum, sealed with electrical tape, and brought out of the glovebox. 95 mg of NFSI (0.20 mmol, 2 equiv.) in 0.3 mL of THF was prepared under argon atmosphere and the NFSI solution was transferred to the vial containing reaction mixture *via* a syringe. The reaction solution was stirred for additional 2 hours at 23 °C and then quenched by exposure to air. The crude mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and then transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 3% ethyl acetate in hexanes; gradient: 3% to 5% to 7% ethyl acetate in hexanes) yielded 19 mg (0.069 mmol, 69% yield) of product as a white solid. **1H NMR** (500 MHz, chloroform-*d*, 23 °C): δ 7.4 –7.40 (m, 2H), 7.35 (t, $J_{HH} = 7.7$ Hz, 2H), 7.32–7.27 (m, 1H), 2.95–2.90 (m, 1H), 2.28–2.13 (m, 1H), 2.07–1.93 (m, 1H), 1.90–1.82 (m, 1H), 1.81–1.74 (m, 1H), 1.67–1.59 (m, 2H), 1.44–1.37 (m, 1H), 1.33–1.12 (m, 11H; should be 9H but

contains grease), 0.85 (t, $J_{HH} = 7.1$ Hz, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** (126 MHz, chloroform-*d*, 23 °C): δ 212.5 (d, $^2J_{CF} = 28.8$ Hz), 138.5 (d, $^2J_{CF} = 22.5$ Hz), 128.5 (d, $^4J_{CF} = 2.0$ Hz), 128.0 (d, $^5J_{CF} = 0.6$ Hz), 124.4 (d, $^3J_{CF} = 10.2$ Hz), 103.5 (d, $^1J_{CF} = 188.5$ Hz), 45.6, 38.7 (d, $^2J_{CF} = 22.2$ Hz), 29.8, 29.0 (d, $^4J_{CF} = 1.4$ Hz), 28.4 (d, $^4J_{CF} = 2.2$ Hz), 25.9, 25.7 (d, $^3J_{CF} = 5.1$ Hz), 25.4 (d, $^4J_{CF} = 2.8$ Hz), 22.8, 14.0. **^{19}F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -171.04 (ddd, $^3J_{FH} = 26.8$, 23.6 Hz, $^4J_{FH} = 3.4$ Hz). **HRMS** (ESI+) *m/z* calculated for $\text{C}_{18}\text{H}_{25}\text{FO}$ ([M+H] $^+$) 277.1962, found *m/z* 277.1964.

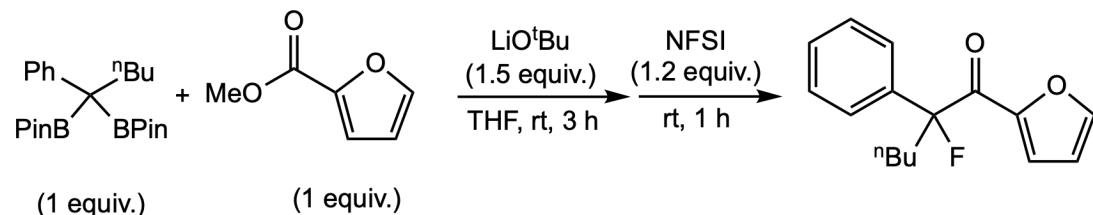
2-Phenyl-2-(prop-2-yn-1-yl)-1-(4-(trifluoromethyl)phenyl)hexan-1-one 17b.



In the glovebox, a scintillation vial with a magnetic stir bar was charged with 40 mg of *n*-pentylbenzene-benzylboronate (0.10 mmol, 1 equiv.), 20 mg of methyl 4-(trifluoromethyl)benzoate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiO^tBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours. The vial was capped with a rubber septum, sealed with electrical tape, and brought out of the glovebox. To the mixture was added 22 μL of propargyl bromide solution (80 wt. % in toluene, 0.20 mmol, 2 equiv.) *via* a microsyringe and the mixture was allowed to stir at 40 °C for 2 hours. Then, the reaction mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 4% ethyl acetate in hexanes; gradient: 4% to 5% to 6% ethyl acetate in hexanes) yielded 26 mg (0.073 mmol, 73% yield) of product as a white solid. **^1H NMR**

(500 MHz, chloroform-*d*, 23 °C): δ 7.4–7.40 (m, 2H), 7.35 (t, J_{HH} = 7.7 Hz, 2H), 7.32–7.27 (m, 1H), 2.95–2.90 (m, 1H), 2.28–2.13 (m, 1H), 2.07–1.93 (m, 1H), 1.90–1.82 (m, 1H), 1.81–1.74 (m, 1H), 1.67–1.59 (m, 2H), 1.44–1.37 (m, 1H), 1.33–1.12 (m, 11H; should be 9H but contains grease), 0.85 (t, J_{HH} = 7.1 Hz, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** (126 MHz, chloroform-*d*, 23 °C): δ 212.5 (d, $^2J_{CF}$ = 28.8 Hz), 138.5 (d, $^2J_{CF}$ = 22.5 Hz), 128.5 (d, $^4J_{CF}$ = 2.0 Hz), 128.0 (d, $^5J_{CF}$ = 0.6 Hz), 124.4 (d, $^3J_{CF}$ = 10.2 Hz), 103.5 (d, $^1J_{CF}$ = 188.5 Hz), 45.6, 38.7 (d, $^2J_{CF}$ = 22.2 Hz), 29.8, 29.0 (d, $^4J_{CF}$ = 1.4 Hz), 28.4 (d, $^4J_{CF}$ = 2.2 Hz), 25.9, 25.7 (d, $^3J_{CF}$ = 5.1 Hz), 25.4 (d, $^4J_{CF}$ = 2.8 Hz), 22.8, 14.0. **^{19}F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -171.04 (ddd, $^3J_{FH}$ = 26.8, 23.6 Hz, $^4J_{FH}$ = 3.4 Hz). **HRMS** (ESI+) *m/z* calculated for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{O}$ ([M+H]⁺) 359.1617, found *m/z* 359.1613.

2-Fluoro-1-(furan-2-yl)-2-phenylhexan-1-one 17c.



In the glovebox, a scintillation vial with a magnetic stir bar was charged with 40 mg of *n*-pentylbenzene-benzyldiboronate (0.10 mmol, 1 equiv.), 13 mg of methyl furanoate (0.10 mmol, 1 equiv.), and 2 mL of THF. 12 mg of LiOtBu (0.15 mmol, 1.5 equiv.) was then added all at once as a solid. The resulting solution was stirred at 23 °C for 3 hours after which 38 mg of NFSI (0.12 mmol, 1.2 equiv.) was added. The mixture was then stirred at rt for 1 h. The reaction mixture was diluted with ethyl acetate and saturated aqueous ammonium chloride solution, and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel packed with hexanes; loaded with 7% ethyl acetate in hexanes; eluent: 7% ethyl acetate in hexanes) yielded 16 mg (0.061 mmol, 62% yield) of product. **^1H NMR** (300 MHz, chloroform-*d*, 23 °C): δ 7.66–

7.58 (m, 1H), 7.50 (d, $J_{HH} = 7.4$ Hz, 2H), 7.46–7.40 (m, 1H), 7.38–7.29 (m, 3H), 6.49 (dd, $J_{HH} = 3.5$, 1.4 Hz, 1H), 2.52–2.33 (m, 1H), 2.30–2.06 (m, 1H), 1.46–1.17 (m, 4H), 0.87 (t, $J = 6.9$ Hz, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** (126 MHz, chloroform-*d*, 23 °C): δ 186.3 (d, $^2J_{CF} = 28.5$ Hz), 149.5 (d, $^3J_{CF} = 4.2$ Hz), 147.7, 138.7 (d, $^2J_{CF} = 22.4$ Hz), 128.7, 128.3, 124.4 (d, $^3J_{CF} = 9.8$ Hz), 122.36 (d, $^3J_{CF} = 15.8$ Hz), 112.39 (d, $^4J_{CF} = 3.1$ Hz), 102.88 (d, $^1J_{CF} = 188.7$ Hz), 38.55 (d, $^2J_{CF} = 22.1$ Hz), 25.19 (d, $^3J_{CF} = 3.2$ Hz), 22.83, 14.03. **^{19}F NMR** (282 MHz, chloroform-*d*, 23 °C): δ -166.34 (td, $J_{FH} = 26.0$, 4.6 Hz). **HRMS** (ESI+) *m/z* calculated for $\text{C}_{16}\text{H}_{17}\text{FO}_2$ ([M+H]⁺) 261.1285, found *m/z* 261.1288.

VI. Spectroscopic Data

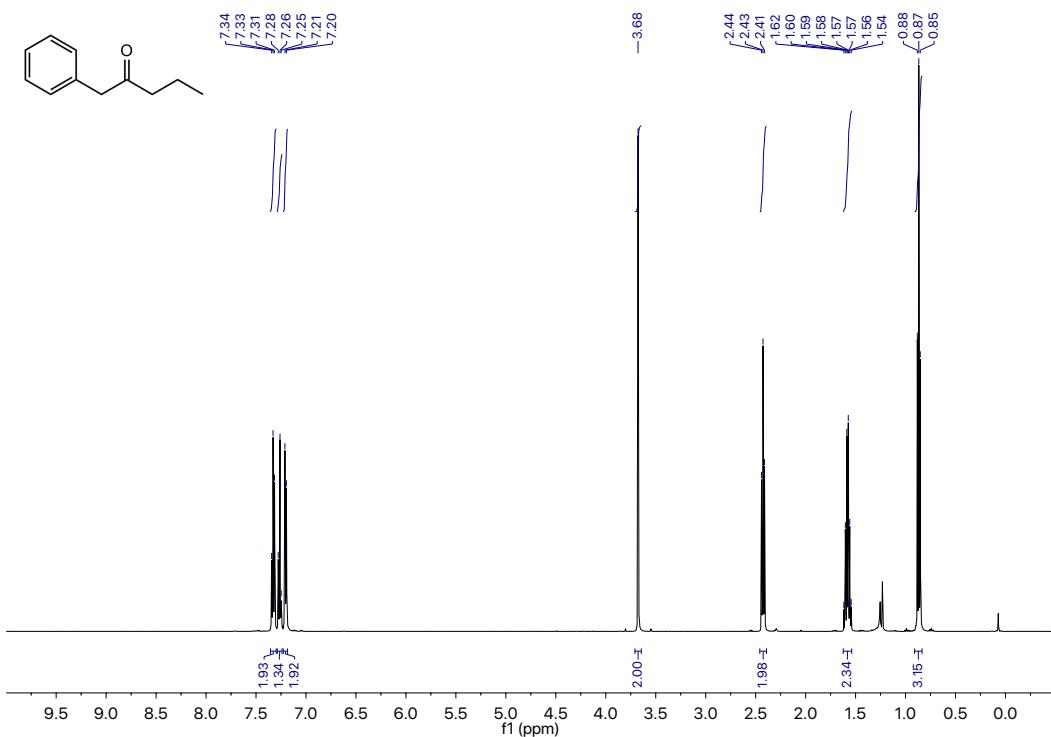


Figure S75. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3a**.

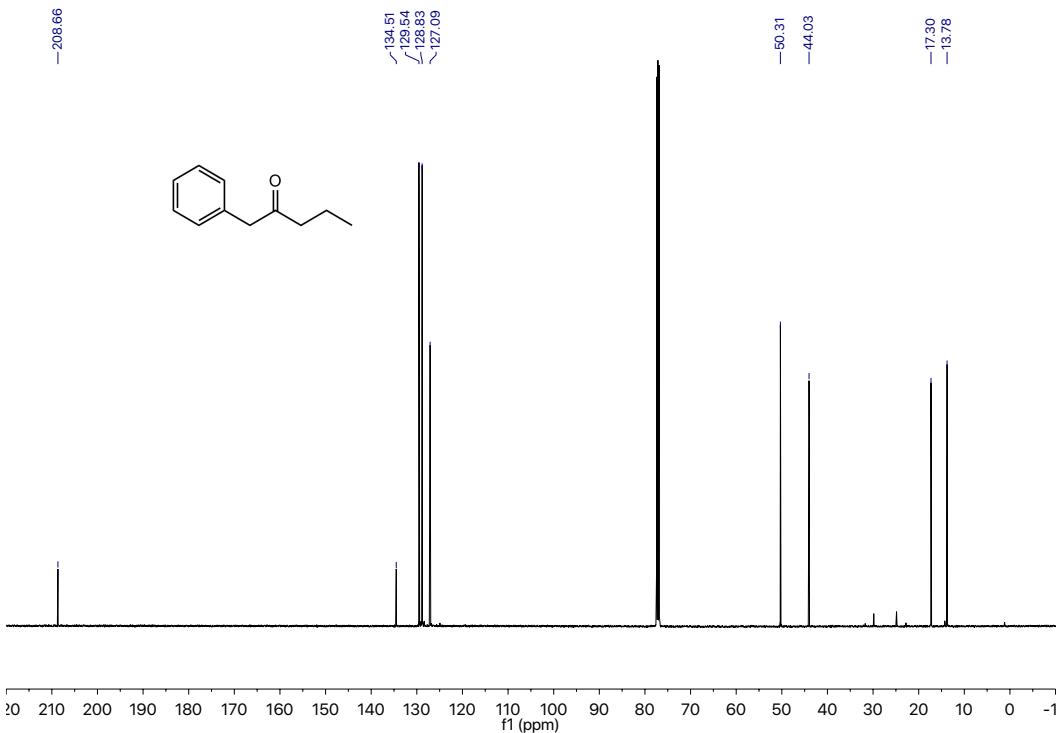


Figure S76. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3a**.

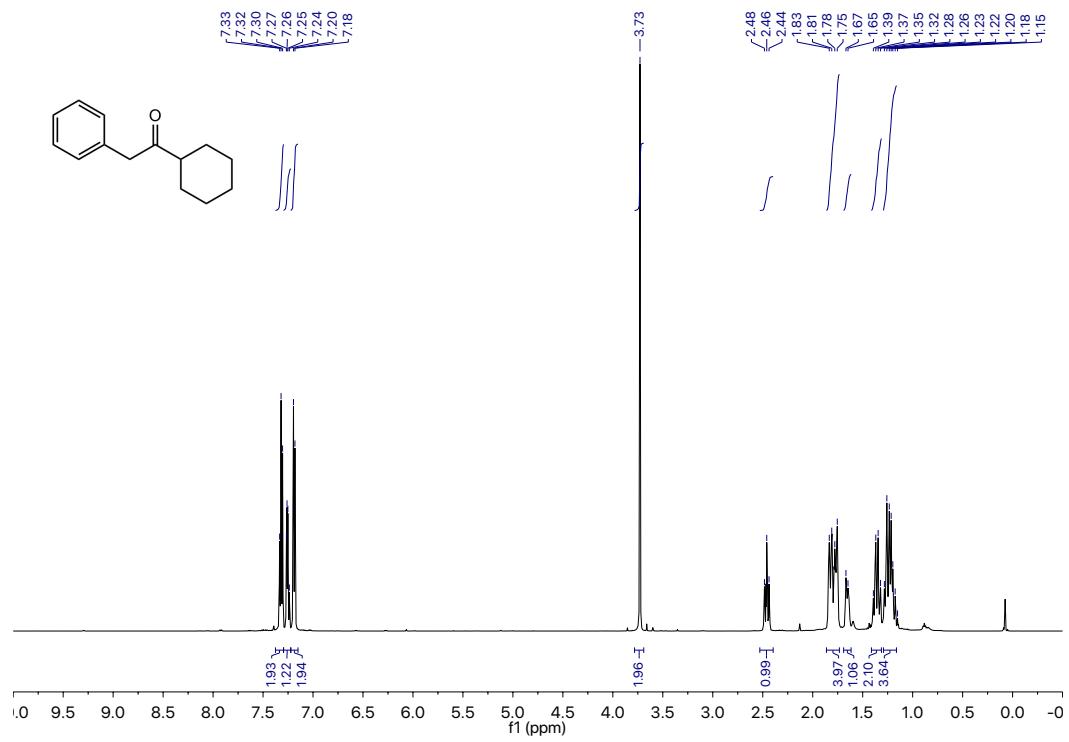


Figure S77. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3b**.

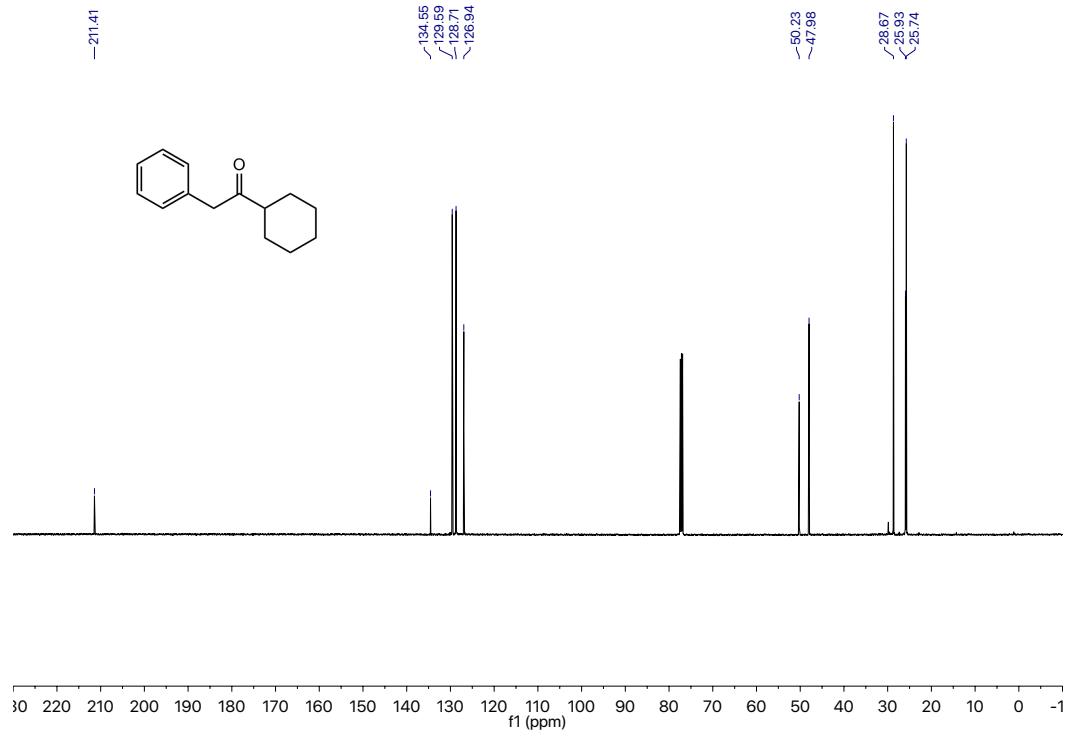


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3b**.

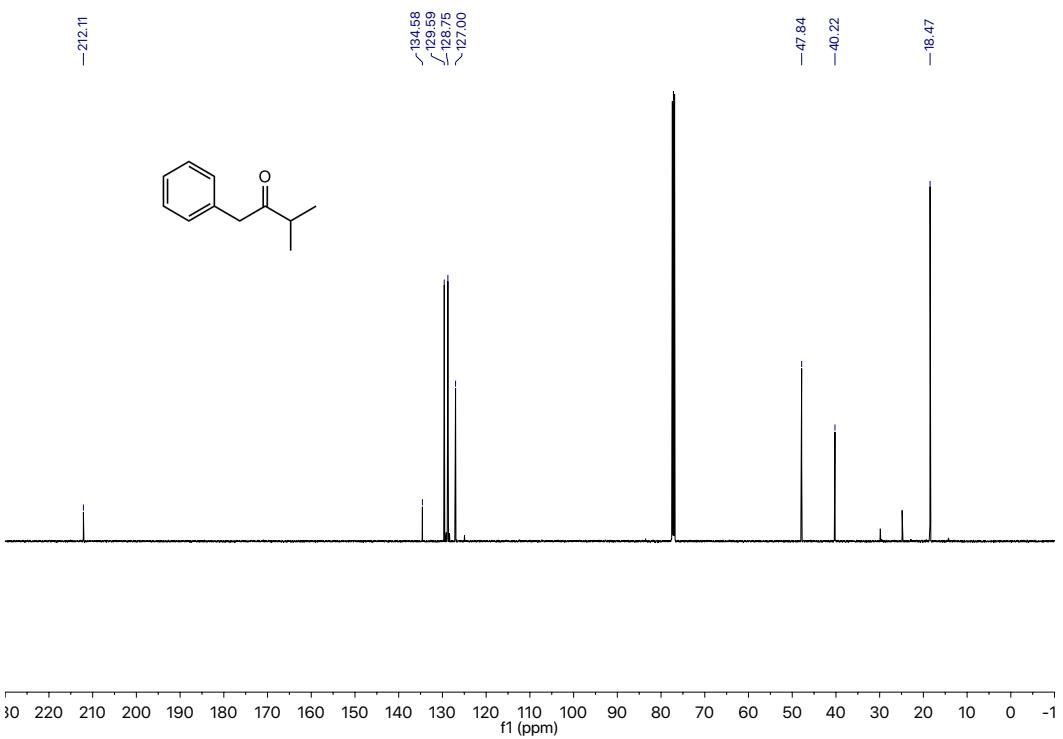
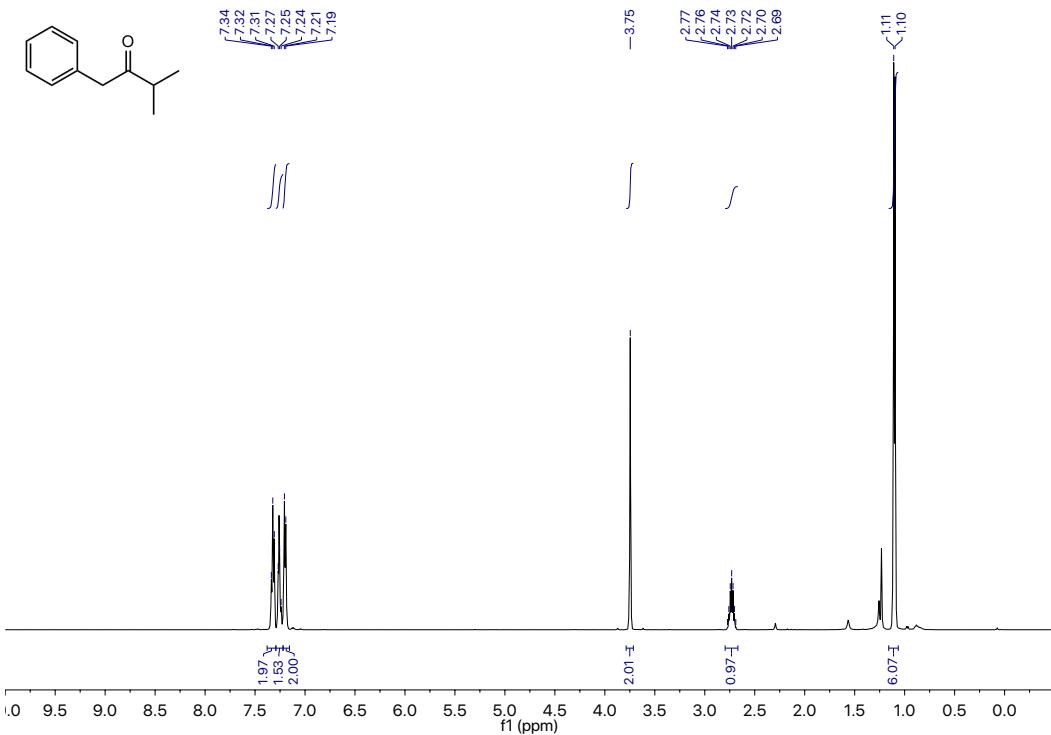


Figure S80. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3c**.

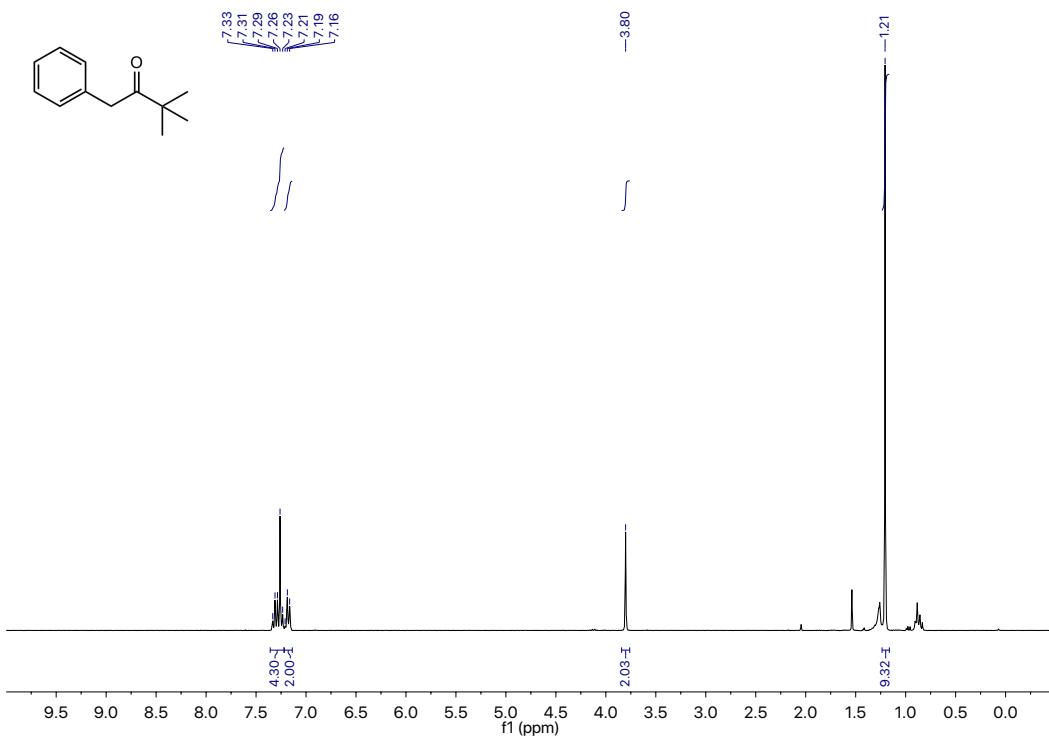


Figure S81. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **3d**.

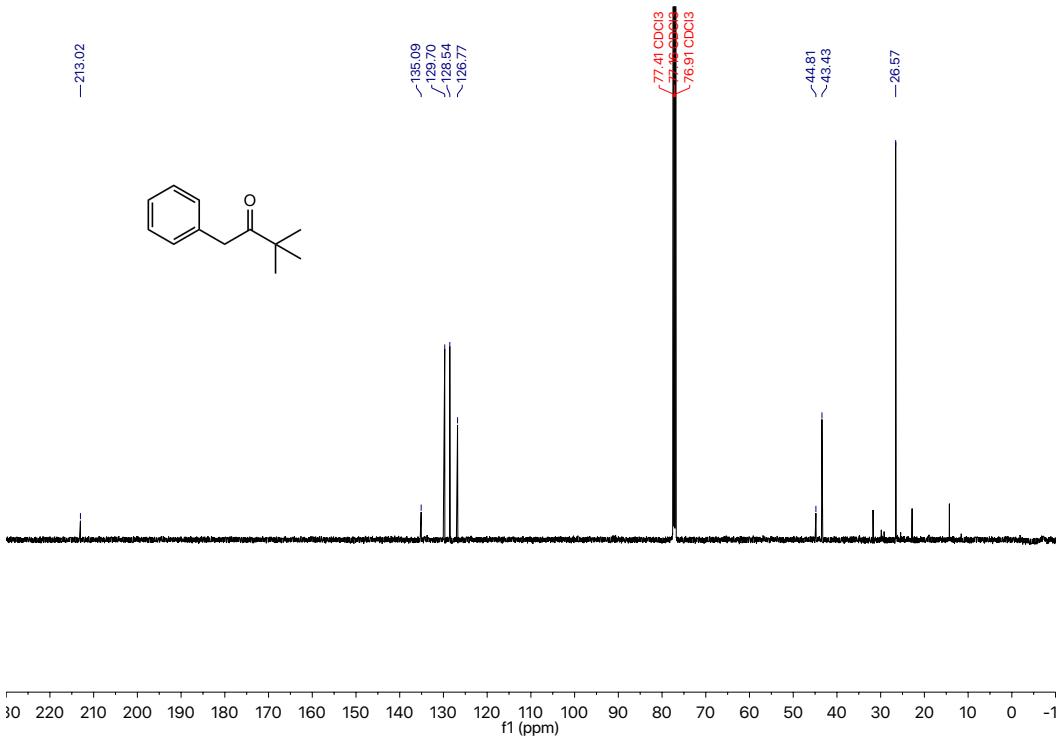
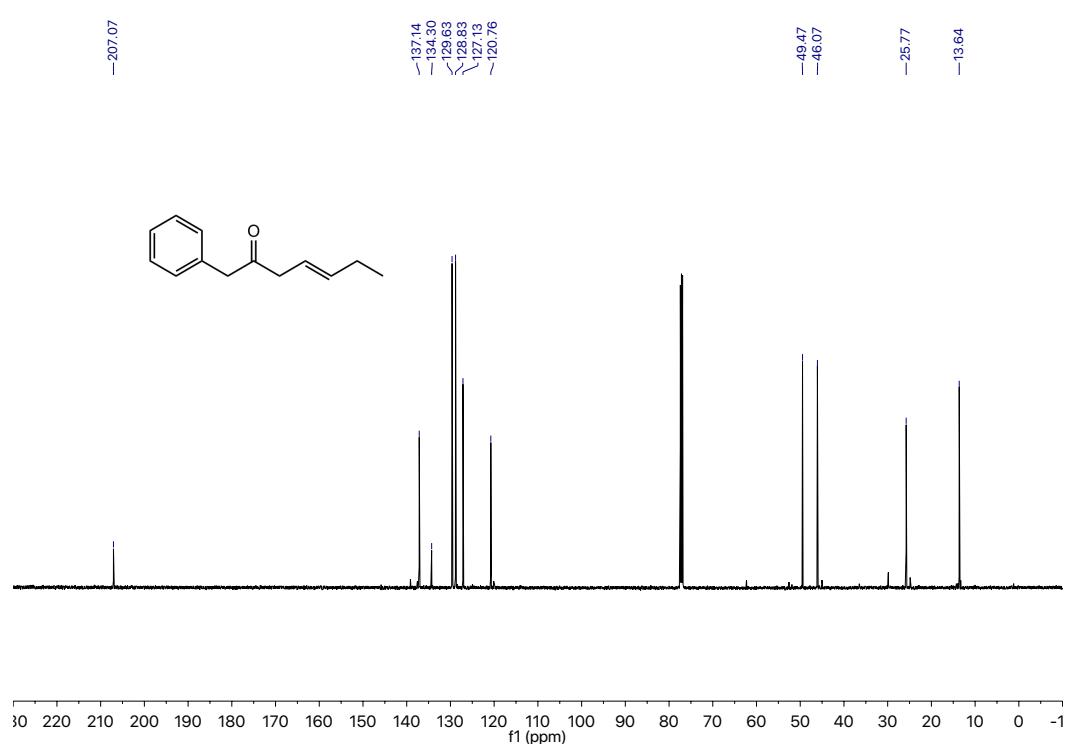
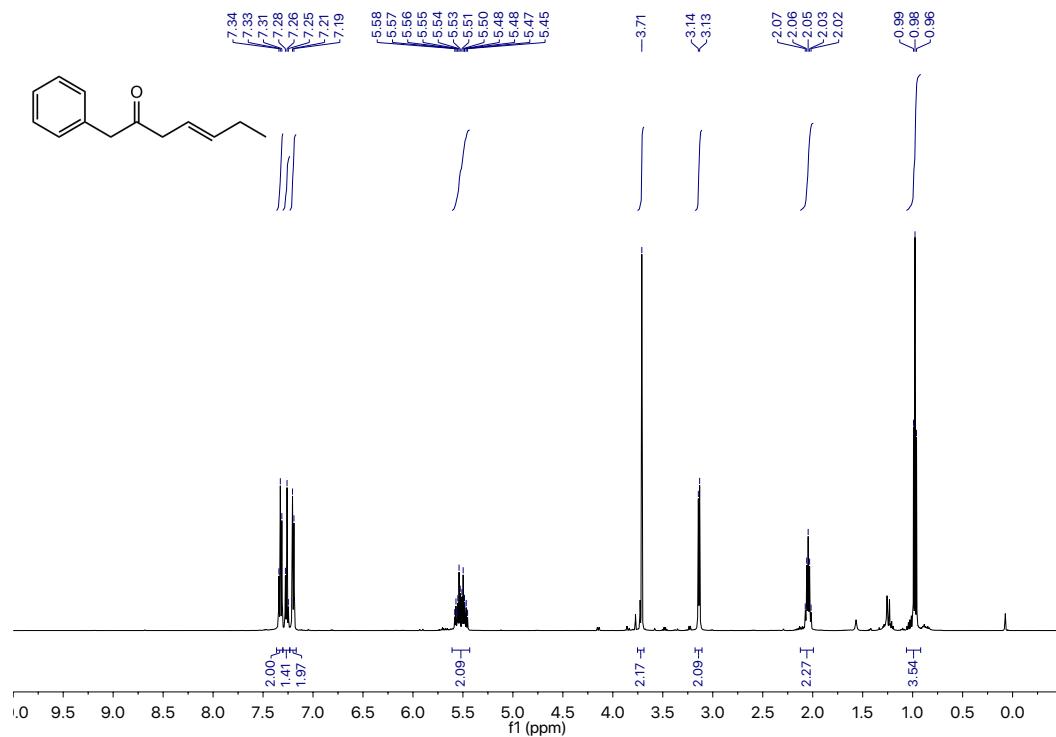


Figure S82. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3d**.



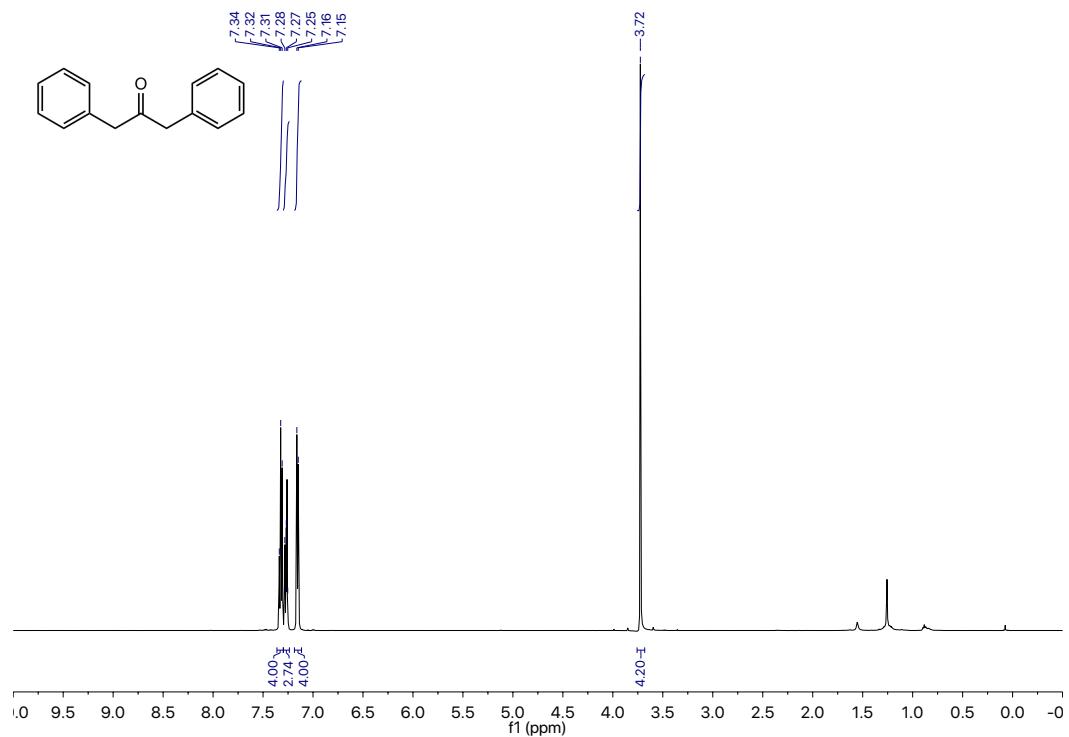


Figure S85. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of 3f.

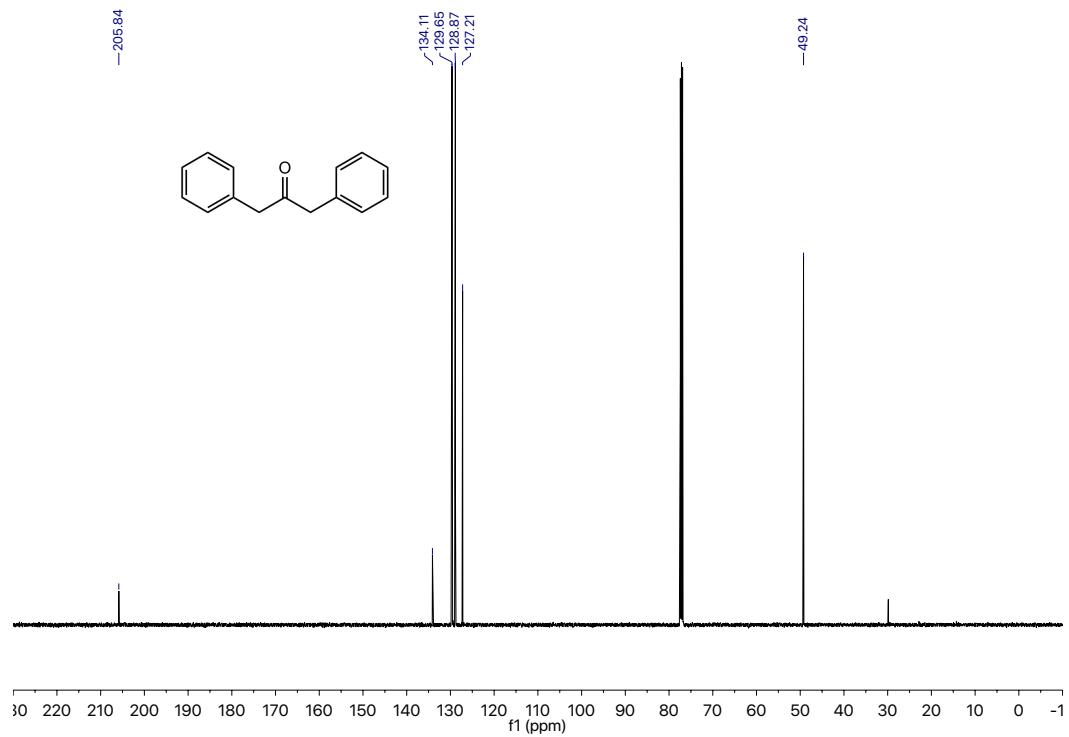


Figure S86. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 3f.

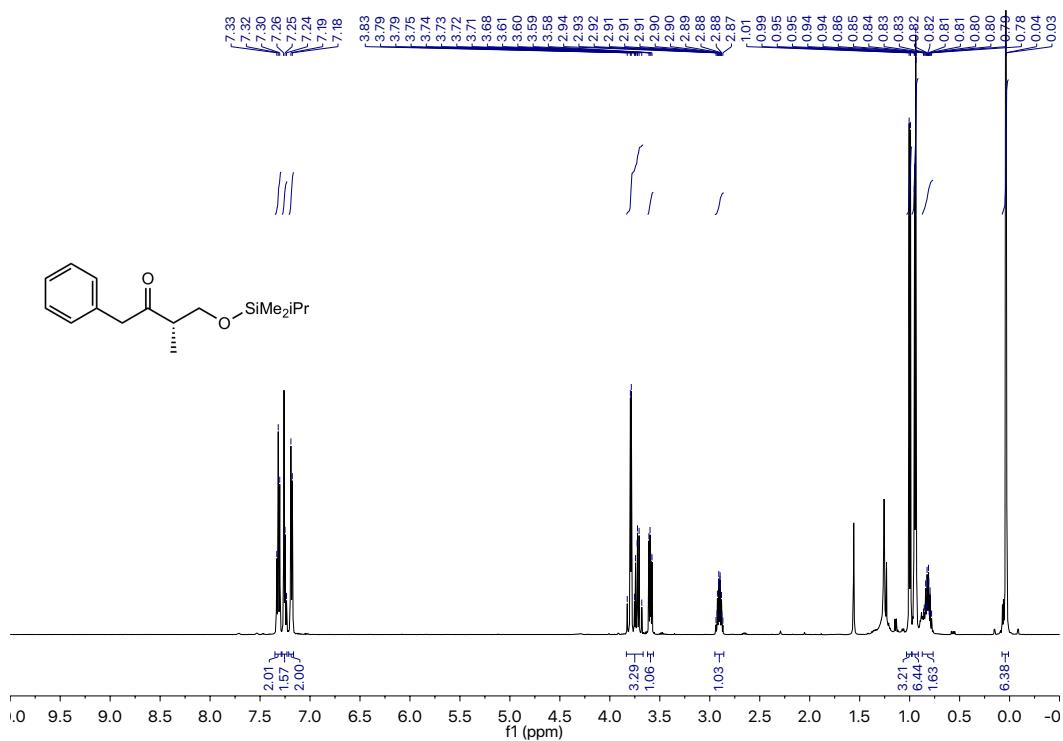


Figure S87. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3g**.

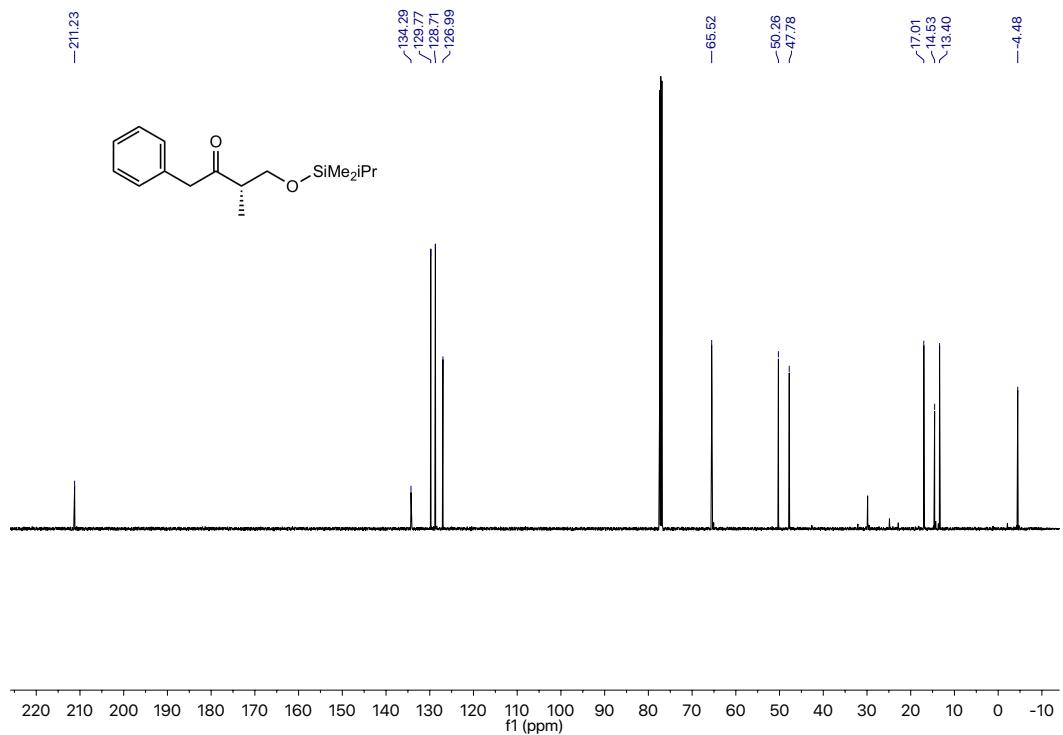


Figure S88. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3g**.

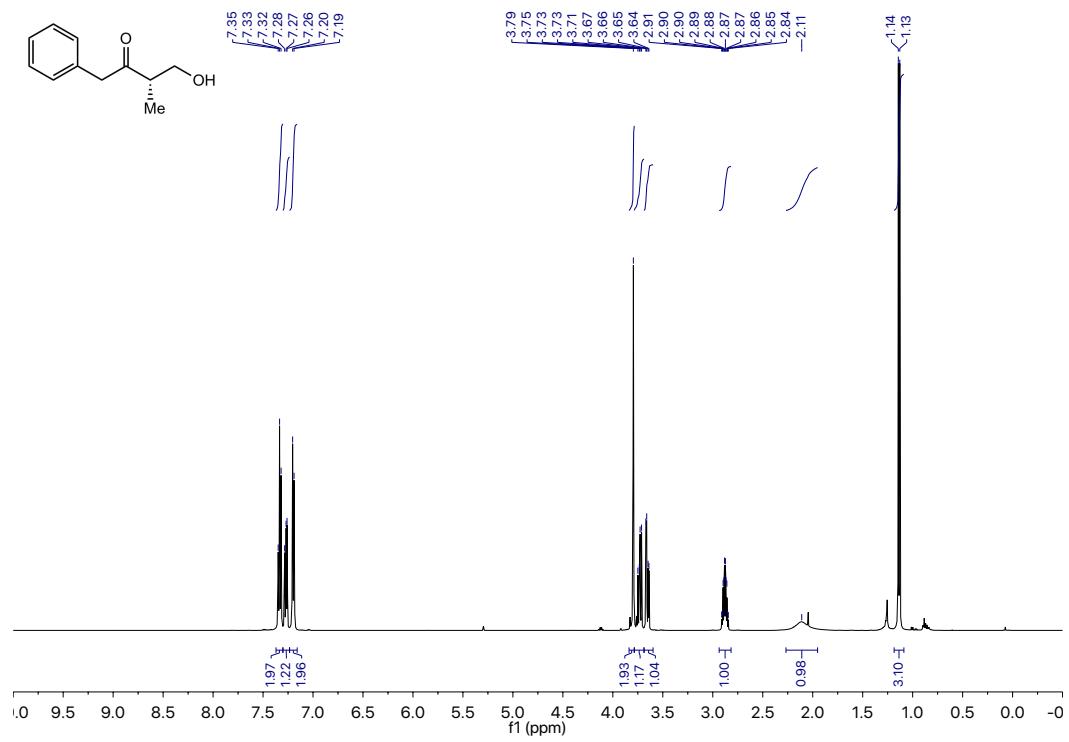


Figure S89. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3h**.

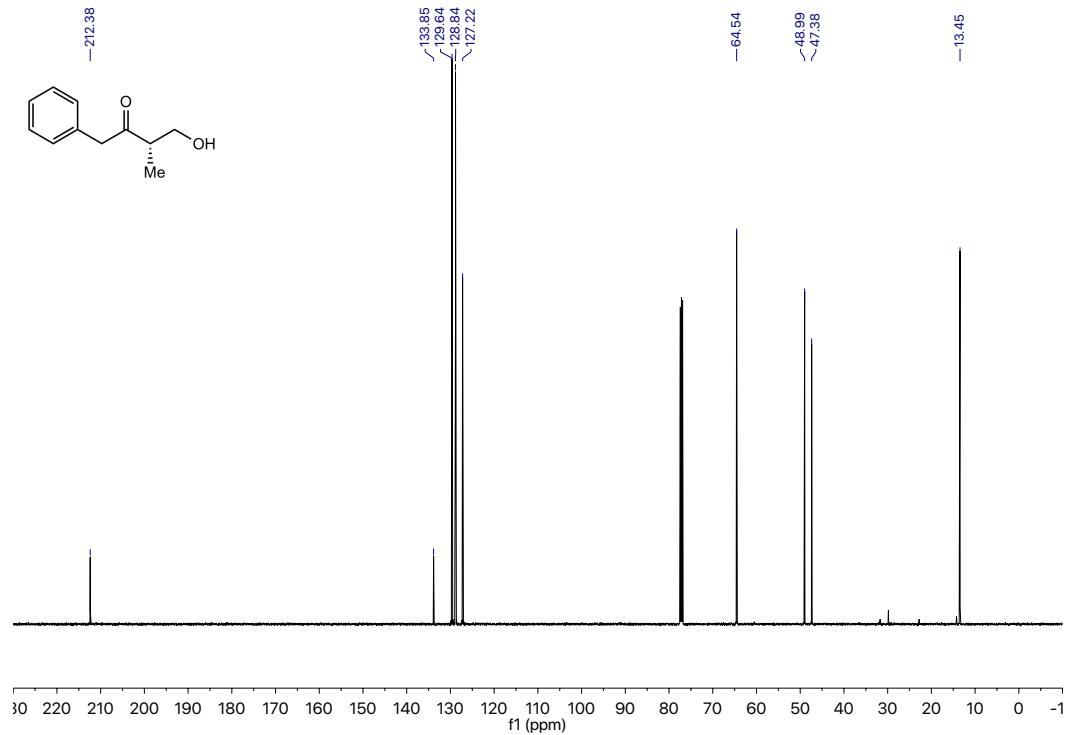


Figure S90. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3h**.

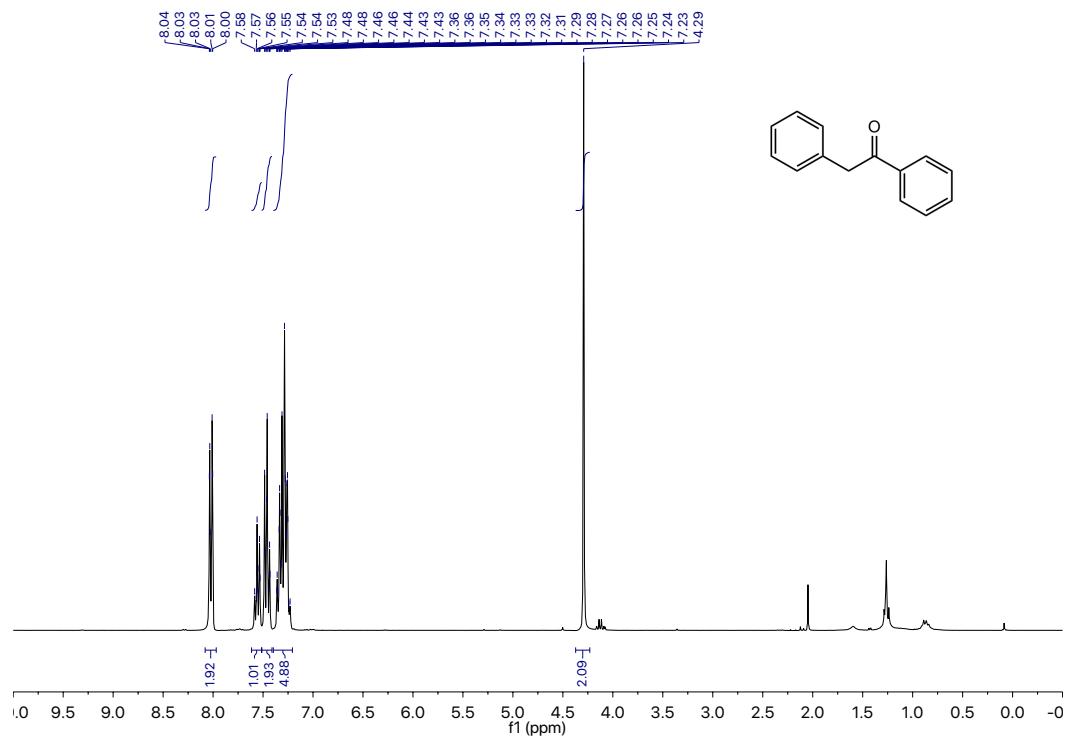


Figure S91. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3i**.

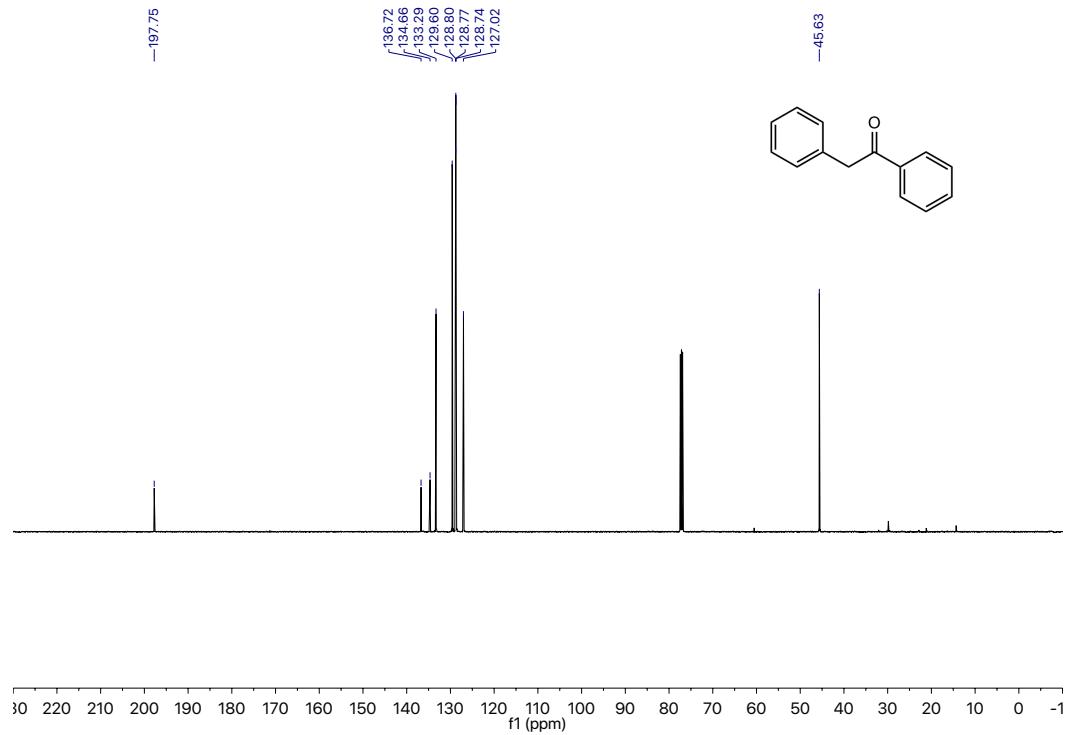


Figure S92. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3i**.

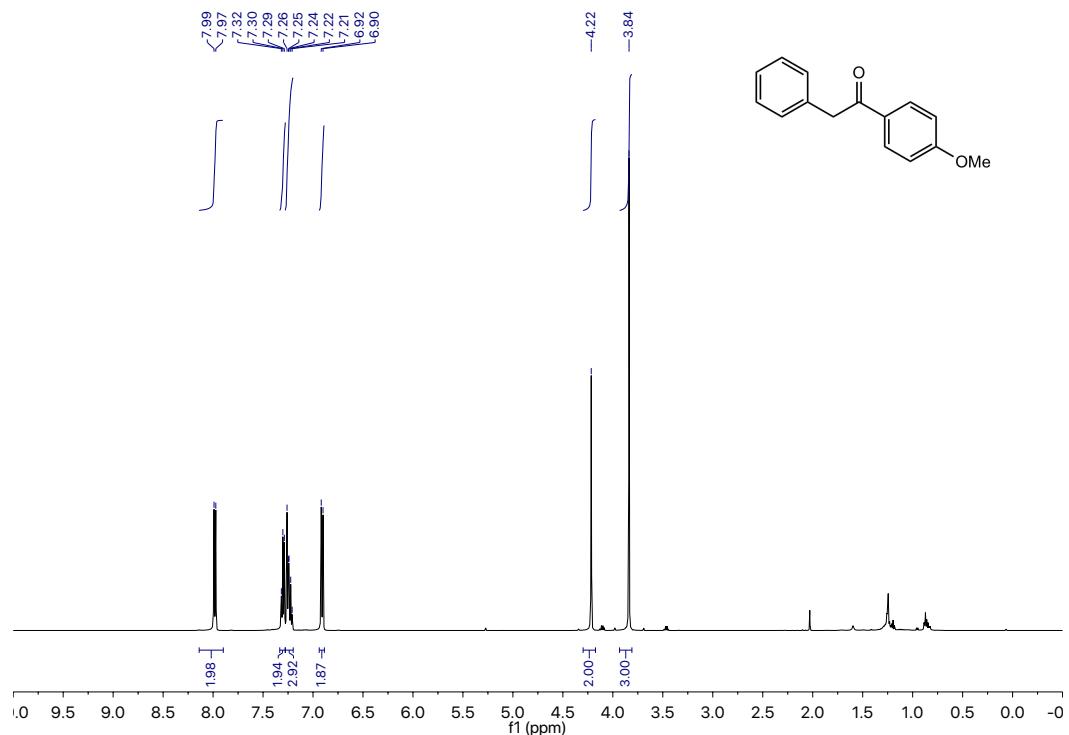


Figure S93. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3j**.

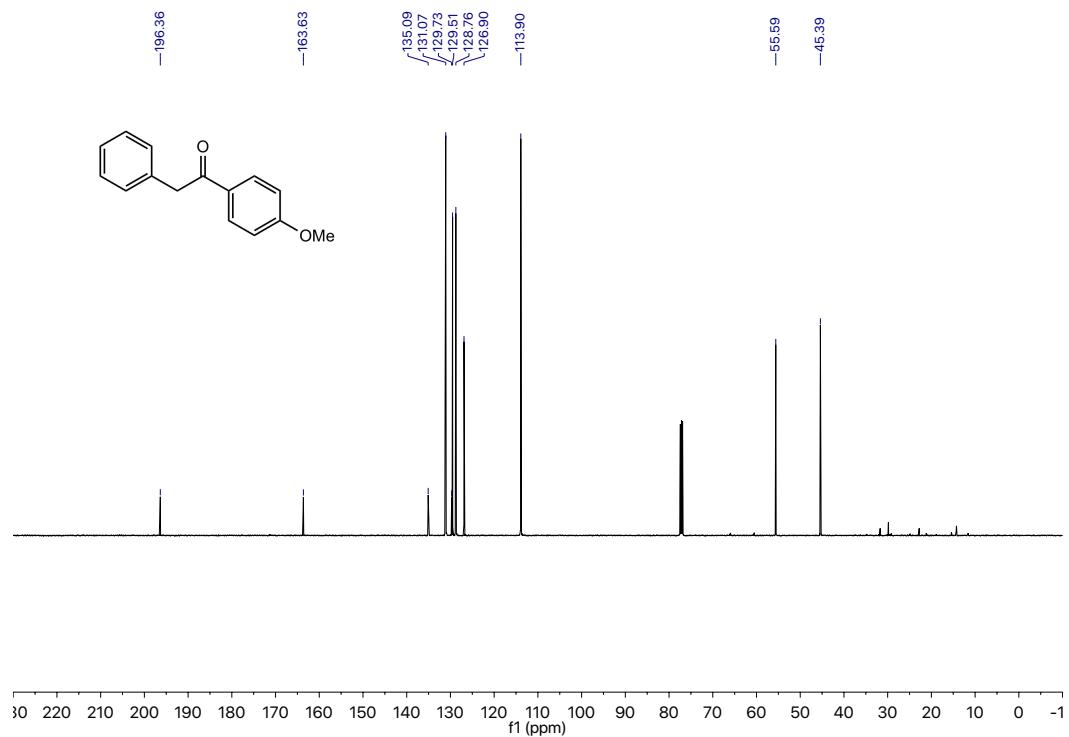


Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3j**.

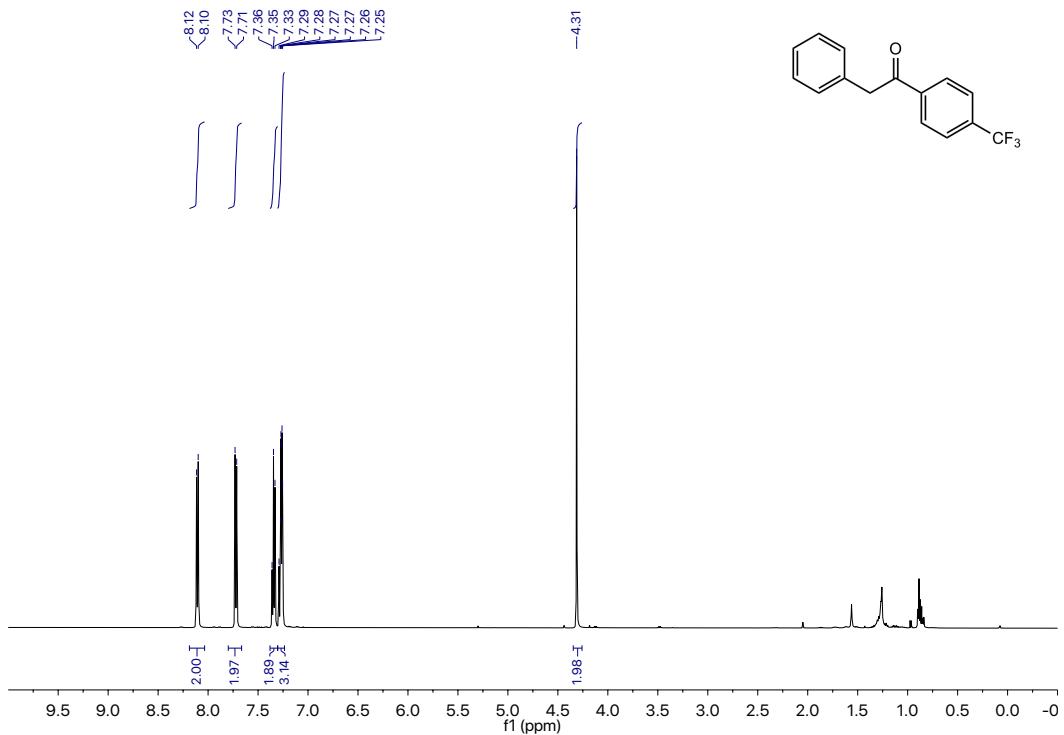


Figure S95. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3k**.

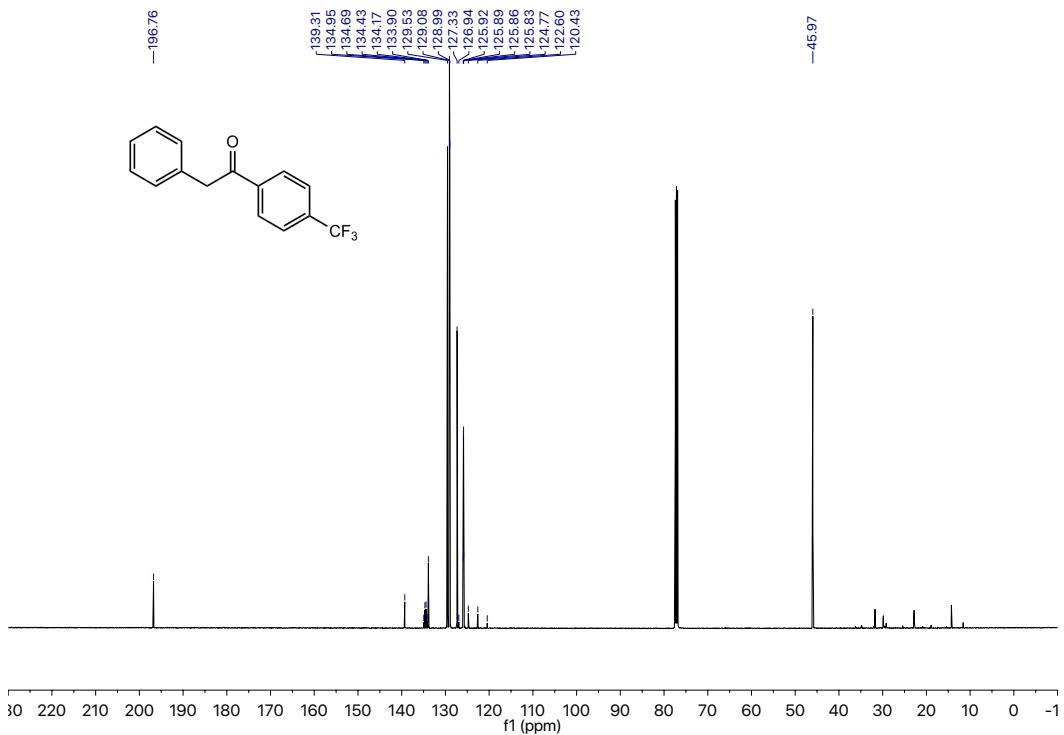


Figure S96. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3k**.

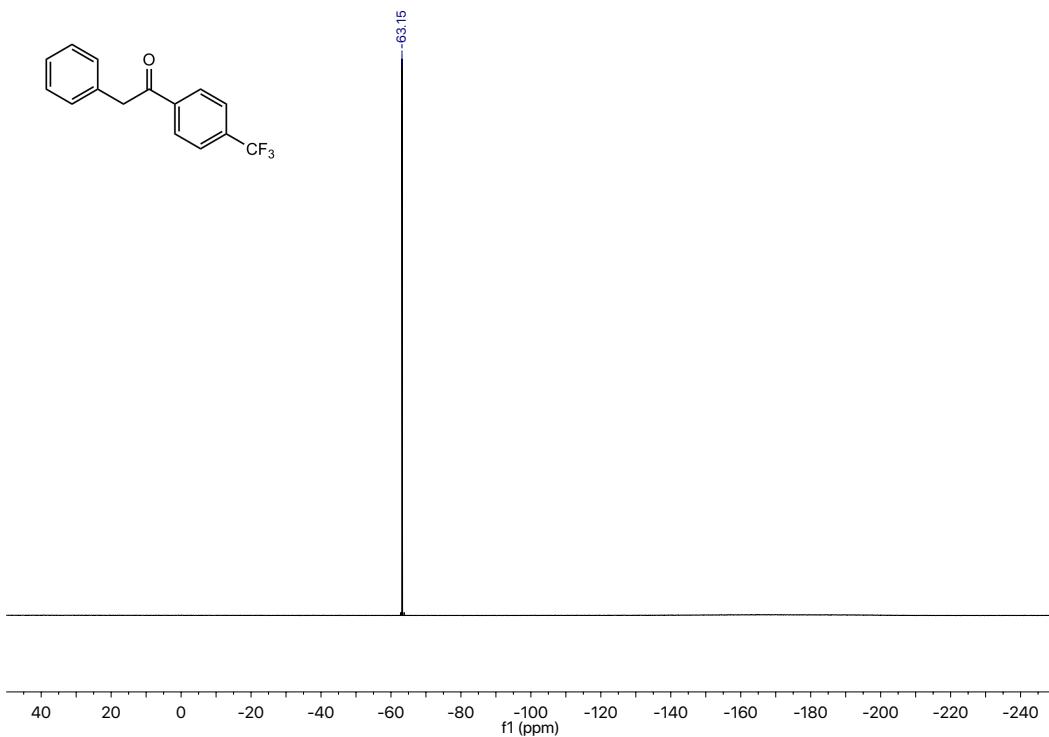


Figure S97. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3k**.

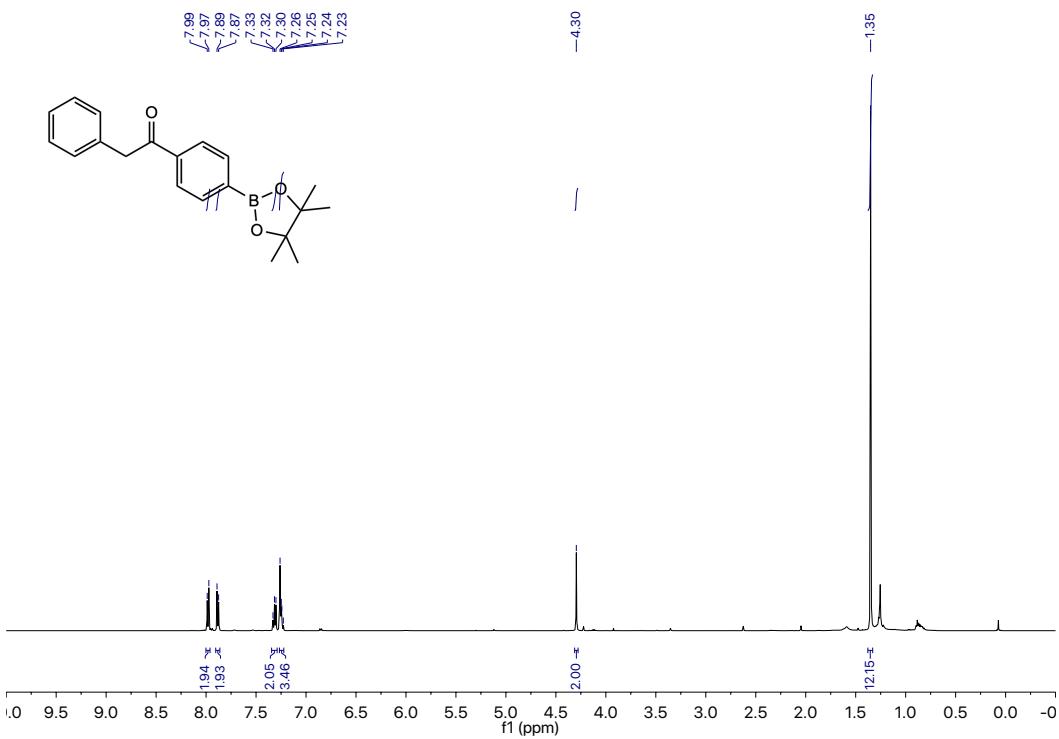


Figure S98. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3l**.

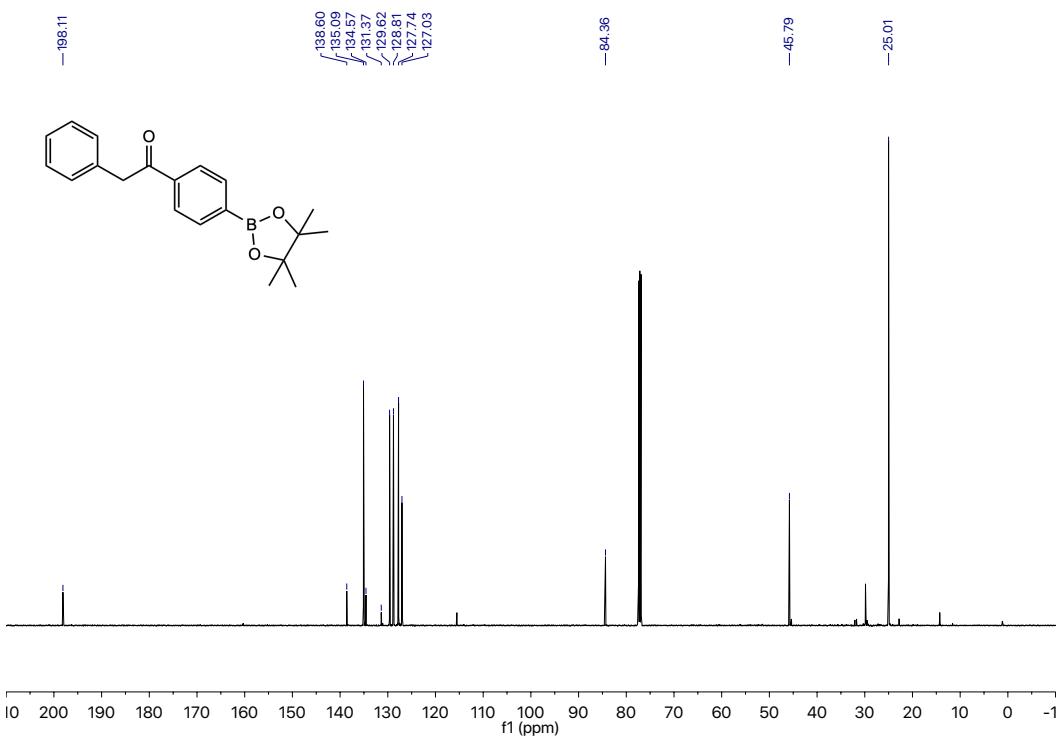


Figure S99. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3I**.

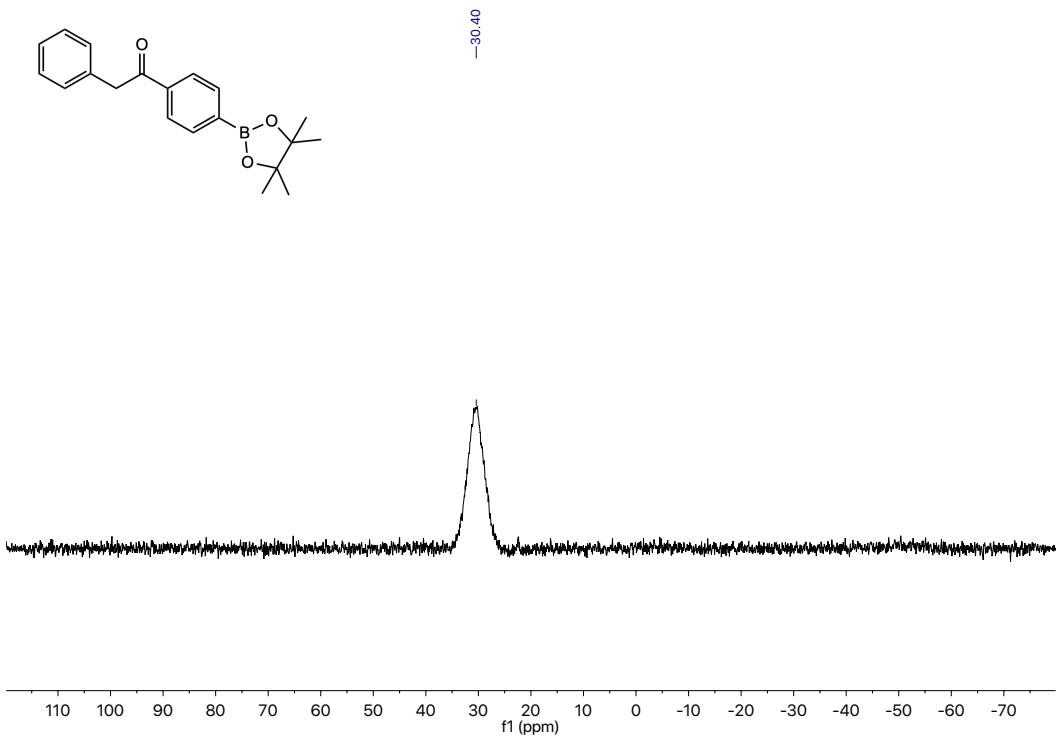


Figure S100. ^{11}B NMR spectrum (96 MHz, chloroform-*d*, 23 °C) of **3I**.

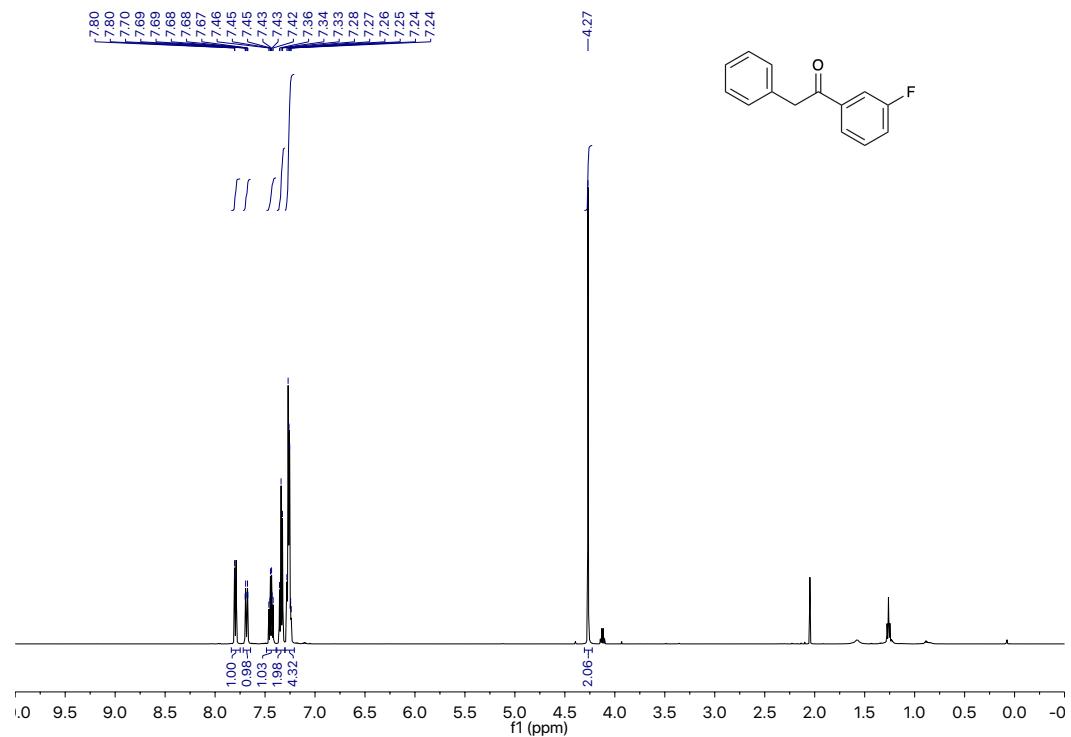


Figure S101. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3m**.

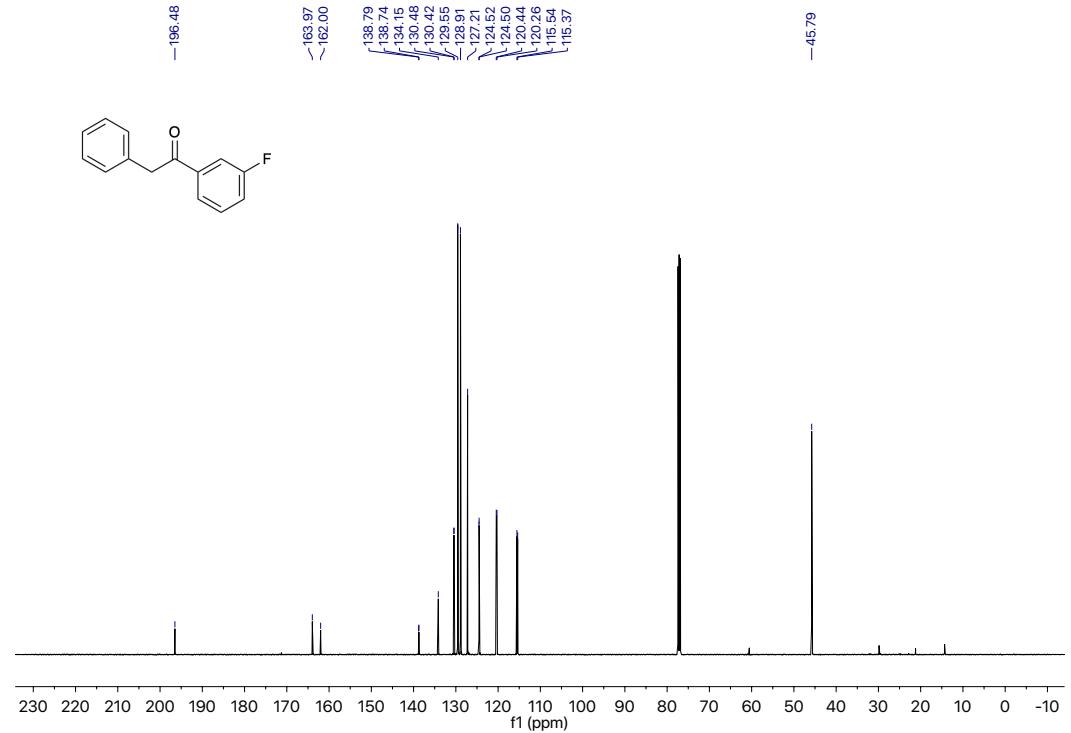


Figure S102. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3m**.

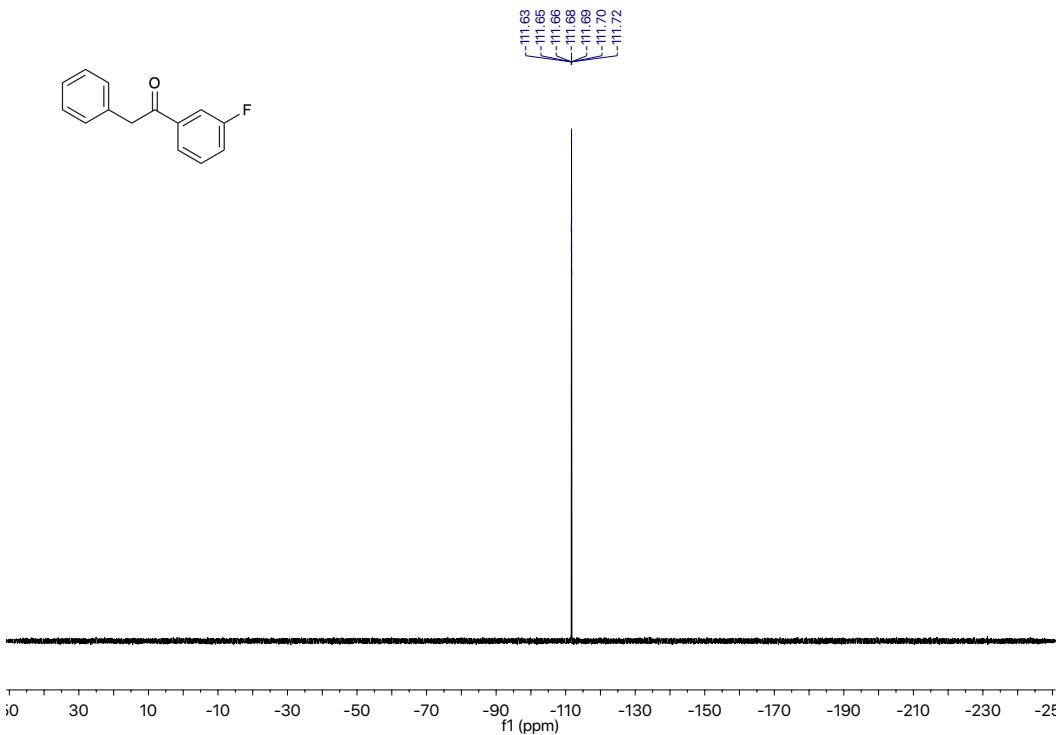


Figure S103. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3m**.

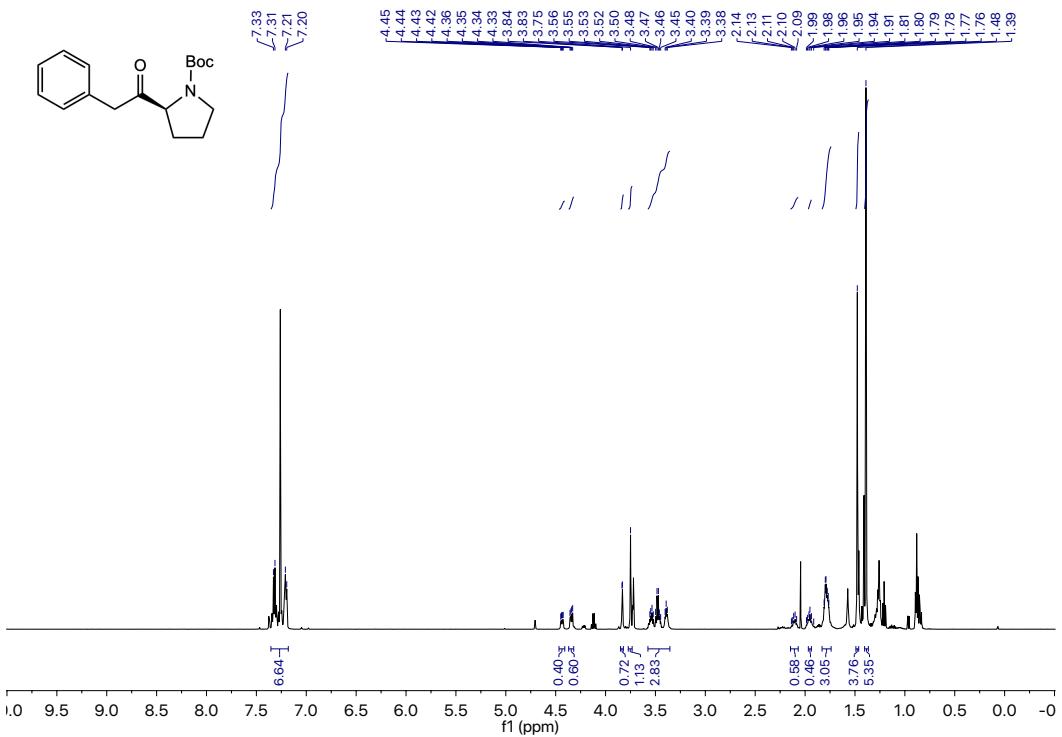
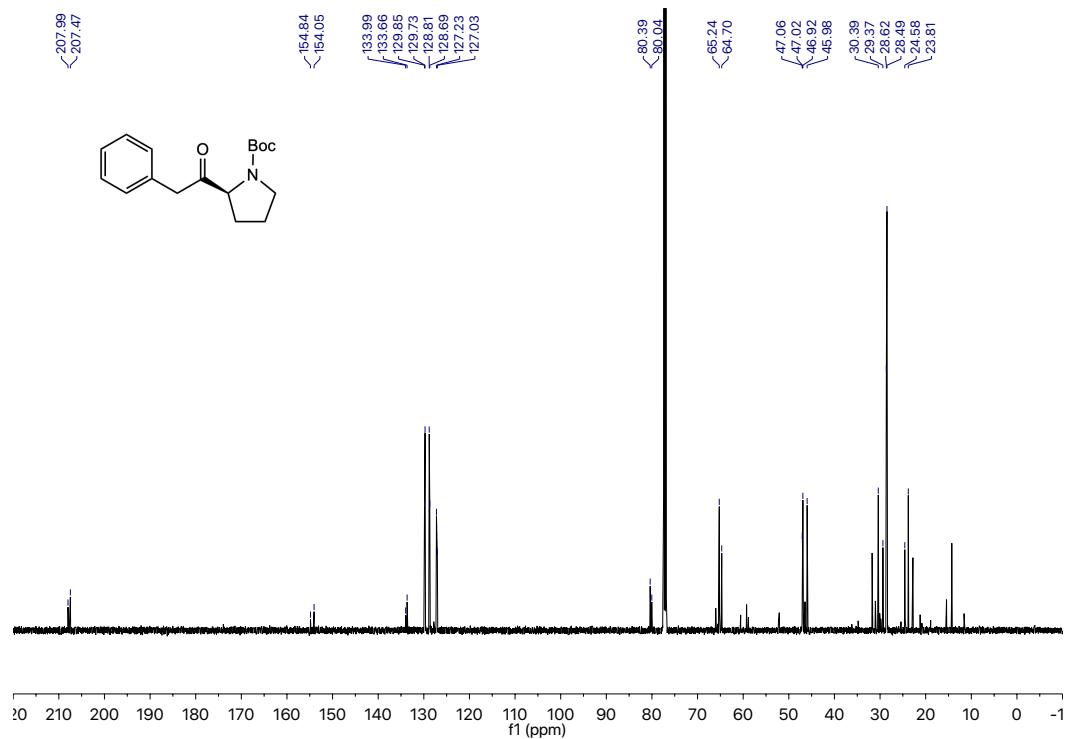


Figure S104. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3n**.



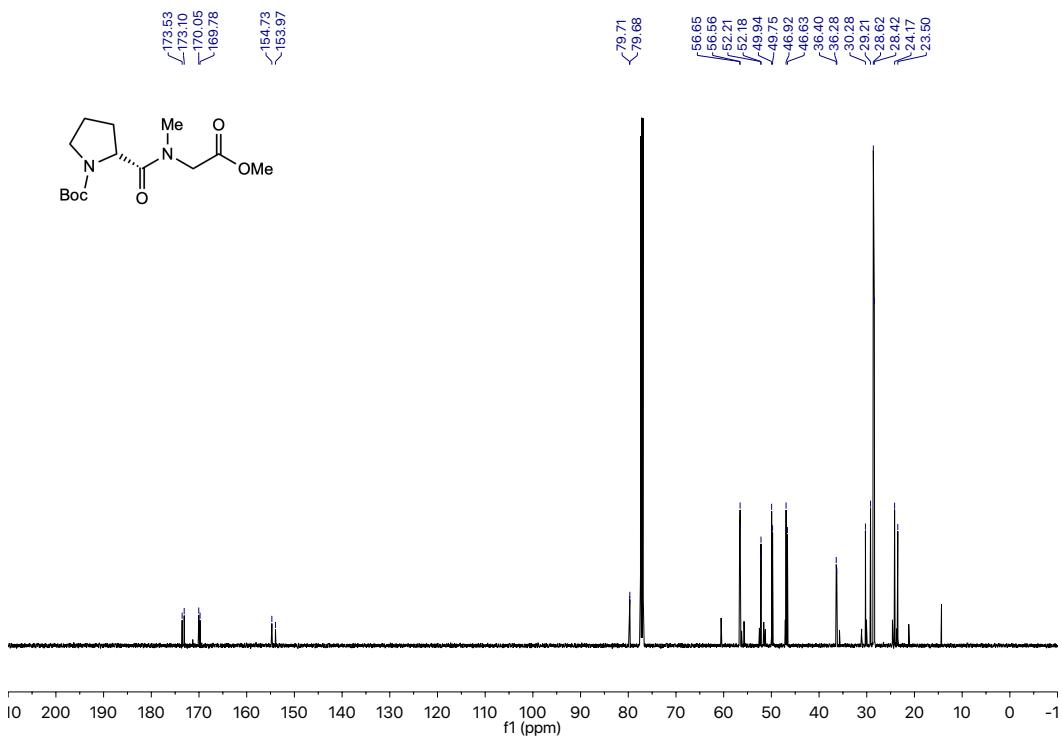


Figure S107. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of Boc-Pro-Sar-OMe.

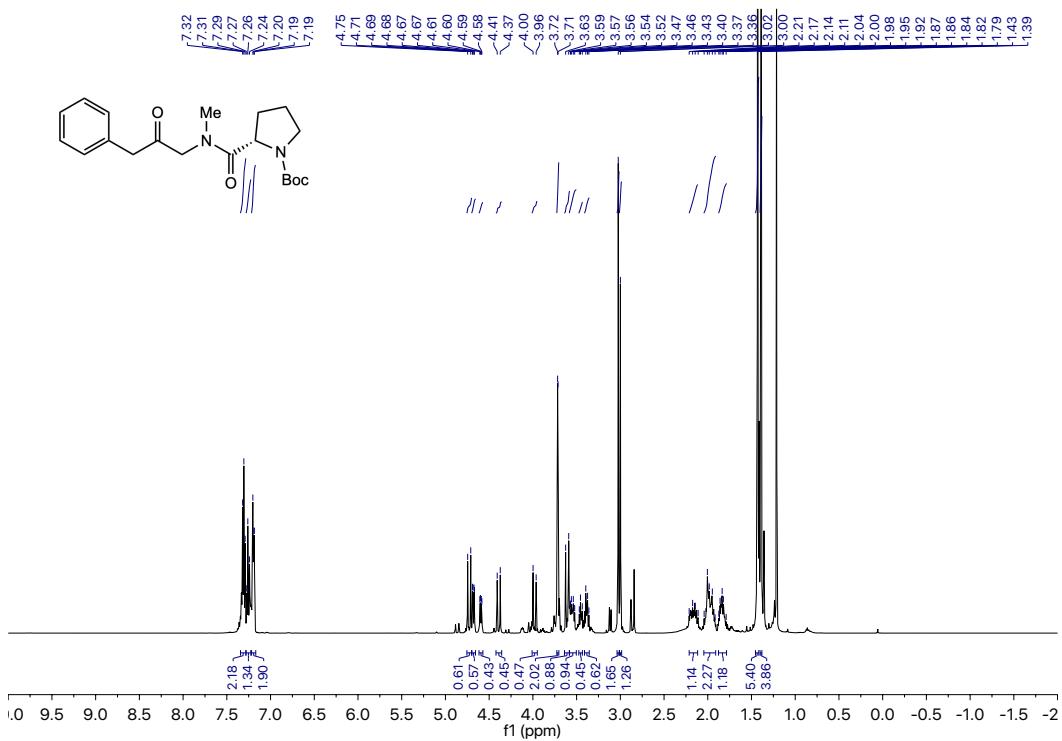


Figure S108. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3o**.

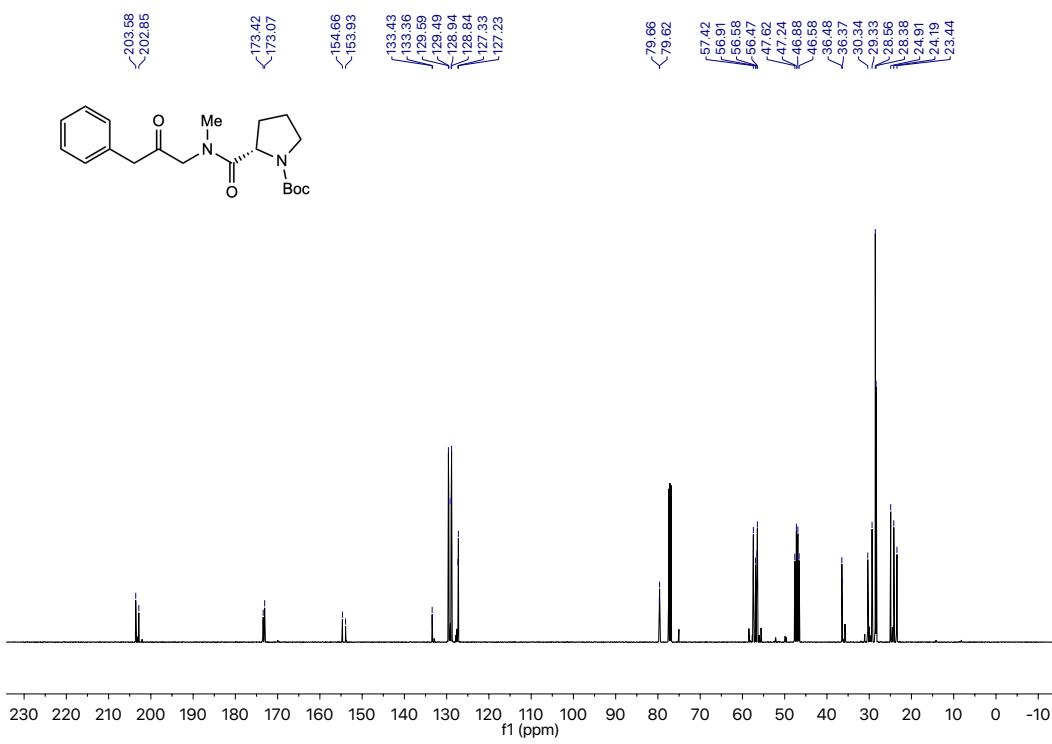


Figure S109. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3o**.

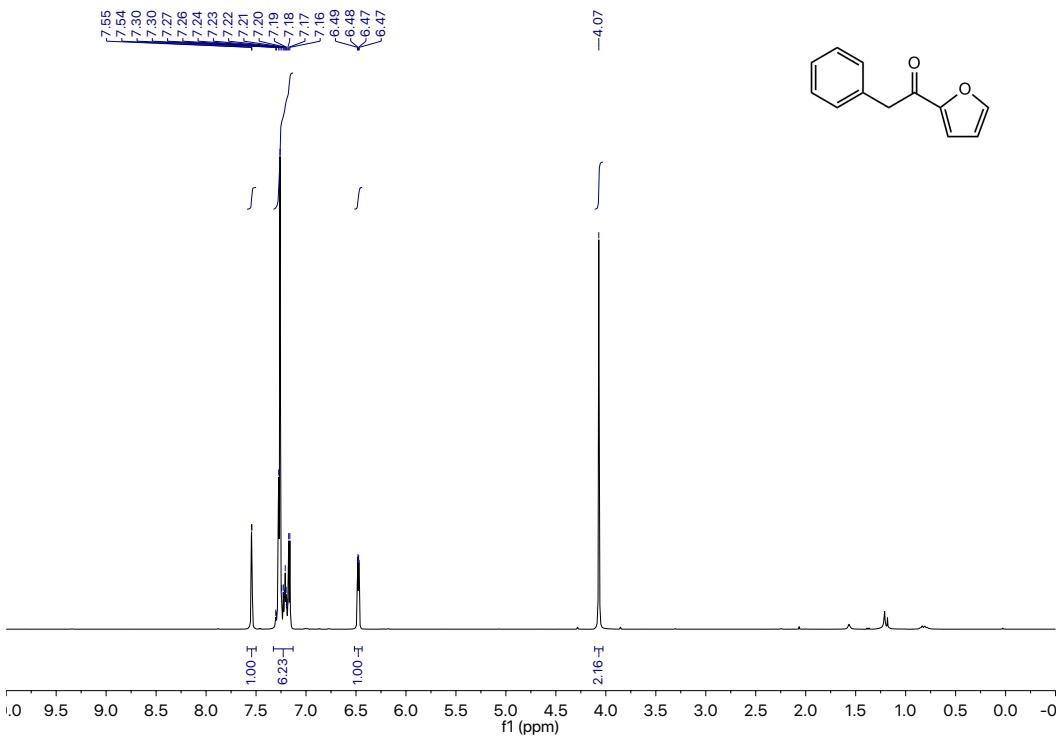


Figure S110. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **3p**.

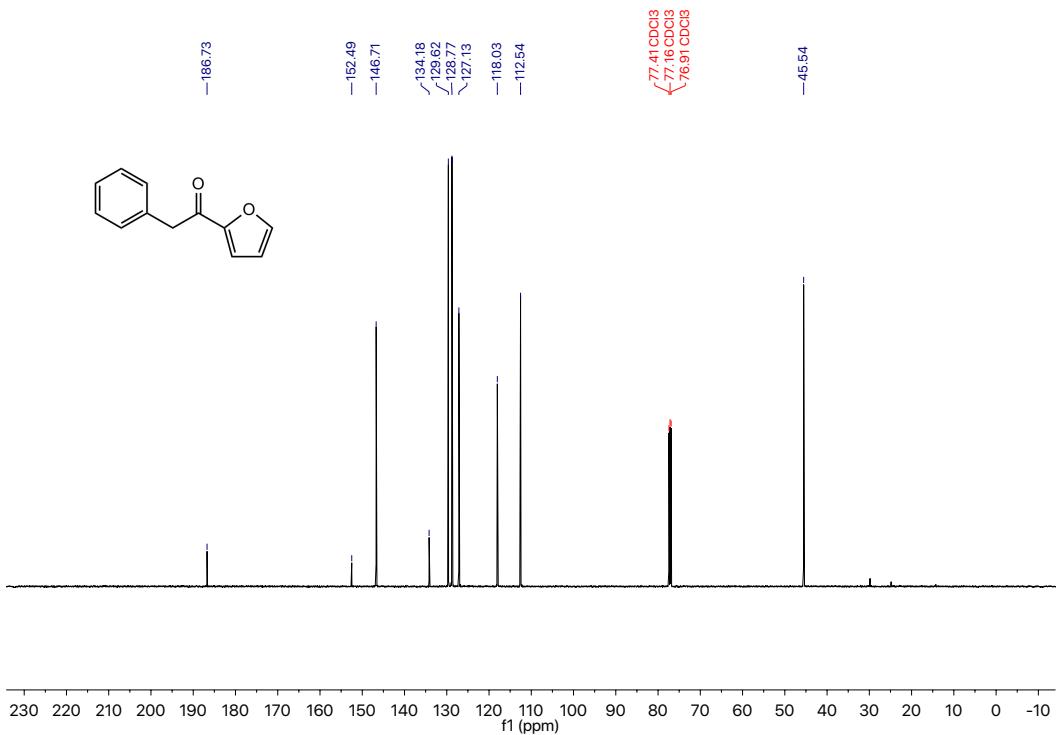


Figure S111. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3p**.

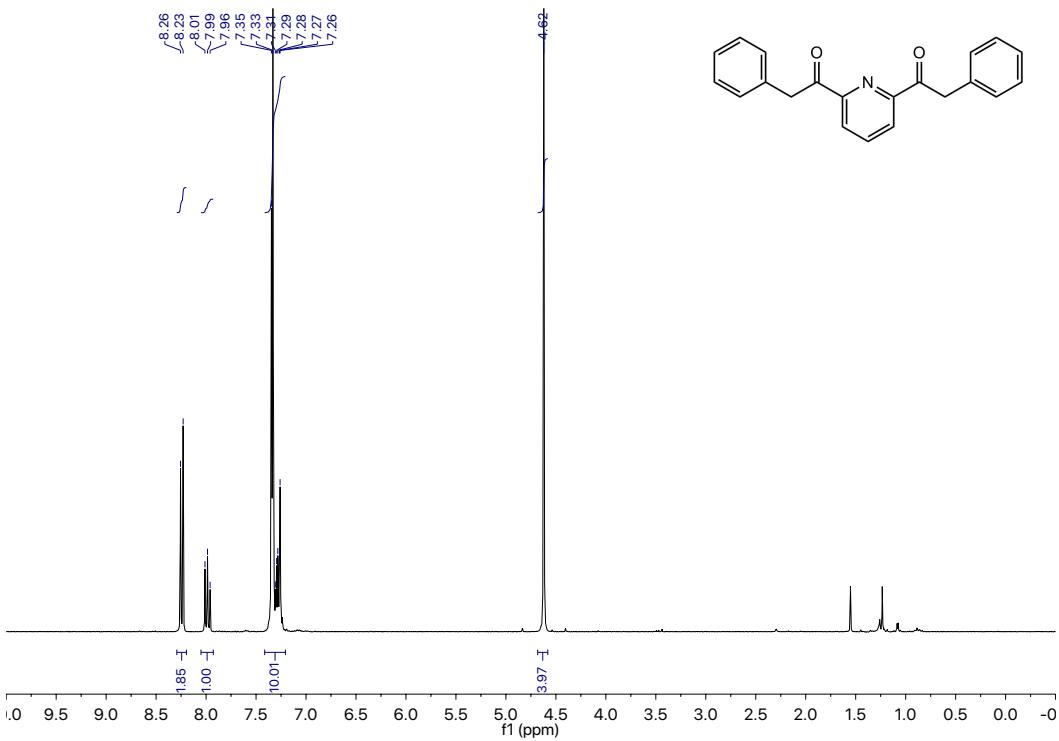


Figure S112. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **3q**.

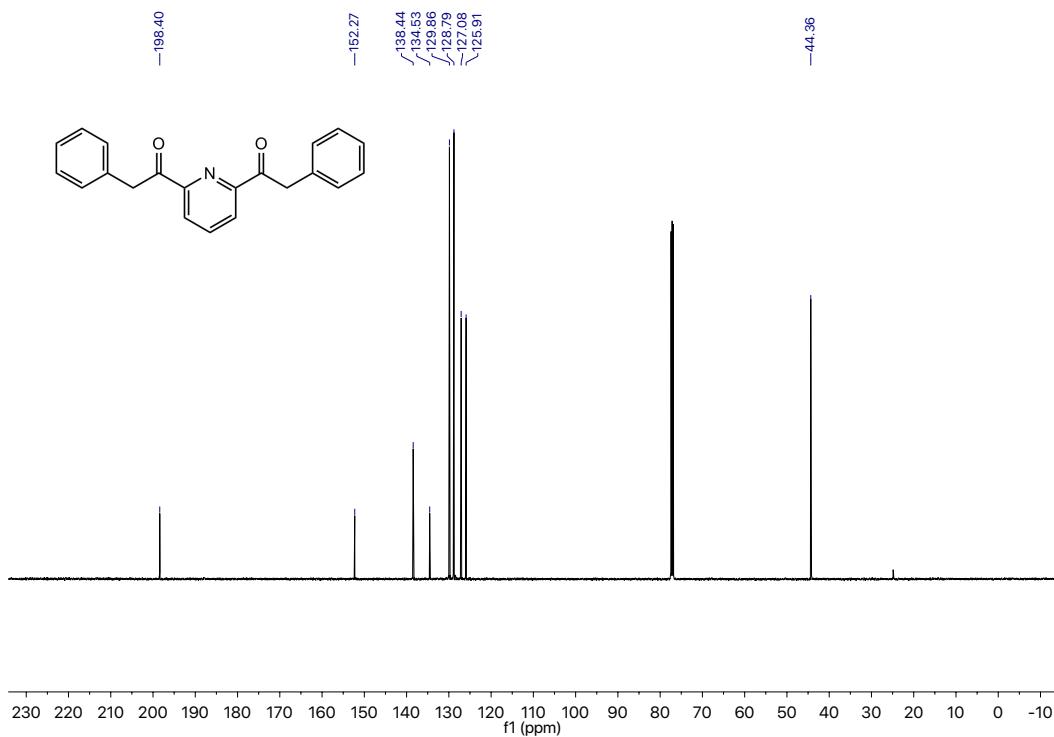


Figure S113. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 3q.

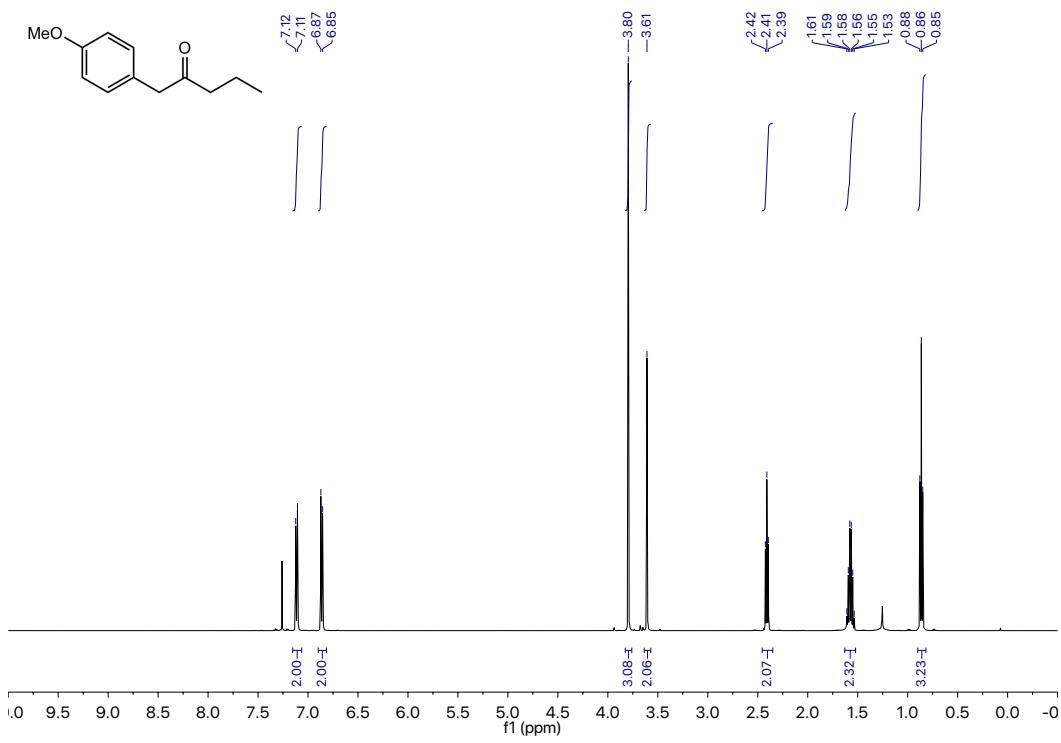


Figure S114. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of 3r.

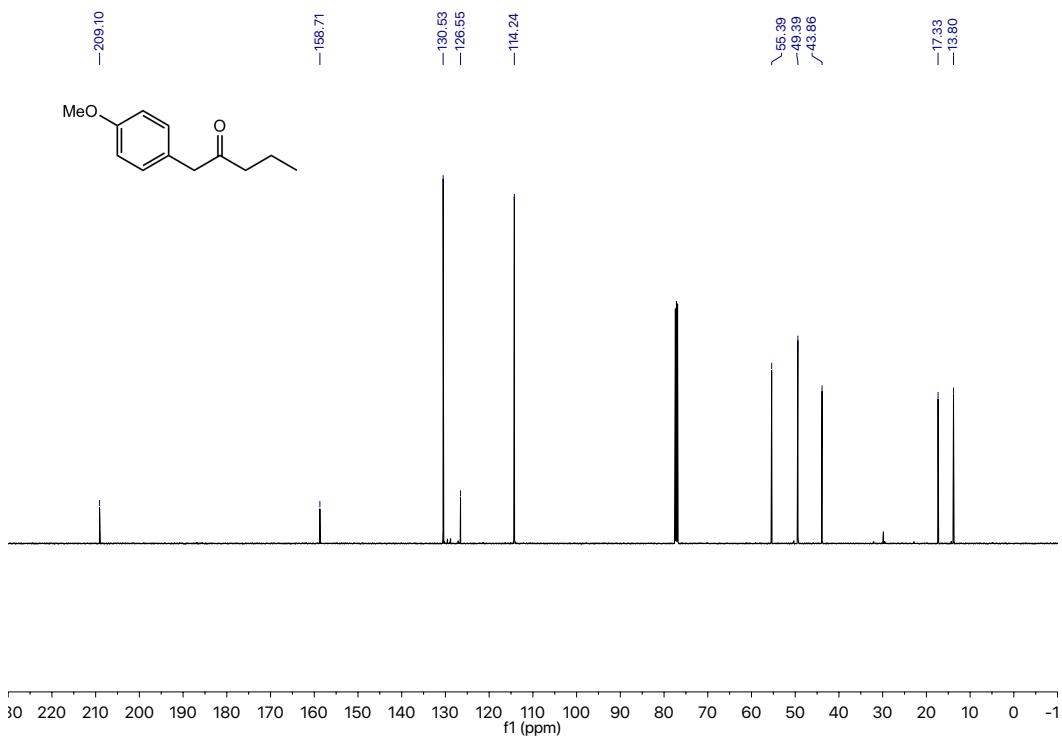


Figure S115. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3r**.

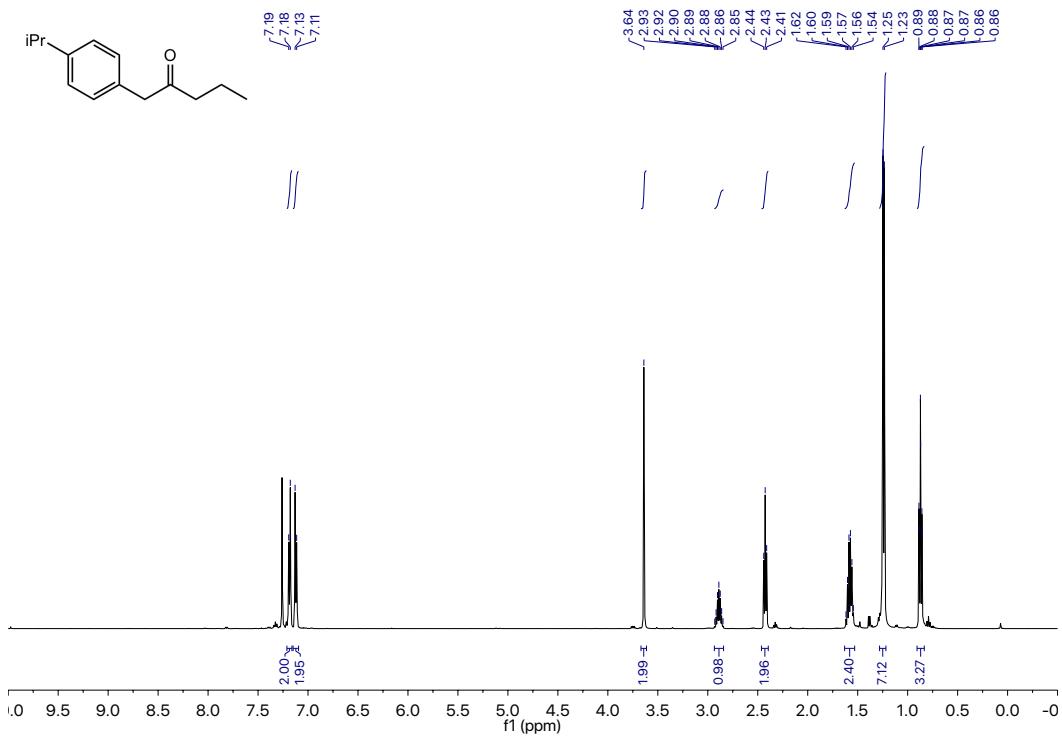


Figure S116. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3s**.

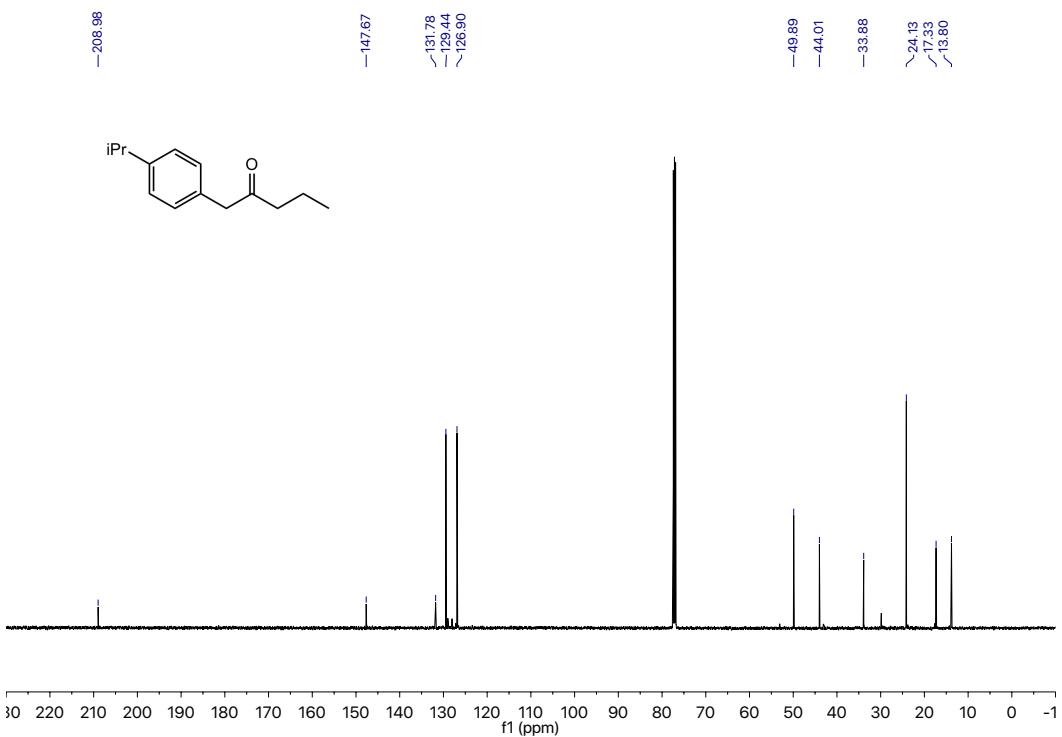


Figure S117. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3s**.

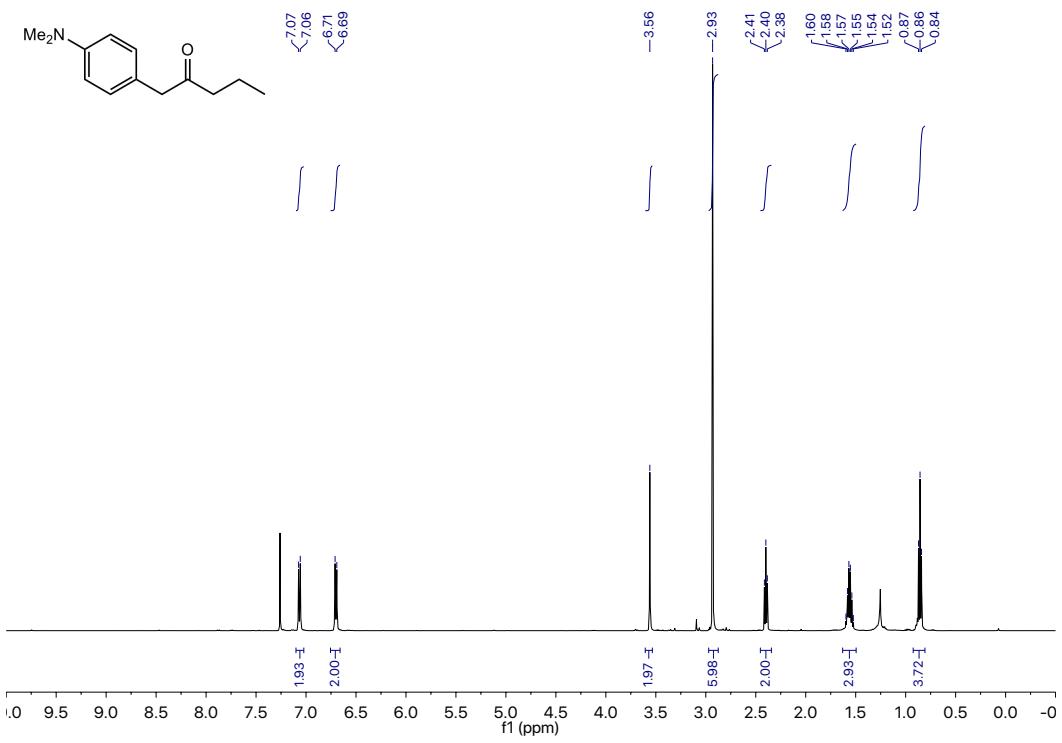


Figure S118. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3t**.

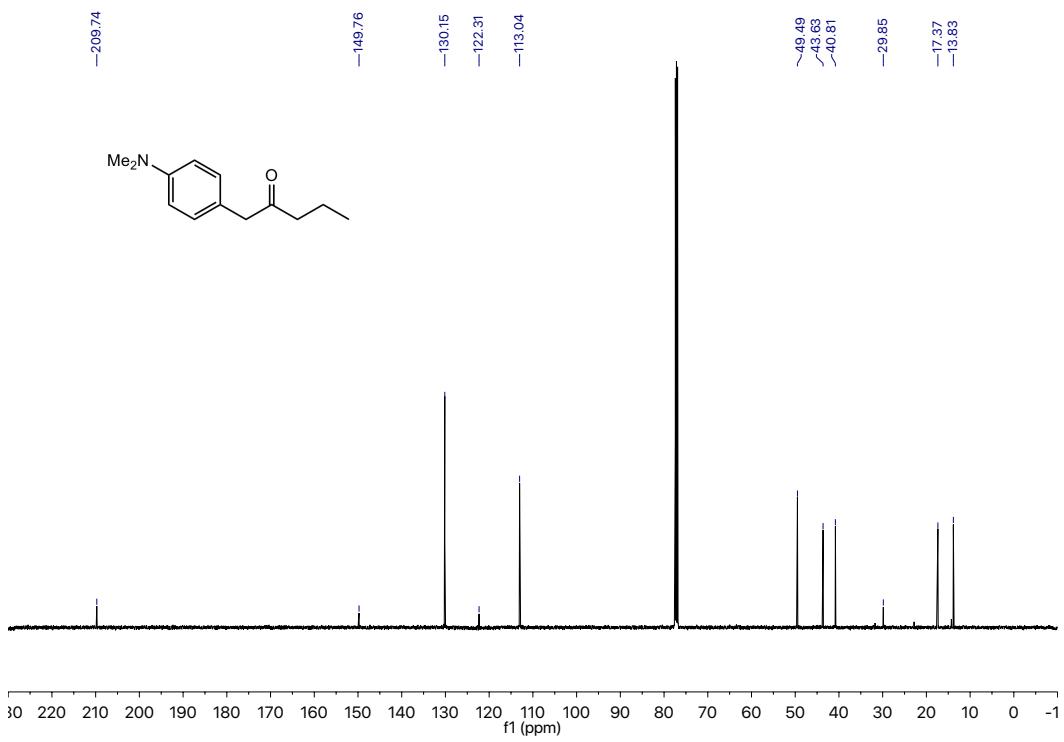


Figure S119. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 3t.

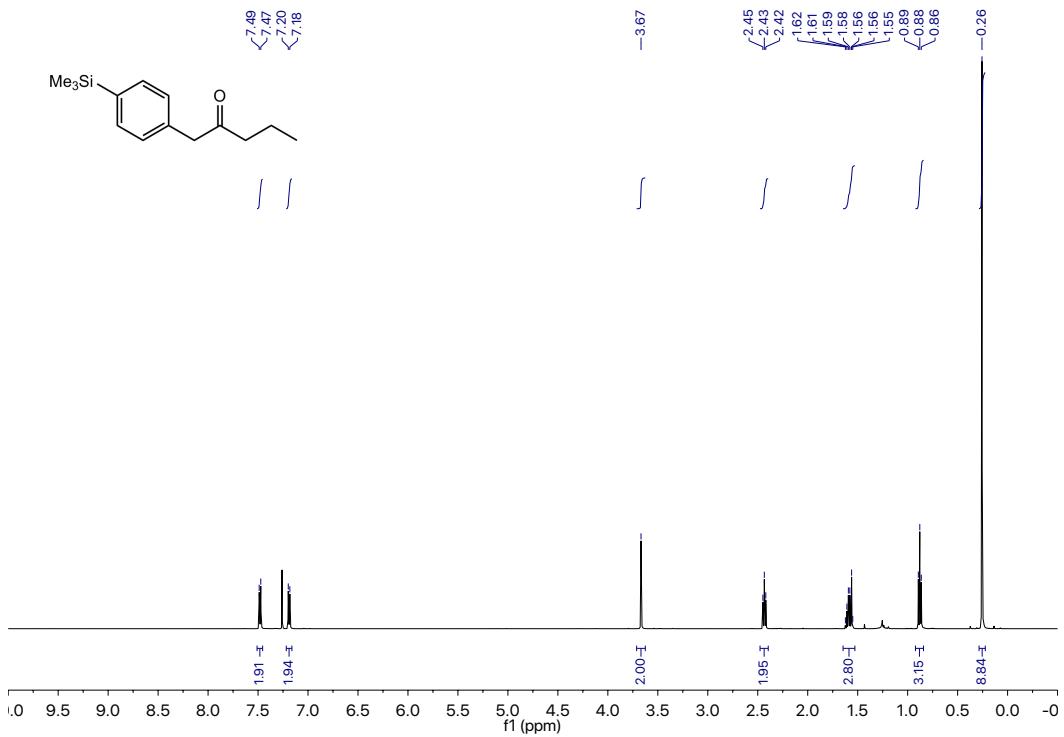


Figure S120. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of 3u.

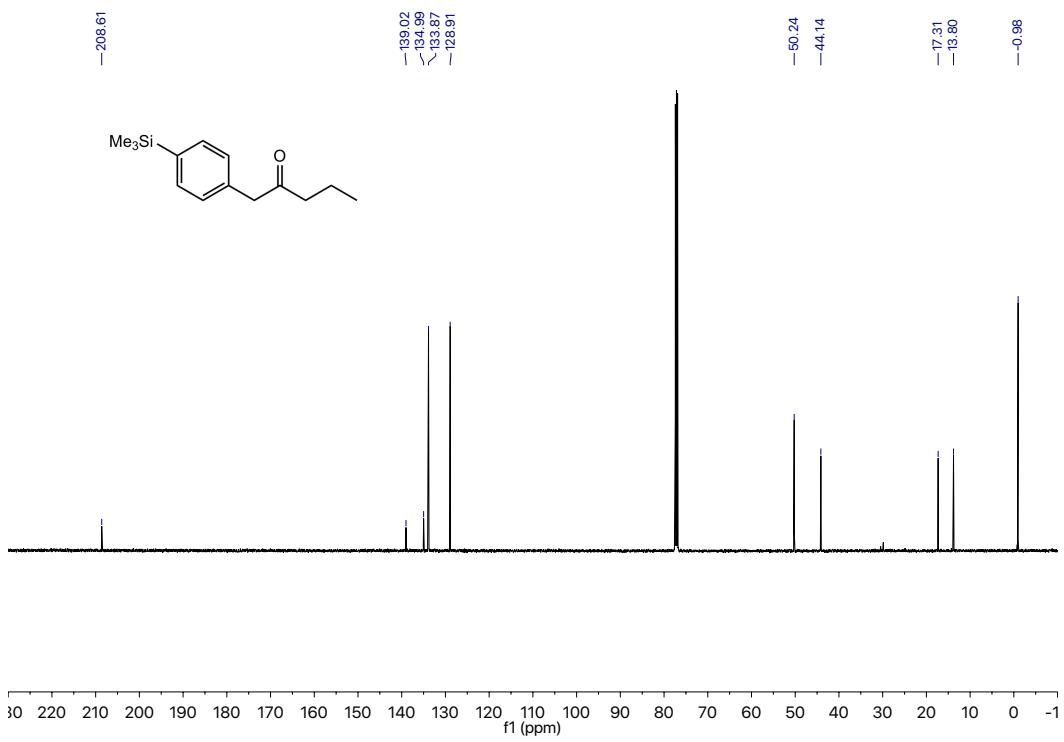


Figure S121. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3u**.

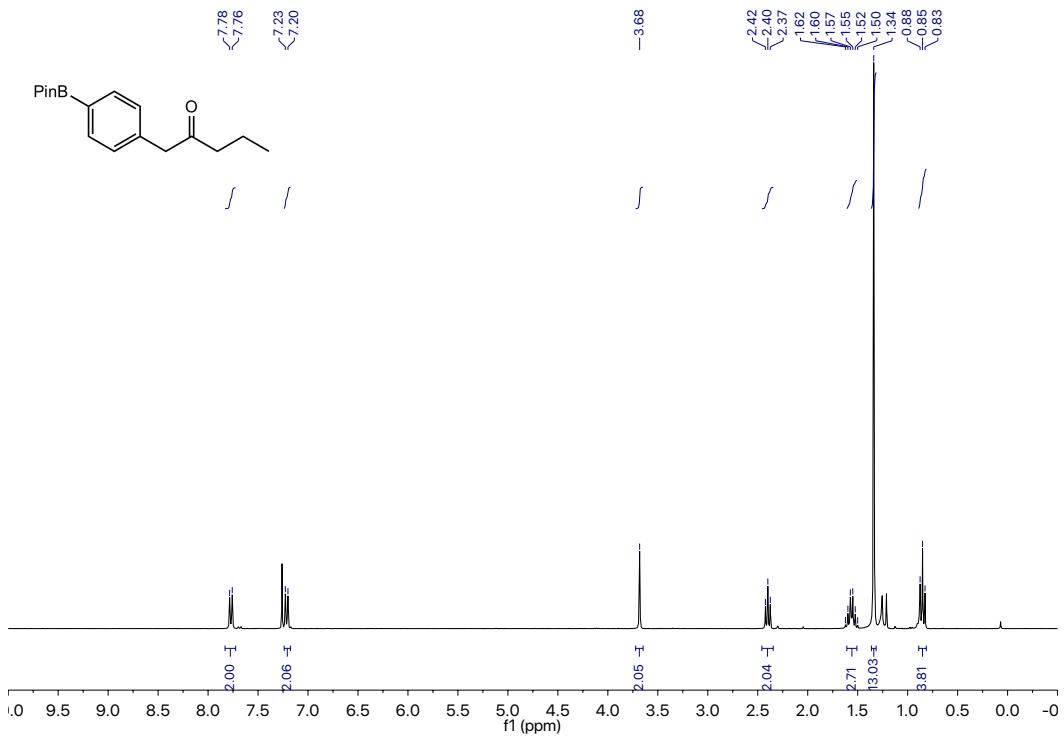


Figure S122. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **3v**.

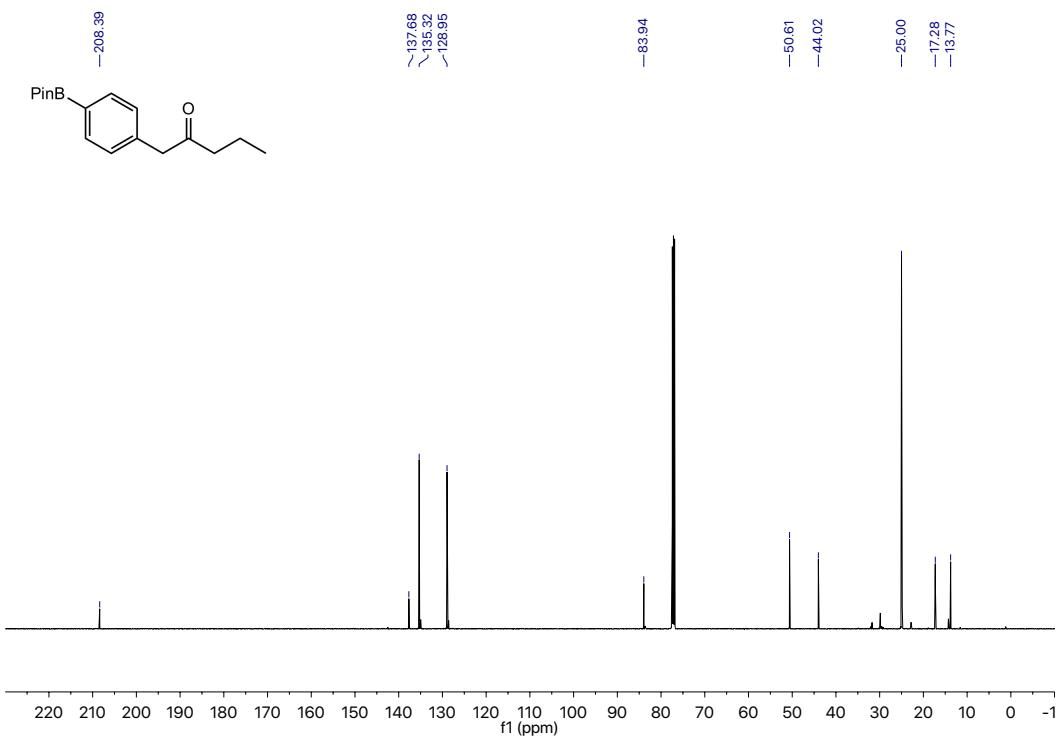


Figure S123. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 3v.

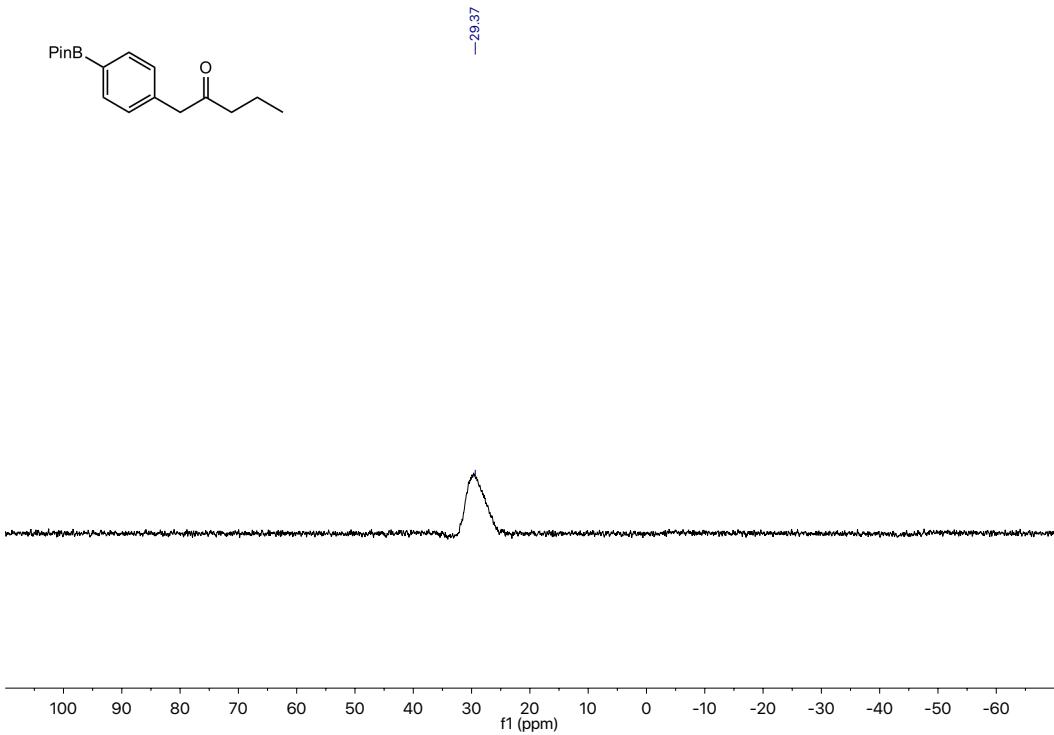


Figure S124. ^{11}B NMR spectrum (96 MHz, chloroform-*d*, 23 °C) of 3v.

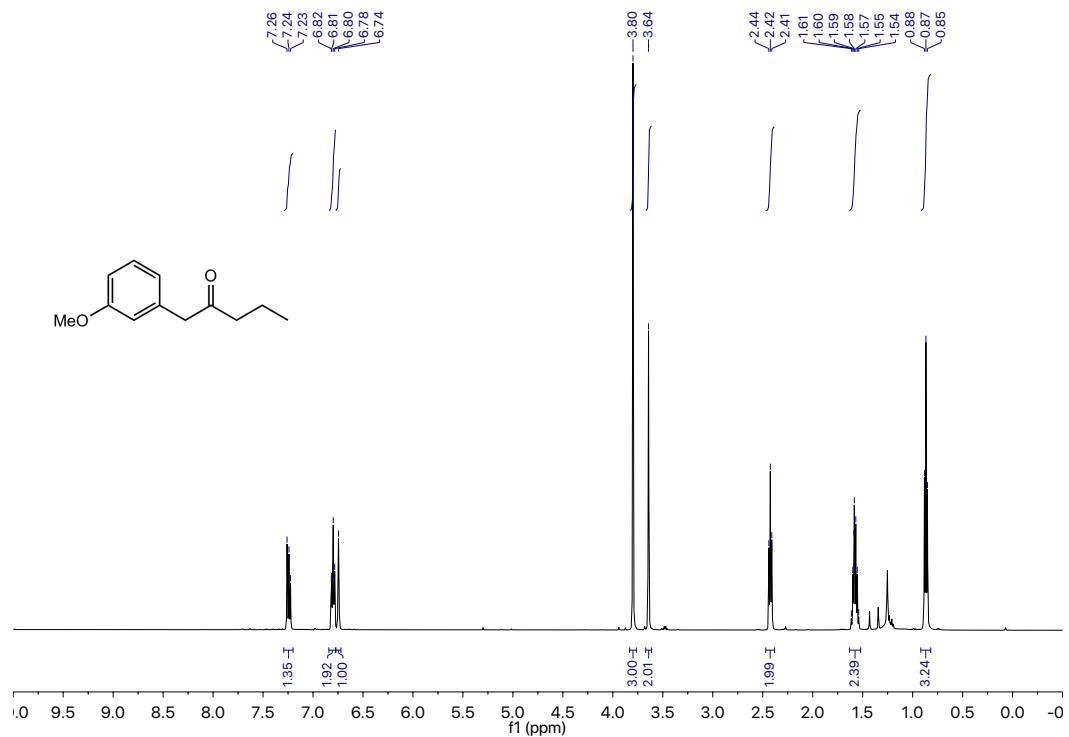


Figure S125. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3w**.

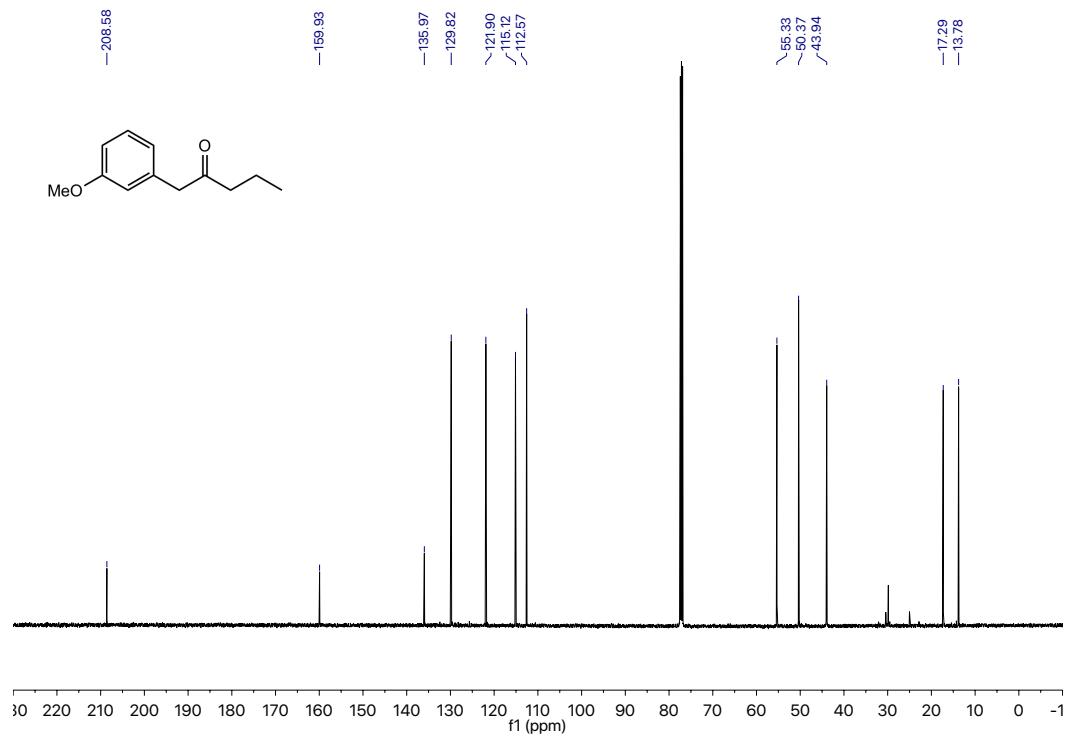


Figure S126. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3w**.

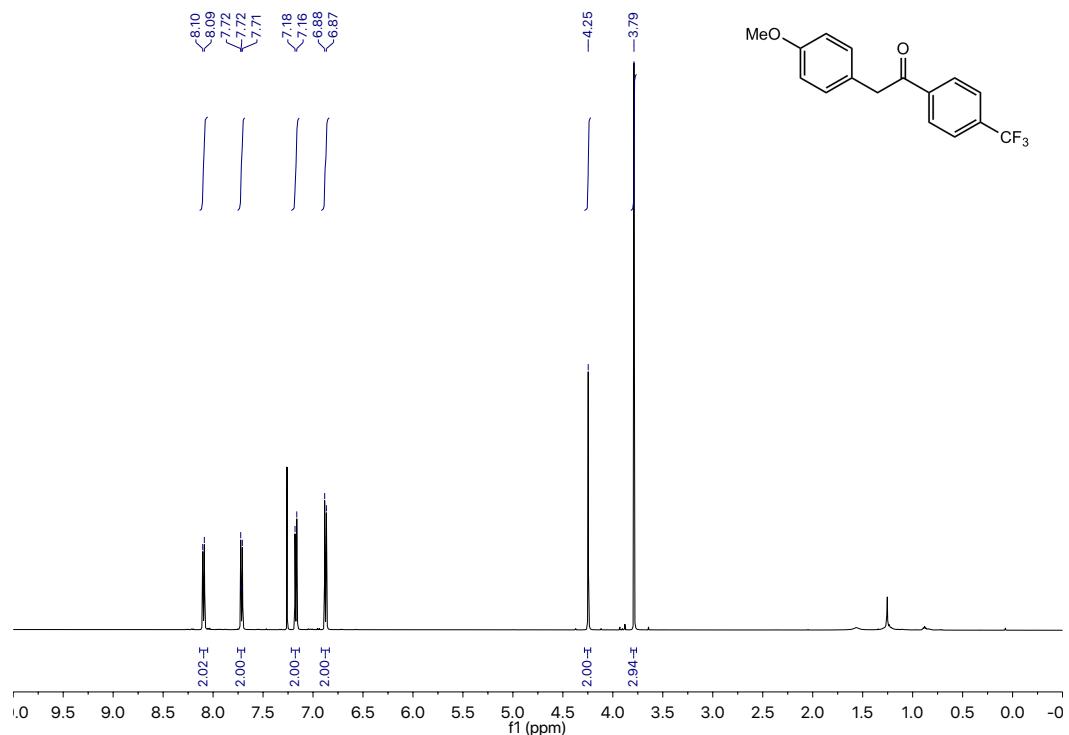


Figure S127. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3x**.

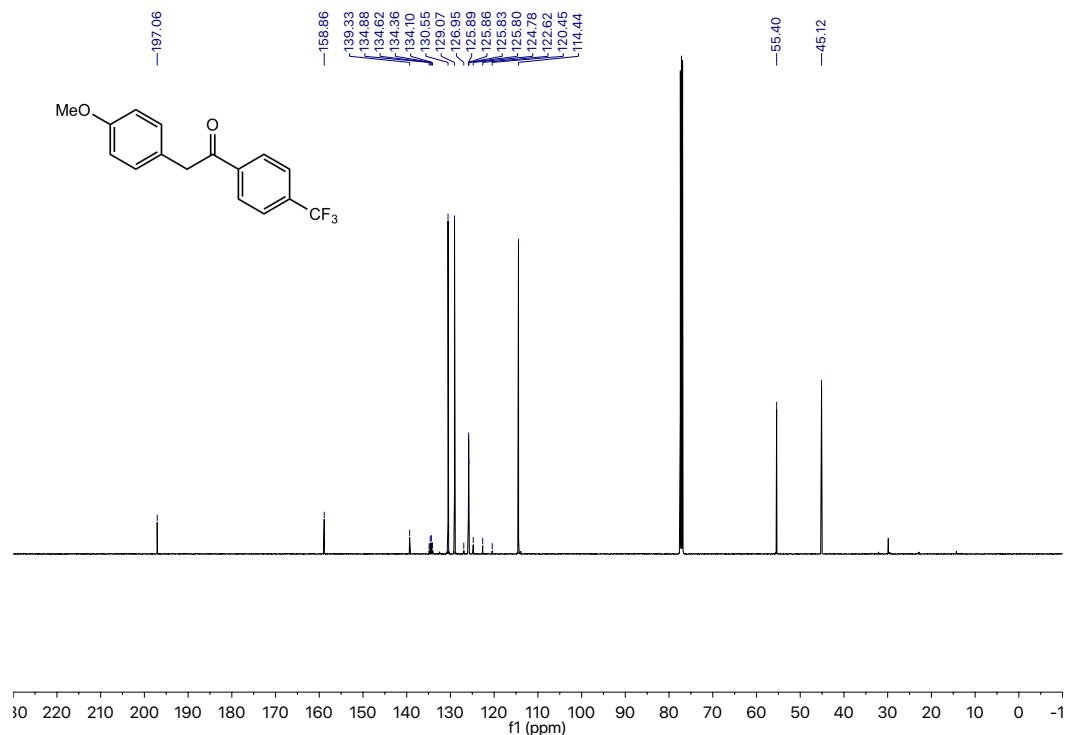


Figure S128. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3x**.

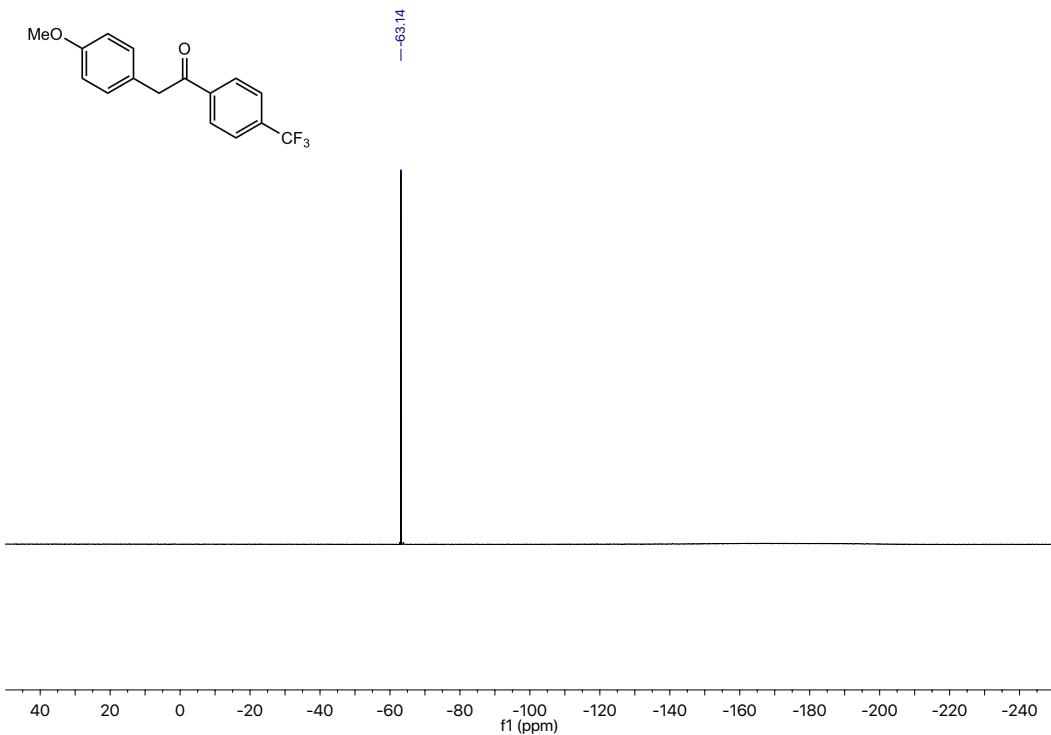


Figure S129. ¹⁹F NMR spectrum (282 MHz, chloroform-d, 23 °C) of **3x**.

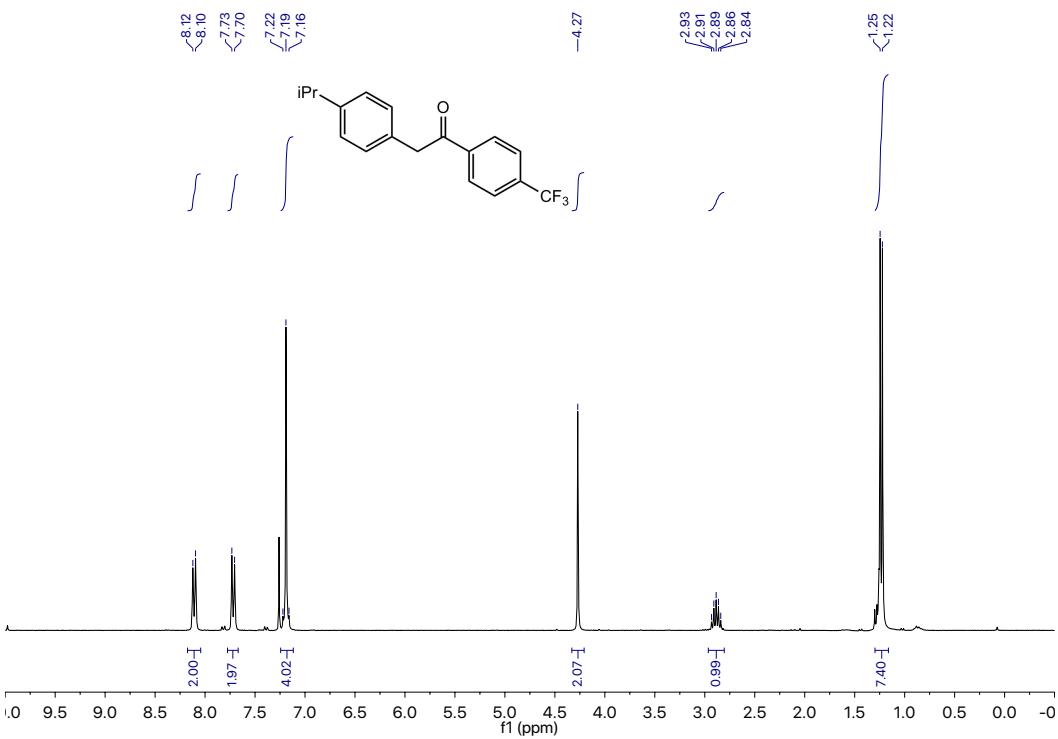


Figure S130. ¹H NMR spectrum (500 MHz, chloroform-d, 23 °C) of **3y**.

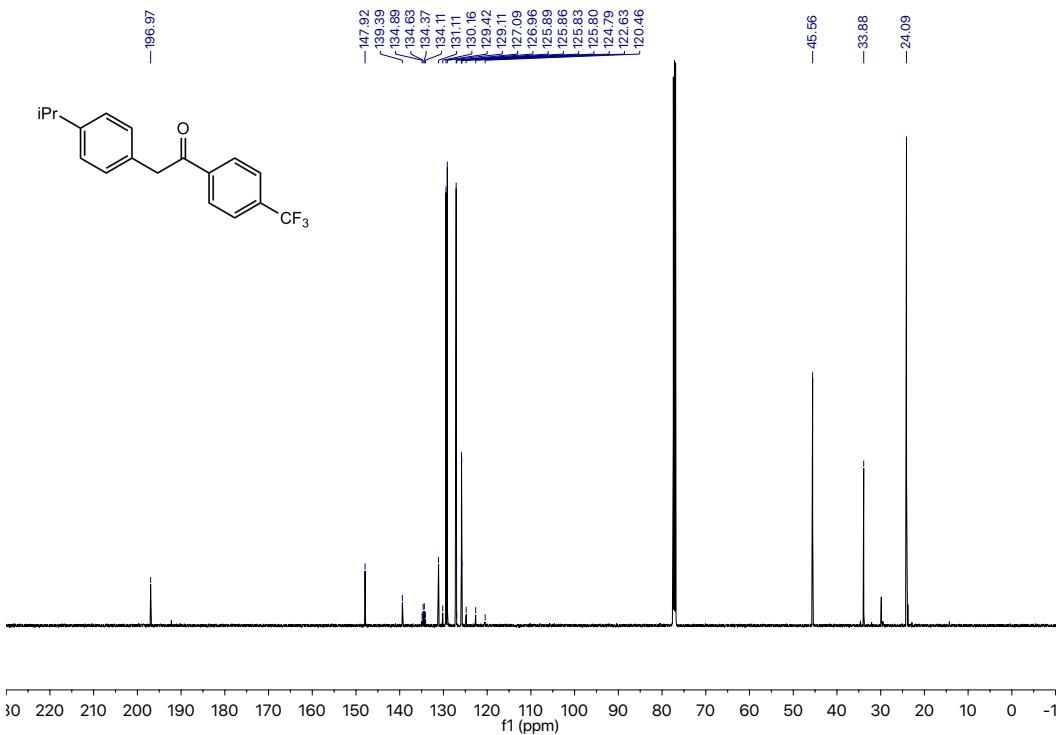


Figure S131. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3y**.

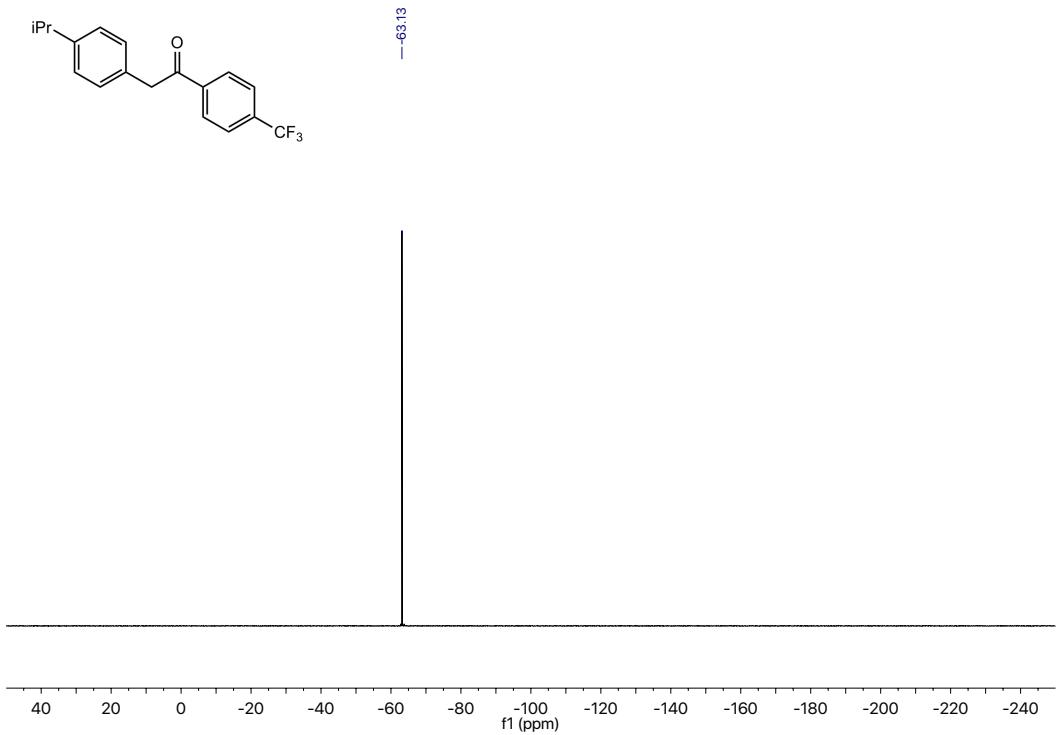


Figure S132. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3y**.

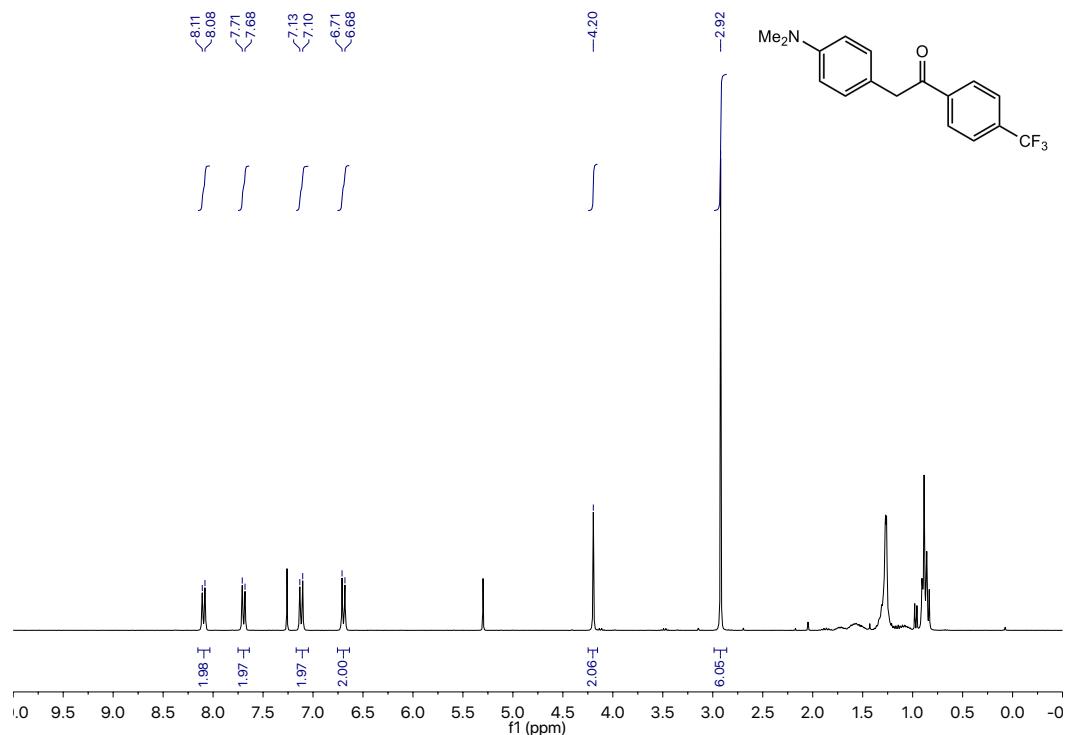


Figure S133. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **3z**.

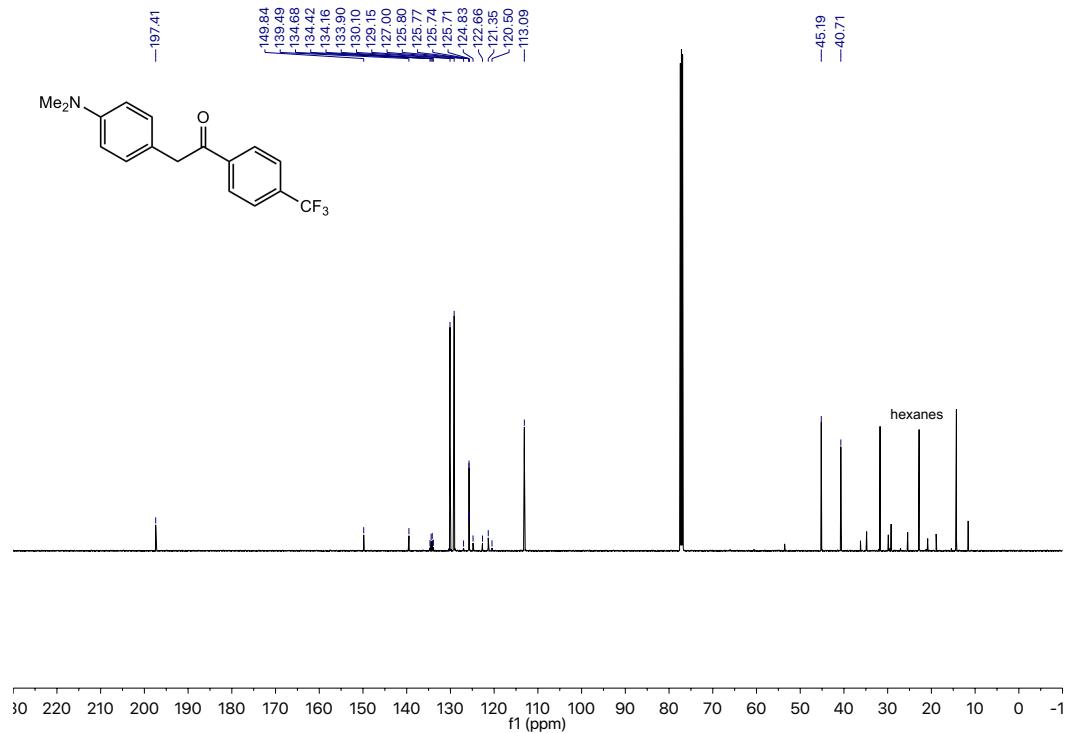


Figure S134. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3z**.

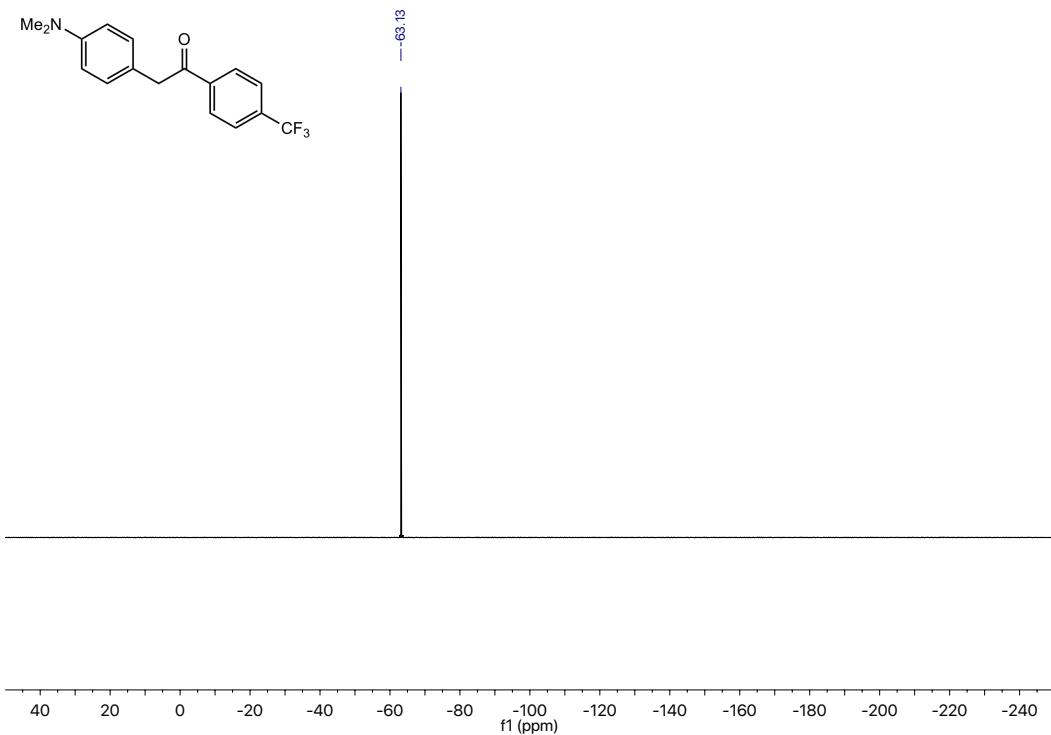


Figure S135. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3z**.

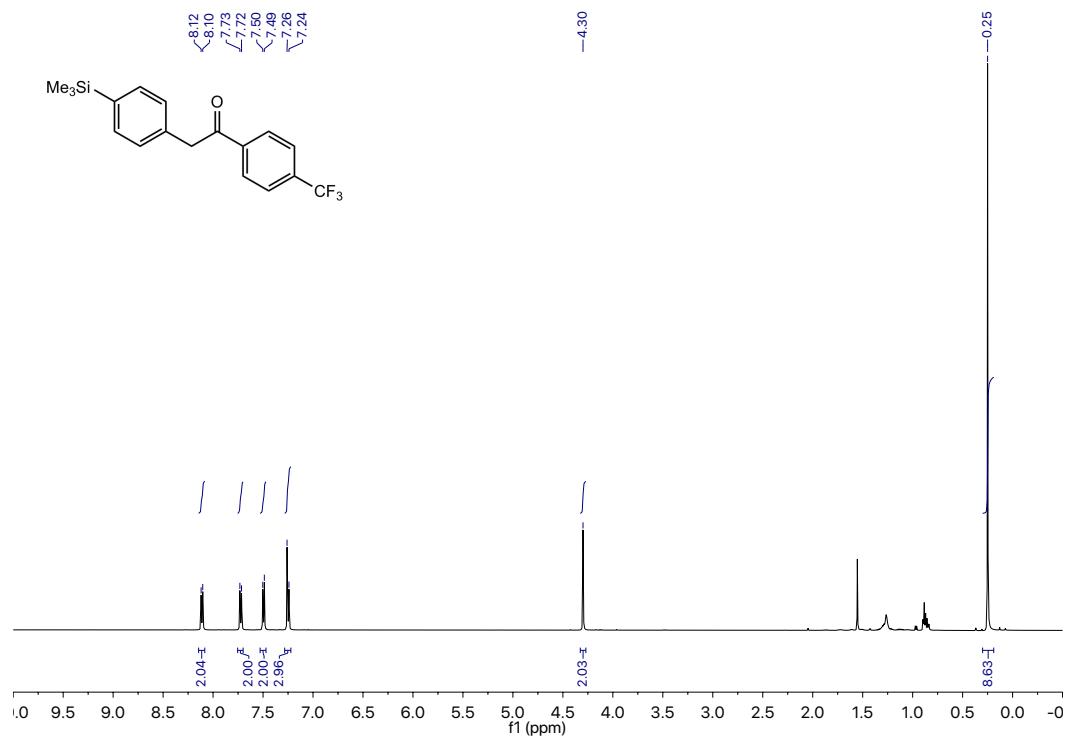


Figure S136. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3aa**.

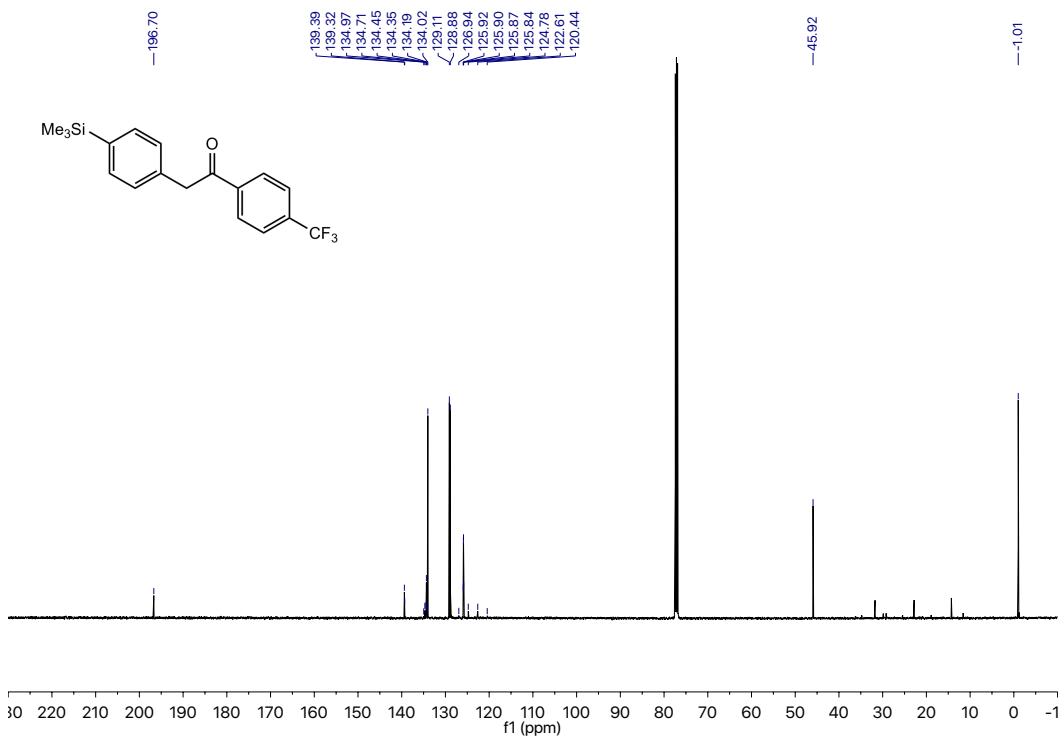


Figure S137. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 3aa.

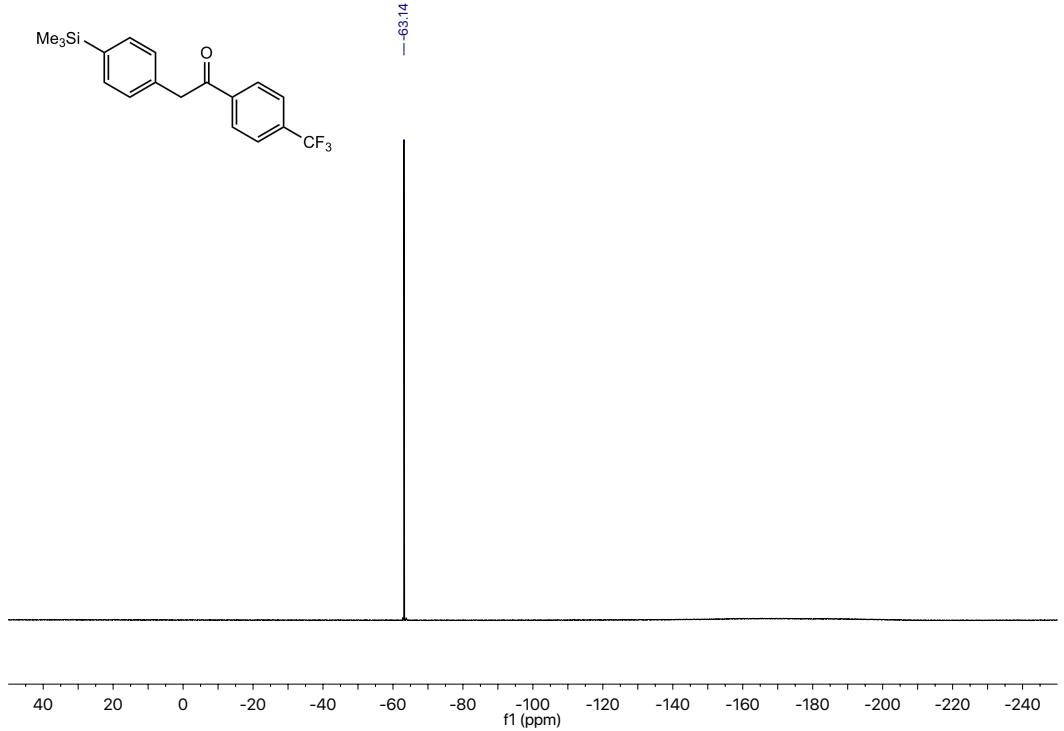


Figure S138. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of 3aa.

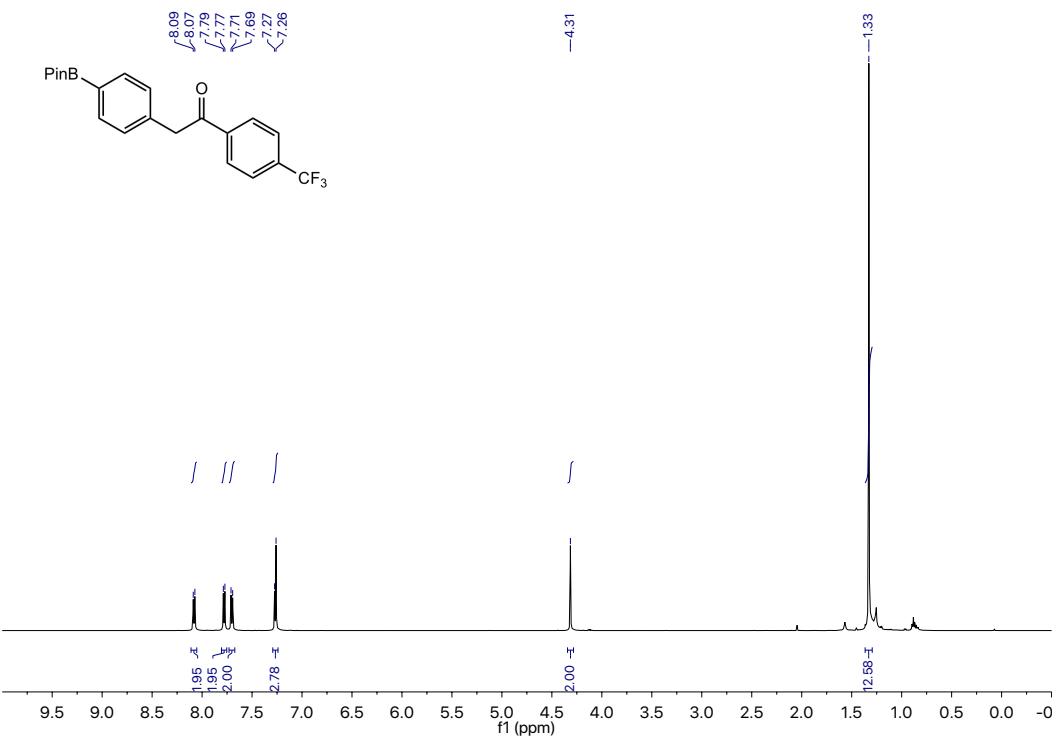


Figure S139. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3ab**.

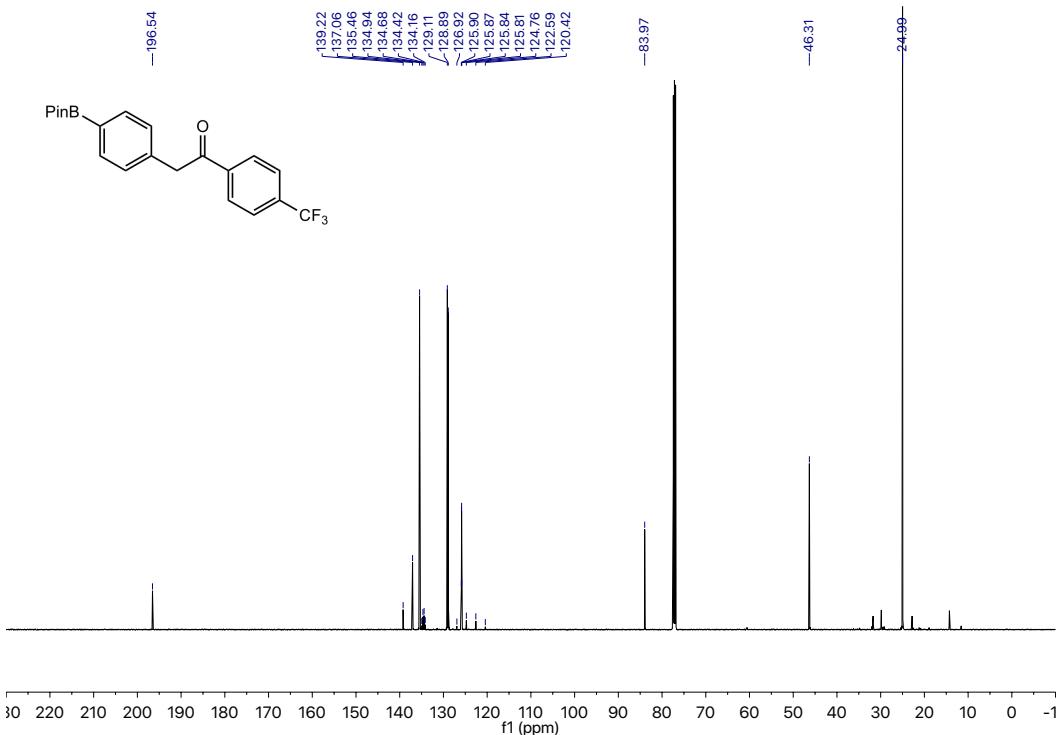


Figure S140. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3ab**.

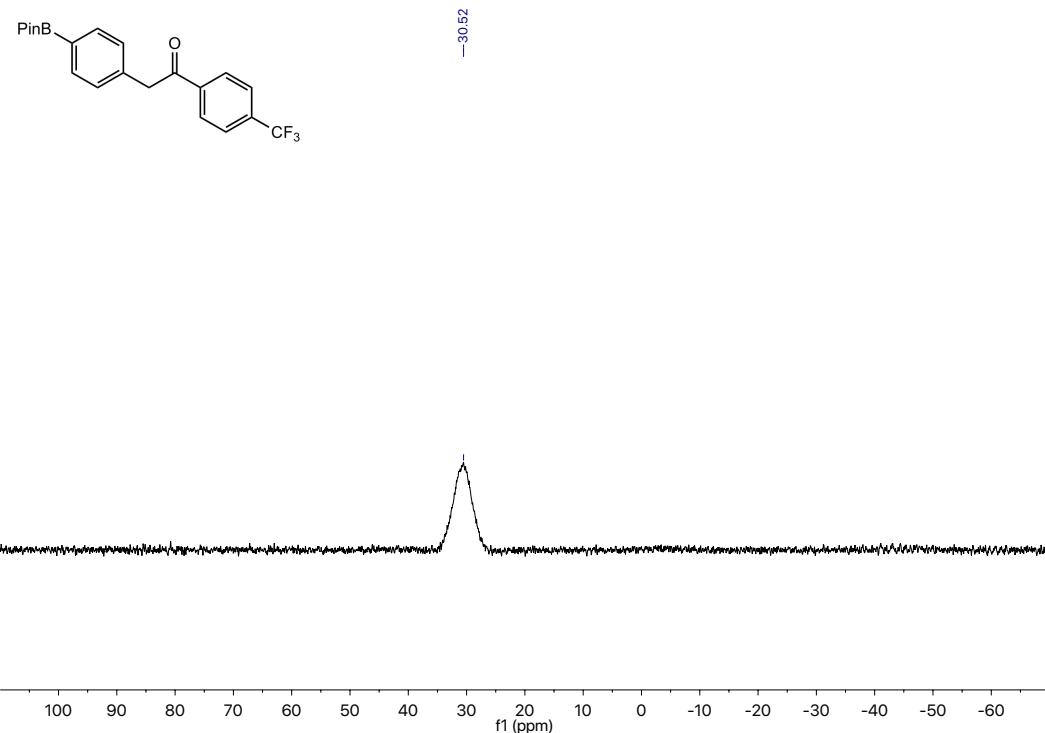


Figure S141. ^{11}B NMR spectrum (96 MHz, chloroform-*d*, 23 °C) of **3ab**.

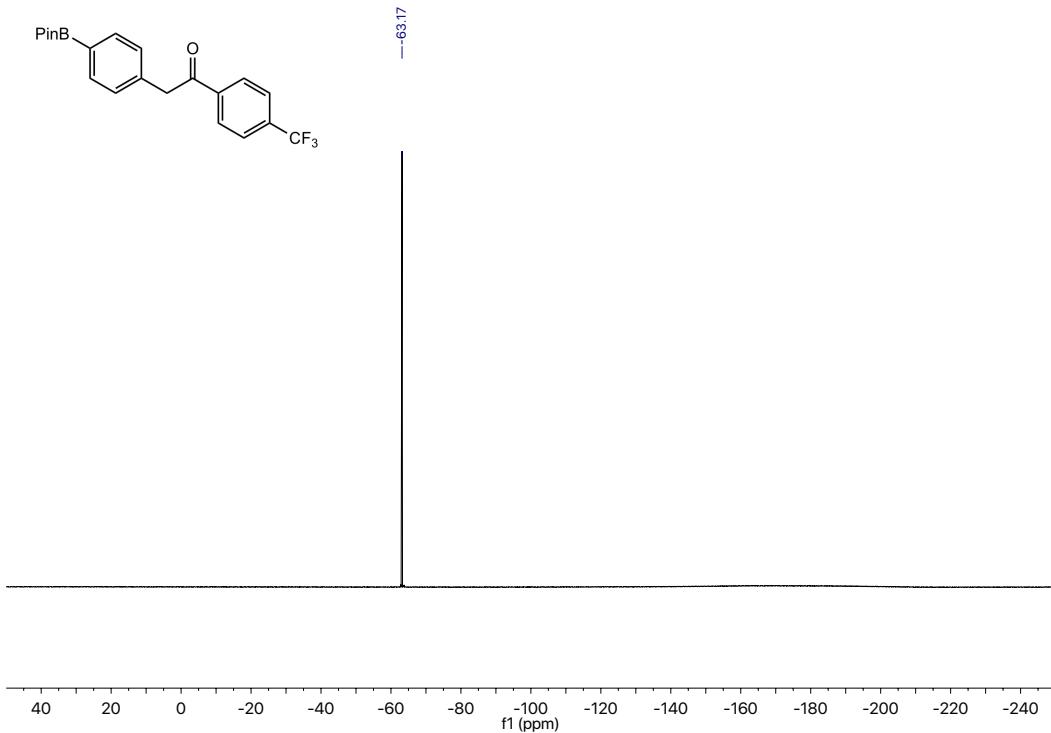


Figure S142. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3ab**.

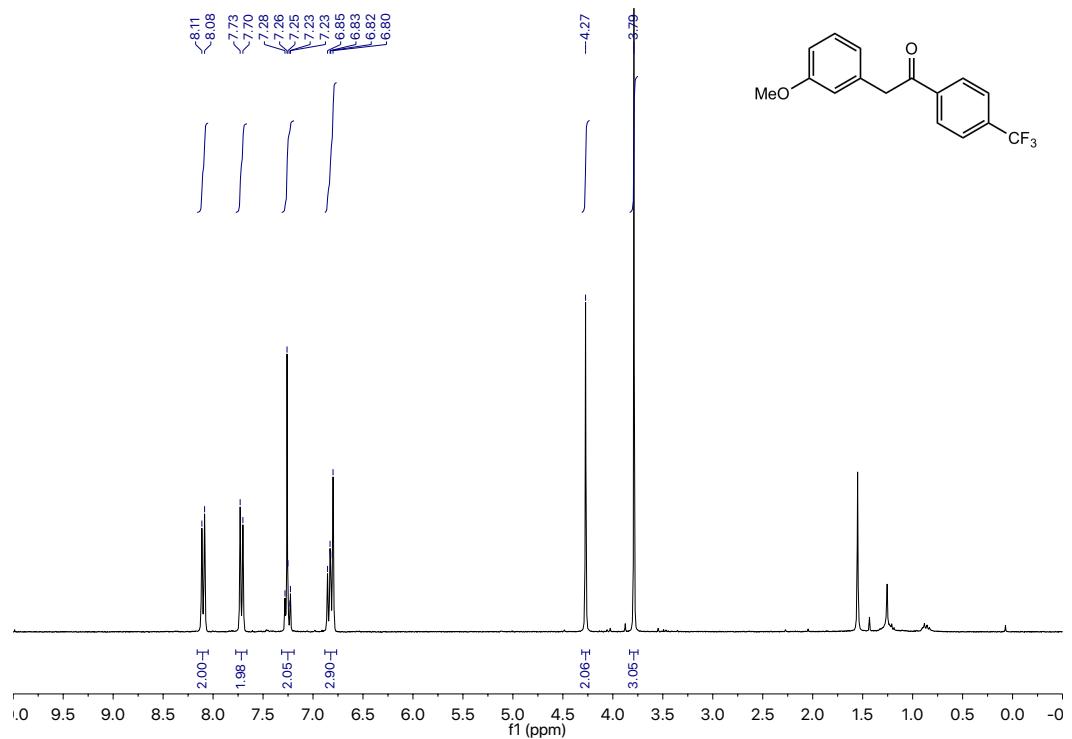


Figure S143. ¹H NMR spectrum (300 MHz, chloroform-d, 23 °C) of 3ac.

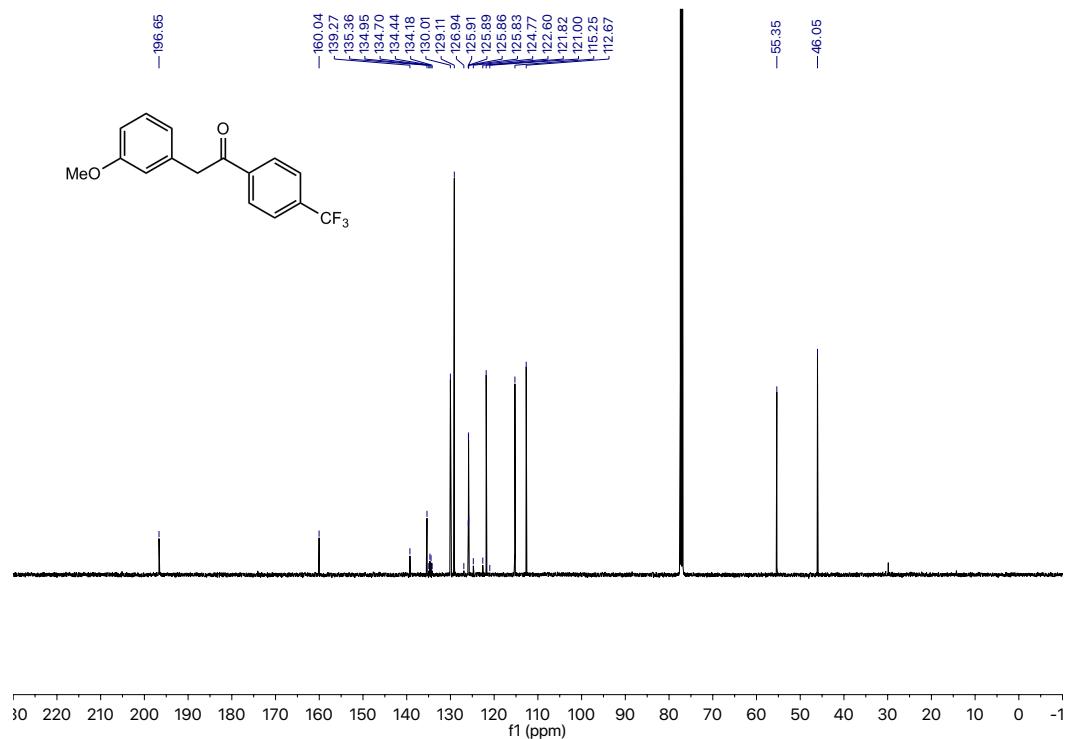


Figure S144. ¹³C{¹H} NMR spectrum (126 MHz, chloroform-d, 23 °C) of 3ac.

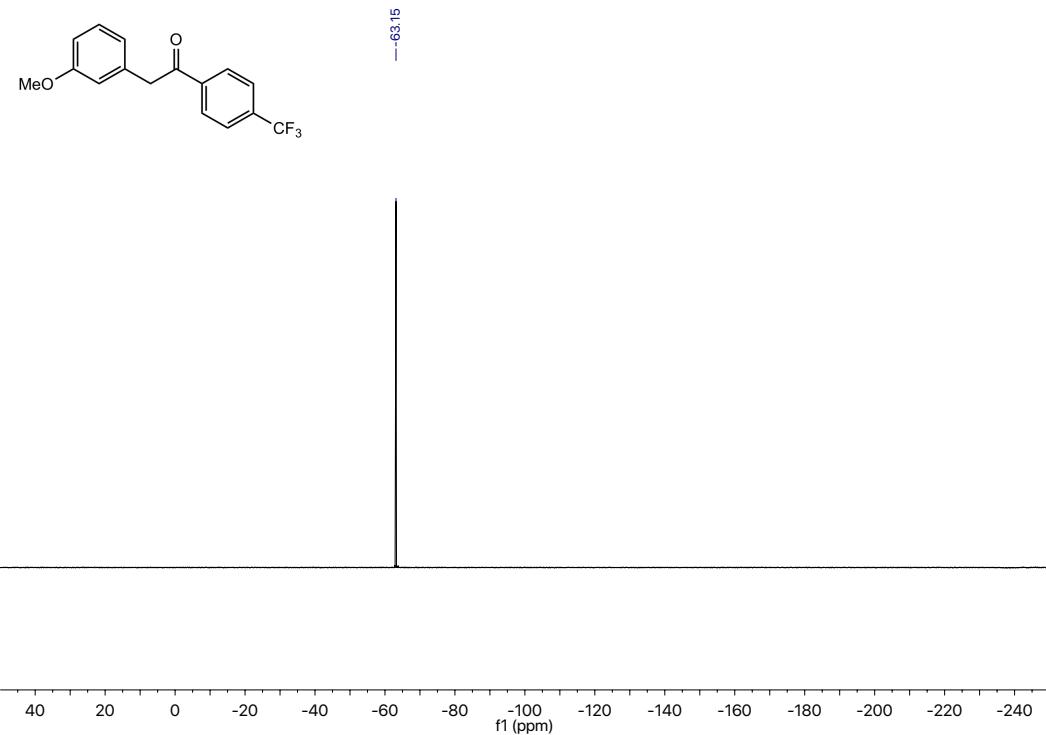


Figure S145. ¹⁹F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **3ac**.

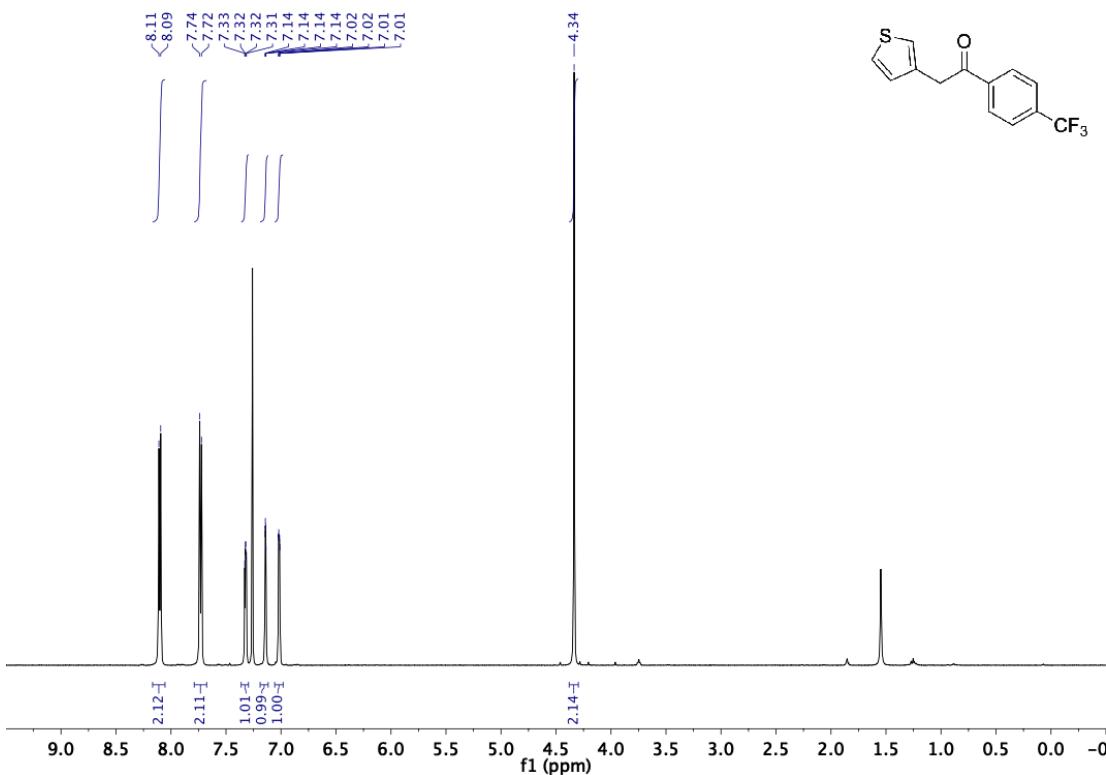


Figure S146. ¹H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3ad**.

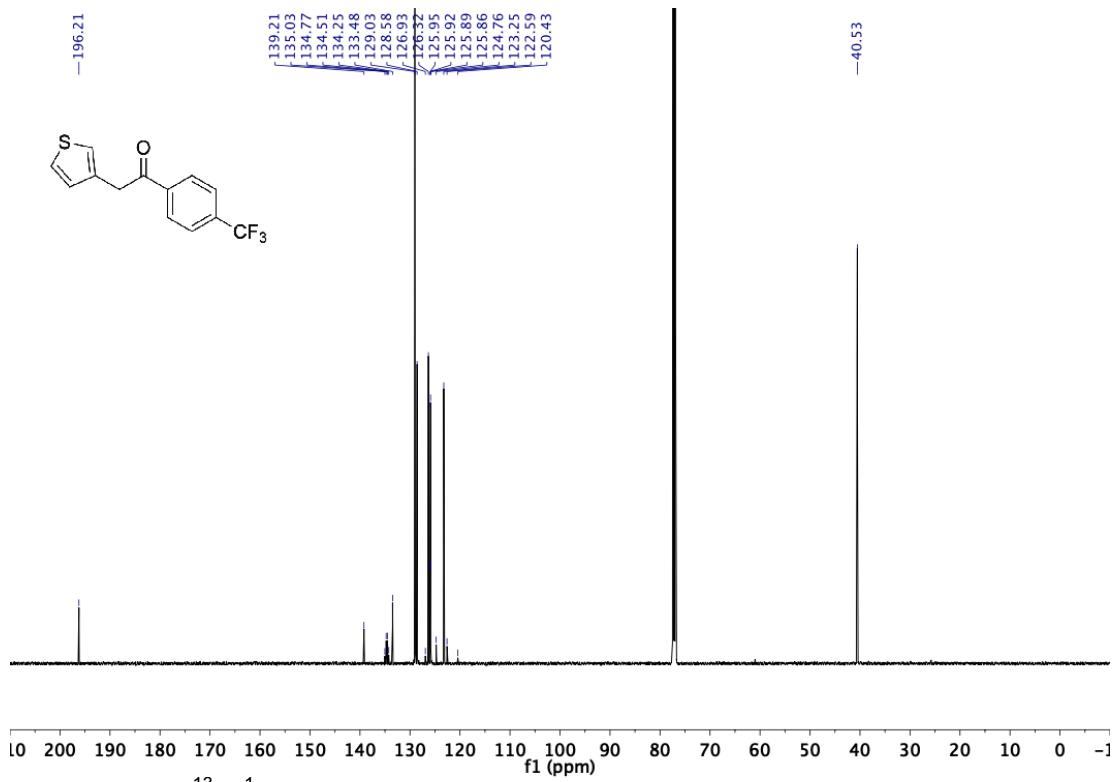


Figure S147. $^{13}\text{C}\{\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C) of 3ad.

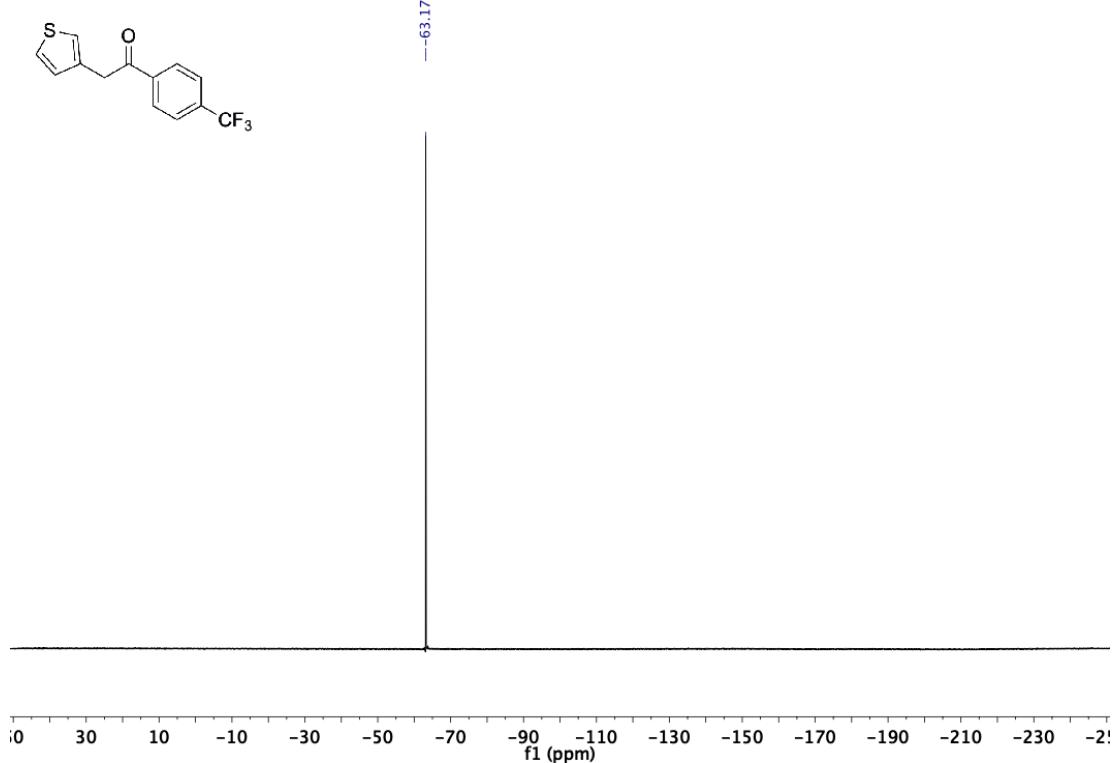


Figure S148. ^{19}F NMR (282 MHz, chloroform-*d*, 23 °C) of 3ad.

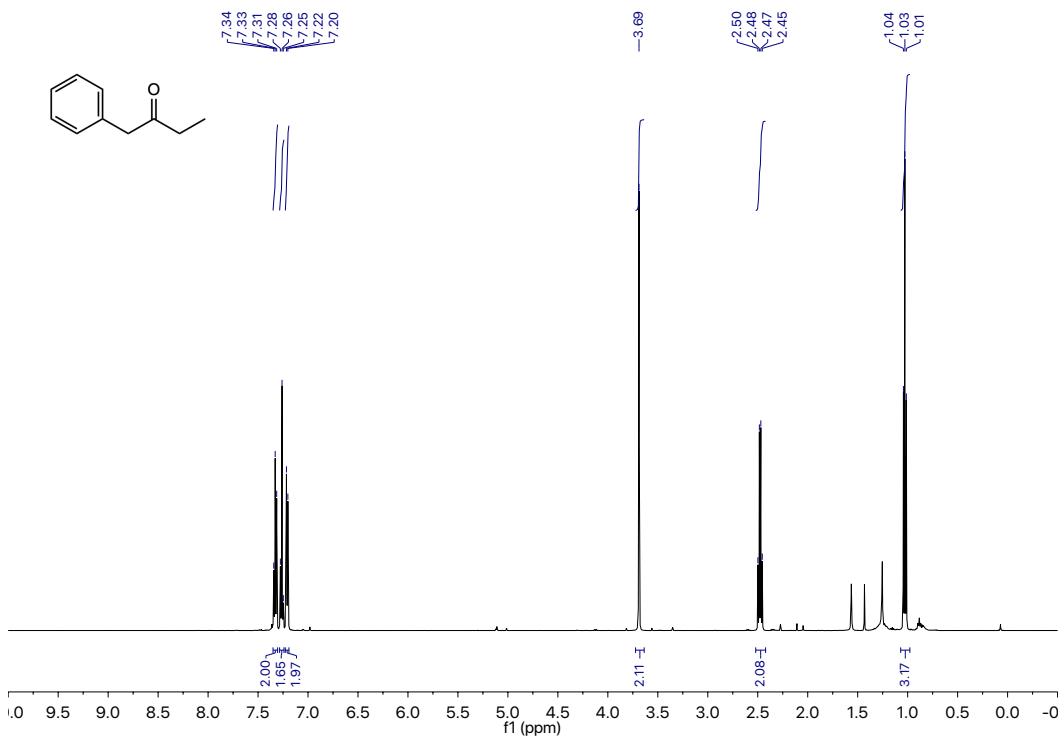


Figure S149. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3ae**.

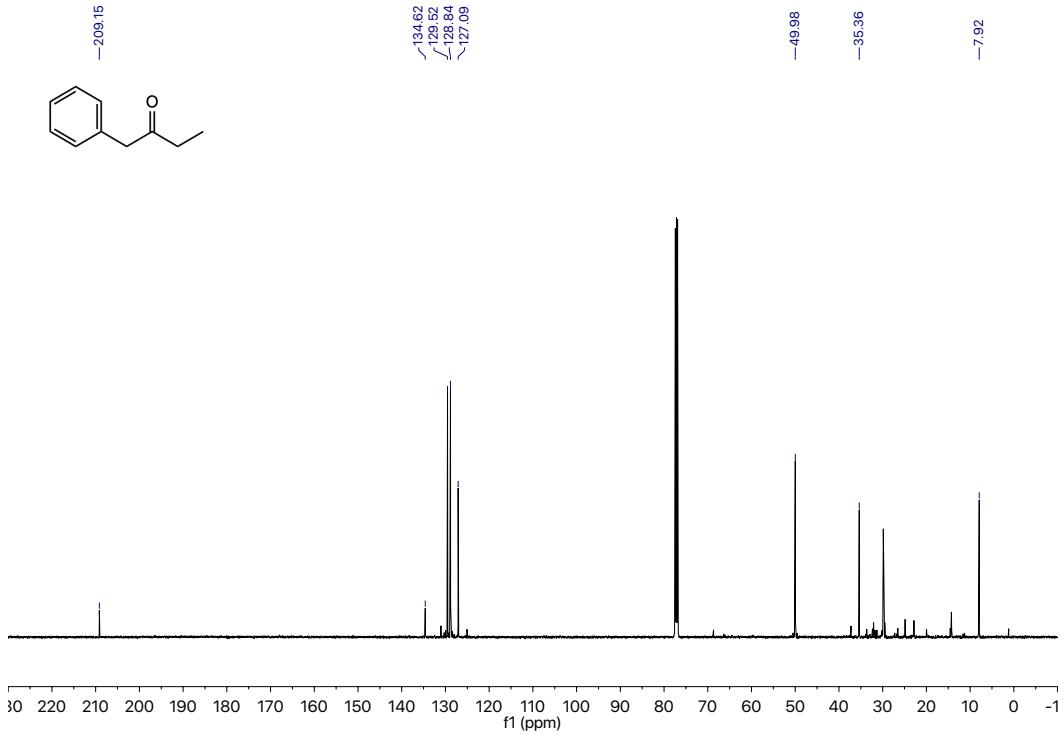


Figure S150. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3ae**.

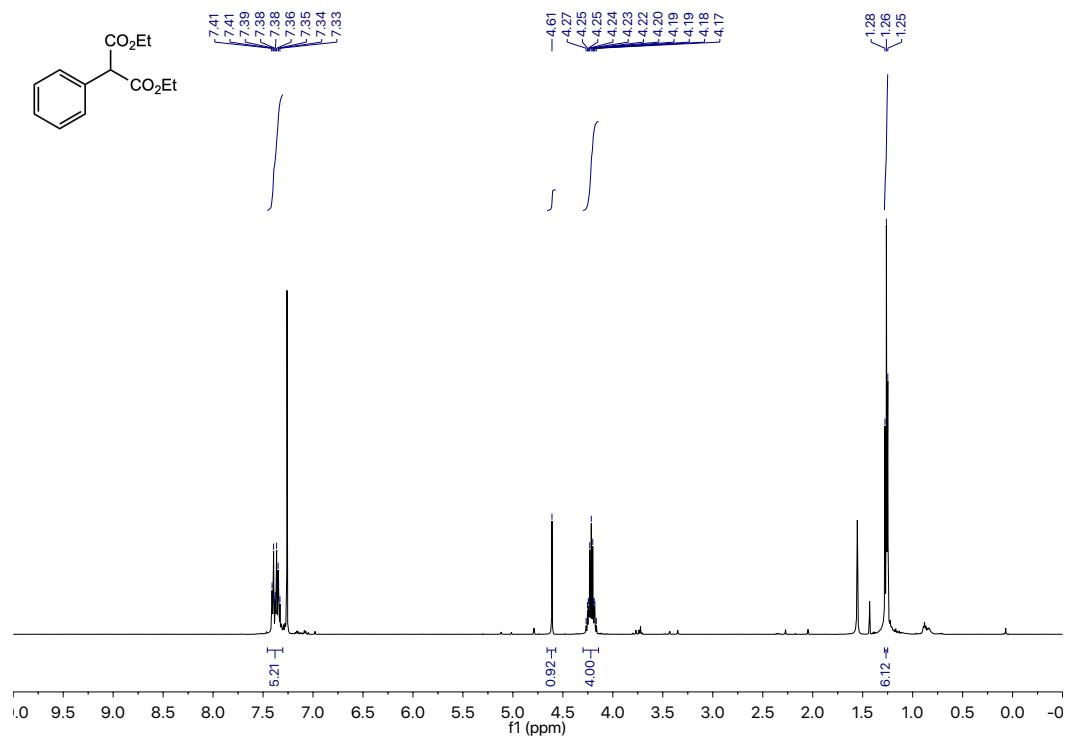


Figure S151. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **3af**.

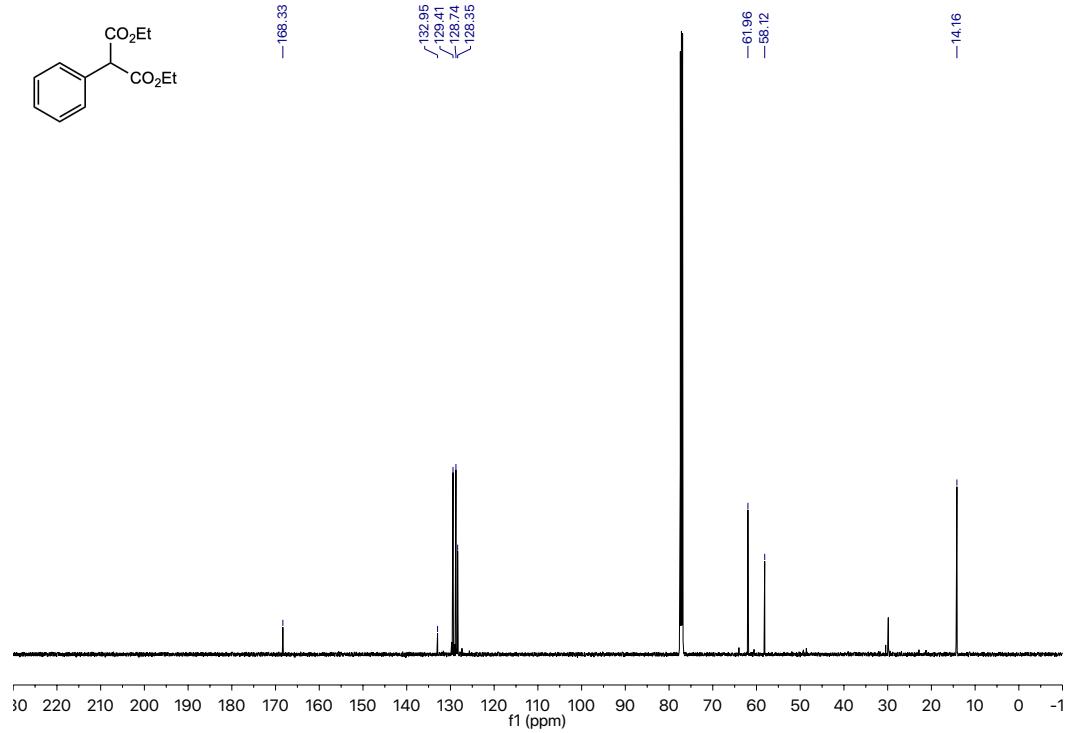


Figure S152. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **3af**.

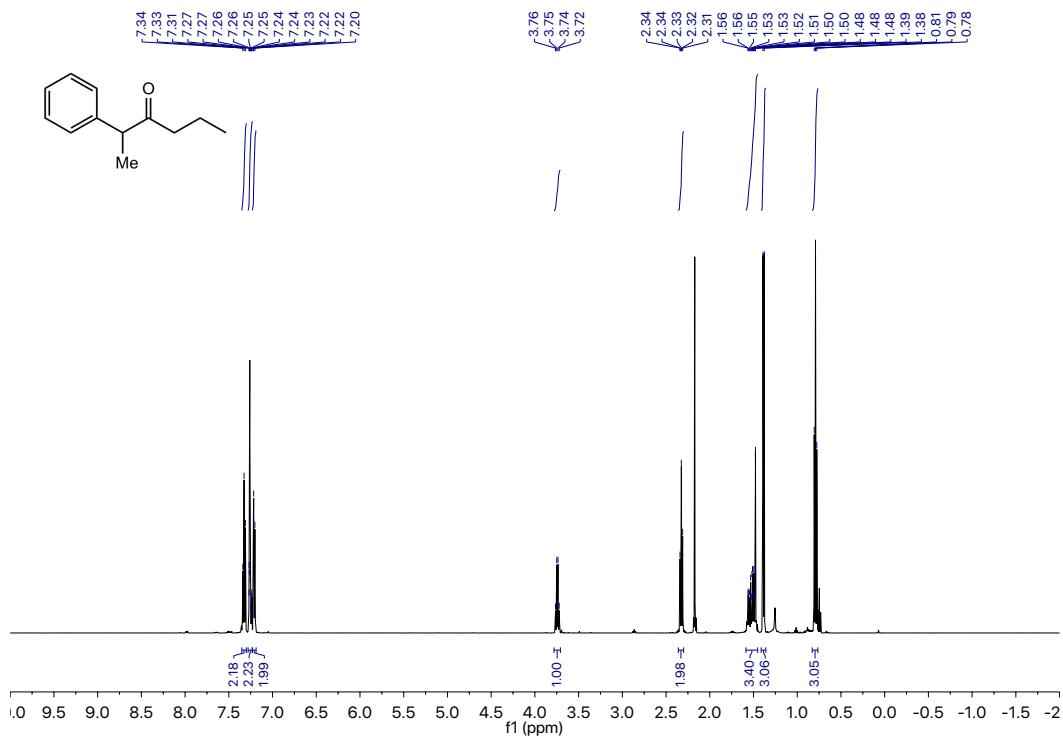


Figure S153. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of 14a.

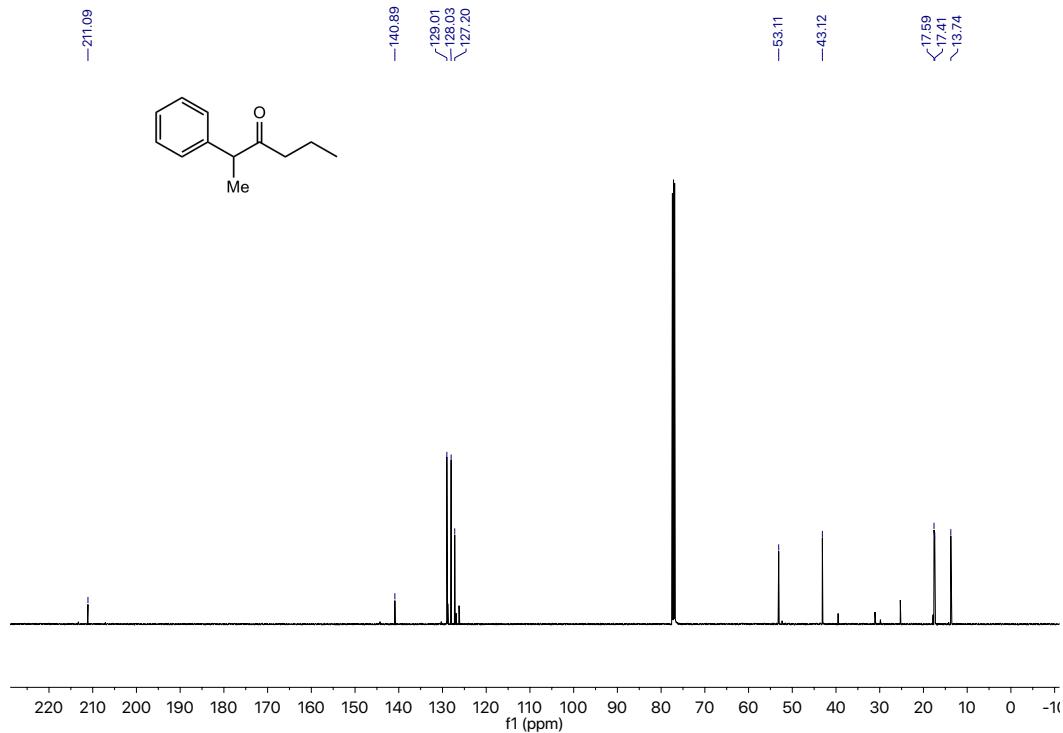


Figure S154. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 14a.

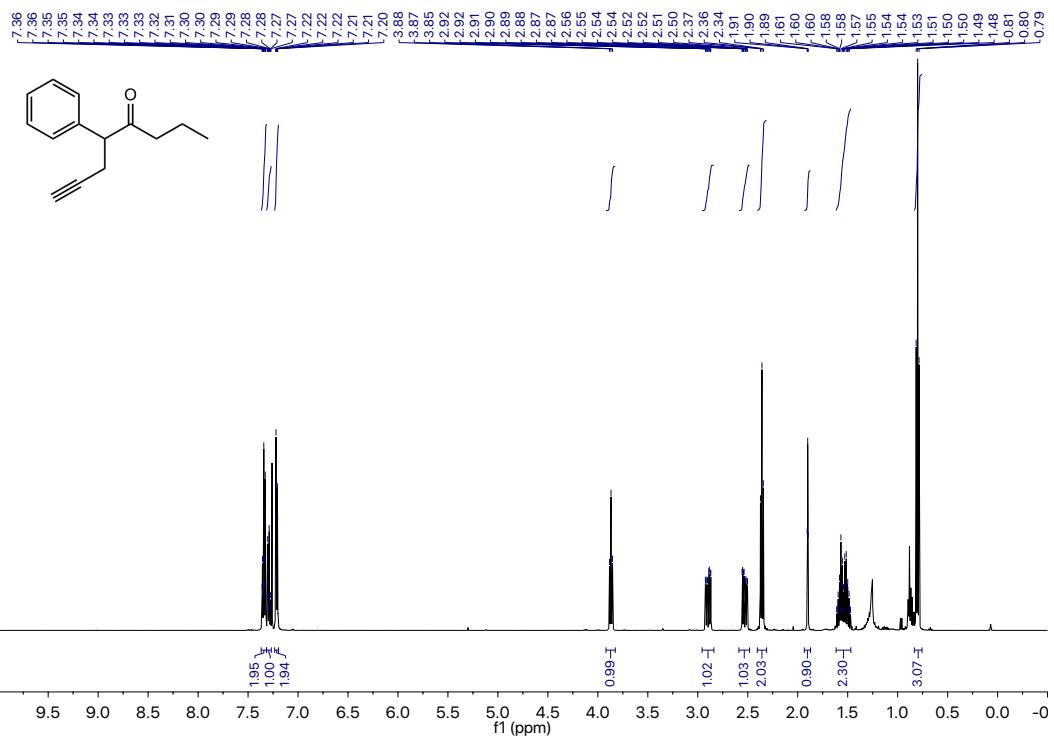


Figure S155. ¹H NMR spectrum (500 MHz, chloroform-d, 23 °C) of **14b**.

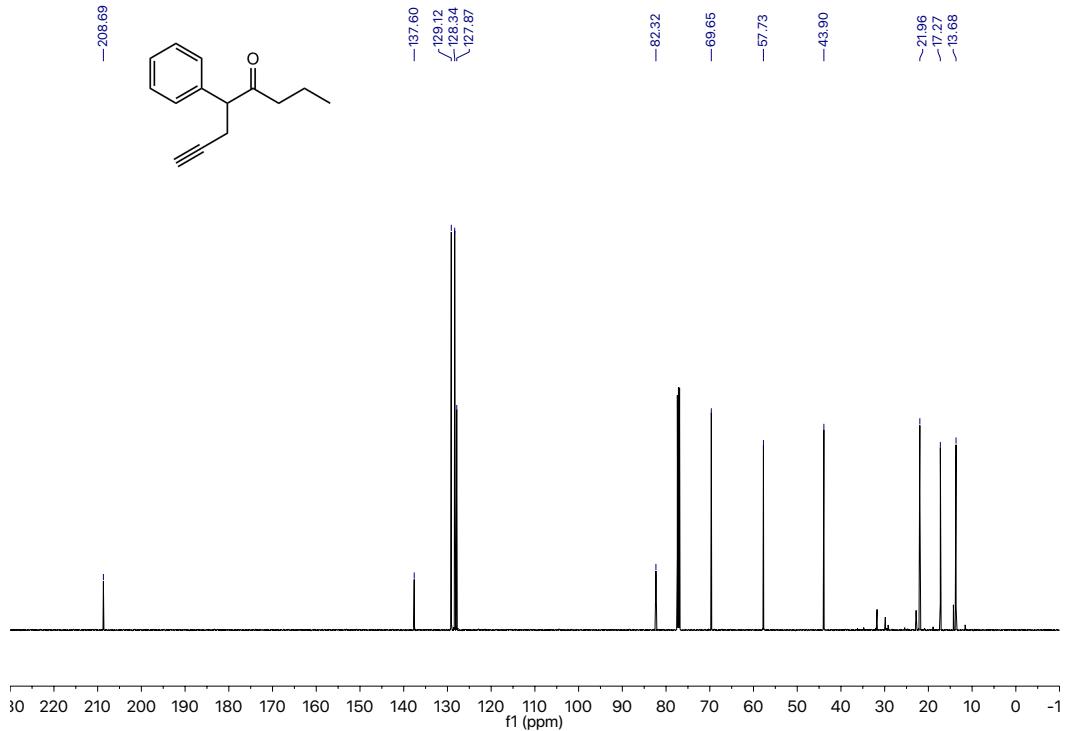
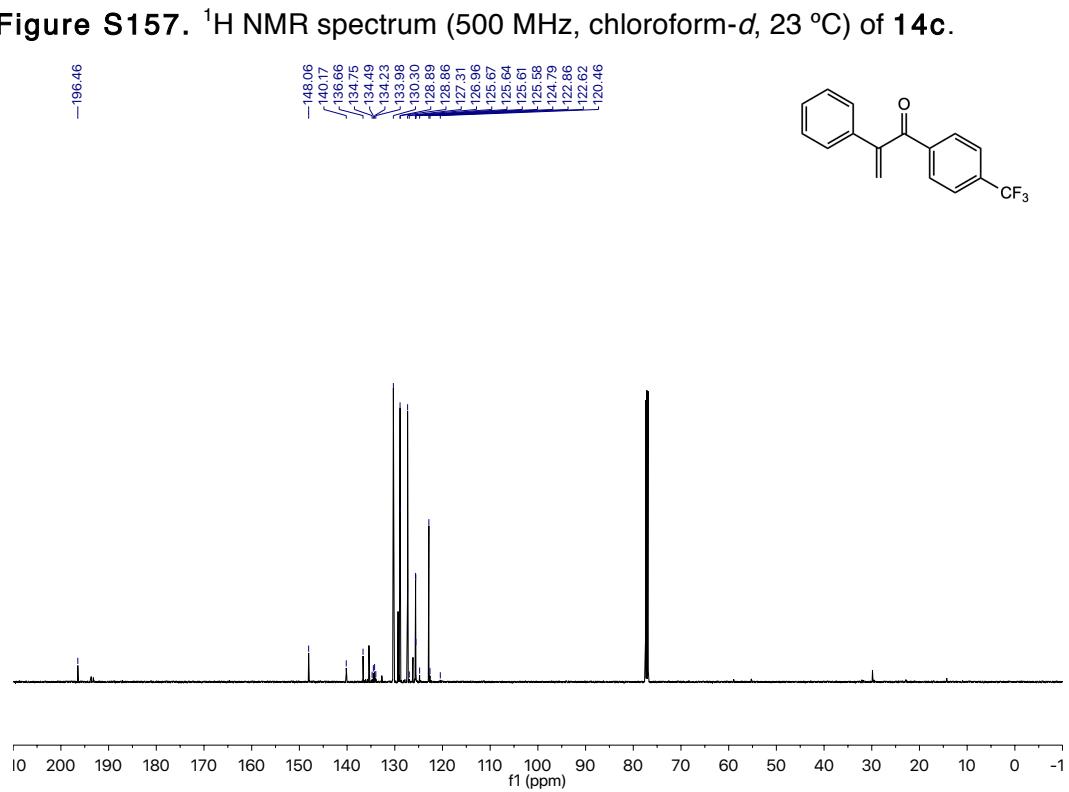
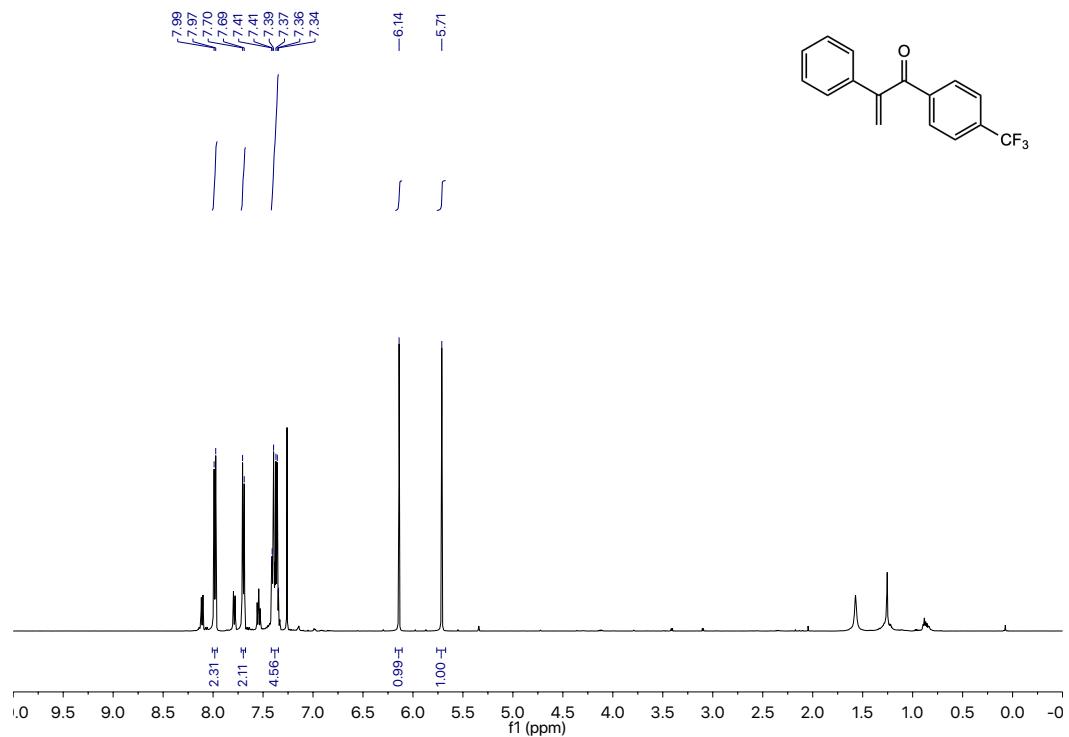


Figure S156. ¹³C{¹H} NMR spectrum (126 MHz, chloroform-d, 23 °C) of **14b**.



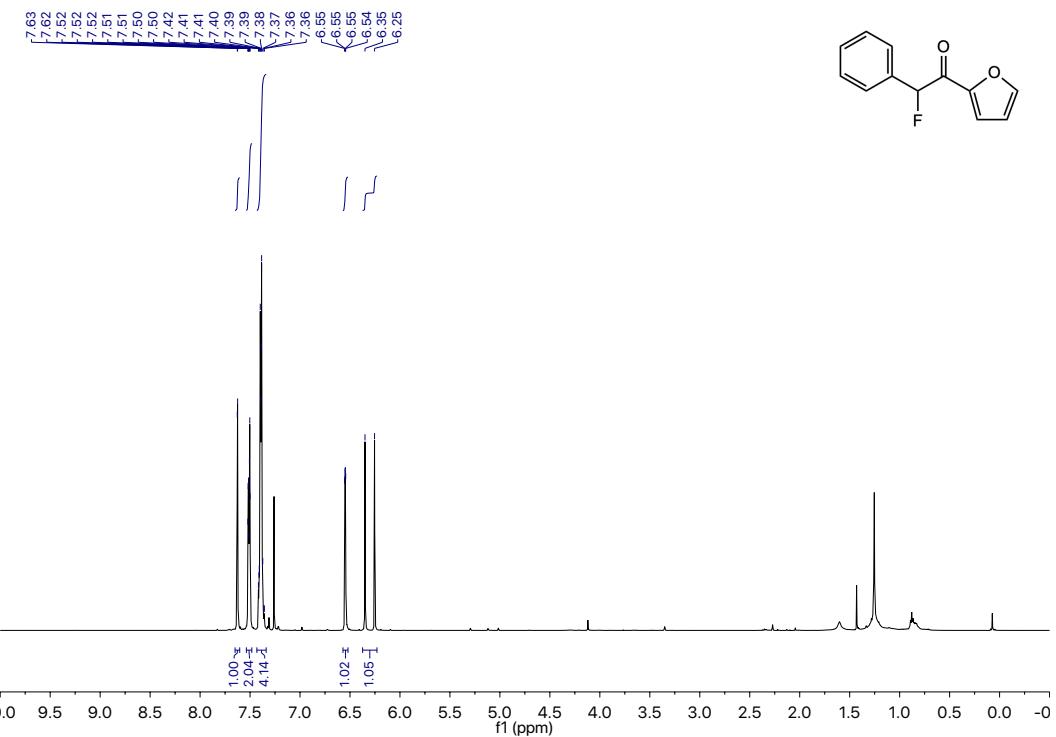


Figure S159. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **14d**.

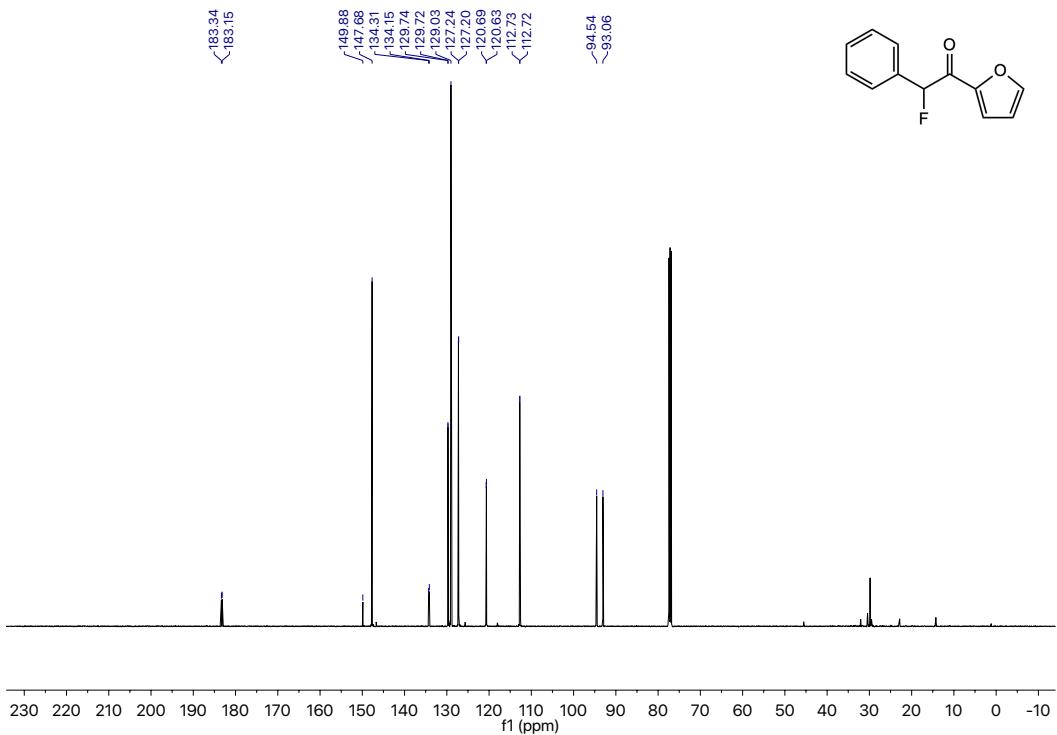


Figure S160. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **14d**.

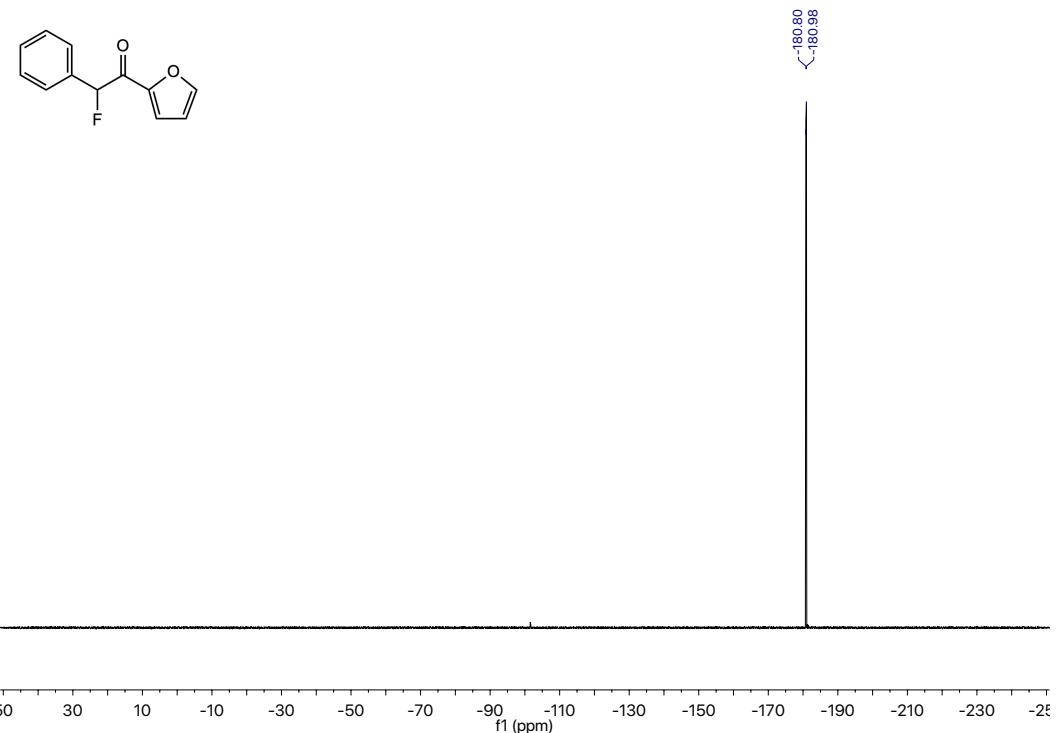


Figure S161. ¹⁹F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **14d**.

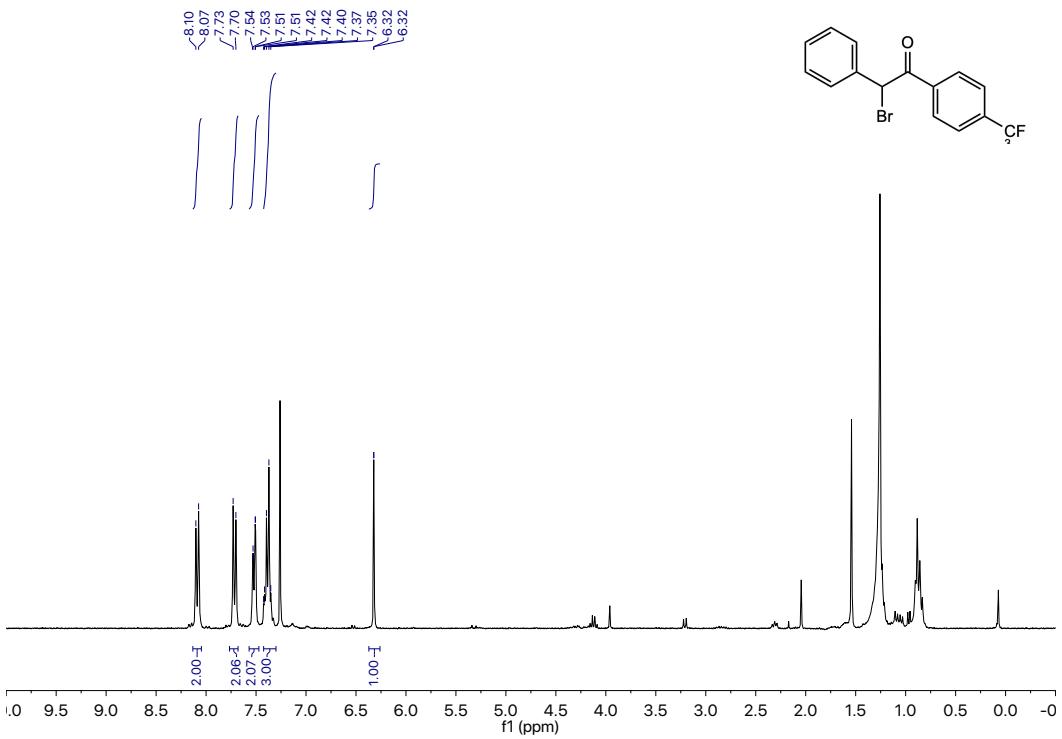


Figure S162. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **14e**

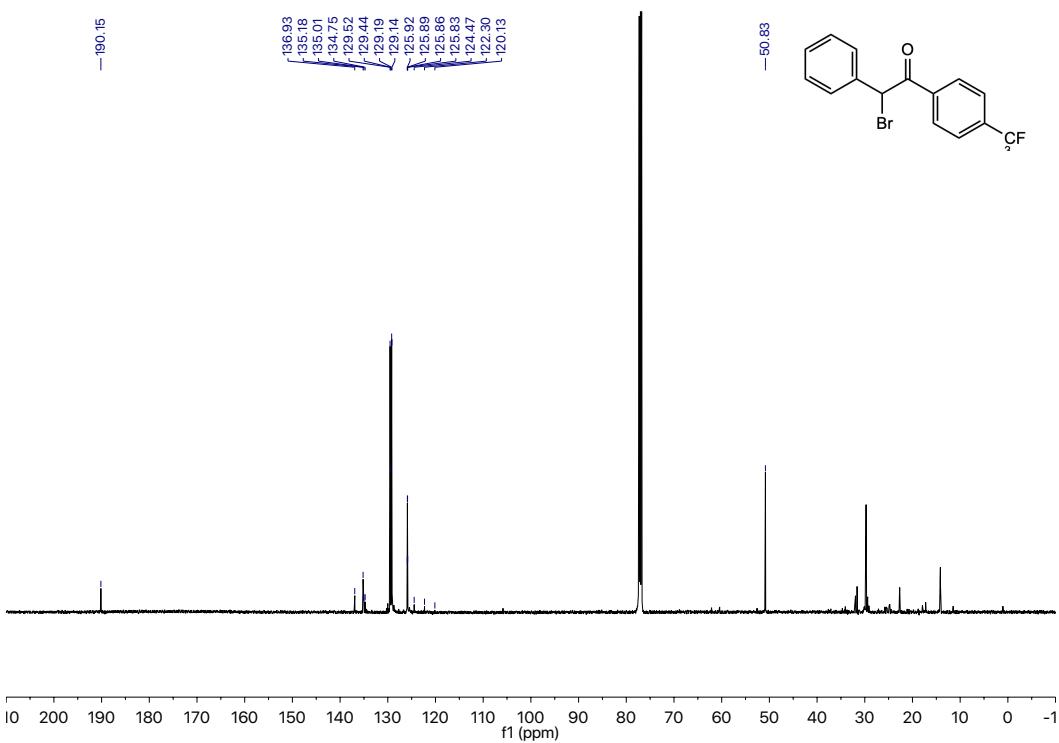


Figure S163. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **14e**.

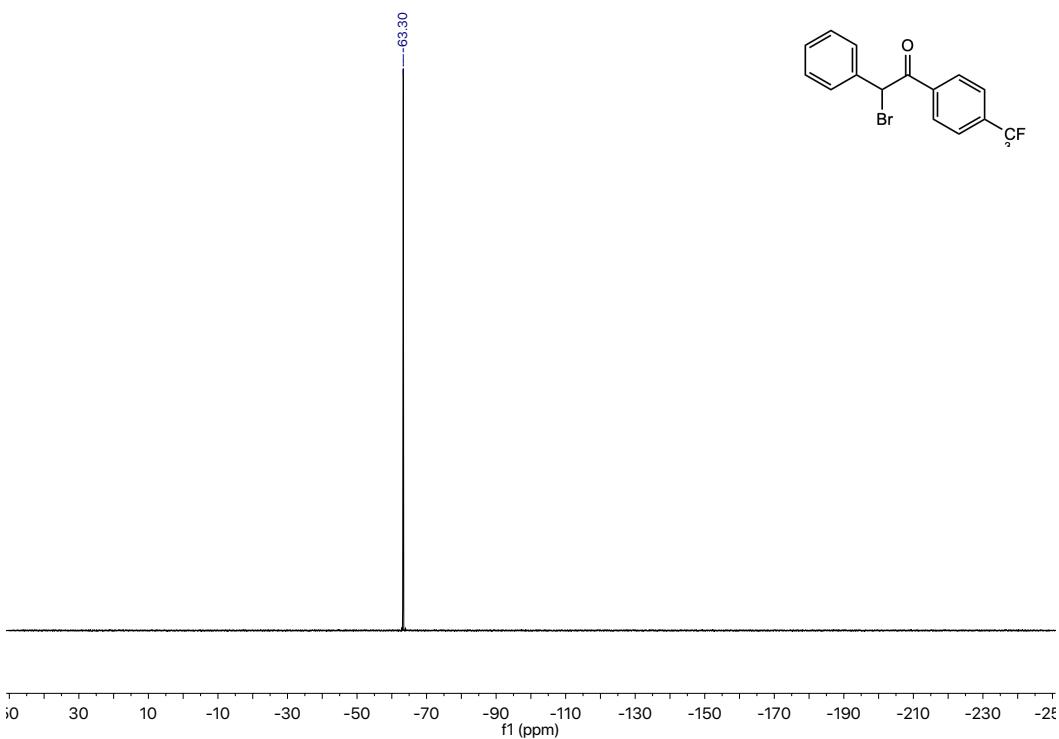


Figure S164. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **14e**.

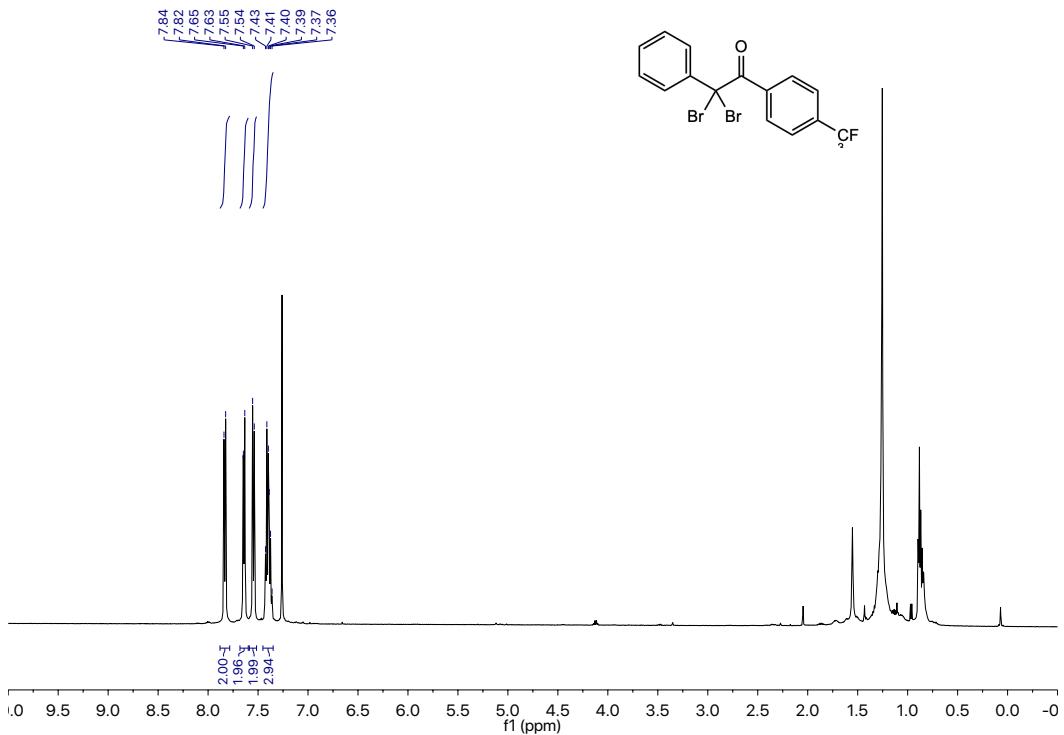


Figure S165. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **14f**.

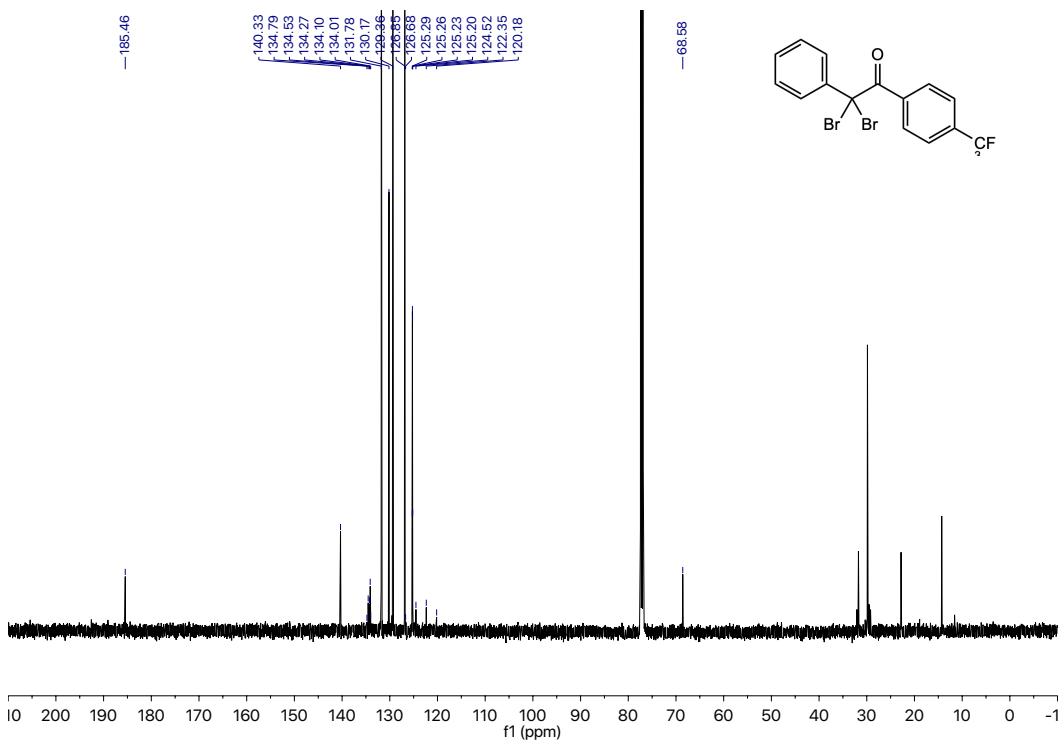


Figure S166. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **14f**.

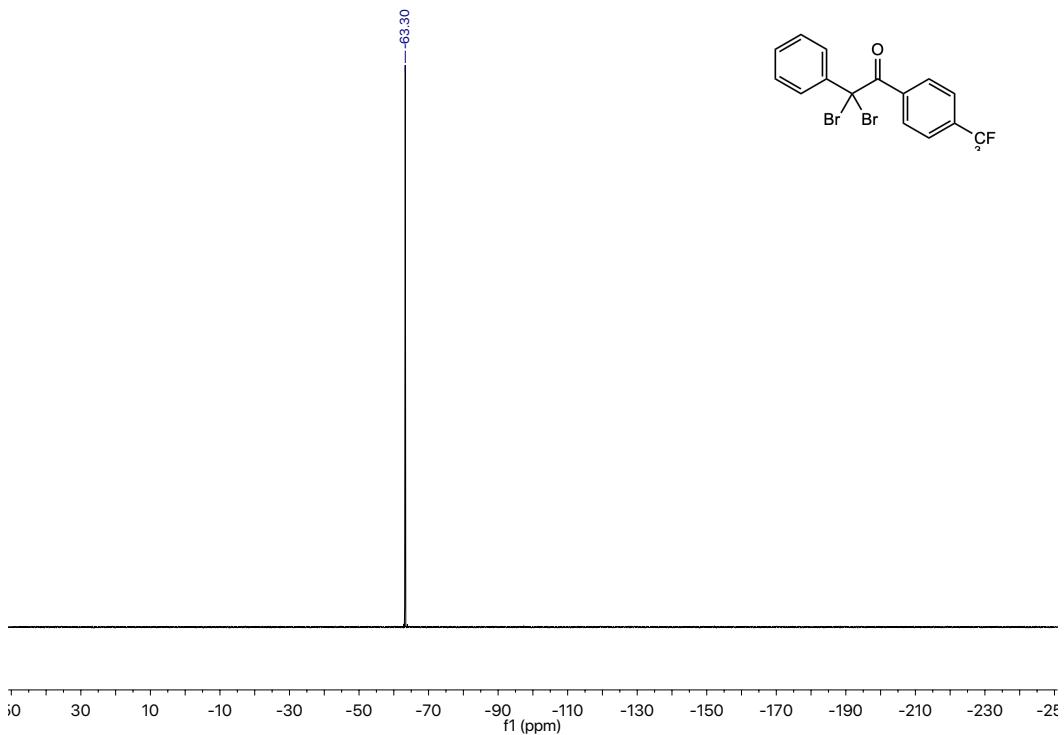


Figure S167. ¹⁹F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **14f**.

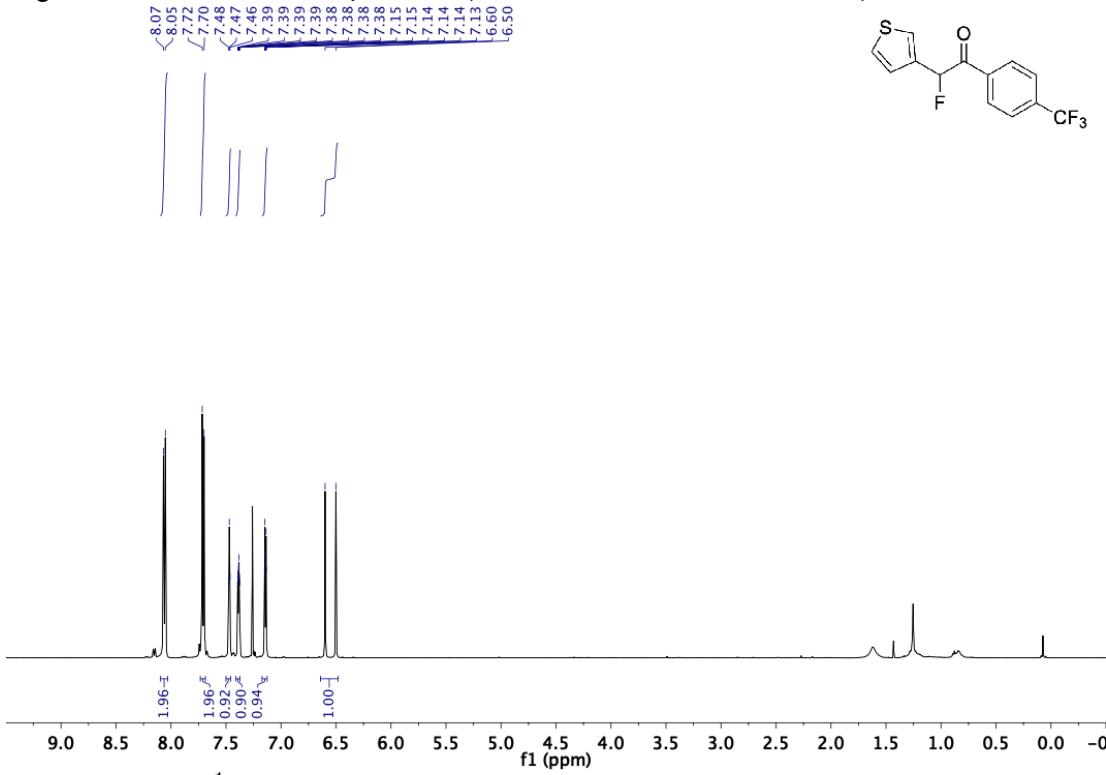


Figure S168. ¹H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **14g**.

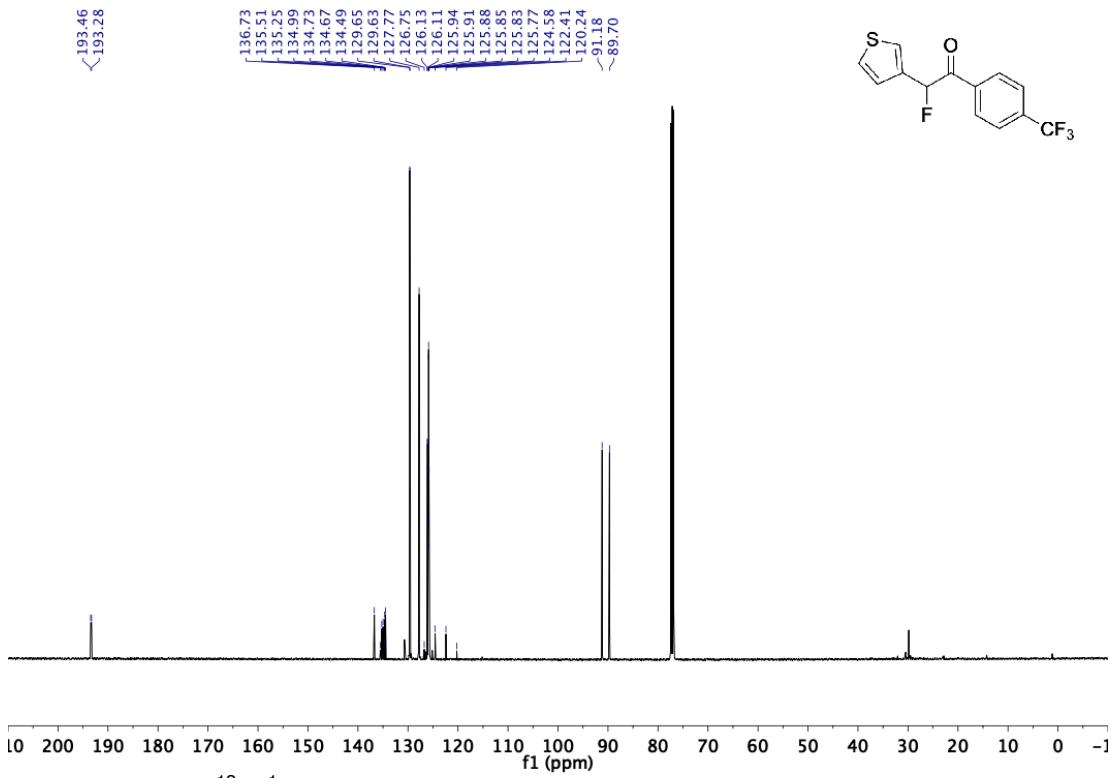


Figure S169. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*, 23 °C) of **14g**.

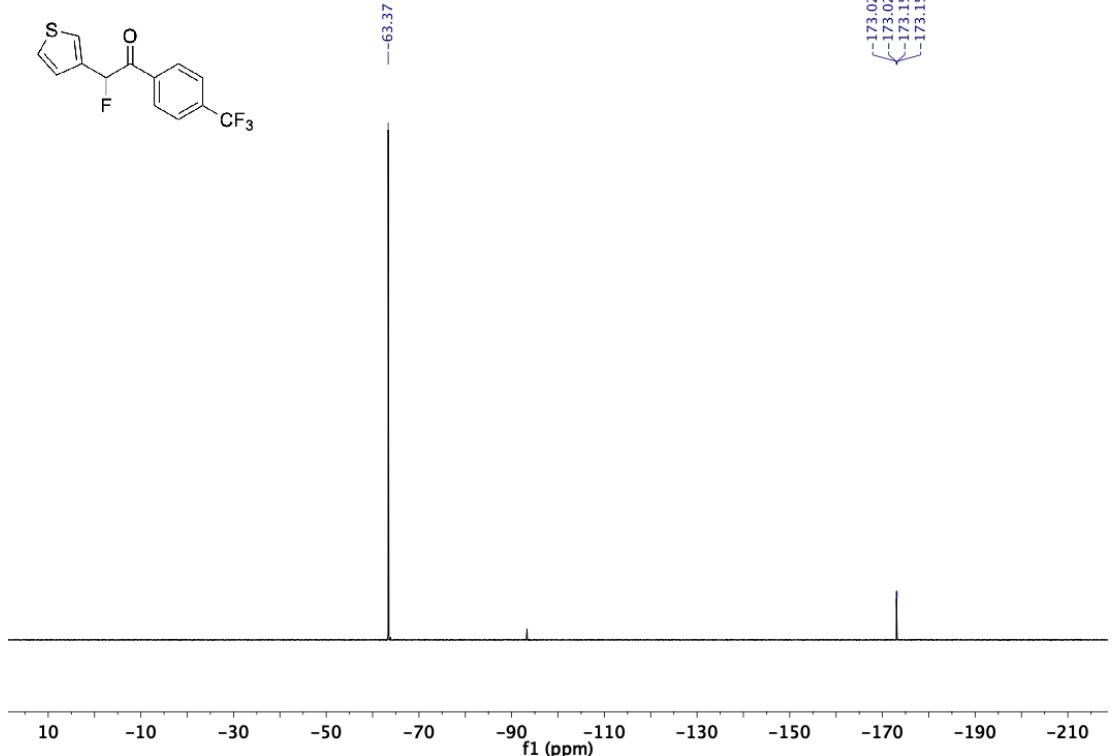


Figure S170. ^{19}F NMR (376 MHz, chloroform-*d*, 23 °C) of **14g**.

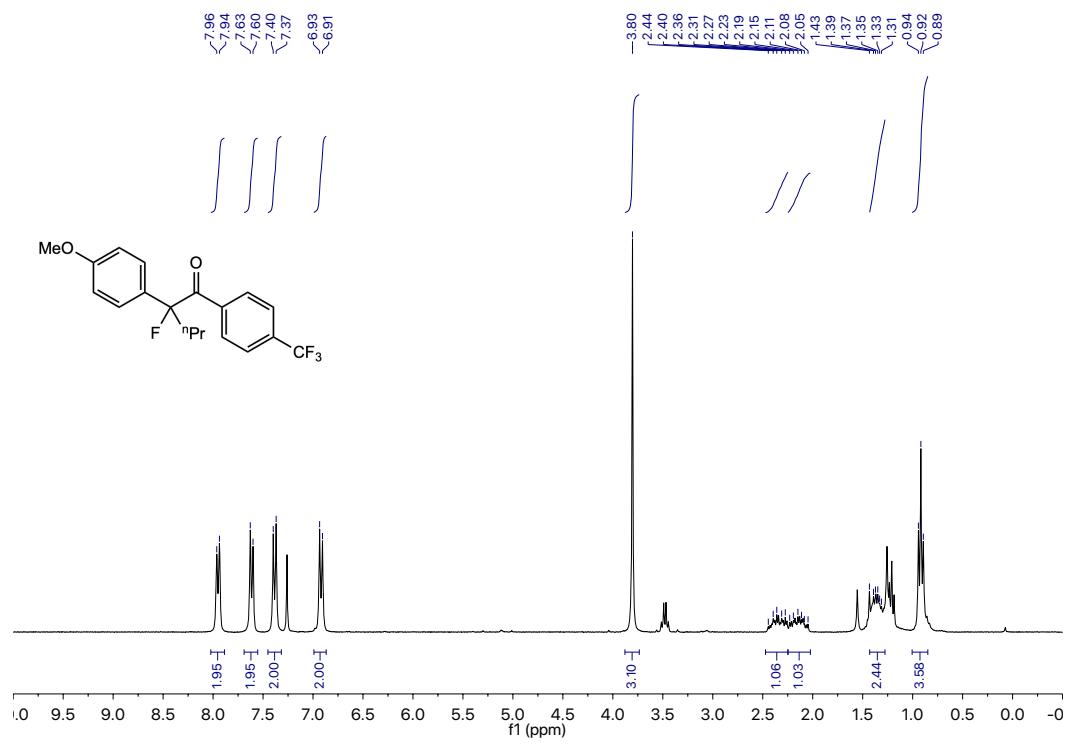


Figure S171. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **15a**.

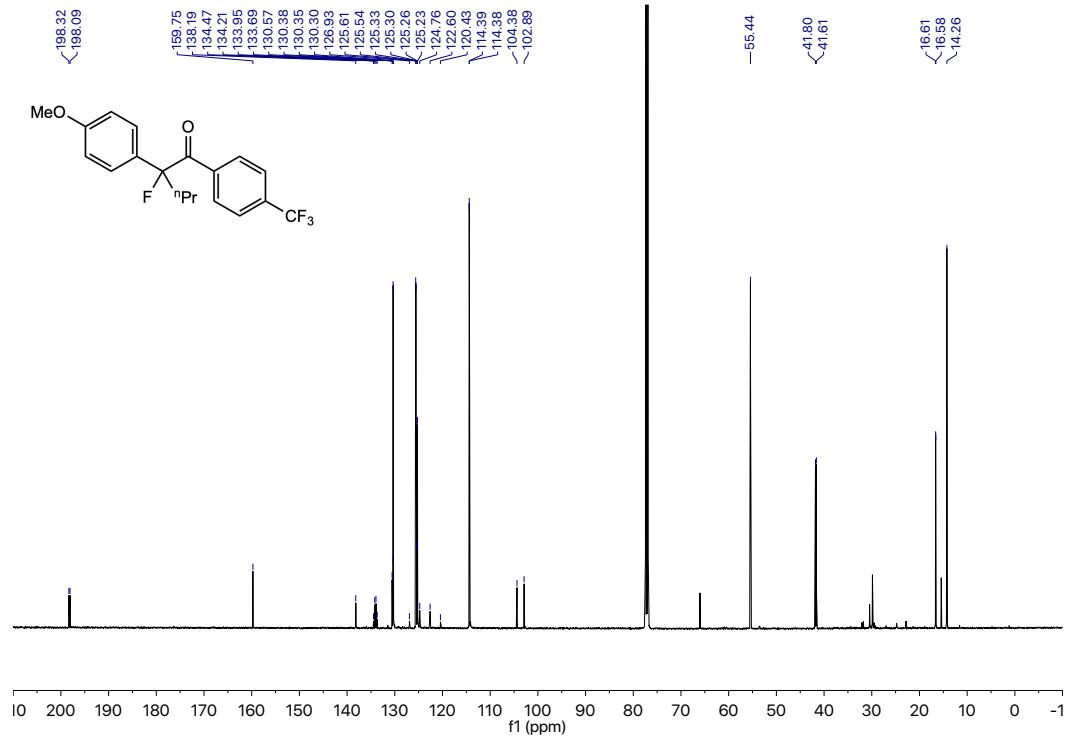


Figure S172. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **15a**.

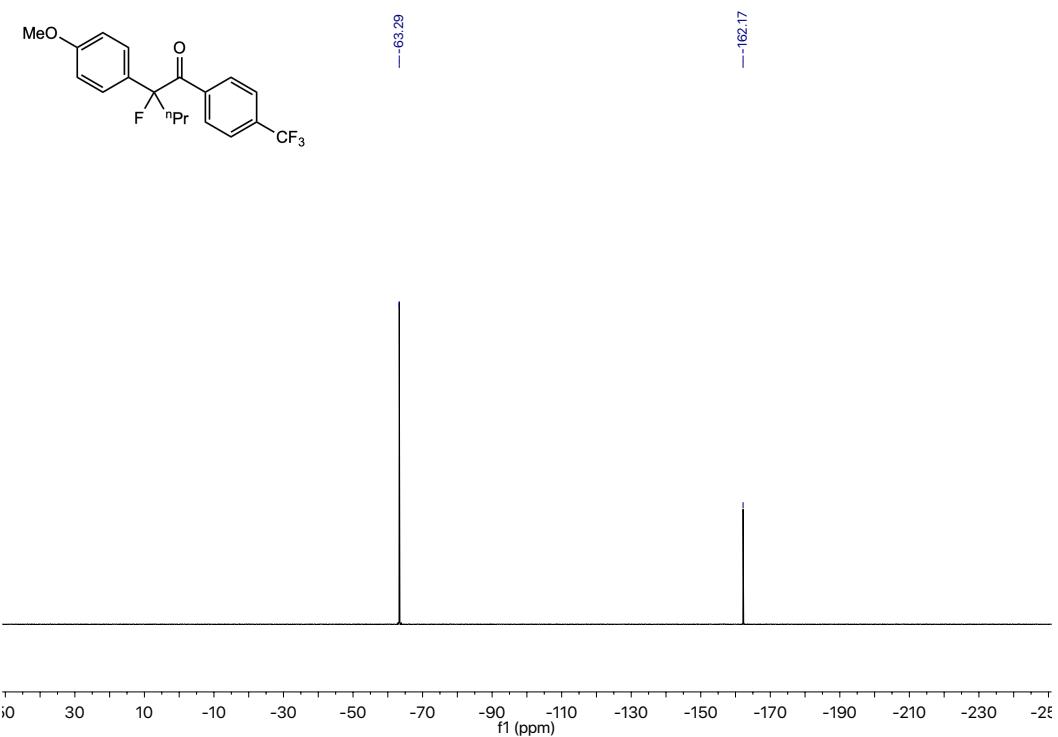


Figure S173. ¹⁹F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **15a**.

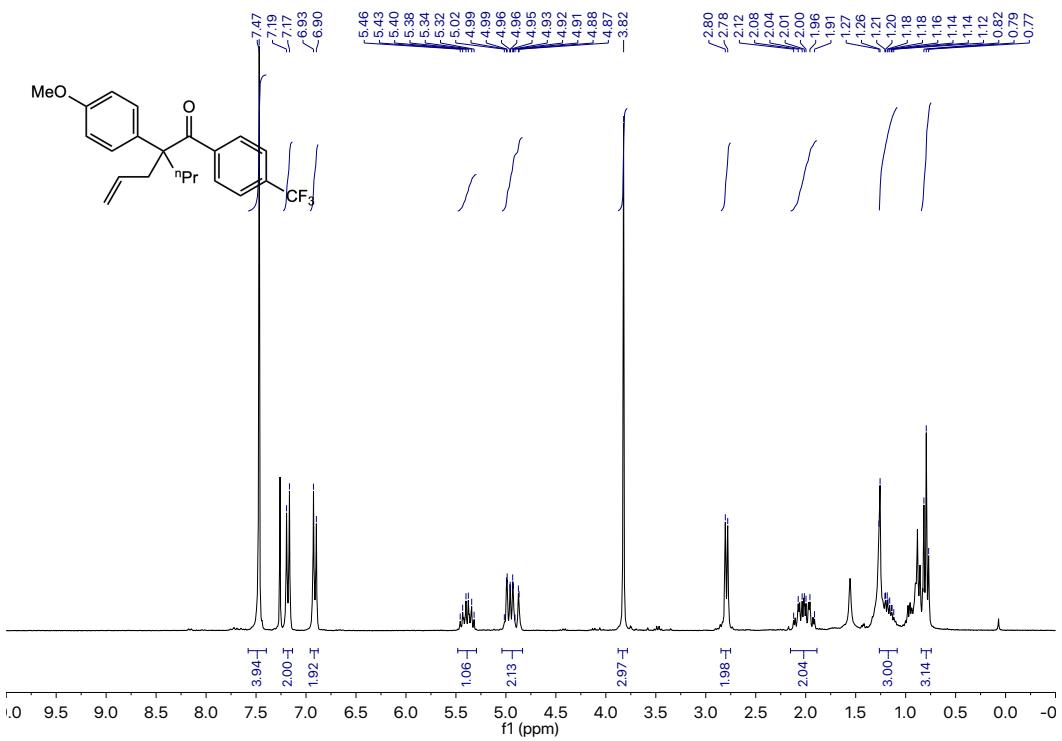


Figure S174. ¹H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **15b**.

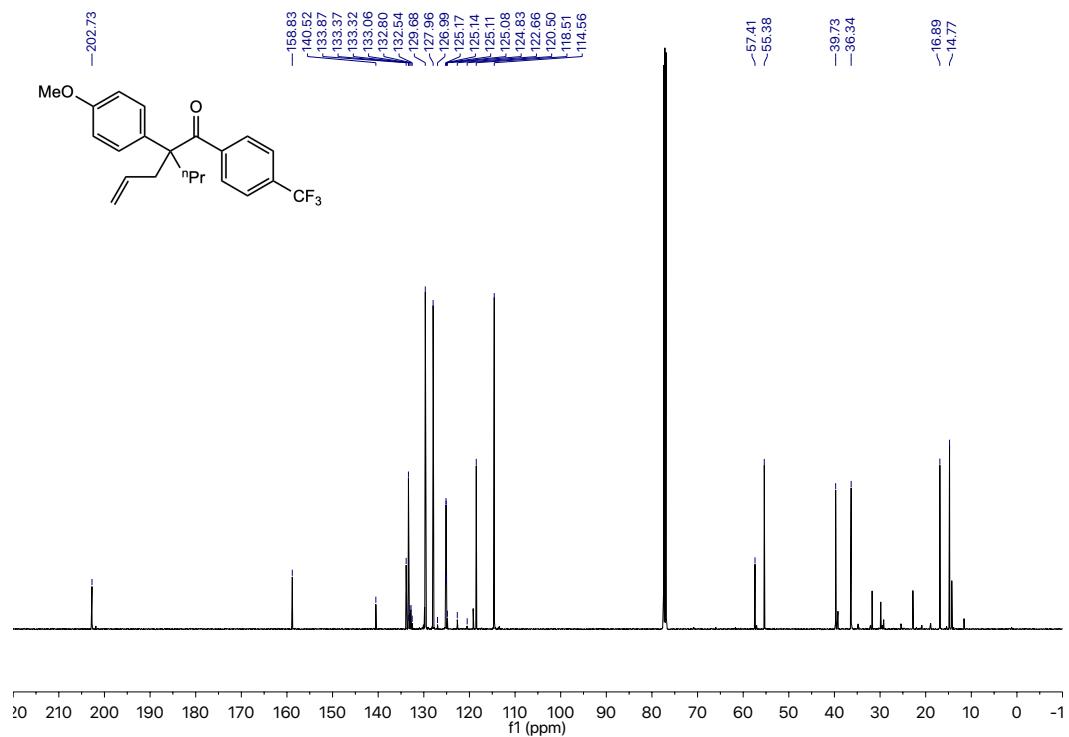


Figure S175. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **15b**.

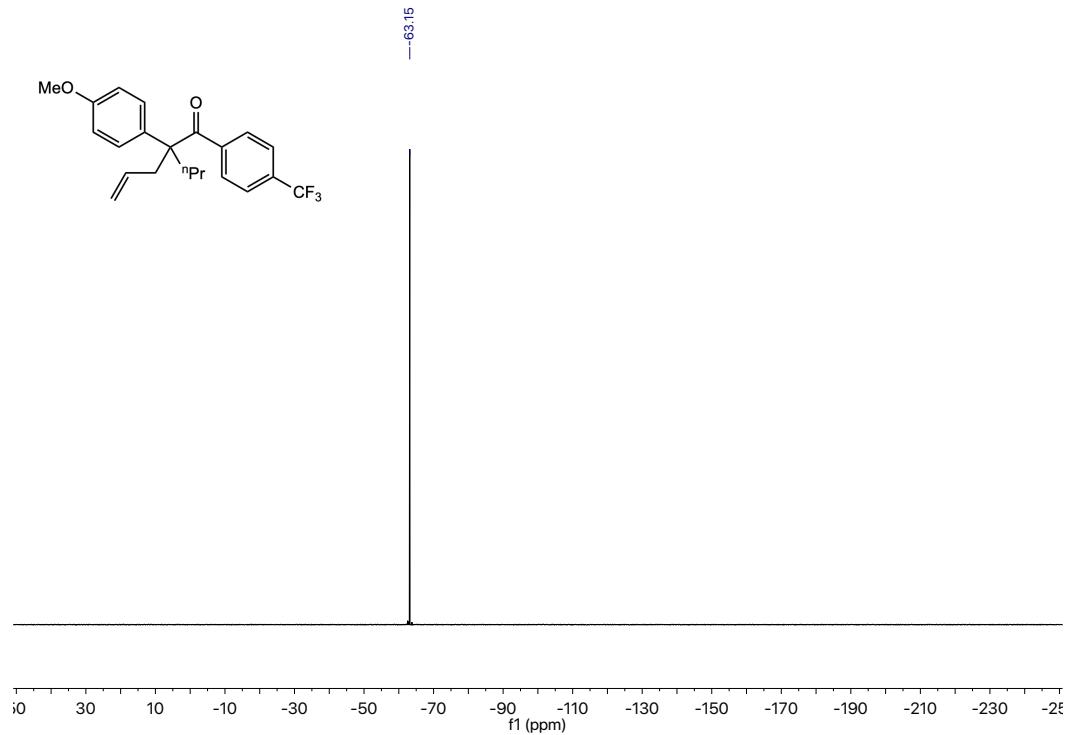


Figure S176. ^{19}F NMR spectrum (282 MHz, chloroform-d, 23 °C) of **15b**.

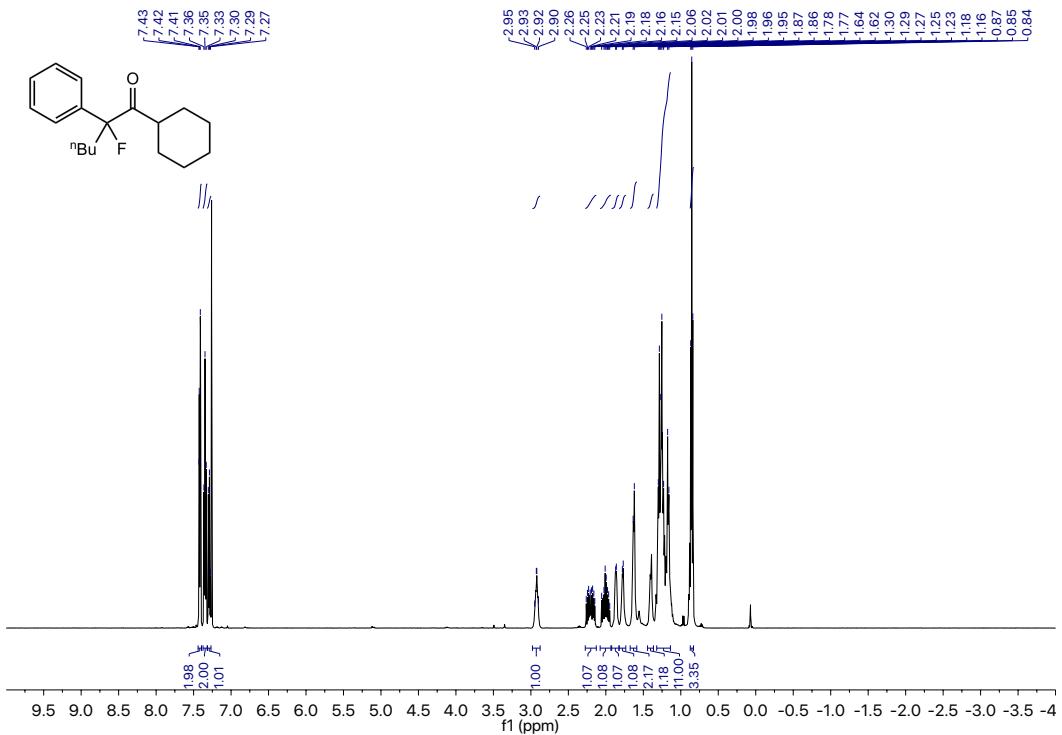


Figure S177. ^1H NMR spectrum (500 MHz, chloroform-*d*, 23 °C) of **17a**.

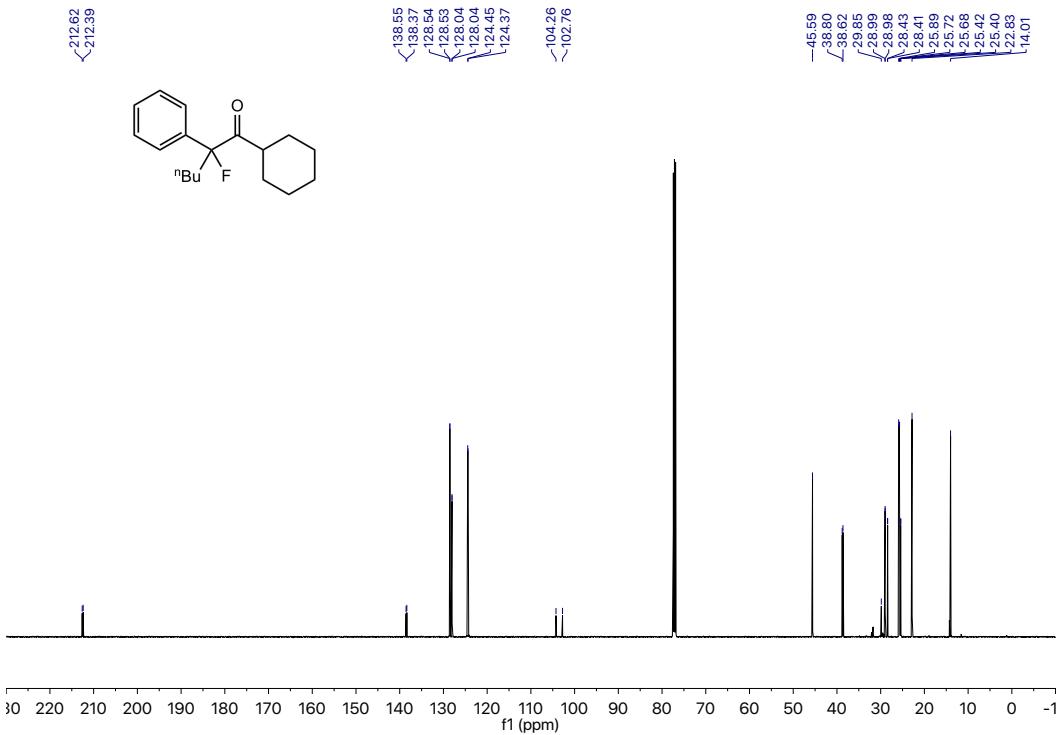


Figure S178. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-d, 23 °C) of **17a**.

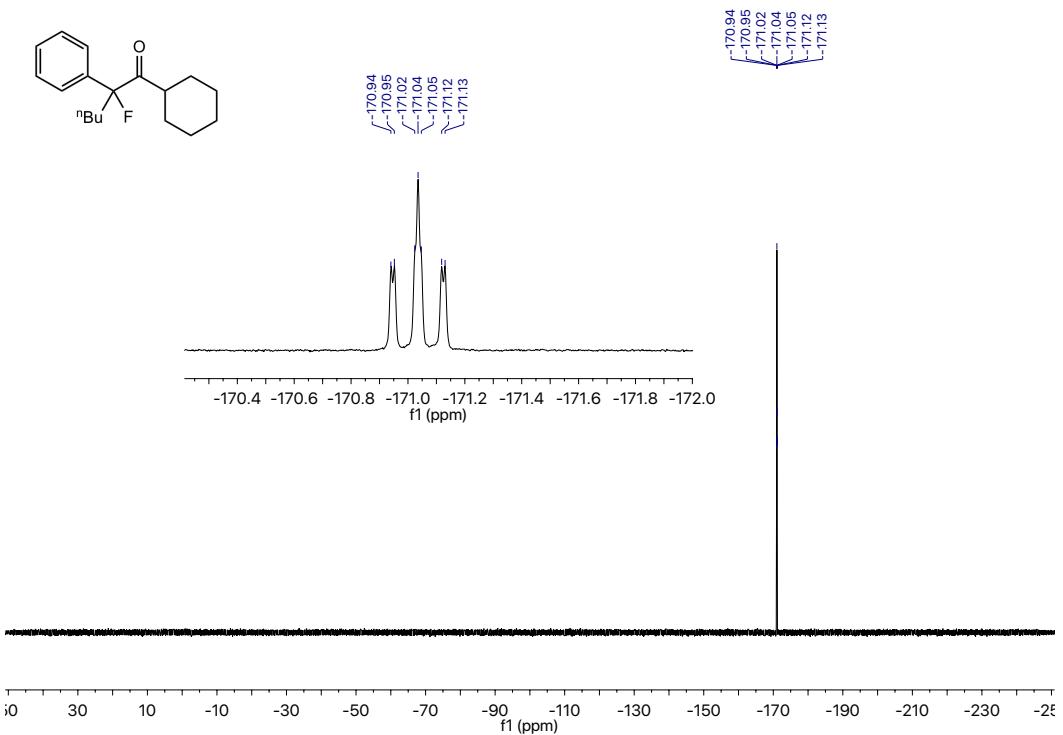


Figure S179. ^{19}F NMR spectrum (282 MHz, chloroform-d, 23 °C) of **17a**.

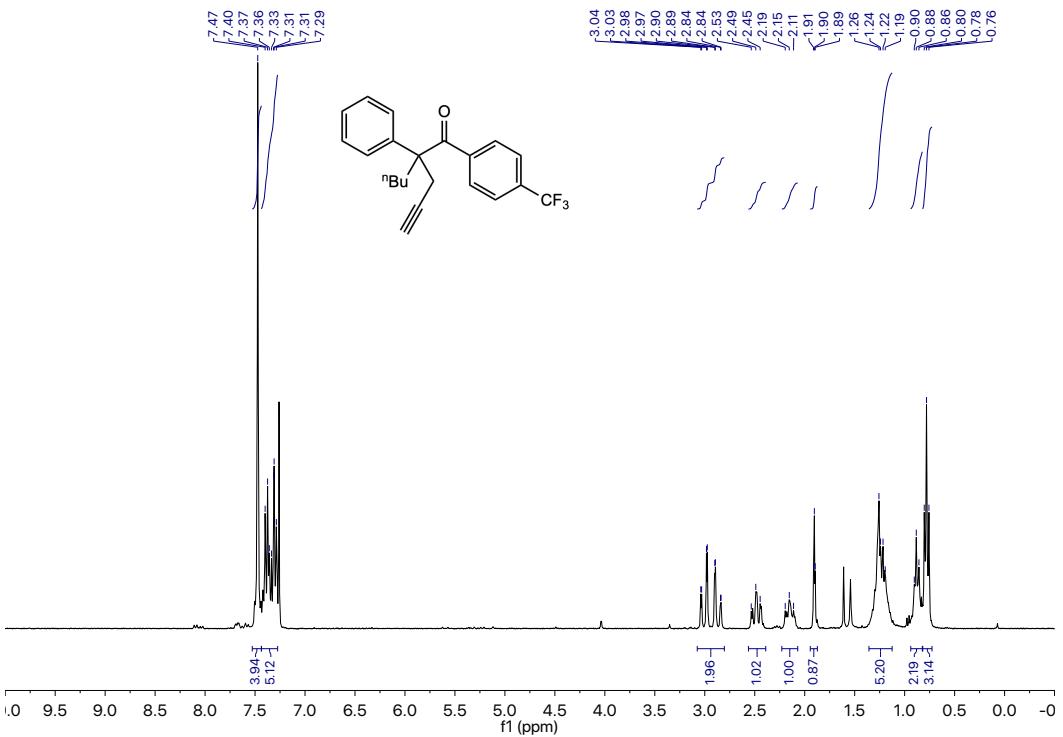


Figure S180. ^1H NMR spectrum (500 MHz, chloroform-d, 23 °C) of **17b**.

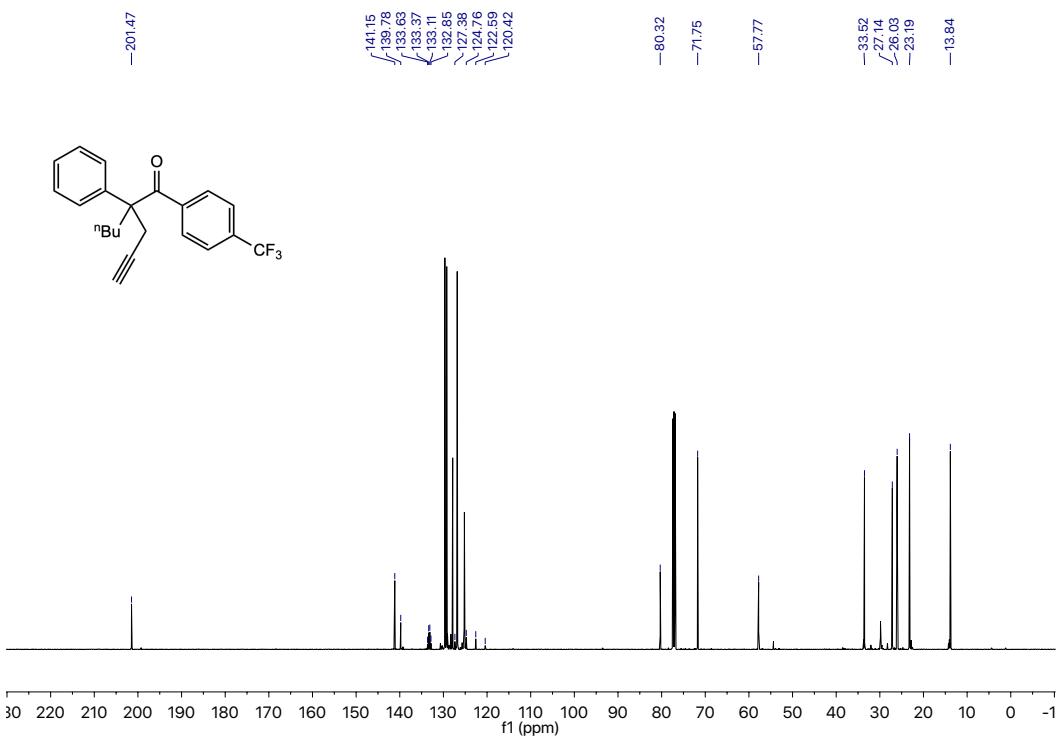


Figure S181. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of 17b.

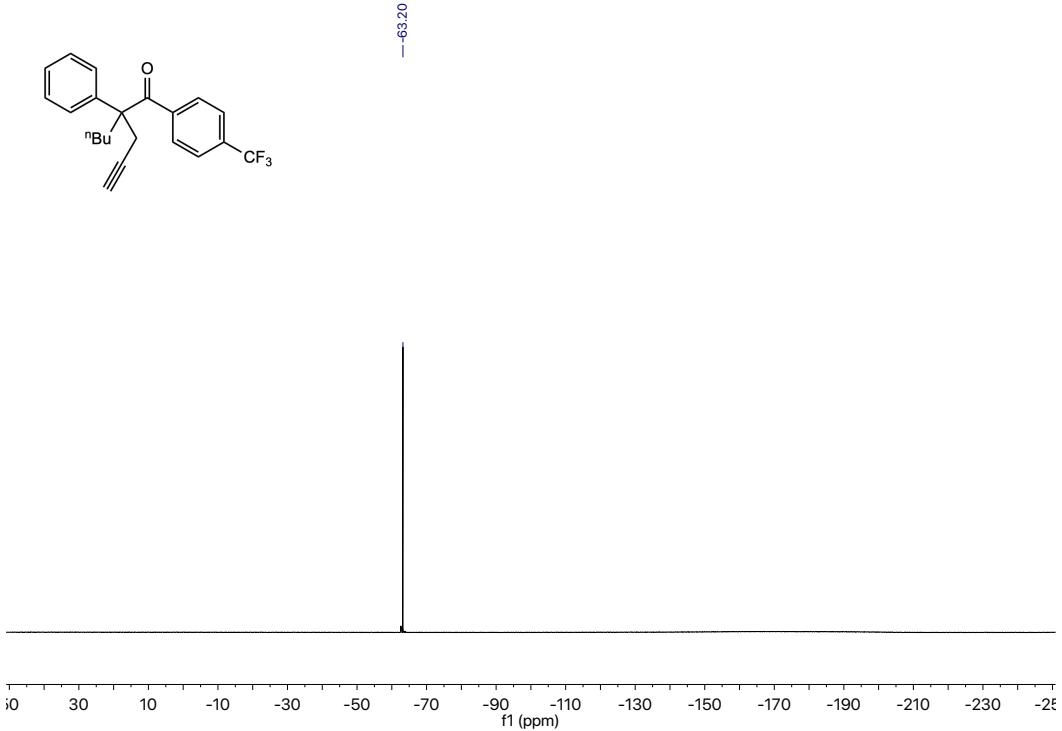


Figure S182. ^{19}F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of 17b.

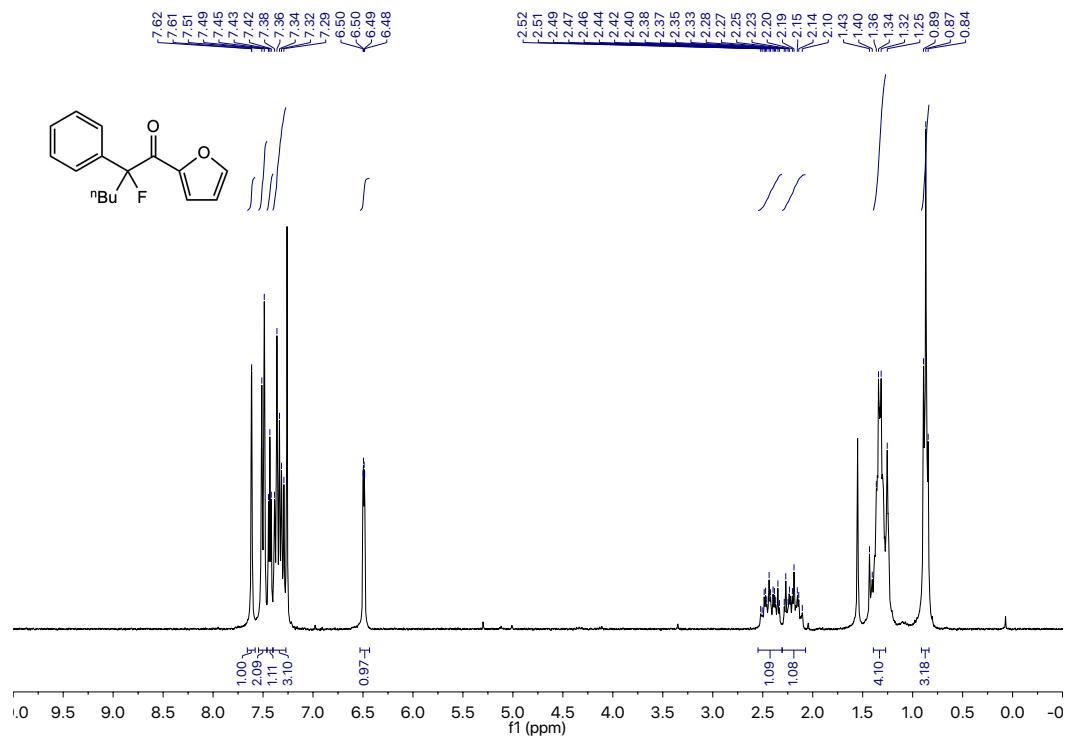


Figure S183. ^1H NMR spectrum (300 MHz, chloroform-*d*, 23 °C) of **17c**.

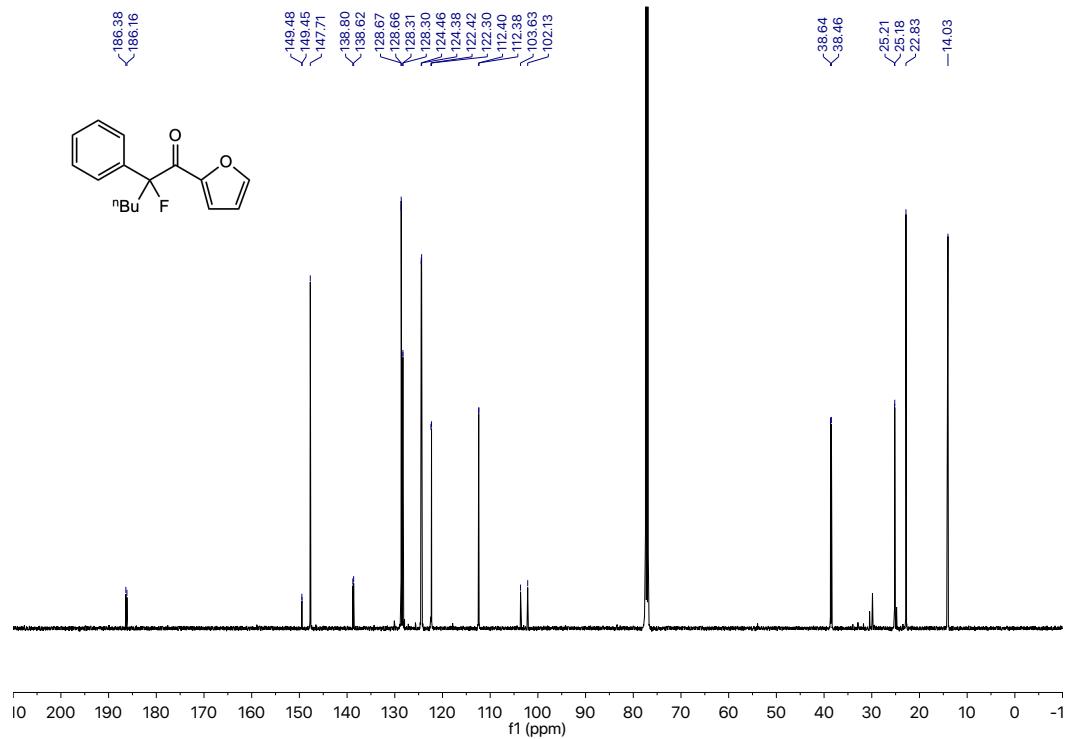


Figure S184. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, chloroform-*d*, 23 °C) of **17c**.

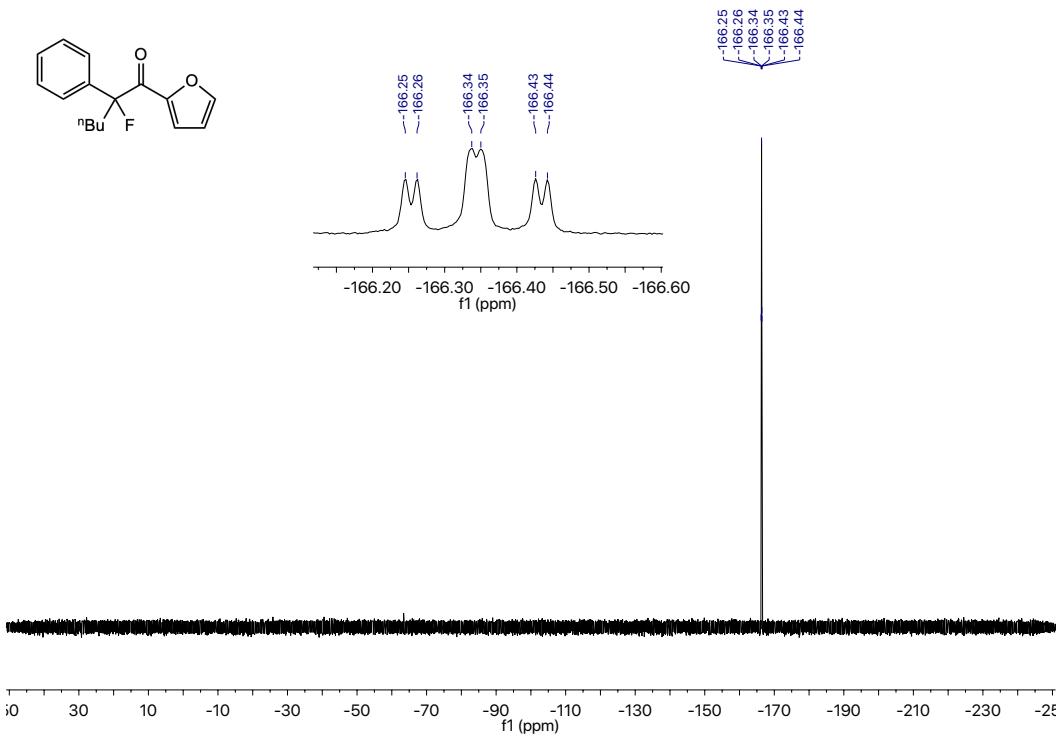


Figure S185. ¹⁹F NMR spectrum (282 MHz, chloroform-*d*, 23 °C) of **17c**.

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