Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

An evaluation of palladium-based catalysts for the base-free borylation of alkenyl carboxylates

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1. General Information

All solvents and chemicals were purchased from commercial suppliers without any further purification. All air-free manipulations were performed under nitrogen-atmosphere using an MBraun glovebox. $Pd(OAc)_2$, $Pd(PCy_3)_2$, $(dppf)PdCl_2$•0.5 DCM, P(*o*-OMePh)$_3$, XPhos, SPhos, and dppf were purchased from Strem Chemicals and stored under inert atmosphere. B_2Pin_2 was purchased from AK Scientific and stored under inert atmosphere.

All NMR spectra were acquired on either a Bruker AVANCE 300 MHz spectrometer or a Bruker AVANCE Neo 500 MHz spectrometer. All ^1H and ^{13}C chemical shifts are calibrated to residual protio-solvents. All data is processed using Bruker TopSpin 4.07.

Microscale screening experiments were performed in sealed aluminum blocks (1 mL shell vials) or with aluminum crimp-caps (2 mL HPLC vials), with heating/stirring done using rare-earth magnetic tumble stirrers from V&P Scientific.

2. Microscale Screening

a. Catalyst Screening (Figure 2, main text)

$Pd(OAc)_2$ and $Pd_2(dba)_3$•$CHCl_3$ were dispensed as stock solutions in dichloromethane into 5 x 1 mL vials (0.0057 mmol and 0.0029 mmol respectively). ^{DMP}DAB-Pd-MAH and $[Pd(acetanilide)OAc]_2$ were dispensed using acetone into 5 x 1 mL vials (0.0057 mmol and 0.0029 mmol respectively). Solvent was then removed using a Genevac EZ-2 (Medium BP setting, no heat). These vials were then brought under N_2 atmosphere (glovebox). A stock solution of each ligand (P(*o*-OMePh)$_3$, SPhos and Xphos: 0.114 M, or dppf: 0.057 M) was dispensed in 100 µl toluene. A stock solution of substrate **1a** (0.57 M) and 1,3,5-trimethoxybenzene (0.057 M) was dispensed in 100 µl toluene. B_2Pin_2 (0.9 M) was dispensed using 100 µl toluene. 100 µl toluene was then added to each vial. Additional experiments using single-component precatalysts were also performed: one using $Pd(PCy_3)_2$ (3.8 mg, 0.0057 mmol), and one using $(dppf)PdCl_2$•DCM (4.7 mg, 0.0057 mmol). A further two control experiments were run: one with no palladium catalyst, and one with no palladium catalyst and no B_2Pin_2. Therefore, the reactions are performed at 0.145 M in substrate **1a** and 0.218 M in B_2Pin_2, and (with respect to substrate **1a**) 10 mol% $Pd(OAc)_2$, 20 mol% monodentate ligand (or 10 mol% bidentate ligand) and 10 mol% 1,3,5-trimethoxybenzene (internal standard) in 400 µl toluene. The reaction plate was sealed, removed from the glovebox, and stirred for 18 hours at 100 °C. The conversion and yield are determined by ^1H NMR spectroscopy via relative peak integrations versus the internal standard.

b. Full Factorial Screening (Figure 3, main text)

$Pd(OAc)_2$ was dispensed as a stock solution in dichloromethane into 9 x 2 mL vials (1.8 mg, 0.008 mmol, or 3.4 mg, 0.015 mmol, or 4.6 mg, 0.02 mmol). Dichloromethane was then removed using a Genevac EZ-2 (Medium BP setting, no heat). These vials were then brought under N_2 atmosphere (glovebox). A stock solution of SPhos (0.081 M, or 0.046 M) in toluene was dispensed to each plate. A stock solution of **1a** (2.0 M) and 1,3,5-trimethoxybenzene (0.2 M, internal standard) in toluene was dispensed to each plate. A stock solution of B_2Pin_2 (2.23M, 1.52 M, or 1.62 M) in toluene was dispensed to each plate. Toluene was then dispensed to each appropriate vial to ensure total volumes of 1.1 mL. The vials were sealed using crimp caps, removed from N_2 atmosphere, and stirred for 18 hours at 100 °C. The conversion and yield are determined by ^1H NMR spectroscopy via relative peak integrations versus the internal standard.

c. Substrate Concentration Study (Figure 3, main text)

Under a N_2 atmosphere, 4 x 1 dram vials were charged with $Pd(OAc)_2$ (4.9 mg, 0.022 mmol) and SPhos (13.5 mg, 0.033 mmol). A separate set of 4 x 1 dram vials were charged with **1a** (40 mg, 0.22 mmol; 80 mg, 0.44 mmol; 120 mg, 0.66 mmol; or 160 mg, 0.88 mmol) and 1,3,5-trimethoxybenzene (internal standard; 3.7 mg, 0.022 mmol; 7.4 mg, 0.044 mmol; 11.1 mg, 0.066 mmol; 14.8 mg, 0.088 mmol). 4 x 2 mL vials were charged with B_2Pin_2 (111.5 mg, 0.44 mmol; 223.0 mg, 0.88 mmol; 334.5 mg, 1.32 mmol; or 445.9 mg, 1.76 mmol). The solids in the $Pd(OAc)_2$/SPhos vials were dissolved in 1.1 mL toluene, transferred to the vials with **1a** and 1,3,5-trimethoxybenzene. Dissolution was ensured prior to transfer of the solution to the 2 mL vials with B_2Pin_2. Therefore, the reactions are 0.2 M, 0.4 M, 0.6 M, and 0.8 M with respect to **1a**. With 2.0 eq. B_2Pin_2, 0.1 equiv. 1,3,5-trimethoxybenzene, $Pd(OAc)_2$ (2.5 mol%, 3.33 mol%, 5 mol%, and 10 mol%), and SPhos (3.75 mol%, 5.00 mol%, 7.5 mol% and 15 mol%). The reaction vials were sealed using crimp caps, removed from N_2 atmosphere, and stirred for 18 hours at 100°C. The conversion and yield are determined by ^{1}H NMR spectroscopy via relative peak integrations versus the internal standard.

d. $Pd(PCy_3)_2(OAc)_2$ Study

Under a N_2 atmosphere 1 dram vials are charged with $Pd(PCy_3)_2(OAc)_2$ (17.3 mg, 0.022 mmol), B_2Pin_2 (61.5 mg, 0.242 mmol) and toluene (1.1 ml, 0.2 M with respect to substrate). The vials are removed from the glovebox and stirred for 10 minutes at 100 °C (Method **D**), or 16 hours at 70°C (Method **E**). The vials are returned to the N_2 atmosphere and charged with the respective substrate (0.22 mmol) and 1,3,5-trimethoxybenzene (3.7 mg, 0.022 mmol). The vials are then removed from the glovebox and stirred for 18 hours at 100 °C. The conversion and yield are determined by ^{1}H-NMR.

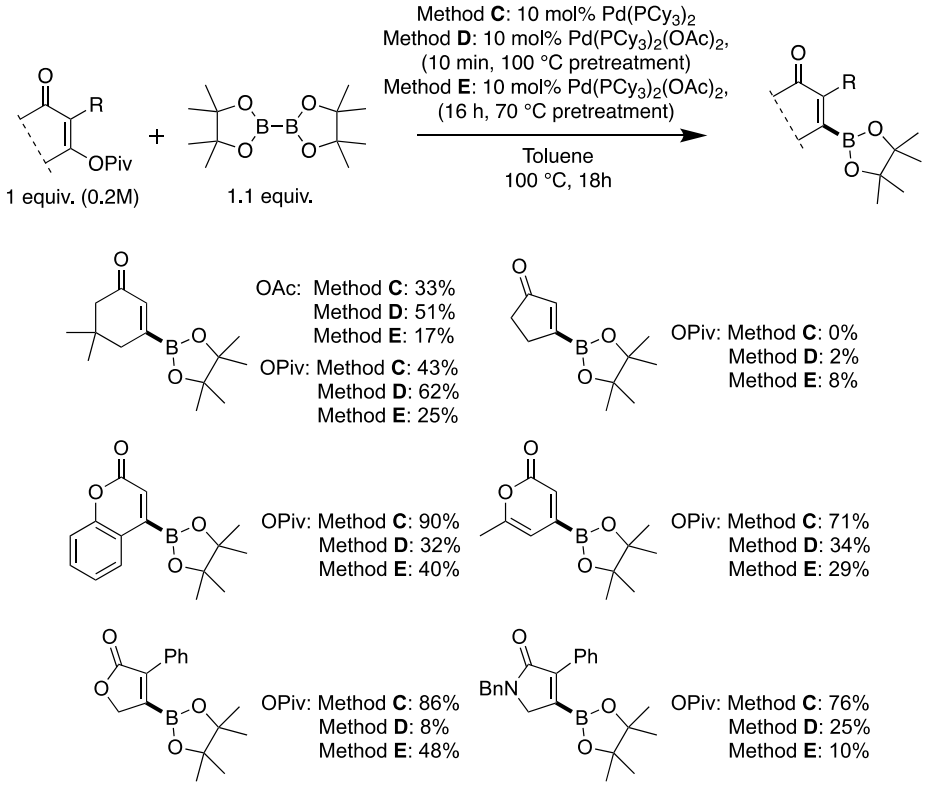


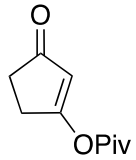
Figure S1: Yields from study using $Pd(PCy_3)_2(OAc)_2$. Method **C**: (10 mol% $Pd(PCy_3)_2$, toluene (0.2M), 18h, 100 °C shown for reference.

3. Synthesis and Characterization

a. Substrates

Compounds prepared using literature procedures: 5,5-dimethyl-3-oxocyclohex-1-en-1-yl acetate (**1a**),[1] 5,5-dimethyl-3-oxocyclohex-1-en-1-yl pivalate (**1b**),[1] 1-acetyloxycyclopent-1-en-3-one,[2] 4-acetoxy-6-methyl-2-pyrone,[3] 2-oxo-2H-chromen-4-yl acetate,[3] 4-pivalyloxybenzopyran-2-one,[4] 4-acetyloxy-3-phenylpyran-3-en-2-one,[5] 4-acetyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one.[5]

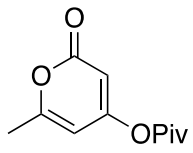
1-pivalyloxycyclopent-1-en-3-one:



A 250 mL round bottom flask was charged with 1,3-cyclopentandione (3.0 g, 30.58 mmol), and DCM (60 mL). While stirring, DIPEA (10.65 mL, 61.16 mmol) was added. The round bottom flask was then submerged in an ice bath and trimethylacetyl chloride (3.84 mL, 31.19 mmol) was added dropwise over 20 minutes. The round bottom flask was removed from the ice bath and allowed to stir at room temperature overnight. The solution was filtered through a frit, washed three times with 1M HCl and reduced to dryness resulting in a brown oil. The crude product was then isolated by column chromatography using a hexanes/ethyl acetate solvent system on a Biotage Selekt unit. A dark orange oil was collected that solidified upon freezing. Dark orange oil (3.98 g, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 6.23 (s, 1H), 2.80-2.76 (m, 2H), 2.50-2.46 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 206.8, 180.1, 174.0, 116.4, 39.6, 33.3, 28.7, 26.8. HRMS: Cal'd for $C_{10}H_{15}O_3$ $[M+H]^+$: 183.10212; found: 183.10157.

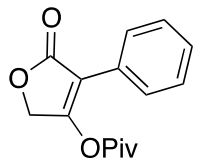
4-pivalyloxy-6-methyl-2-pyrone:



A 500 mL round bottom flask was charged with 6-methyl-4-hydroxypyrone (10 g, 79.3 mmol) and DCM (150 mL). While stirring, DIPEA (18.0 mL, 103 mmol) was added. The round bottom flask was then submerged in an ice bath and trimethylacetyl chloride (10.0 mL, 81.3 mmol) was added dropwise over 10 minutes. The round bottom flask was removed from the ice bath and allowed to stir at room temperature for two hours. The reaction mixture was washed with 1M HCl, dried using $MgSO_4$, filtered, and evaporated to dryness. A colourless oil was collected that solidified upon freezing. Colourless oil, (15.0 g, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 5.93 (dd, J=2.0, 0.5, 1H), 5.86-5.84 (m, 1H), 2.19 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 174.7, 163.8, 163.6, 163.2, 101.4, 101.1, 39.5, 26.8, 20.1. HRMS: Cal'd for $C_{11}H_{15}O_4$ $[M+H]^+$: 211.09704; found: 211.09647.

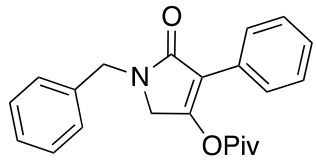
4-pivalyloxy-3-phenylpyran-3-en-2-one



A 100 mL round bottom flask was charged with 3-phenylpyran-3-en-2,4-dione[6] (533 mg, 3.0 mmol) and DCM (20 mL). While stirring, DIPEA (1.1 mL, 6.0 mmol) was added. The round bottom flask was then submerged in an ice bath and trimethylacetyl chloride (0.44 mL, 3.6 mmol) was added dropwise over 10 minutes. The round bottom flask was removed from the ice bath and allowed to stir at room temperature overnight. The reaction mixture was washed with 1M HCl, dried using $MgSO_4$, filtered, and evaporated to dryness. The crude product was then isolated by column chromatography using hexanes/ethyl acetate on a Biotage Selekt unit. A beige solid was collected (790 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.84 (d, J=7.3 Hz, 2H), 7.46 (t, J=7.7 Hz, 2 H), 7.39 (t, J=7.6 Hz), 5.29 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 174.0, 170.8, 163.9, 128.7, 128.4, 128.2, 127.9, 110.6, 67.6, 39.6, 26.9. HRMS: Cal'd for $C_{15}H_{17}O_4$ $[M+H]^+$: 261.11269; found: 261.11212.

4-pivalyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one



A 100 mL round bottom flask was charged with 1-benzyl-3-phenylpyrrolidin-3-en-2,4-dione[7] (1.2 g, 4.5 mmol) and DCM (20 mL). While stirring, DIPEA (1.6 mL, 9.0 mmol) was added. The round bottom flask was then submerged in an ice bath and trimethylacetyl chloride (0.66 mL, 5.4 mmol) was added dropwise over 10 minutes. The round bottom flask was removed from the ice bath and allowed to stir at room temperature overnight. The reaction mixture was washed with 1M HCl, dried using $MgSO_4$, filtered, and evaporated to dryness. The crude product was then isolated by column chromatography using hexanes/ethyl acetate on a Biotage Selekt unit. A beige solid was collected (1.45 g, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.83 (d, J=7.6 Hz, 2H), 7.46-7.29 (m, 8H), 4.73 (s, 2H), 4.27 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 174.8, 168.9, 157.1, 137.1, 129.4, 128.8, 128.6, 128.3, 128.2, 128.1, 127.7, 117.8, 49.2, 45.9, 39.4, 26.9. HRMS: Cal'd for $C_{22}H_{24}NO_3$ $[M+H]^+$: 350.17562; found: 350.17489.

b. Precatalysts

Compounds prepared using literature references: $Pd_2(dba)_3{\cdot}CHCl_3$,[8] ^{DMP}DAB-Pd-MAH,[9] $[Pd(acetanilide)OAc]_2$.[10]

c. Borylation Products

Method evaluation (Figure 4, main text)

Method A:
A 1 dram vial was charged with the respective alkenyl carboxylate precursor (0.120 mmol), B_2Pin_2 (33.5 mg, 0.132 mmol), $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), P(*o*-OMePh)$_3$ (1.6 mg, 0.005 mmol), 1,3,5-trimethoxybenzene (2.0 mg, 0.012 mmol), and 10:1 acetone:water (v/v) (0.6 M in alkenyl carboxylate). The reaction mixture was stirred at room temperature for 18 hours. The solutions were then evaporated to dryness, and NMR spectroscopic analysis conducted in $CDCl_3$ (0.6 mL).

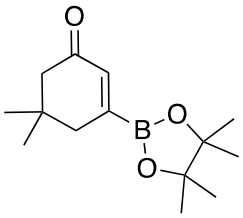
Method B:
A 2 mL vial was charged with the respective alkenyl carboxylate precursor (0.878 mmol), B_2Pin_2 (245.3 mg, 0.966 mmol), $Pd(OAc)_2$ (4.9 mg, 0.022 mmol), SPhos (13.5 mg, 0.033 mmol), 1,3,5-trimethoxybenzene (14.8 mg, 0.088 mmol), and toluene (0.8 M in alkenyl carboxylate). The reaction mixture was stirred at 100 °C for 18 hours. The solutions were then evaporated to dryness, and NMR spectroscopic analysis conducted in $CDCl_3$ (0.6 mL).

Method C:
A J. Young NMR tube was charged with the respective vinyl carboxylate precursor (0.120 mmol), B_2Pin_2 (33.5 mg, 0.132 mmol), $Pd(PCy_3)_2$ (8.0 mg, 0.012 mmol), 1,3,5-trimethoxybenzene (2.0 mg, 0.012 mmol), and d_8-toluene (0.2 M in alkenyl carboxylate). The tubes were immersed in an oil bath set to 100 °C for 18 hours. ^{1}H NMR spectra were then obtained. These samples were then evaporated to dryness and NMR spectroscopic analysis was conducted in $CDCl_3$ (0.6 mL) for consistency with Methods A and B.

Isolation of new compounds

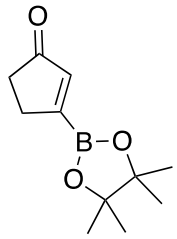
Products **4-7** were synthesized using **Method C** at 0.5 mmol scale in toluene (2.5 mL, 0.2 M) with respect to the vinyl carboxylate precursor, no internal standard was added, and the reactions were conducted in 1-dram vials with stirring at 100 °C. The crude products were filtered through Celite, washed three times with 5 ml saturated NaCl solution (brine). The organic layer was then dried with $MgSO_4$, filtered, and evaporated to dryness before characterization. Purification by silica gel chromatography was not successful due to the propensity of these compounds to give wide elution bands.

2. 1-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-5,5-dimethylcyclohex-1-en-3-one



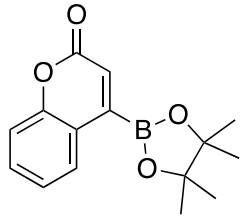
NMR spectral data are consistent with previous literature reports.[11]

3. 1-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)cyclopent-1-en-3-one



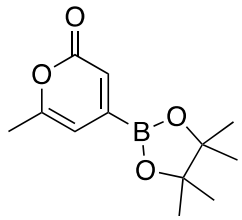
NMR spectral data consistent with previous literature reports.[12]

4. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzopyran-2-one



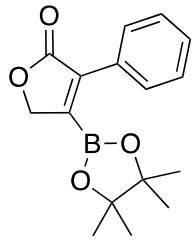
^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 8.21 (dd, J=8.0, 0.7 Hz, 1H), 7.51 (t, J = 7.6 Hz 1H), 7.29 (q, J = 8.1 Hz, 2H), 6.91 (s, 1H), 1.41 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 160.2, 153.8, 131.3, 128.8, 125.5, 124.3, 120.6, 116.8, 85.1, 24.9. HRMS: Cal'd for $C_{15}H_{17}BO_4$ $[M+H]^+$: 273.12982; found: 273.12928.

5. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-6-methyl-2*H*-pyran-2-one



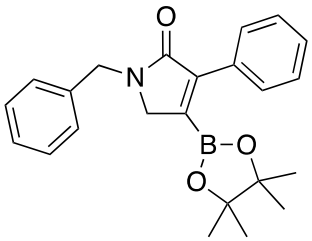
^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 6.59 (s, 1H), 6.20 (s, 1H), 2.24 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 162.4, 161.3, 120.5, 105.8, 85.0, 24.5, 19.7. HRMS: Cal'd for $C_{12}H_{18}BO_4$ $[M+H]^+$: 237.12982; found: 237.12931.

6. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-3-phenylpyran-3-en-2-one



^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.74-7.69 (m, 2H), 7.42-7.37 (m, 3H), 4.98 (s, 1H), 1.30 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 173.4, 144.4, 140.2, 130.5, 129.2, 127.9, 84.9, 72.8, 24.7. HRMS: Cal'd for $C_{12}H_{17}BO_4$: 236.12199; found: 237.12931.
HRMS: Cal'd for $C_{16}H_{19}BO_4$ $[M+H]^+$: 287.14547; found: 287.14511.

7. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-1-benzyl-3-phenylpyrrolidin-3-en-2-one



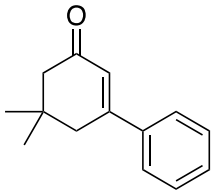
^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 7.75-7.70 (m, 2H), 7.45-7.29 (m, 8H), 4.73 (s, 2H), 4.00 (s, 2H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): 170.0, 137.4, 129.5, 128.7, 128.6, 128.4, 128.3, 128.1, 127.6, 127.0, 84.2, 53.1, 46.8, 24.6. HRMS: Cal'd for $C_{23}H_{27}BNO_3$ [M+H]: 376.20840; found: 376.20806.

d. Cross-Coupling Products

Cross-coupling products were prepared by borylation using one of **Method A**, **B**, or **C** (1.0 mmol scale with respect to alkenyl pivalate precursor unless otherwise noted), followed by evaporating the reaction mixture to dryness, and then subjecting the crude product to the following cross-coupling procedure:

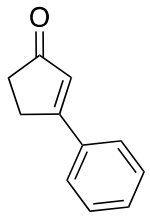
The crude boronate ester was dissolved in toluene (10 ml), filtered through a pad of Celite, washed three times with saturated NaCl (10 ml), dried with $MgSO_4$, filtered, and then evaporated to dryness in a 20 mL vial with a septum cap. The vial was brought into the glovebox, and charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), XPhos (14.3 mg, 0.03 mmol), K_3PO_4 (425.7 mg, 2.0 mmol), bromobenzene (157 mg, 1.0 mmol) and toluene (5 mL, 0.2 M in alkenyl carboxylate). The vial was brought outside the glovebox, degassed H_2O (1 mL) was injected through the septum, and the reaction mixture stirred at 80 °C for 18 hours. The solution was then filtered through a pad of celite and evaporated to dryness. The crude product was then isolated by column chromatography using hexanes/ethyl acetate on a Biotage Selekt unit (see section 4 for details).

8: **1-phenyl-5,5-dimethylcyclohex-1-en-3-one**[5]



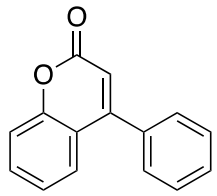
This product is prepared by borylation via **Method B** (3.3 mmol scale) followed by the cross-coupling procedure described above. NMR spectral data is consistent with that previously reported. Yield: 297.8 mg (45%, yellow oil).

9: **1-phenylcyclopent-1-en-3-one**[5]



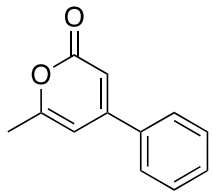
This product is prepared by borylation via **Method A** followed by the cross-coupling procedure described above. NMR spectral data is consistent with that previously reported. Yield: 48.9 mg (24%, yellow solid).

10: **4-phenylbenzopyran-2-one**[5]



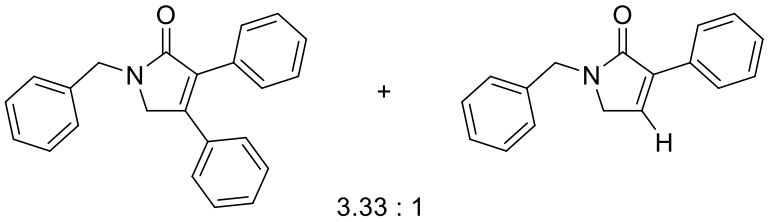
This product is prepared by borylation via **Method C** followed by the cross-coupling procedure described above. NMR spectral data is consistent with that previously reported. Yield: 35.1 mg (16%, brown solid). The protodeboronation product (i.e. coumarin) was also obtained.[13] Yield: 46.7 mg (32%).

11: **4-phenyl-6-methyl-2*H*-pyran-2-one**[14]



This product is prepared by borylation via **Method C** followed by the cross-coupling procedure described above. NMR spectral data is consistent with that previously reported. Yield: 59.0 mg (32%, beige solid).

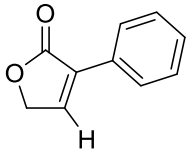
12: **4-phenyl-1-benzyl-3-phenylpyrrolidin-3-en-2-one**[5]



This product was attempted to be prepared by borylation via **Method C** followed by the cross-coupling procedure described above. Upon isolation using automated chromatography, we observe a 3.33 : 1 mixture of **12** and 1**4**. NMR spectral data for **12** is consistent with that previously reported. Yield: 151.7 mg (49% based on observed product ratio, yellow oil).

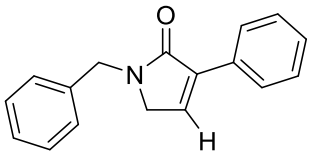
e. Protodeboronation Products

13: 3-phenylfuran-2(5H)-one[15]



This product was prepared by borylation via **Method C** (0.500 mmol scale), followed by filtration of the crude reaction solution through Celite. The organic phase (~5 mL total volume toluene) was then washed with 3 x 5 mL saturated $NaHCO_3$, and the organic layer dried over $MgSO_4$ before concentration in vacuo. The crude product was then isolated by column chromatography using hexanes/ethyl acetate on a Biotage Selekt unit (see section 4 for details). NMR spectral data is consistent with that previously reported. Yield: 52.8 mg (66%, yellow solid).

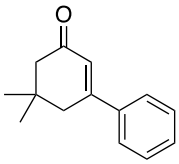
14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one[16]

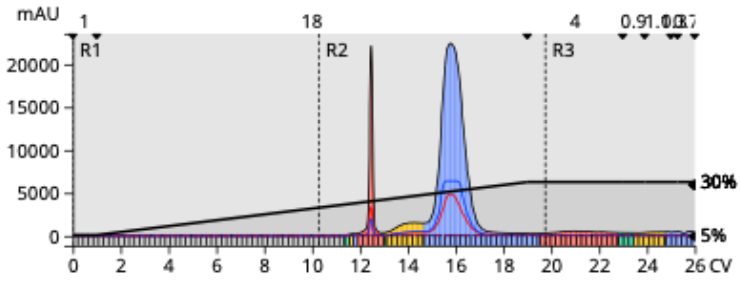


This product was prepared by borylation via **Method C** (0.500 mmol scale), followed by filtration of the crude reaction solution through Celite. The organic phase (~5 mL total volume toluene) was then washed with 3 x 5 mL saturated $NaHCO_3$, and the organic layer dried over $MgSO_4$ before concentration in vacuo. The crude product was then isolated by column chromatography using hexanes/ethyl acetate on a Biotage Selekt unit (see section 4 for details). NMR spectral data is consistent with that previously reported. Yield: 53.9 mg (43%, yellow oil).

4. Purification Chromatograms

8. 1-phenyl-5,5-dimethylcyclohex-1-en-3-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1 (Collect)	254 nm	40 mAU
UV2 (Collect)	280 nm	40 mAU

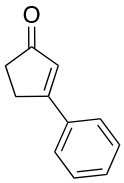
Gradient

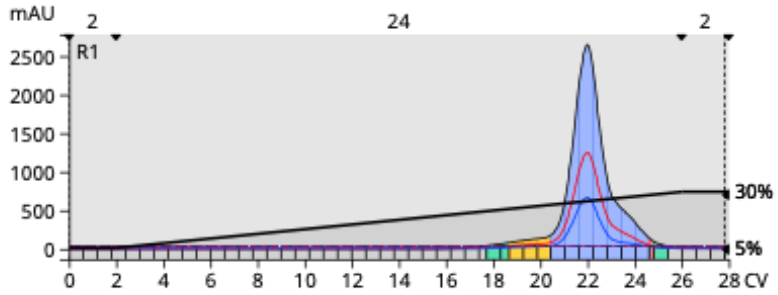
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

5-5%	Ethyl acetate in n-Hexane	1 CV	
5-30%	Ethyl acetate in n-Hexane	18 CV	
30-30%	Ethyl acetate in n-Hexane	4 CV	
30-30%	Ethyl acetate in n-Hexane	0.9 CV	
30-30%	Ethyl acetate in n-Hexane	1.1 CV	Auto extended
30-30%	Ethyl acetate in n-Hexane	0.3 CV	
30-30%	Ethyl acetate in n-Hexane	0.7 CV	

Figure S2: Chromatography Results for **8**.

9. 1-phenylcyclopent-1-en-3-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1 (Collect)	280 nm	40 mAU
UV2 (Collect)	254 nm	40 mAU

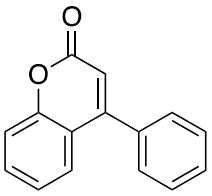
Gradient

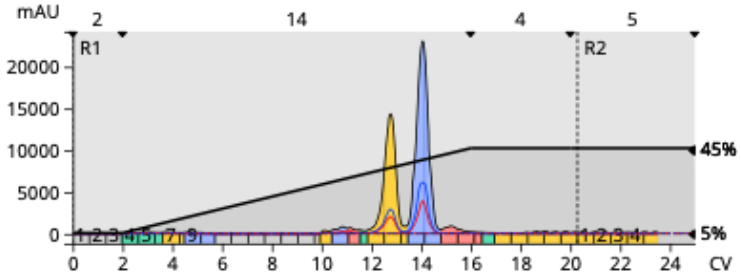
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

5-5%	Ethyl acetate in n-Hexane	2 CV
5-30%	Ethyl acetate in n-Hexane	24 CV
30-30%	Ethyl acetate in n-Hexane	2 CV

Figure S3: Chromatography Results for **9**.

10. 4-phenylbenzopyran-2-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1 (Collect)	254 nm	40 mAU
UV2 (Collect)	280 nm	40 mAU

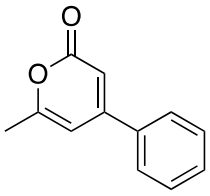
Gradient

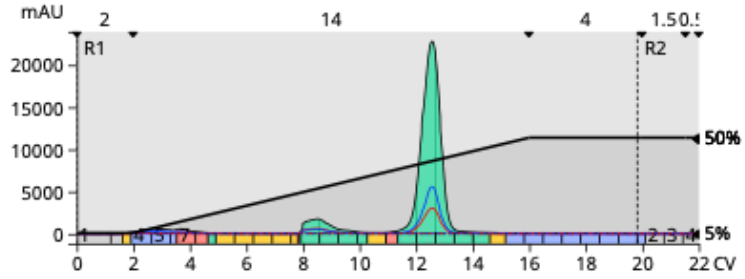
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

5-5%	Ethyl acetate in n-Hexane	2 CV	
5-45%	Ethyl acetate in n-Hexane	14 CV	
45-45%	Ethyl acetate in n-Hexane	4 CV	
45-45%	Ethyl acetate in n-Hexane	5 CV	Auto extended

Figure S4: Chromatography Results for **10**.

11. 4-phenyl-6-methyl-2*H*-pyran-2-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1 (Collect)	280 nm	40 mAU
UV2 (Collect)	254 nm	40 mAU

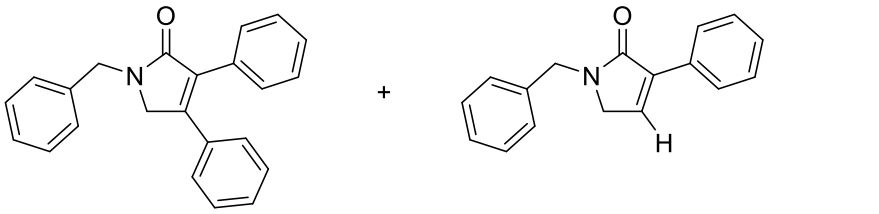
Gradient

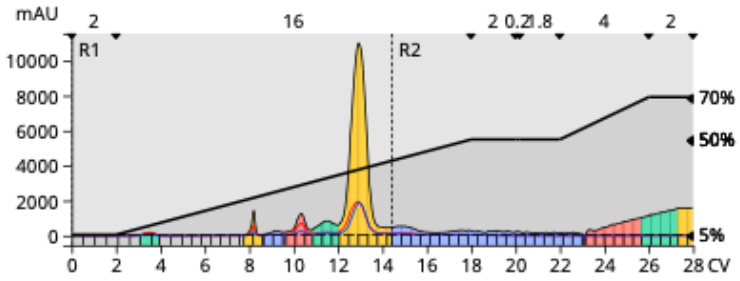
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

5-5%	Ethyl acetate in n-Hexane	2 CV	
5-50%	Ethyl acetate in n-Hexane	14 CV	
50-50%	Ethyl acetate in n-Hexane	4 CV	
50-50%	Ethyl acetate in n-Hexane	1.5 CV	
50-50%	Ethyl acetate in n-Hexane	0.5 CV	Auto extended

Figure S5: Chromatography Results for **11**.

12. 4-phenyl-1-benzyl-3-phenylpyrrolidin-3-en-2-one co-elution with 1-benzyl-3-phenylpyrrolidin-3-en-2-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1	254 nm	
UV2	280 nm	

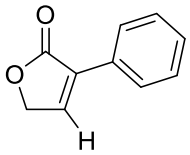
Gradient

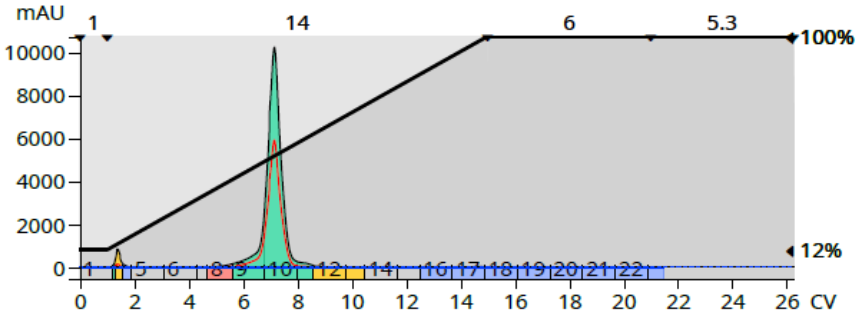
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

5-5%	Ethyl acetate in n-Hexane	2 CV	
5-50%	Ethyl acetate in n-Hexane	16 CV	
50-50%	Ethyl acetate in n-Hexane	2 CV	
50-50%	Ethyl acetate in n-Hexane	0.2 CV	
50-50%	Ethyl acetate in n-Hexane	1.8 CV	Auto extended
50-70%	Ethyl acetate in n-Hexane	4 CV	
70-70%	Ethyl acetate in n-Hexane	2 CV	

Figure S6: Chromatography Results for **12**.

13. 3-phenylfuran-2(5H)-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	40 mAU
UV1 (Collect)	254 nm	40 mAU
UV2 (Collect)	220 nm	40 mAU

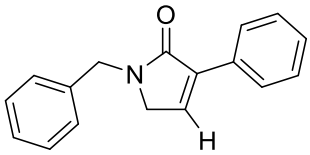
Gradient

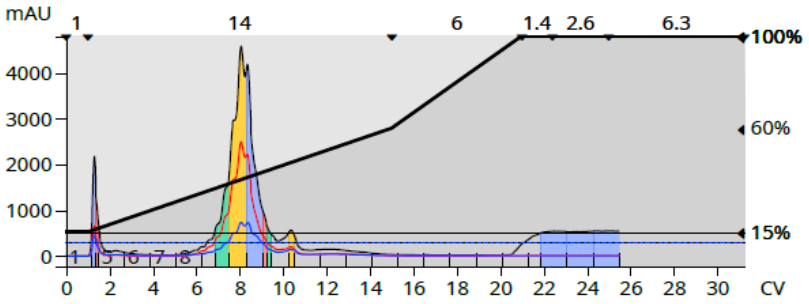
Solvent A: n-Hexane **Solvent B:** Ethyl acetate

12-12%	Ethyl acetate in n-Hexane	1 CV	
12-100%	Ethyl acetate in n-Hexane	14 CV	
100-100%	Ethyl acetate in n-Hexane	6 CV	
100-100%	Ethyl acetate in n-Hexane	5.3 CV	Auto extended

Figure S7: Chromatography Results for **13**.

14. 1-benzyl-3-phenylpyrrolidin-3-en-2-one:





Signal	Wavelength	Threshold
λ-All (Collect)	200 - 400 nm	500 mAU
UV1 (Collect)	254 nm	300 mAU
UV2 (Collect)	280 nm	300 mAU

Gradient

Solvent A: n-Hexane **Solvent B:** Ethyl acetate

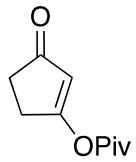
15-15%	Ethyl acetate in n-Hexane	1 CV	
15-60%	Ethyl acetate in n-Hexane	14 CV	
60-100%	Ethyl acetate in n-Hexane	6 CV	
100-100%	Ethyl acetate in n-Hexane	1.4 CV	
100-100%	Ethyl acetate in n-Hexane	2.6 CV	
100-100%	Ethyl acetate in n-Hexane	6.3 CV	Auto extended

Figure S8: Chromatography Results for **14**.

5. NMR and HRMS Spectra

a. Starting Materials

1-pivalyloxycyclopent-1-en-3-one:



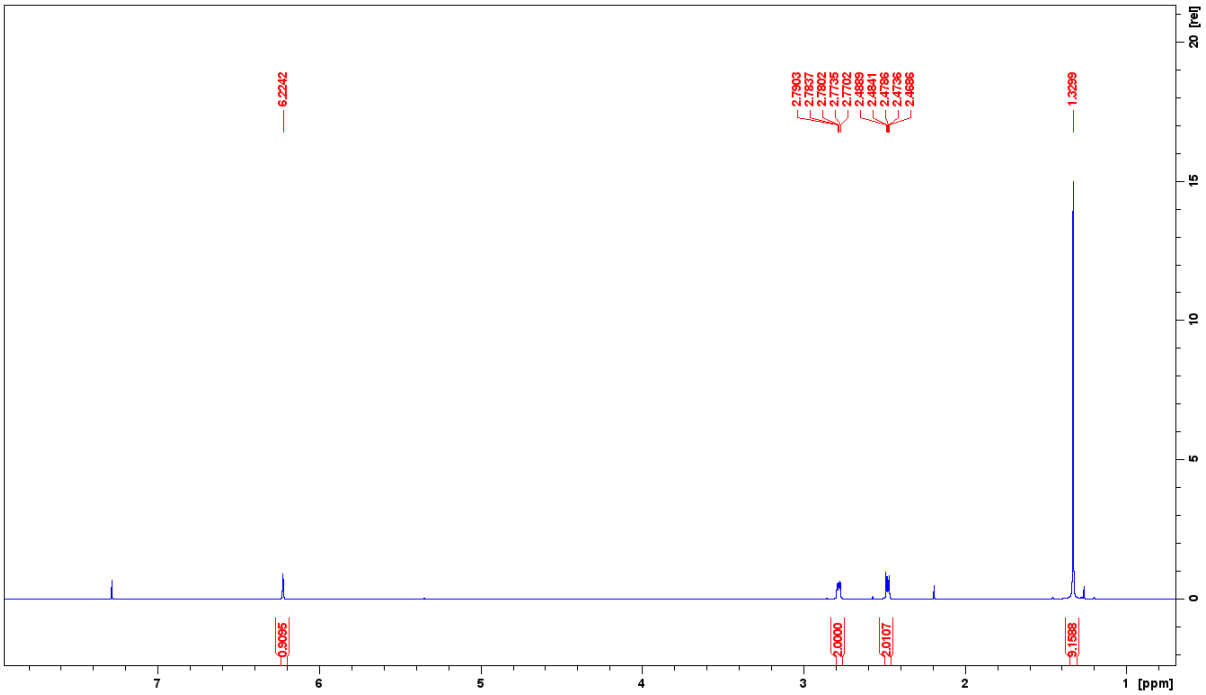


Figure S9: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **1-pivalyloxycyclopent-1-en-3-one**

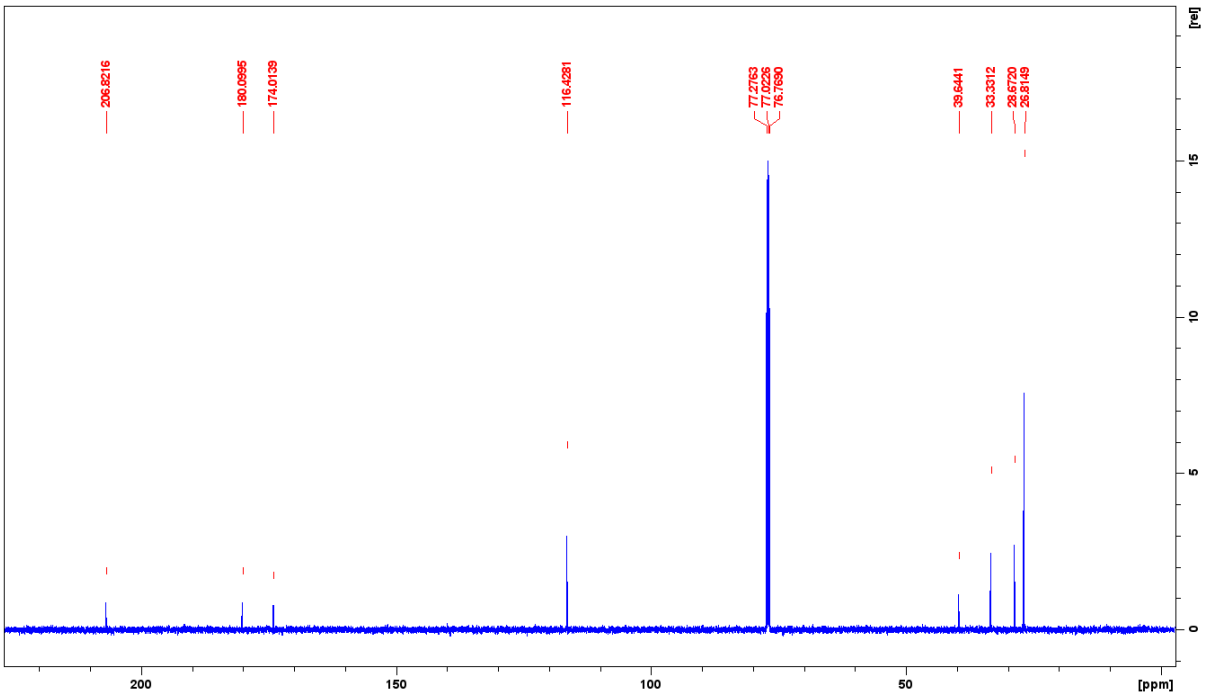


Figure S10: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K) of **1-pivalyloxycyclopent-1-en-3-one**

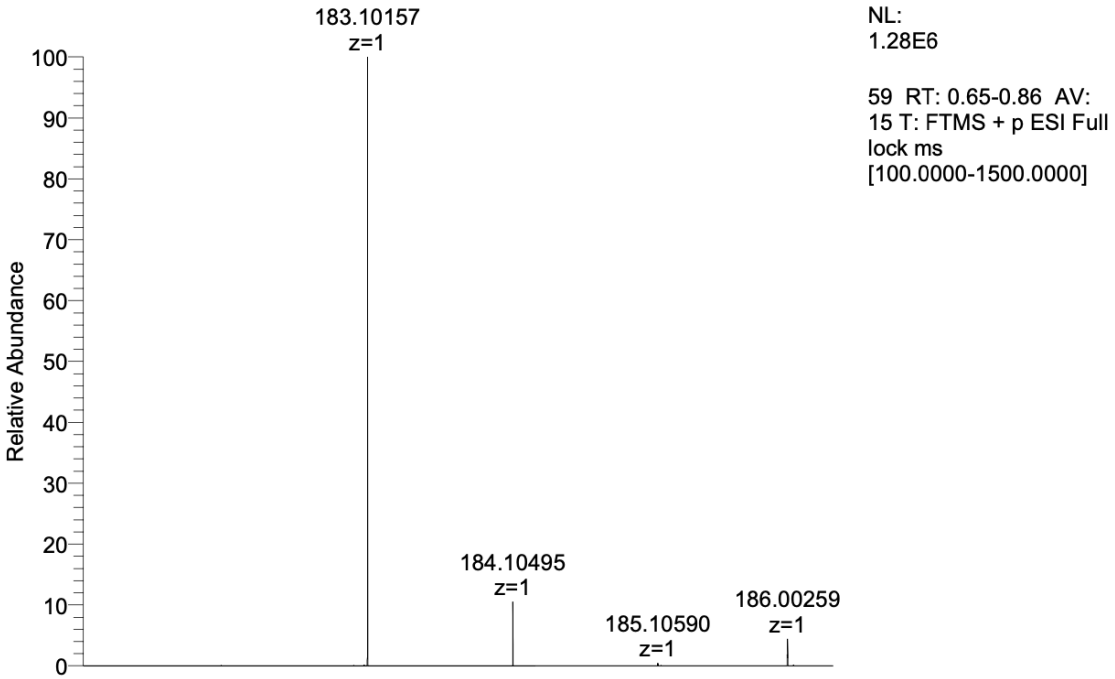
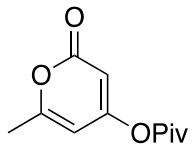


Figure S11: HRMS spectrum of **1-pivalyloxycyclopent-1-en-3-one**

4-pivalyloxy-6-methyl-2-pyrone:



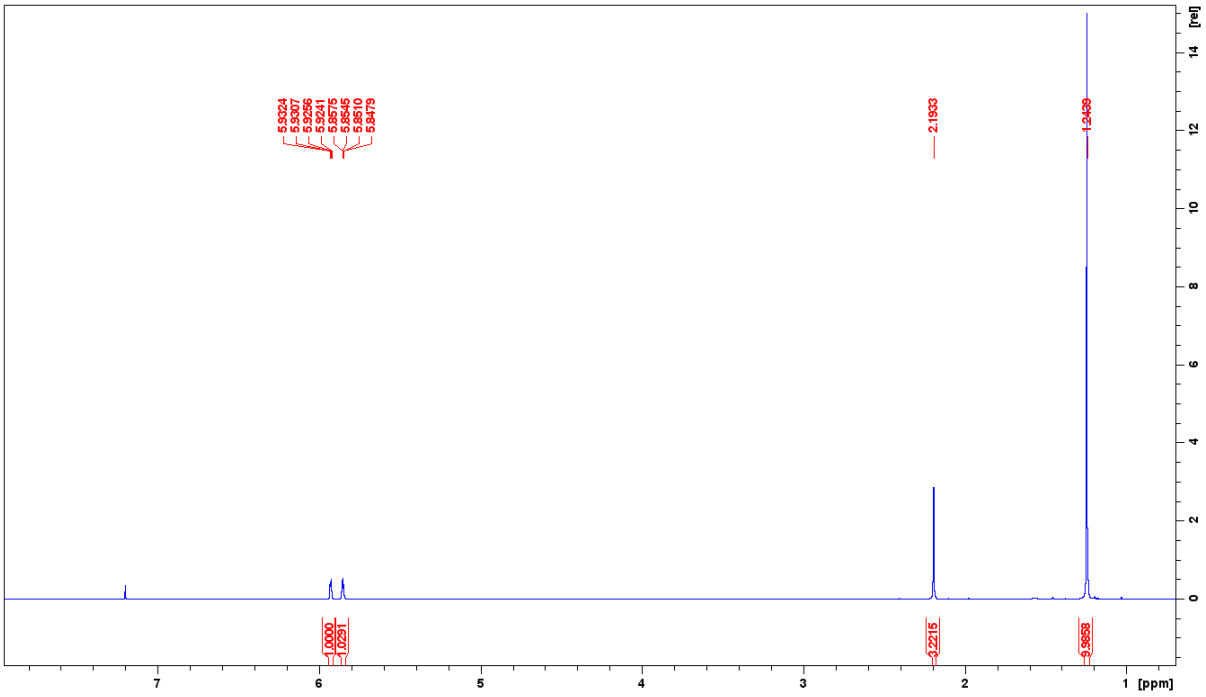


Figure S12: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **4-pivalyloxy-6-methyl-2-pyrone**

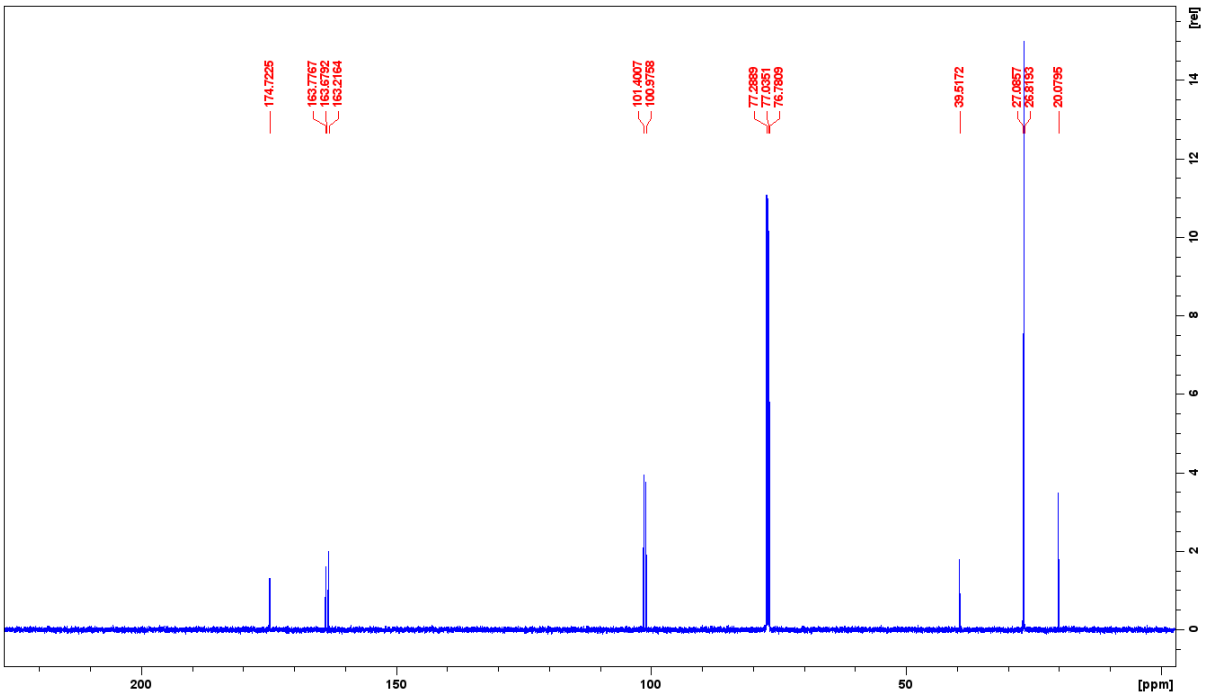


Figure S13: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **4-pivalyloxy-6-methyl-2-pyrone**

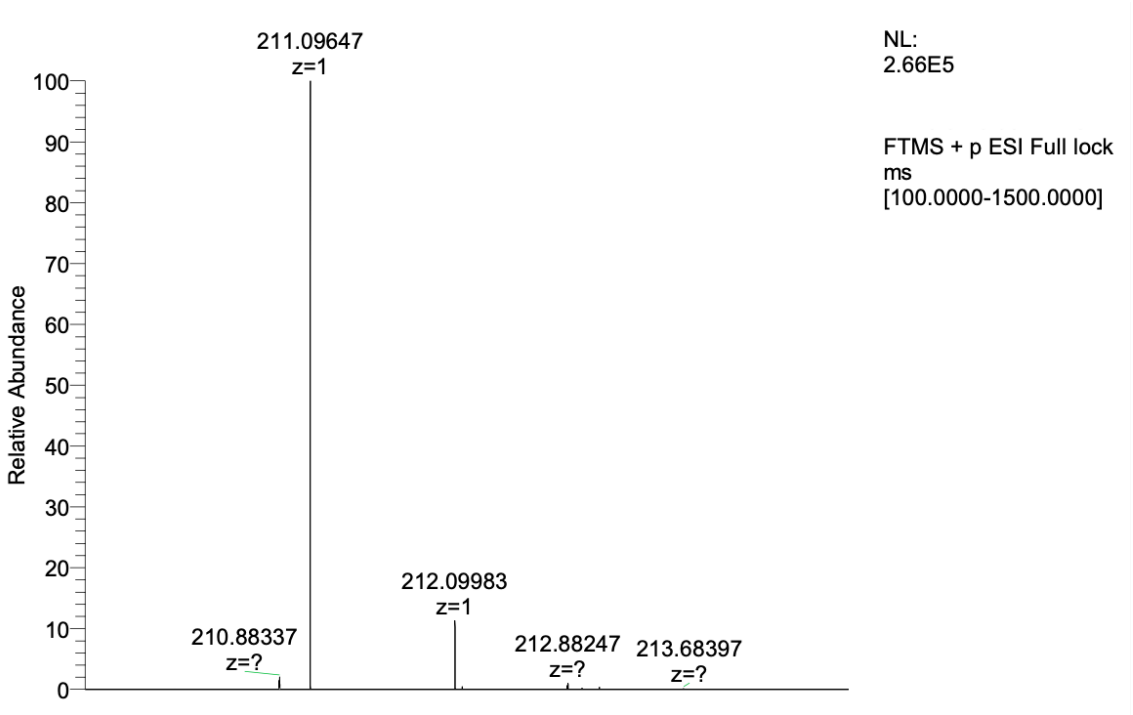
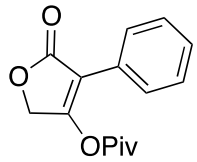


Figure S14: HRMS spectrum of **4-pivalyloxy-6-methyl-2-pyrone**

4-pivalyloxy-3-phenylpyran-3-en-2-one



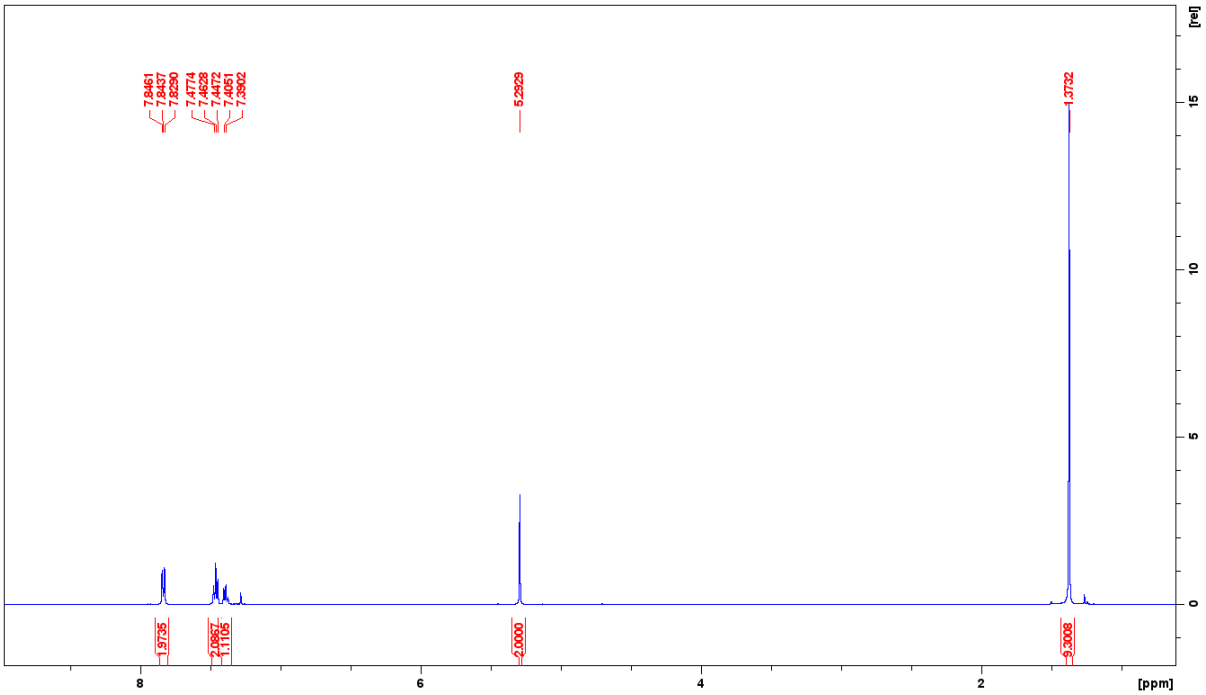


Figure S15: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **4-pivalyloxy-3-phenylpyran-3-en-2-one**

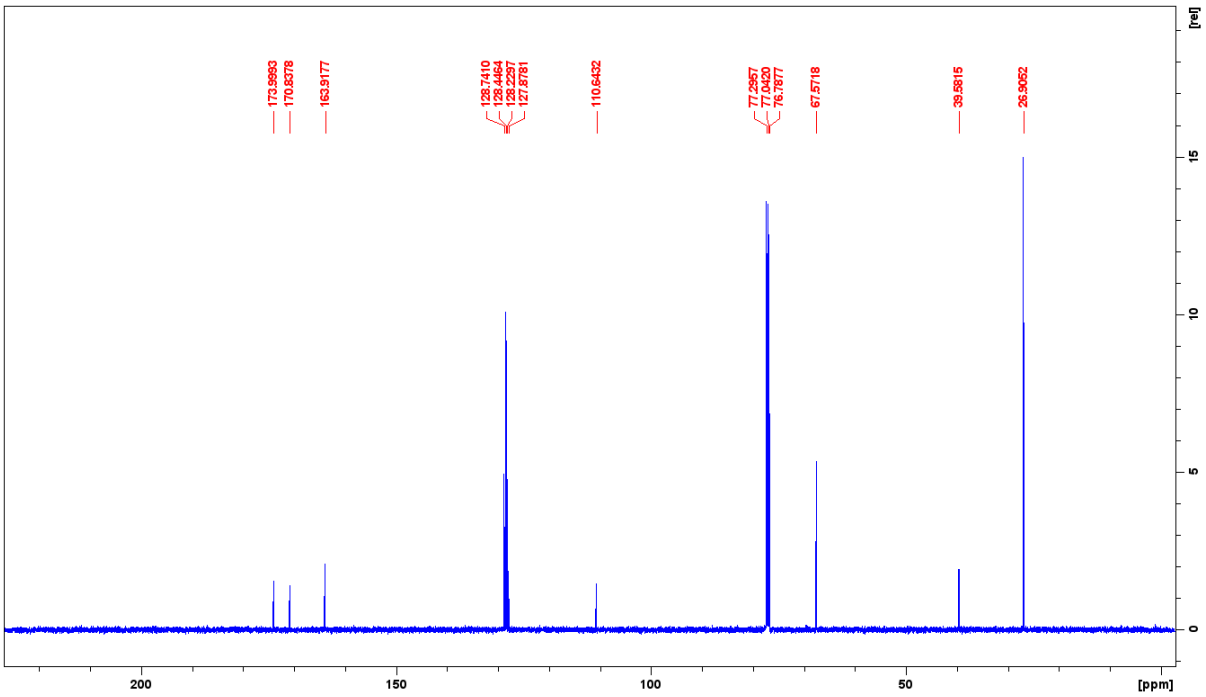


Figure S16: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K) of **4-pivalyloxy-3-phenylpyran-3-en-2-one**

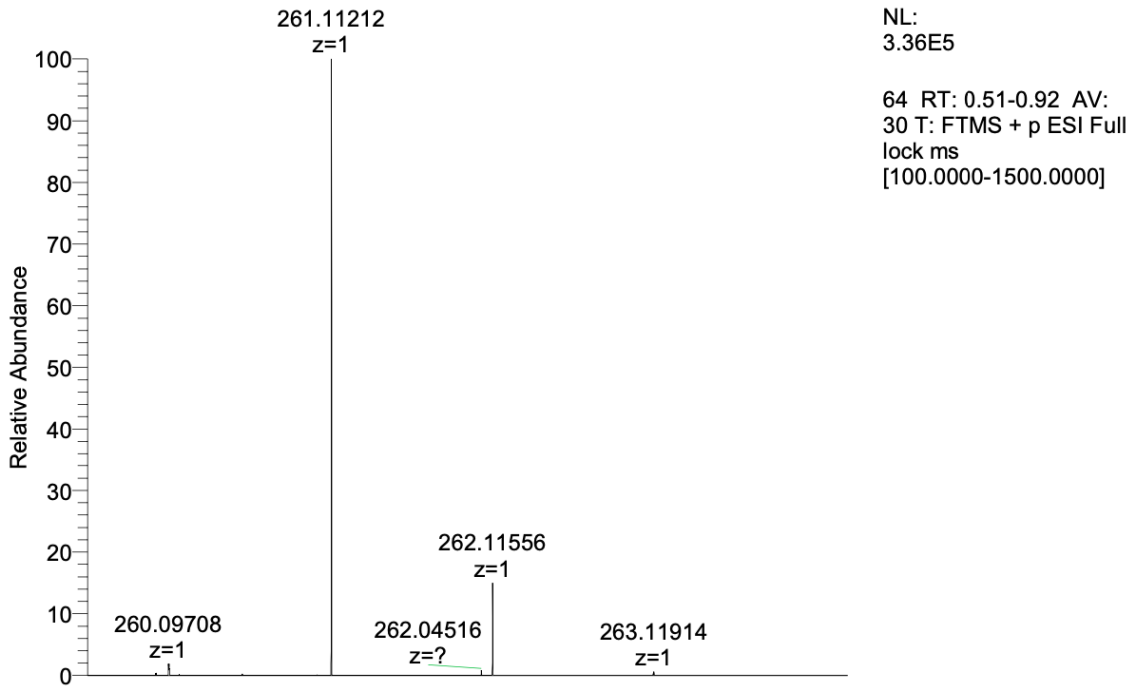
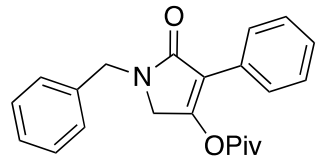


Figure S17: HRMS spectrum of **4-pivalyloxy-3-phenylpyran-3-en-2-one**

4-pivalyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one



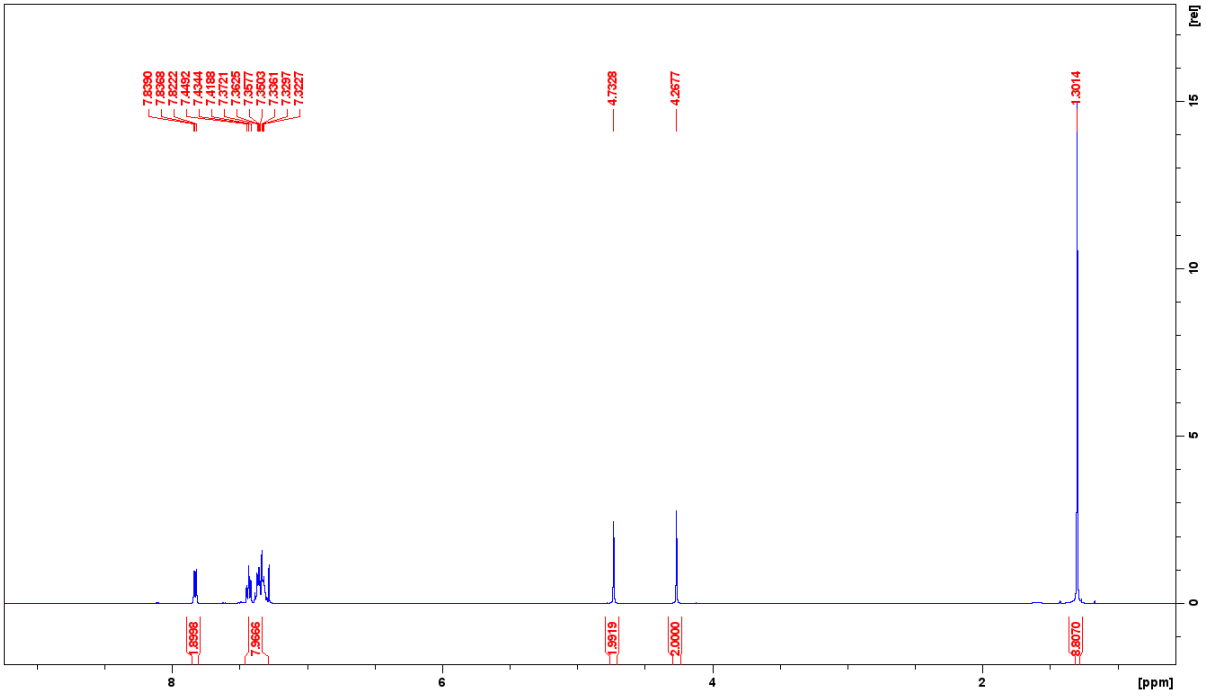


Figure S18: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **4-pivalyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one**

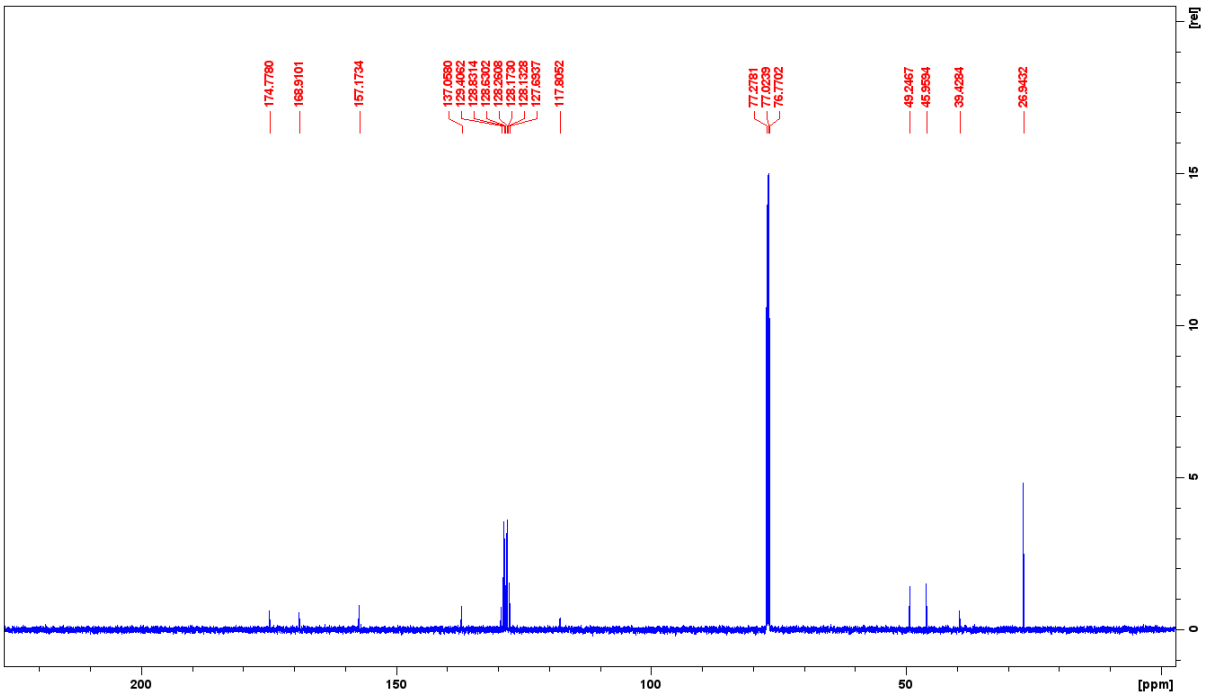


Figure S19: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **4-pivalyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one**

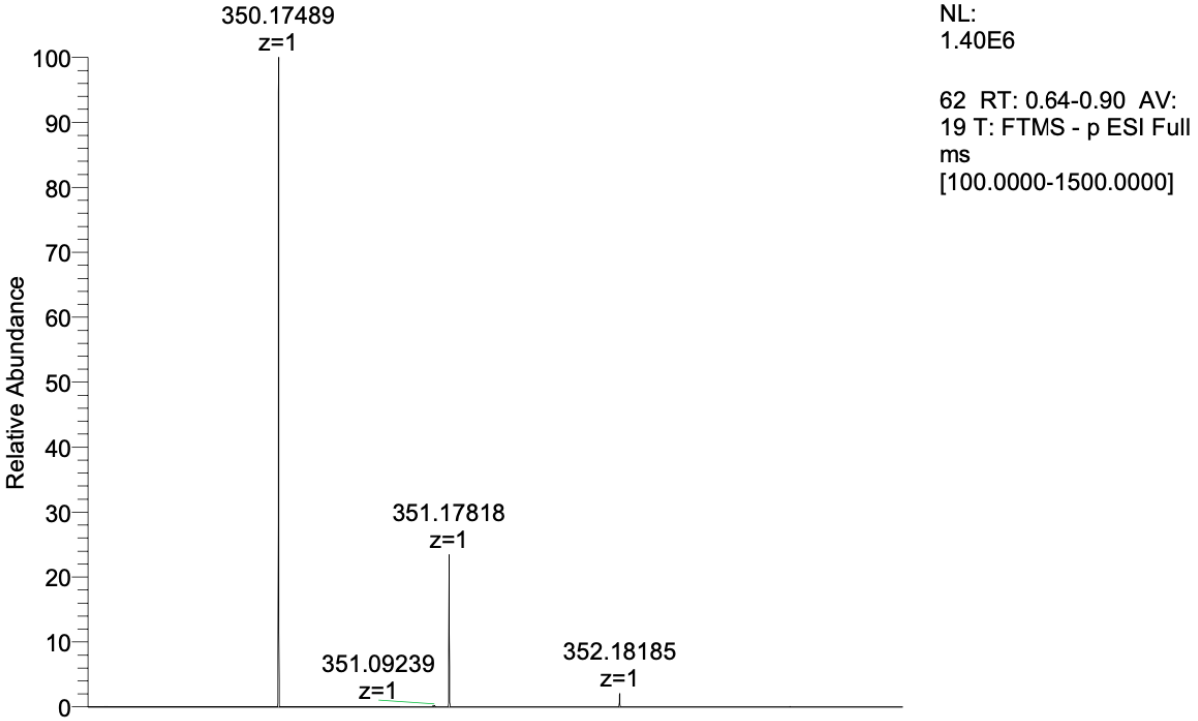
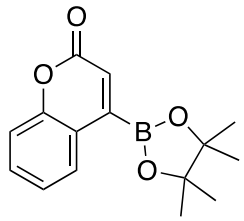


Figure S20: HRMS spectrum of **4-pivalyloxy-1-benzyl-3-phenylpyrrolidin-3-en-2-one**

b. Borylation Products

4. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzopyran-2-one



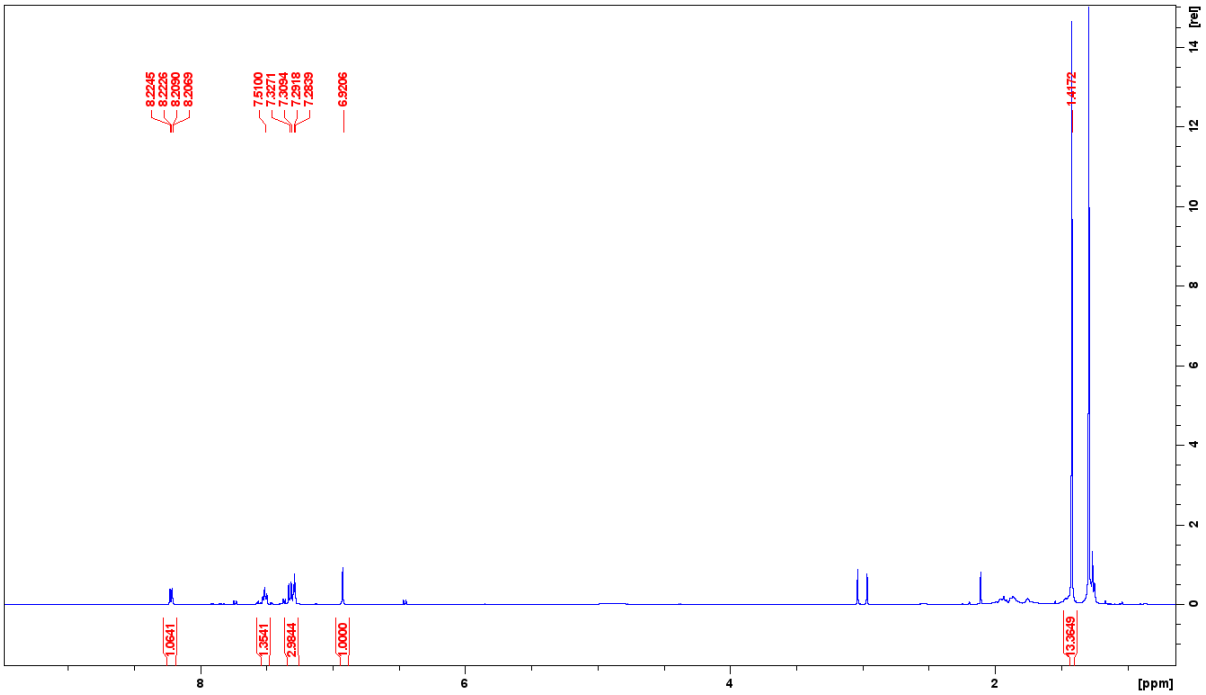


Figure S21: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **4**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzopyran-2-one**

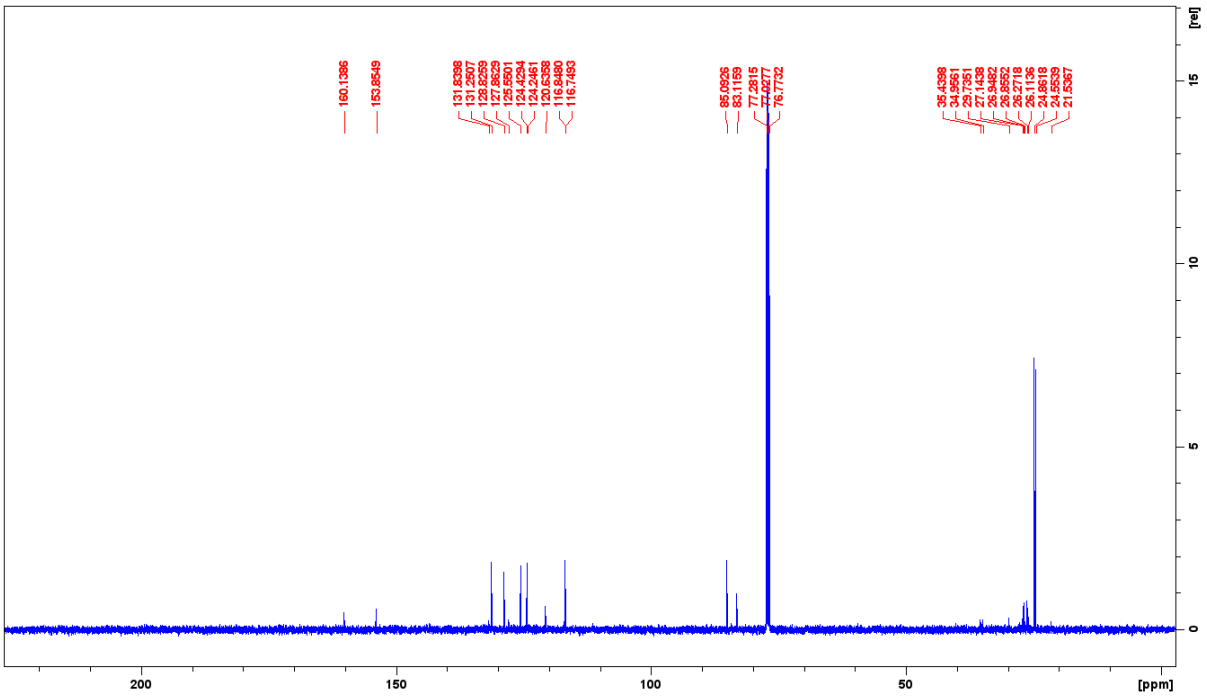


Figure S22: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **4**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzopyran-2-one**

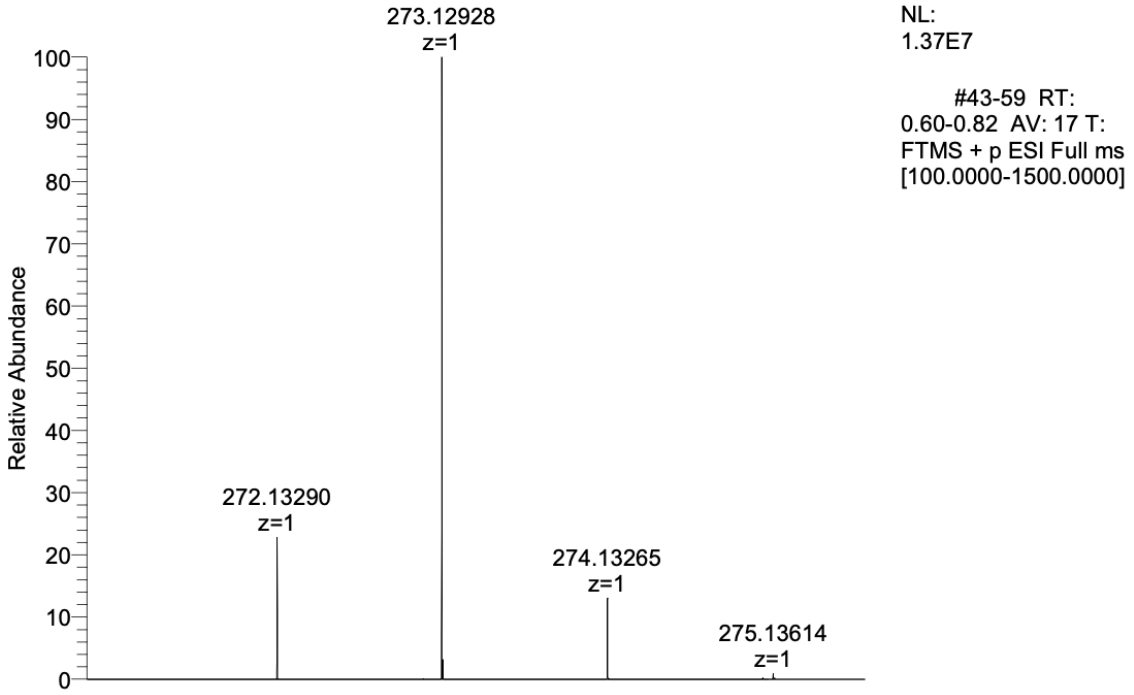
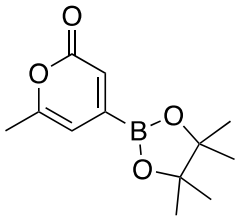


Figure S23: HRMS spectrum of **4**:
4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzopyran-2-one

5. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-6-methyl-2*H*-pyran-2-one



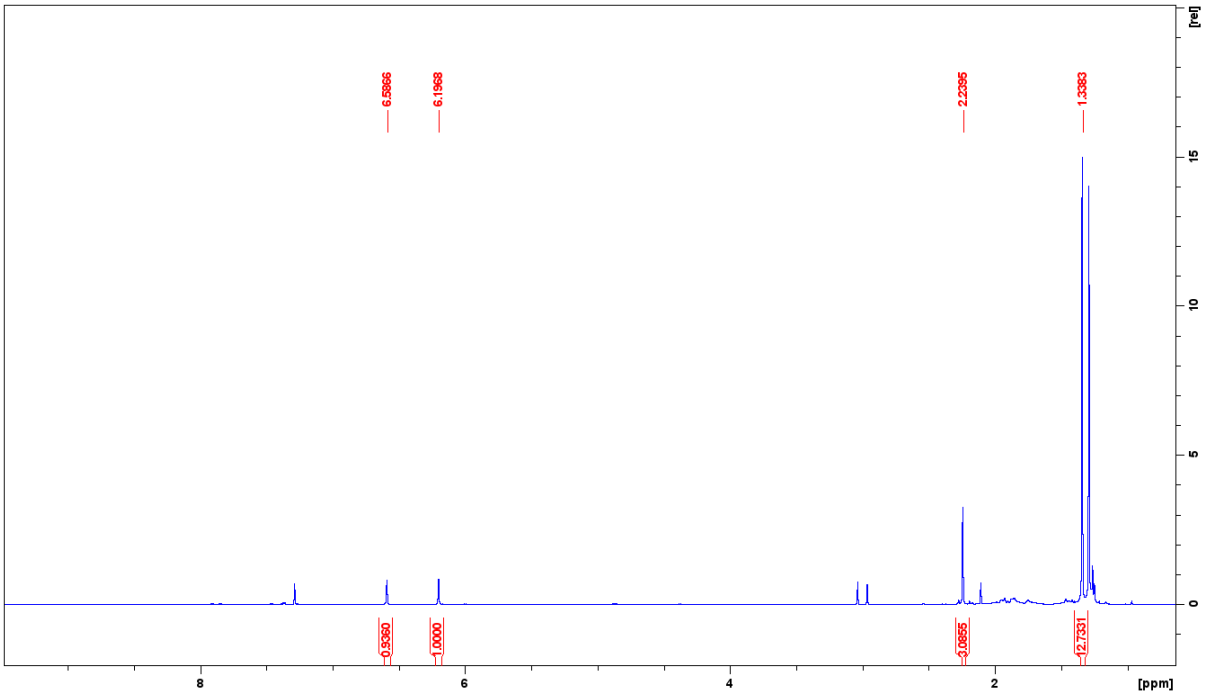


Figure S24: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **5**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-6-methyl-2*H*-pyran-2-one**

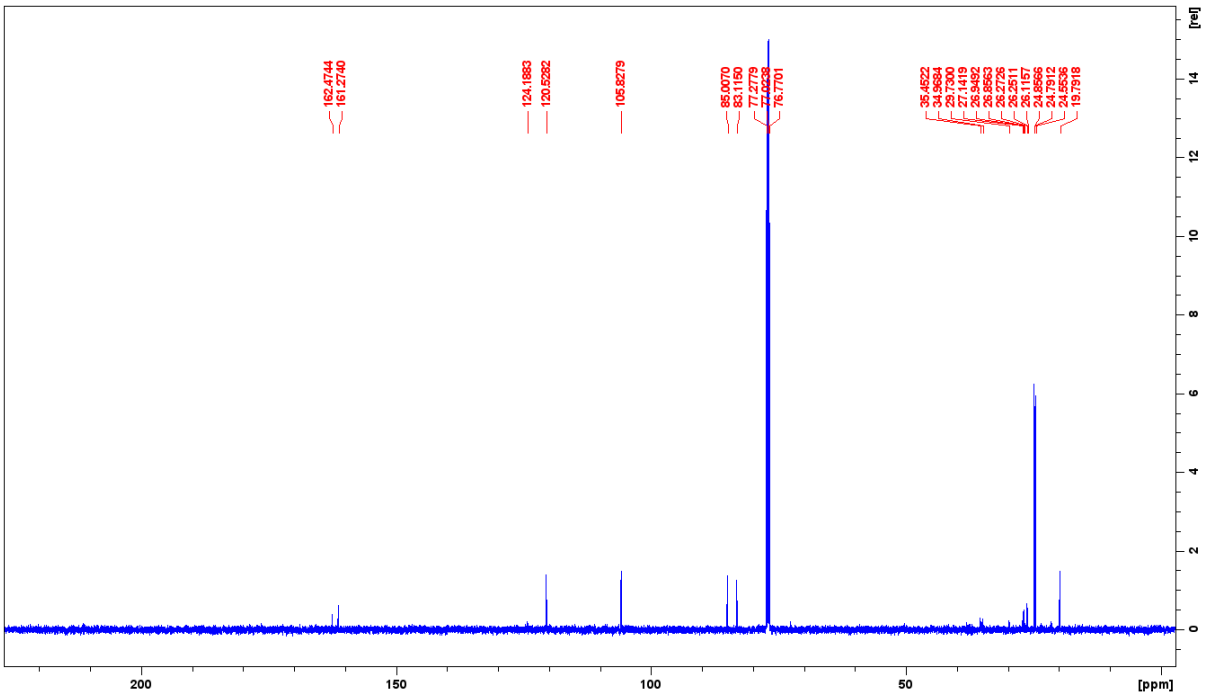


Figure S25: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **5**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-6-methyl-2*H*-pyran-2-one**

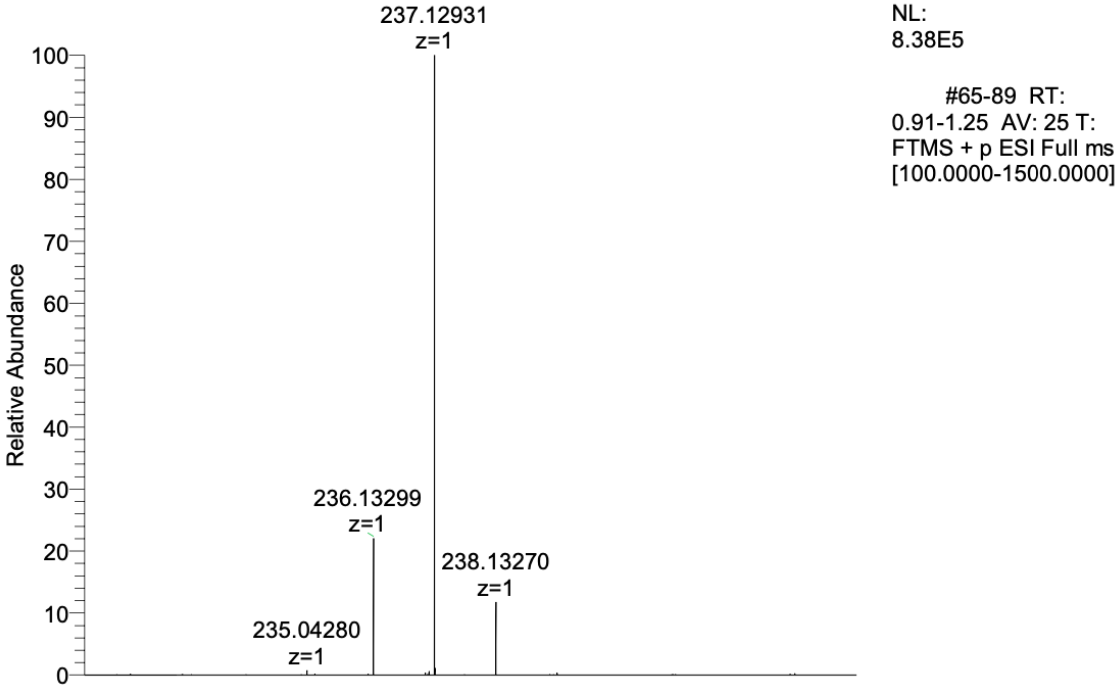
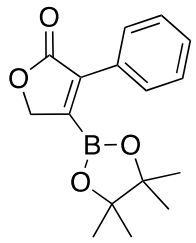


Figure S26: HRMS spectrum of **5**:
4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-6-methyl-2*H*-pyran-2-one

6. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-3-phenylpyran-3-en-2-one



All characterization for **6** was completed prior to any workup. Significant deboronation occurs when subject to any aqueous wash.

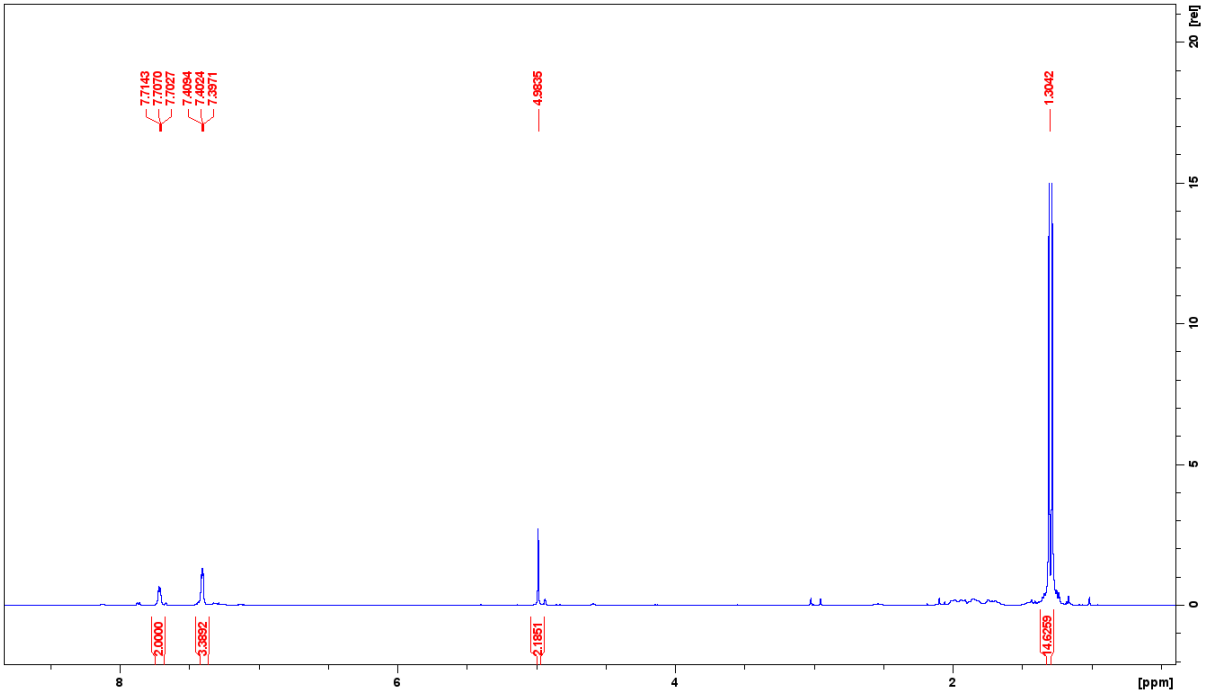


Figure S27: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **6**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-3-phenylpyran-3-en-2-one**

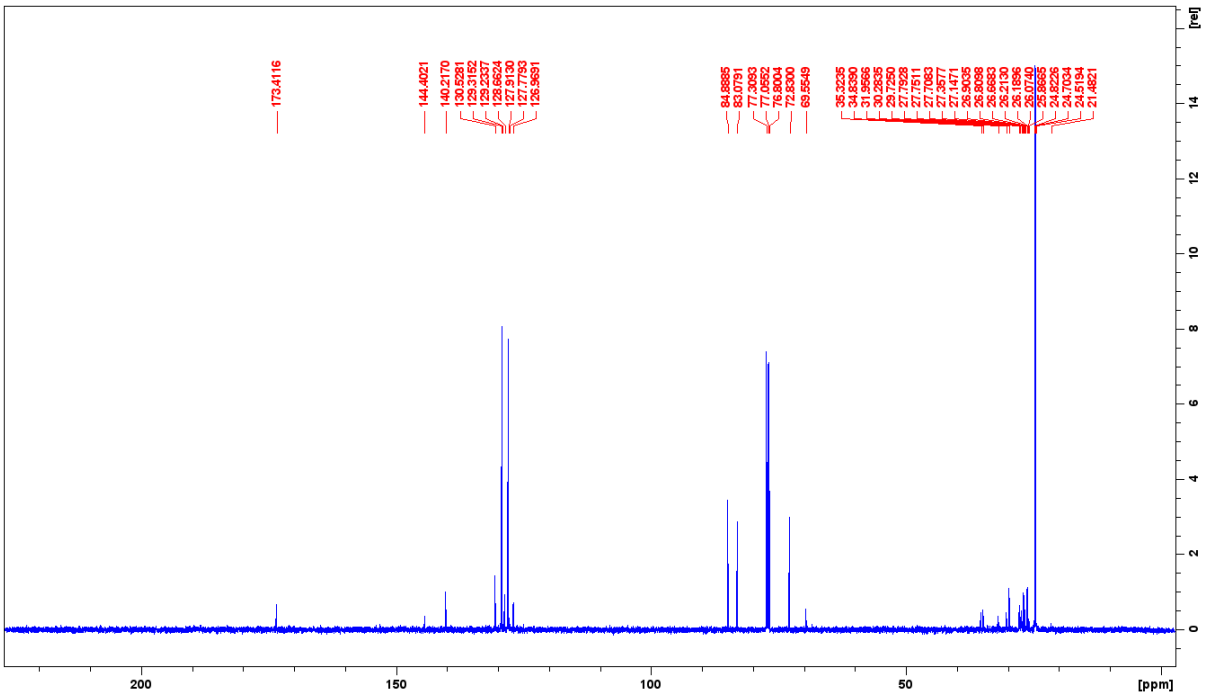


Figure S28: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **6**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-3-phenylpyran-3-en-2-one**

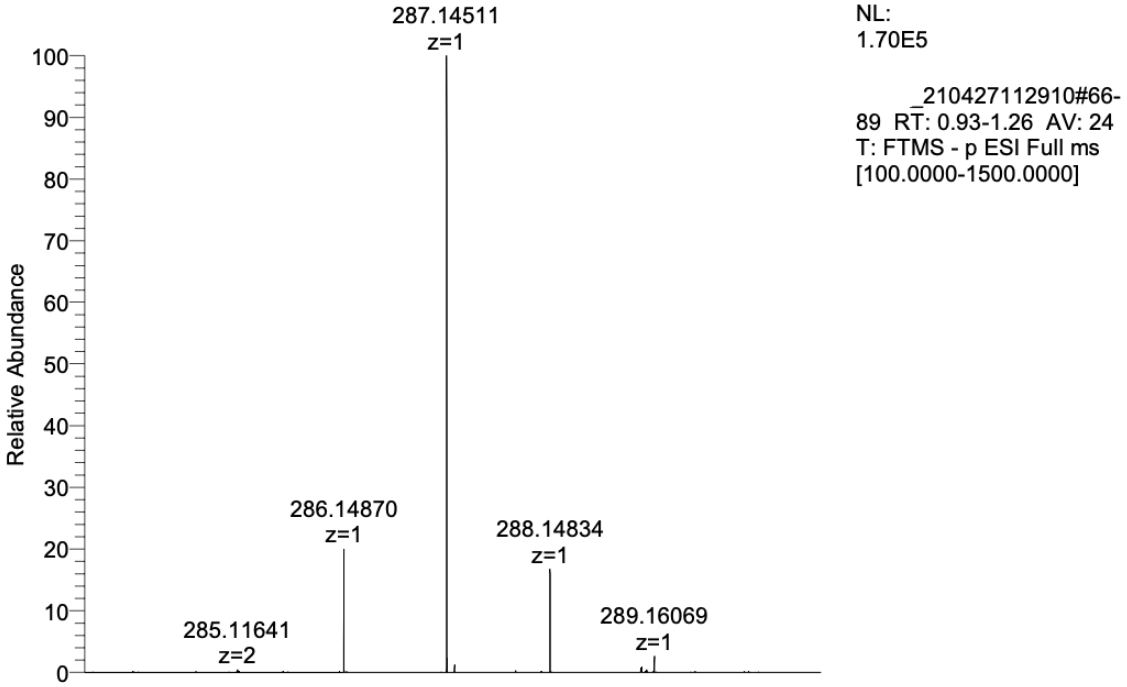


Figure S29: HRMS spectrum of **6**:
4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-3-phenylpyran-3-en-2-one

7. 4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-1-benzyl-3-phenylpyrrolidin-3-en-2-one

After borylation, **7** is isolated as a mixture with **14** (protodeborylation) in a 3.33 : 1 ratio. Attempts to further purify **7** resulted in more protodeboronation to give **14**; therefore, the mixture was characterized as-is; compound **14** was separately characterized after protodeboronation via treatment with aqueous base (see below).

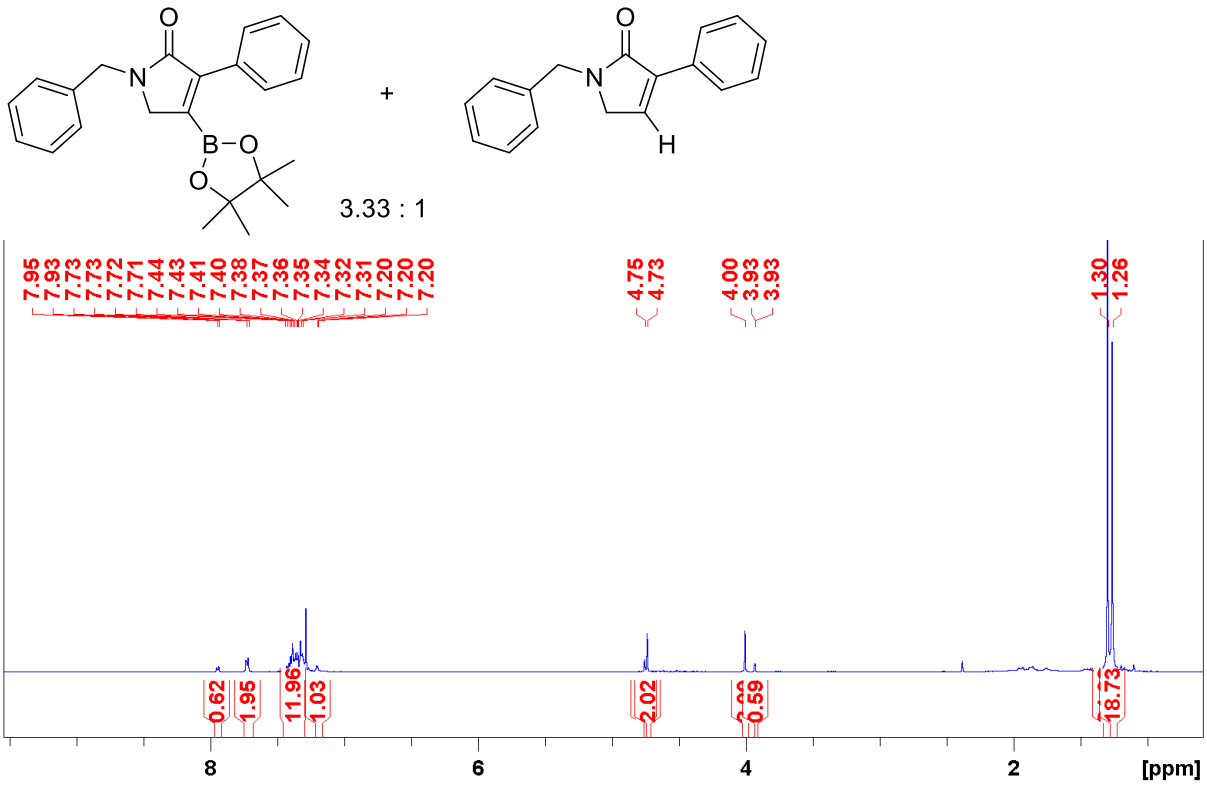


Figure S30: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K) of **7**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-1-benzyl-3-phenylpyrrolidin-3-en-2-one** and **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one** (3.33 : 1 mixture)

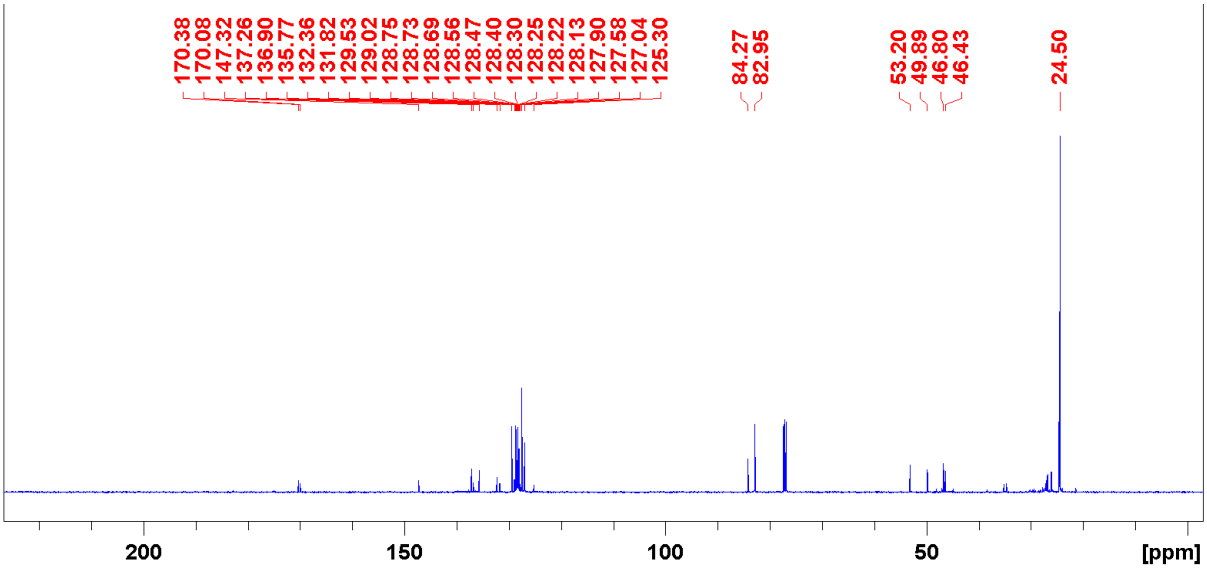


Figure S31: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K) of **7**: **4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-1-benzyl-3-phenylpyrrolidin-3-en-2-one** and **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one** (3.33 : 1 mixture)

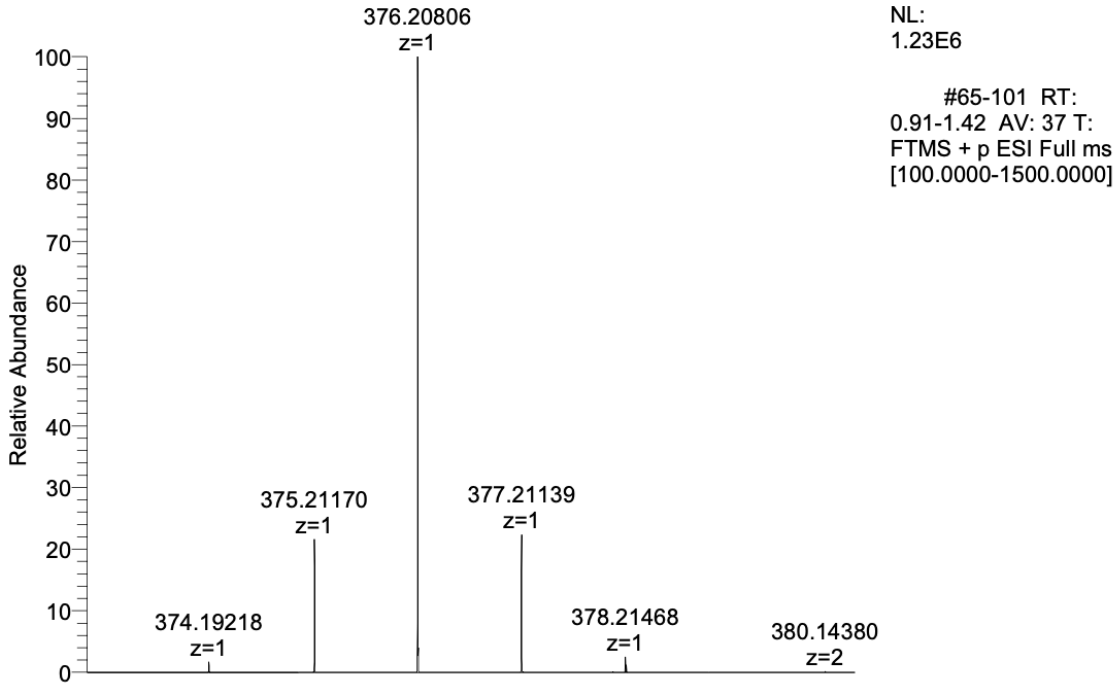
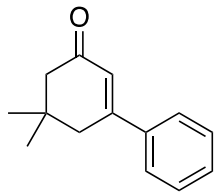


Figure S32: HRMS spectrum of **7**:

4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)-1-benzyl-3-phenylpyrrolidin-3-en-2-one

c. Cross-Coupling Products

8: **1-phenyl-5,5-dimethylcyclohex-1-en-3-one**



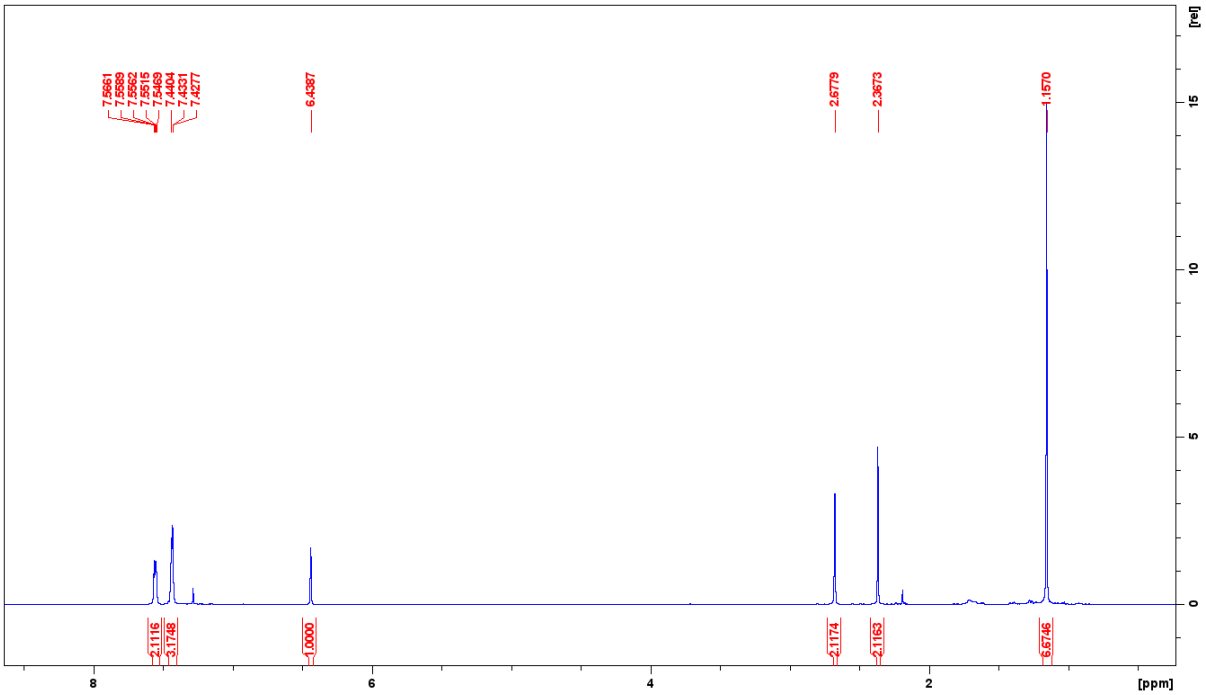


Figure S33: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **8**: **1-phenyl-5,5-dimethylcyclohex-1-en-3-one**

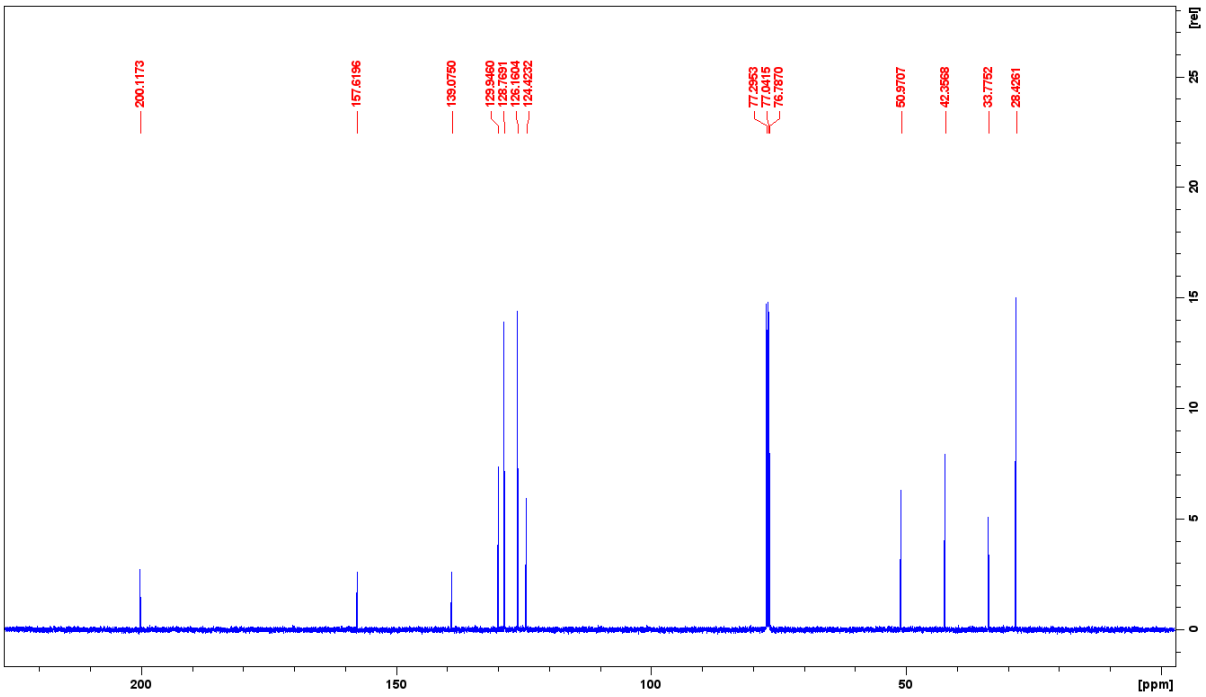
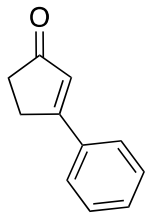


Figure S34: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **8**: **1-phenyl-5,5-dimethylcyclohex-1-en-3-one**

9: **1-phenylcyclopent-1-en-3-one**



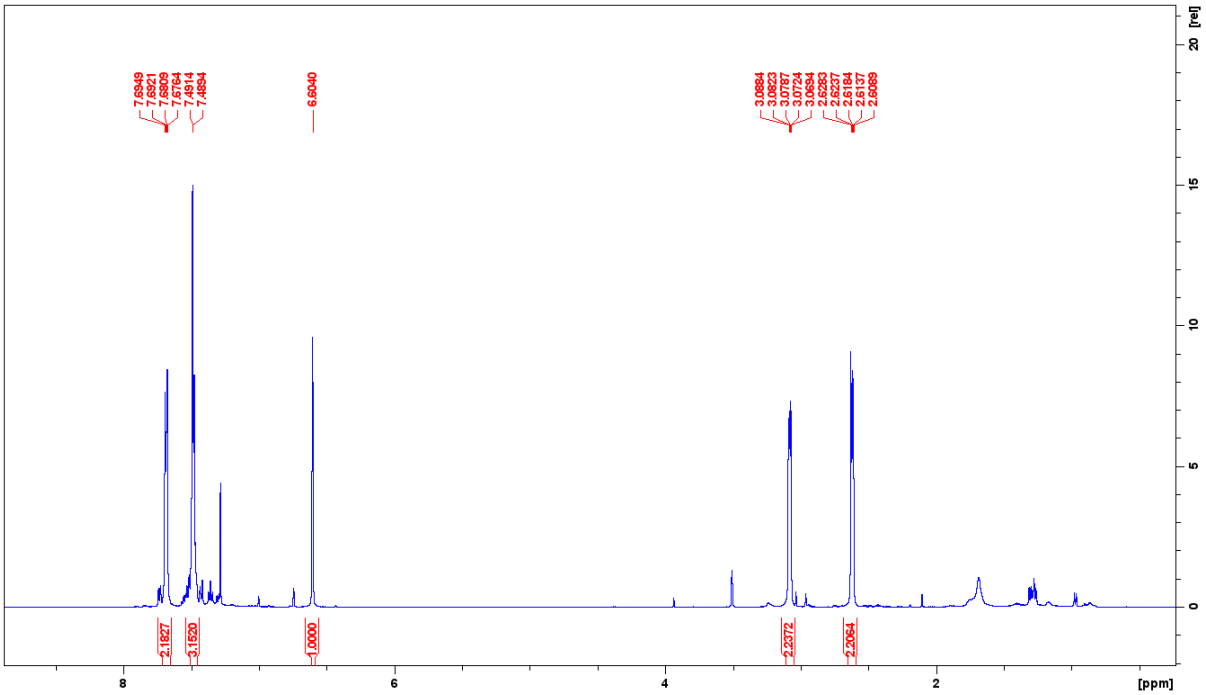


Figure S35: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **9**: **1-phenylcyclopent-1-en-3-one**

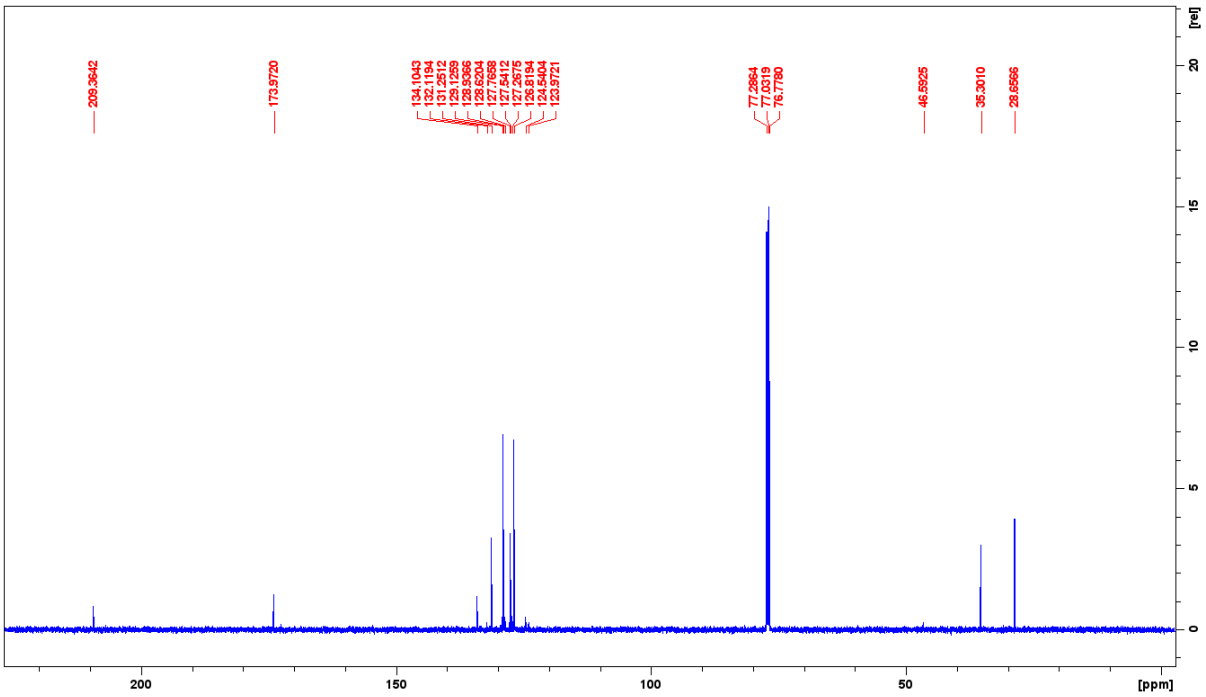
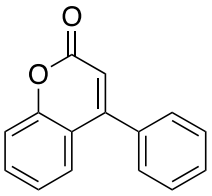


Figure S36: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **9**: **1-phenylcyclopent-1-en-3-one**

10: **4-phenylbenzopyran-2-one**



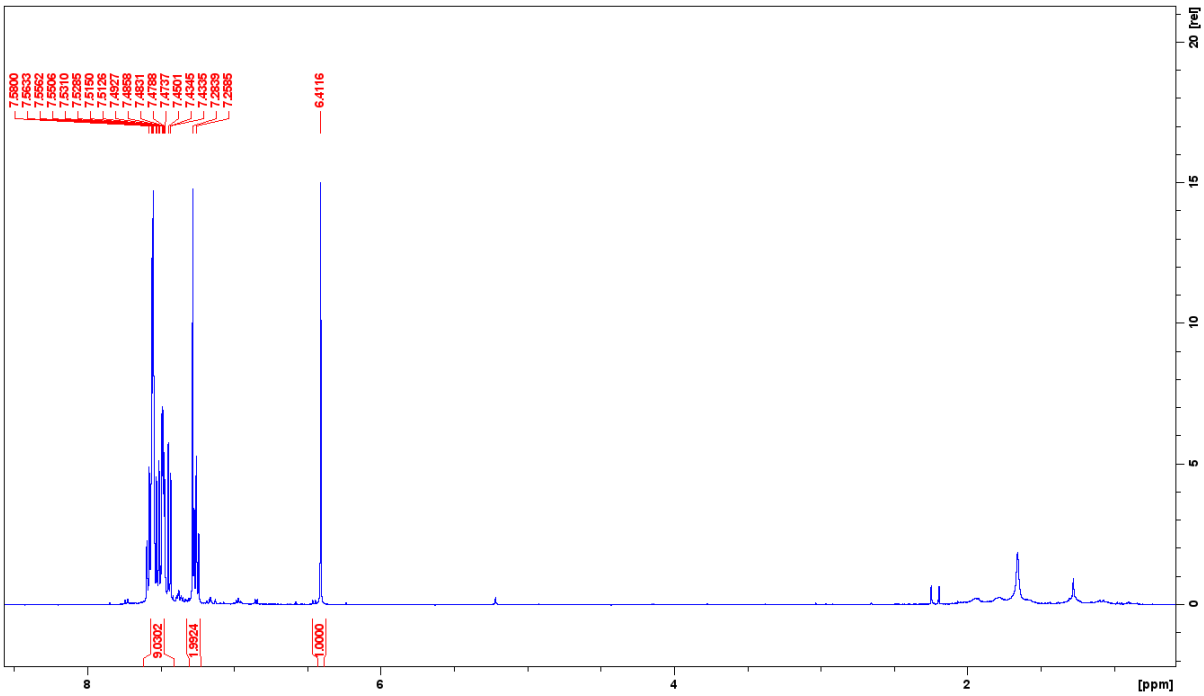


Figure S37: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **10**: **4-phenylbenzopyran-2-one**

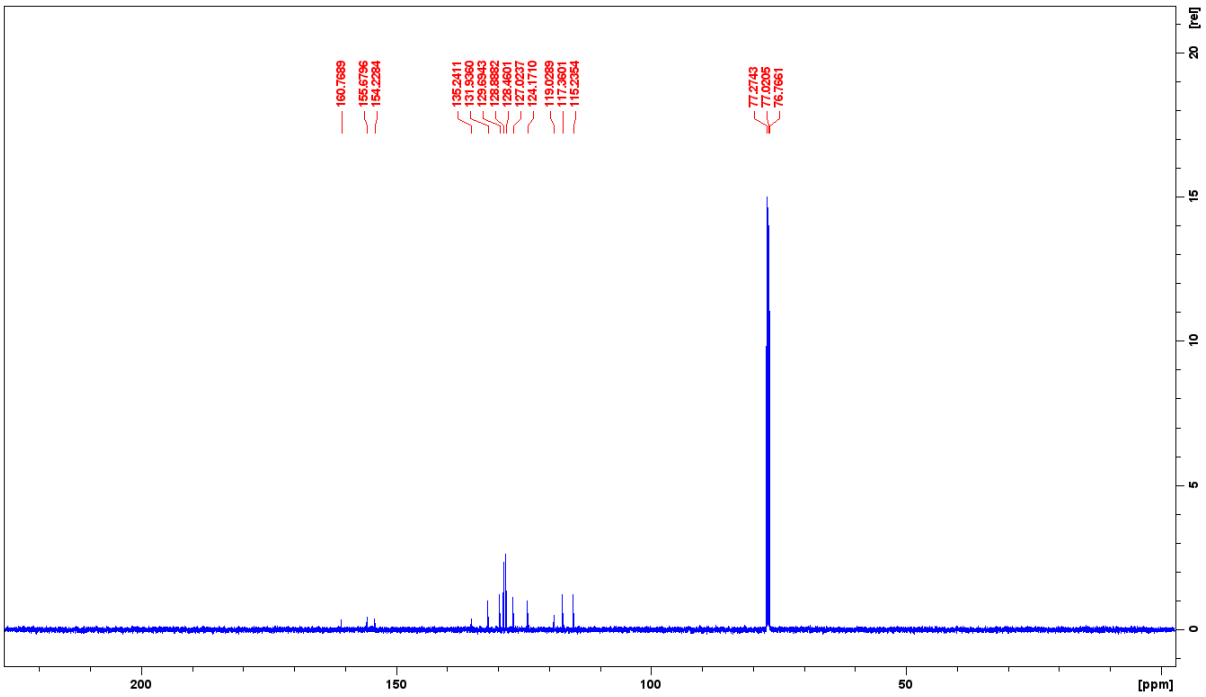
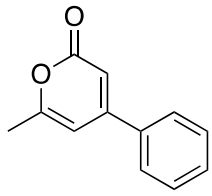


Figure S38: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **10**: **4-phenylbenzopyran-2-one**

11: **4-phenyl-6-methyl-2*H*-pyran-2-one**



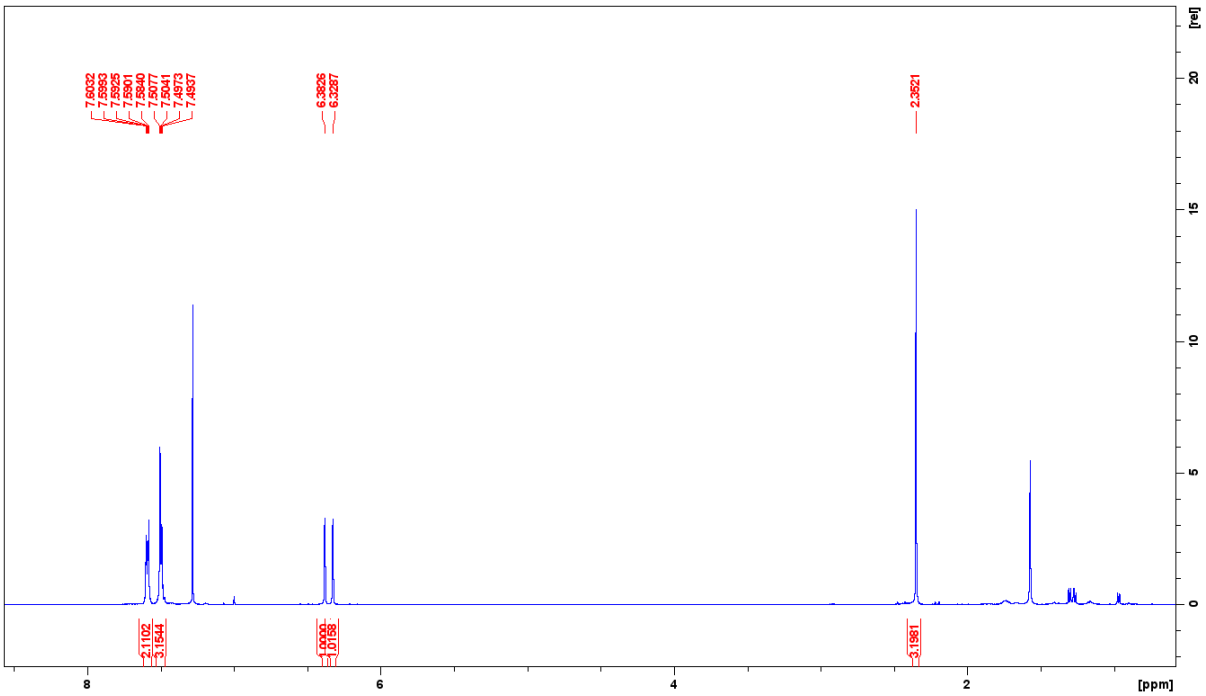


Figure S39: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **11**: **4-phenyl-6-methyl-2*H*-pyran-2-one**

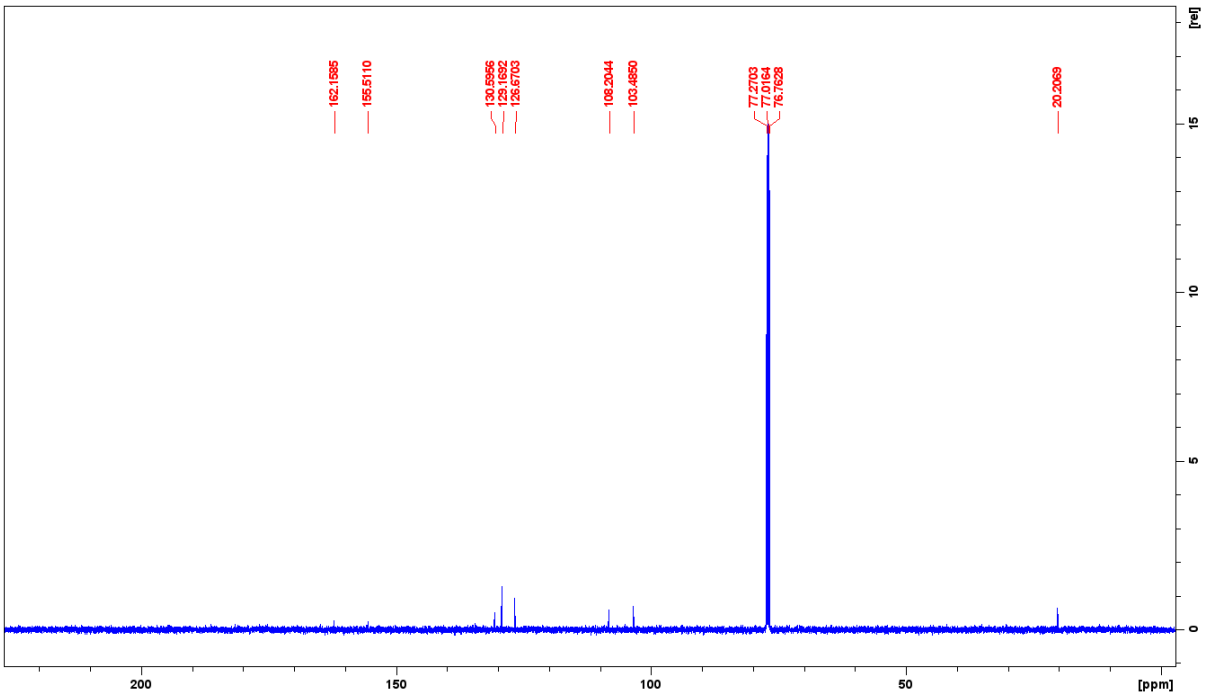
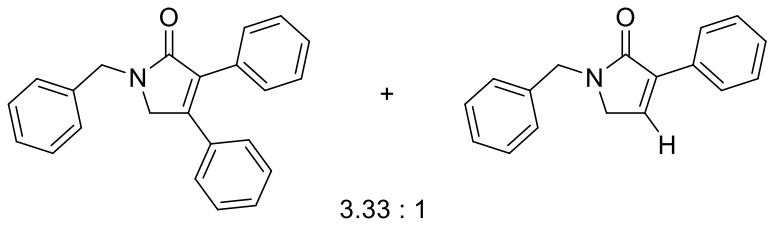


Figure S40: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **11**: **4-phenyl-6-methyl-2*H*-pyran-2-one**

12: **4-phenyl-1-benzyl-3-phenylpyrrolidin-3-en-2-one + 14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one**

Consistent with the ratio of **7** to **14** after borylation catalysis, we observe a 3.33 : 1 ratio of **12** to **14** after Suzuki coupling. These two compounds co-elute during column chromatography.



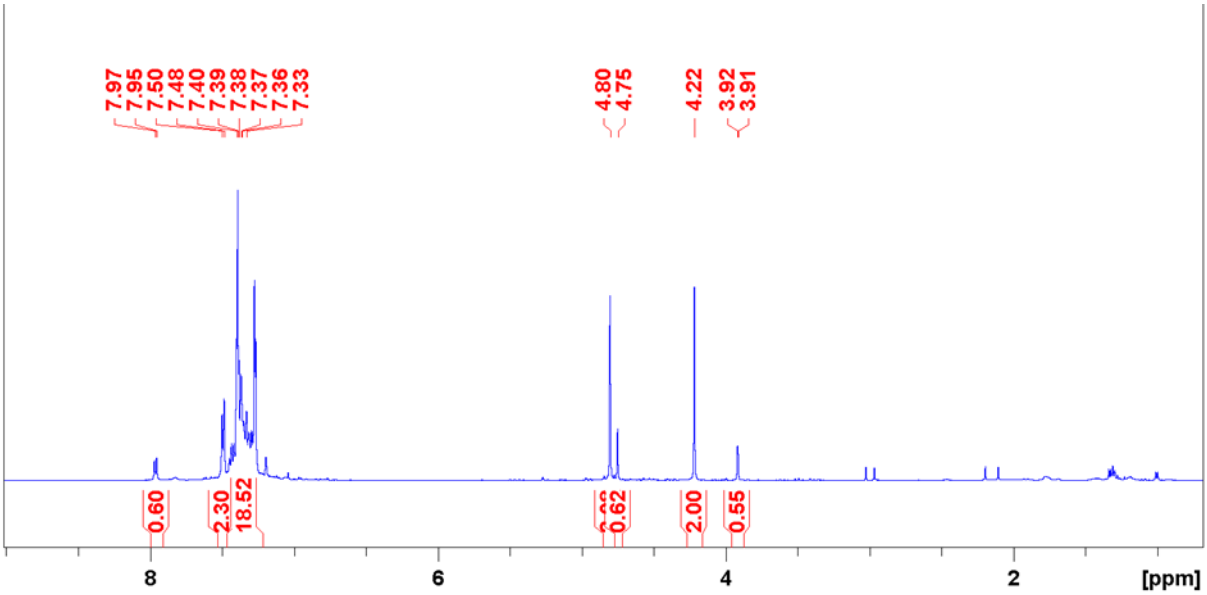


Figure S41: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **12**: **4-phenyl-1-benzyl-3-phenylpyrrolidin-3-en-2-one** and **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one** (3.33 : 1 mixture)

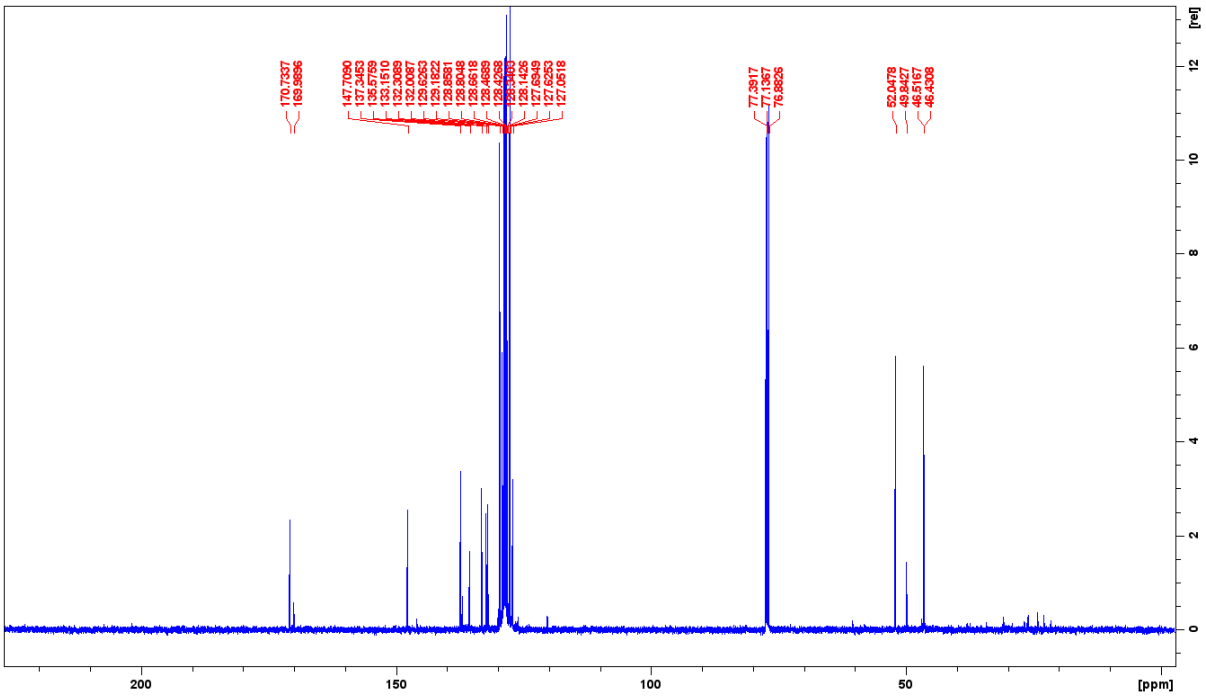
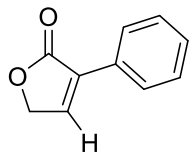


Figure S42: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **12**: **4-phenyl-1-benzyl-3-phenylpyrrolidin-3-en-2-one** and **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one** (3.33:1 mixture)

d. Protodeboronation Products

13. 3-phenylfuran-2(5H)-one:



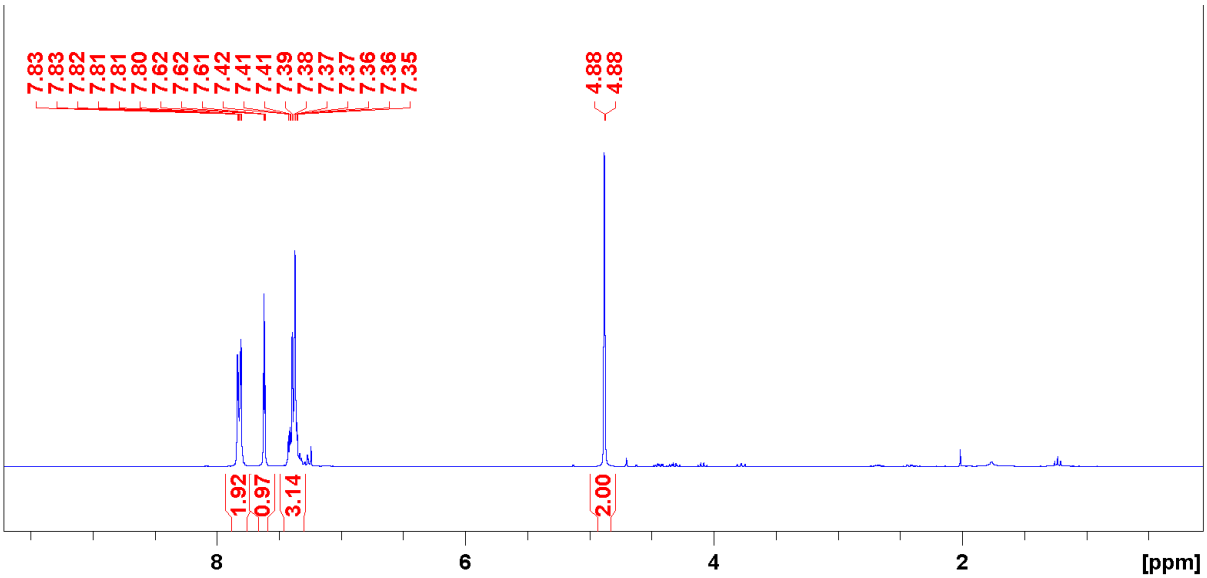
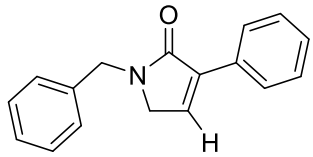


Figure S43: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **13**: **3-phenylfuran-2(5H)-one**

14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one



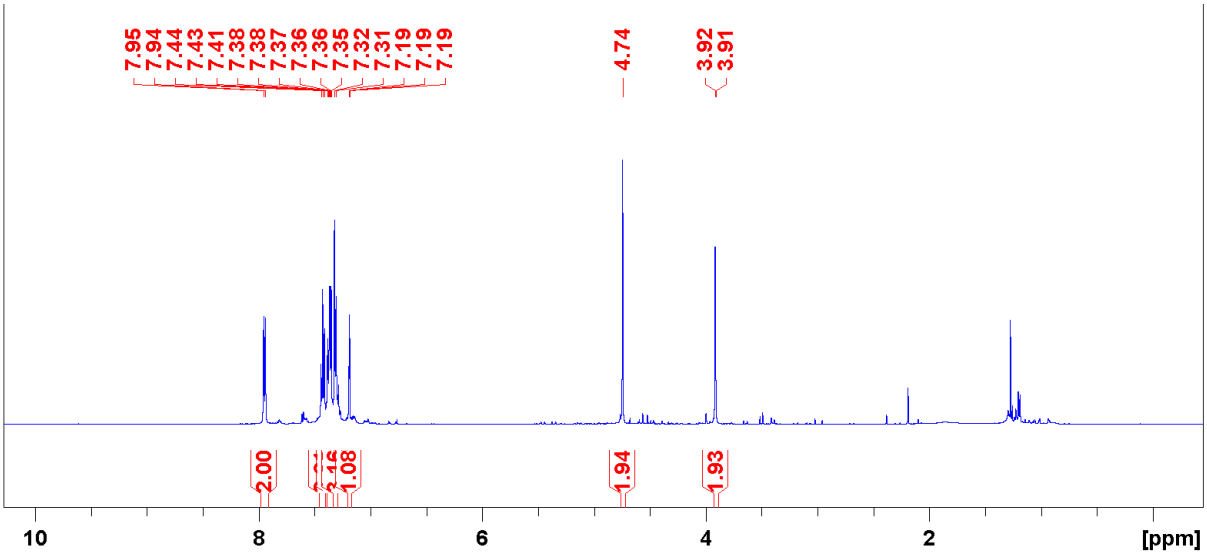


Figure S44: ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 292 K)
of **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one**

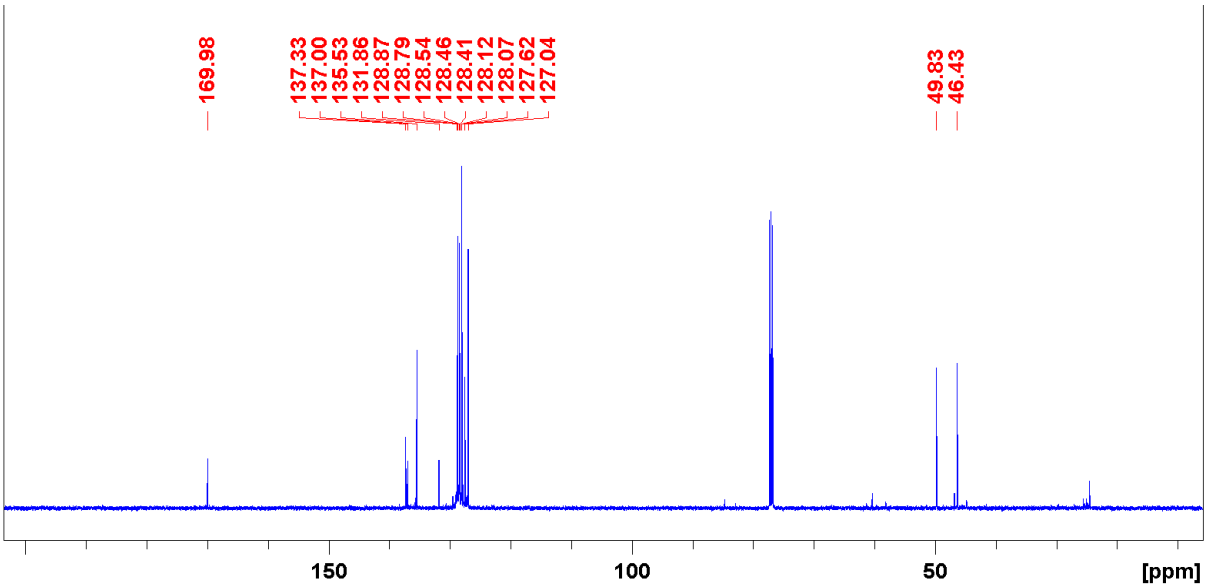


Figure S45: ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 292 K)
of **14: 1-benzyl-3-phenylpyrrolidin-3-en-2-one**

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