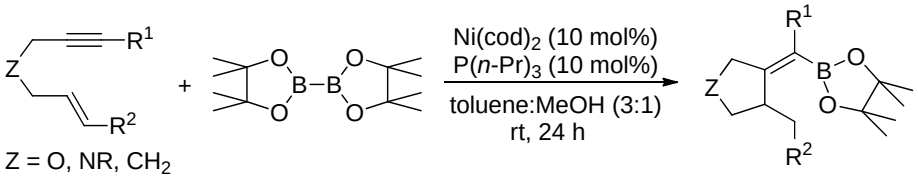
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


## Table of Contents

## General information:

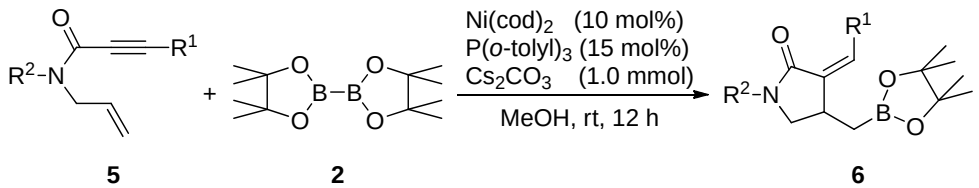
All reagents were purchased from Sigma-Aldrich, Fisher-Acros, TCI, or Alfa-Aesar, and were used without further purification unless otherwise noted. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique. Flash column chromatography was performed using silica gel (230–400 mesh). Analytical thin layer chromatography (TLC) was performed on 60 $F_{254}$ (0.25 mm) plates and visualization was accomplished with UV light (254 and 354 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were recorded on Bruck 400 or 500 spectrometer with $Me_4Si$ or solvent resonance as the internal standard ($^1$H NMR, $Me_4Si$ at 0 ppm, $CHCl_3$ at 7.24 ppm, DMSO at 2.49 ppm; $^{13}$C NMR, $Me_4Si$ at 0 ppm, $CDCl_3$ at 77.0 ppm, $d_6$-DMSO at 39.7 ppm). $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. IR spectral data were recorded on a Brucker TENSOR 37 spectrometer. Melting points (mp) were determined using a SRS OptiMelt MPA100. Starting materials 1, 6-enynes were prepared according to the literature procedure.[1-3]

## General procedure for the borylative cyclization of activated 1,6-enynes (1) with bis(pinacolato)diboron (2):



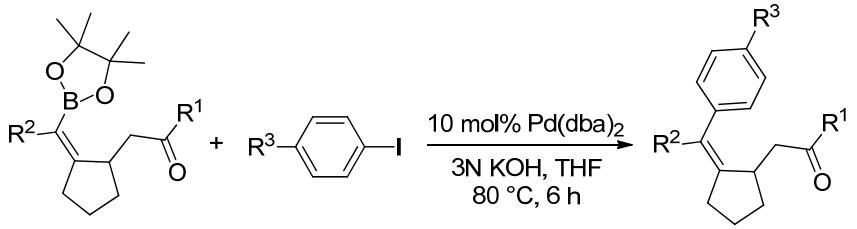

A sealed tube containing $Ni(cod)_2$ (0.025 mmol, 10 mol%), and bis(pinacolato)diboron **2** (0.63 mmol, 2.52 equiv) was evacuated and purged with nitrogen gas for three times. Freshly distilled toluene (0.75 mL) and P(*n*-Pr)$_3$ (0.025 mmol, 10 mol%) were added and the mixture was kept stirring until the solution became yellow. Then enyne **1** (0.25 mmol, 1.0 equiv) and methanol (0.25 mL) were added to the reaction mixture, sealed with cap and stirred at rt. for 24 h. The mixture was filtered through a Celite pad and washed with ethyl acetate/hexane (v/v = 70:30). The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate as eluent to afford the desired products **3**.

## General procedure for the borylative cyclization of unactivated 1,6-enynes (5) with bis(pinacolato)diboron (2):



A sealed tube containing $Ni(cod)_2$ (0.04 mmol, 10 mol%), P(*o*-tolyl)$_3$ (0.06 mmol, 15 mol%), $Cs_2CO_3$ (0.4 mmol, 1.0 equiv), bis(pinacolato)diboron **2** (0.4 mmol, 1.0 equiv) and 1,6-enynes **5** (0.48 mmol, 1.2 equiv) were evacuated and purged with nitrogen for three times. Freshly distilled dry MeOH (2.0 mL) was added to the sealed tube, and then sealed with cap. The reaction mixture was kept stirring at rt. for 12 h, then diluted with dichloromethane and stirred in the air for 10 min. The mixture was filtered through a Celite and silica gel pad, and then washed with dichloromethane. The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate as eluent to afford the desired products **6**.

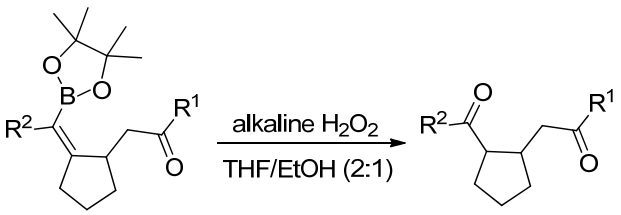
**Procedure for the palladium-catalyzed coupling reaction of aromatic iodides and alkenyl boronates 3:**[4]




**3** **7**

A 10-mL sealed tube containing $Pd(dba)_2$ (0.1 mmol, 10 mol%) was evacuated and purged with nitrogen for three times. Freshly distilled THF (1.0 mL) and iodobenzene (1.0 mmol, 1.0 equiv) were added to the reaction mixture and the system was stirred at rt. for 5 min. Then, alkenyl boronate **3** (1.0 mmol, 1.0 equiv) dissolved in THF (1.0 mL) and an aqueous solution of 3 N KOH (0.25 mL) were sequentially added to the solution and the mixture was heated at 80 °C for stirring 6 h. The mixture was cooled, filtered through a short Celite pad and washed with dichloromethane. The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate (20:1) as eluent to afford the compounds **7**.

**Procedure for the preparation of 2-methyl-1-phenylheptane-1,5-dione (8):**[4]

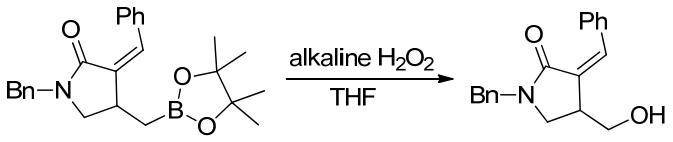



**3** **8**

A 25-mL round-bottomed side-arm flask containing alkenylboronate **3** (1.0 mmol) was dissolved in THF/ethanol (2.0 mL + 1.0 mL) at room temperature. To this solution, 1.0 mL of 30% aq. $H_2O_2$ and 1.0 mL of 1 N NaOH were added and stirred at room temperature for 30 min. The reaction mixture was quenched slowly by aqueous $Na_2S_2O_3$ solution until the

effervescence ceases. Product was extracted with ether, dried in $MgSO_4$ and was purified through a column chromatography by using hexane and ethyl acetate (20:1) as eluent to afford the compounds **8**.

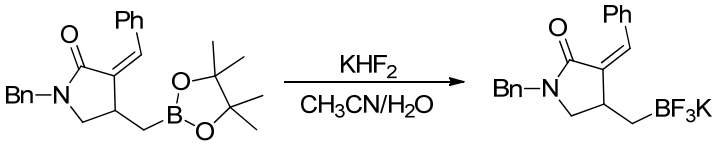
**Procedure for the preparation of *(Z)*-1-benzyl-3-benzylidene-4-(hydroxymethyl) -pyrrolidin-2-one (9):**




**6a** **9**

An aqueous solution of NaOH (3 M, 3.0 equiv) was slowly added to a solution of alkylboronate **6a** (50 mg) in THF (5 mL) at RT. The mixture was then cooled to 0 °C, whereupon a solution of $H_2O_2$ (33 % w/v, 30 equiv) was added dropwise and the resulting mixture was stirred at rt. for 1.5 h. Water and $Et_2O$ were then added, and the aqueous layer was separated and extracted with $Et_2O$ (3×5 mL). The combined organic fractions were dried over anhydrous $MgSO_4$ and filtered through anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the residue was purified through a column chromatography. Primary alcohol **9** was obtained in 90 % yield as light yellow oil.

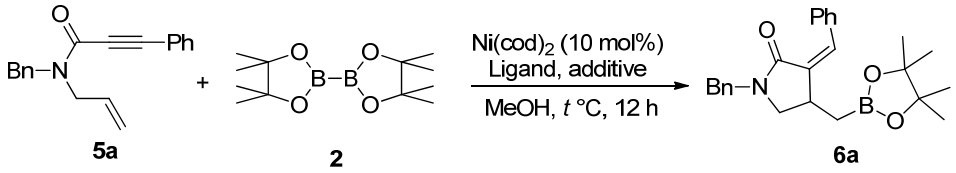
**Procedure for the preparation of potassium (*Z*)-((1-benzyl-4-benzylidene-5-oxo -pyrrolidin-3-yl)methyl) trifluoroborate (10):**




**6a** **10**

A saturated aqueous solution of $KHF_2$ (4.5 M, 4.0 equiv) was slowly added to a solution of alkylboronate **6a** (100 mg) in acetonitrile and kept stirring at rt. for 3 h. The solvent was evaporated, and the remaining white residue was repeatedly extracted with hot acetone, and the combined extracts were filtered to remove inorganic impurities. The solvent was completely removed under vacuum and the resulted white solid was washed with warm $Et_2O$, and then dried under vacuum without further purification. Primary alkyltrifluoroborate salt **10** was obtained in 93% yield as a white solid.

**Table S1. Optimization studies for the borylative cyclization of (5) with (2)[a]**

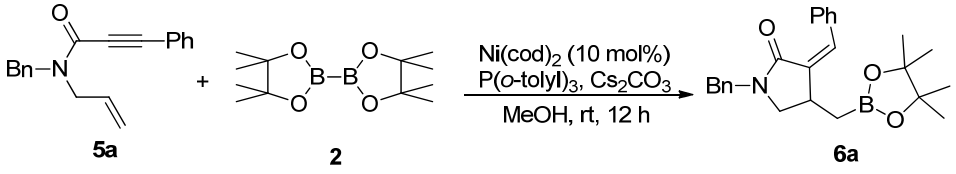



5a 2 6a

| Entry | Ligand (15 mol%) | Additive | Temp (°C) | Yield(%)[b] |
|---|---|---|---|---|
| 1 | $PPh_3$ | $Cs_2CO_3$ | 50 | - |
| 2 | P(*n*-Bu)$_3$ | $Cs_2CO_3$ | 50 | - |
| 3 | P(*t*-Bu)$_3$ | $Cs_2CO_3$ | 50 | 30 |
| 4 | P(anisyl)$_3$ | $Cs_2CO_3$ | 50 | 50 |
| 5 | P(OPh)$_3$ | $Cs_2CO_3$ | 50 | 35 |
| 6 | Dppf | $Cs_2CO_3$ | 50 | 44 |
| 7 | P(*o*-tolyl)$_3$ | $Cs_2CO_3$ | 50 | 54 |
| 8 | P(*o*-tolyl)$_3$ | CsF | 50 | 22 |
| 9 | P(*o*-tolyl)$_3$ | - | 50 | 30 |
| 10 | P(*o*-tolyl)$_3$ | NaO$^t$Bu | 50 | 46 |
| 11 | P(*o*-tolyl)$_3$ | $Cs_2CO_3$ | rt | 62 |
| 12 | P(*o*-tolyl)$_3$ | $K_2CO_3$ | rt | 29 |

[a]All reactions were carried out using 1,6-enynes (**5a**) (0.48 mmol), bis(pinacolato)diboron (**2**) (0.40 mmol), catalyst (0.04 mmol), ligand (0.06 mmol), additive (0.6 mmol) and methanol (2.0 mL) for 12 h. [b]Yields were measured from the crude products by the $^1$H NMR integration method using mesitylene as an internal standard.

**Table S2. Optimization Studies[a]**



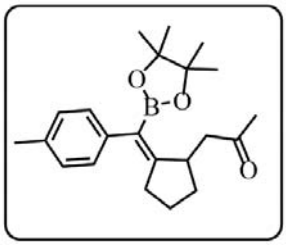

5a 2 6a

| Entry | Ratio (**5a**:**2**) | P(*o*-tolyl)$_3$ (mol%) | $Cs_2CO_3$ (eq.) | Yield(%)[b] |
|---|---|---|---|---|
| 1 | 1 : 1.5 | 10 | 1.5 | 66 |
| 2 | 1 : 1.5 | 15 | 1.5 | 76 |
| 3 | 1 : 1.5 | 20 | 1.5 | 72 |
| 4 | 1 : 1.5 | 15 | 0.5 | 75 |
| 5 | 1 : 1.5 | 15 | 1.0 | 80 |
| 6 | 1 : 1.5 | 15 | 1.5 | 76 |
| 7 | 1 : 1.2 | 15 | 1.5 | 75 |
| **8** | **1.2 : 1** | **15** | **1.0** | **89** |

[a]All reactions were carried out using 1, 6-enynes (**5a**) (0.40–0.48 mmol), bis(pinacolato)diboron (**2**) (0.40–0.60 mmol), catalyst (0.04 mmol), ligand (0.04–0.08 mmol, 10–20 mol%) and methanol (2.0 mL) for 12 h. [b]Yields were measured from the crude products by the $^1$H NMR integration method using mesitylene as an internal standard.

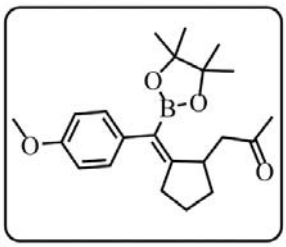
## Spectral data for all products:

***(E)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methylene)cyclopentyl)propan-2-one (3a)**



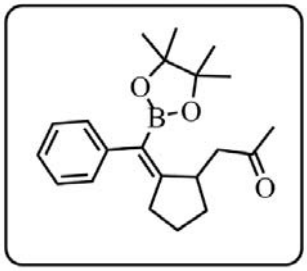
Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.59–3.54 (m, 1H), 2.79 (dd, *J* = 16.0, 2.8 Hz, 1H), 2.41 (dd, *J* = 16.0, 11.2 Hz, 1H), 2.30 (s, 3H), 2.20–2.11 (m, 4H), 1.85–1.78 (m, 1H), 1.64–1.54 (m, 2H), 1.53–1.41 (m, 2H), 1.22 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 208.4, 166.5, 140.2, 134.8, 128.5, 128.4, 83.1, 50.9, 39.9, 32.8, 31.4, 29.5, 24.8, 24.7, 23.2, 21.1; HRMS [(FAB), $M^+$]: 354.2369 (calcd for $C_{22}H_{31}BO_3$ 354.2366); IR (KBr): 2977, 2869, 1712, 1612, 1511, 1349, 1303, 1141, 971, 809, 763 $cm^{-1}$.

***(E)*-1-(2-((4-Methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3b)**



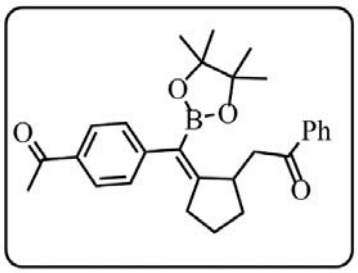
Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.57–3.53 (m, 1H), 2.78 (dd, *J* = 16.0, 2.8 Hz, 1H), 2.40 (dd, *J* = 15.6, 11.6 Hz, 1H), 2.35–2.28 (m, 1H), 2.20 (s, 3H), 1.86–1.75 (m, 1H), 1.64–1.54 (m, 2H), 1.53–1.38 (m, 2H), 1.22 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 208.4, 166.3, 157.3, 135.5, 129.7, 113.1, 83.1, 55.1, 50.9, 39.8, 32.8, 31.4, 29.5, 24.8, 24.7, 23.3; HRMS [(FAB), $M^+$]: 370.2318 (calcd for $C_{22}H_{31}BO_4$ 370.2315); IR (KBr): 2969, 1712, 1604, 1511, 1465, 1349, 1303, 1241, 1141, 971, 809, 709, 694 $cm^{-1}$.

***(E)*-1-(2-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3c)**



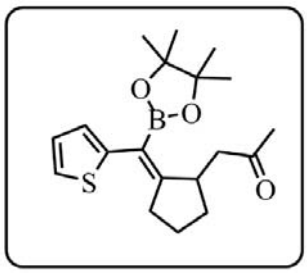
Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.25–7.21 (m, 2H), 7.13–7.09 (m, 1H), 7.04–7.09 (m, 2H), 3.56–3.51 (m, 1H), 2.76 (dd, *J* = 16.0, 2.8 Hz, 1H), 2.38 (dd, *J* = 16.0, 11.6 Hz, 1H), 2.30-2.23 (m, 1H), 2.15 (s, 3H), 2.12–2.07 (m, 1H), 1.82–1.75 (m, 1H), 1.60–1.43 (m, 3H), 1.19 (s, 6H), 1.18 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 208.4, 166.9, 143.3, 128.7, 127.7, 125.4, 83.1, 50.9, 39.8, 32.8,31.5, 29.5, 24.8, 24.7, 23.2; HRMS [(FAB), $(M+H)^+$]: 341.2286 (calcd for $C_{21}H_{30}BO_3$ 341.2288); IR (KBr): 2977, 1712, 1612, 1357, 1303, 1141, 971, 809, 786, 763, 709 $cm^{-1}$.

***(E)*-2-(2-((4-Acetylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)-1-phenylethan-1-one (3d)**



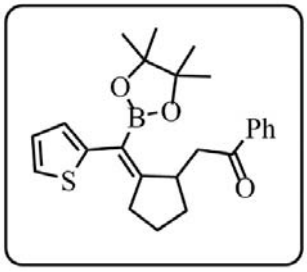
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.75–3.73 (m, 1H), 3.40 (dd, *J* = 16.8, 3.2 Hz, 1H), 2.97 (dd, *J* = 16.4, 10.8 Hz, 1H), 2.57 (s, 3H), 2.41–2.32 (m, 1H), 2.21–2.12 (m, 1H), 1.95–1.86 (m, 1H), 1.71–1.62 (m, 1H), 1.60–1.54 (m, 2H), 1.20 (s, 6H), 1.17 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.1, 198.0, 168.6, 149.0, 137.3, 134.5, 132.8, 128.9, 128.5, 128.1, 128.0, 83.4, 45.8, 40.2, 33.3, 31.9, 26.5, 24.8, 24.6, 23.4; $^{11}$B NMR (160 MHz, $CDCl_3$): δ 29.737; HRMS [(FAB), $M^+$]: 444.2470 (calcd for $C_{28}H_{33}BO_4$ 444.2472); IR (KBr): 2977, 2869, 1681, 1604, 1450, 1357, 1303, 1265, 1141, 971, 802, 740 $cm^{-1}$.

***(E)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methylene)cyclopentyl)propan-2-one (3e)**



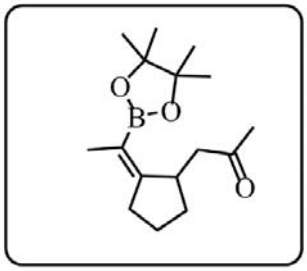
Brown oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 5.2 Hz, 1H), 6.97–6.95 (m, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 3.50–3.45 (m, 1H), 2.74 (dd, *J* = 16.8, 2.0 Hz, 1H), 2.64–2.57 (m, 1H), 2.51–2.43 (m, 2H), 2.14 (s, 3H), 1.83–1.60 (m, 3H), 1.54–1.51 (m, 1H), 1.28 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 207.8, 164.4, 144.6, 126.4, 125.7, 123.8, 83.6, 49.9, 40.9, 33.5, 31.4, 29.9, 24.8, 23.2; HRMS [(FAB), $M^+$]: 346.1777 (calcd for $C_{19}H_{27}BO_3S$ 346.1774); IR (KBr): 2977, 2877, 1712, 1604, 1349, 1303, 1234, 1141, 964, 809, 794, 755 $cm^{-1}$.

***(E)*-1-Phenyl-2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methylene)cyclopentyl)ethan-1-one (3f)**



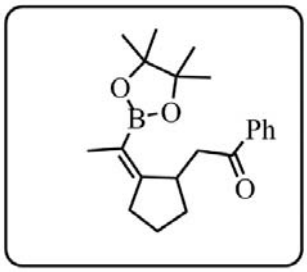
Brown solid, m.p.: 84–85 °C.; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 6.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.20 (dd, *J* = 4.8, 0.8 Hz, 1H), 6.99–6.95 (m, 2H), 3.67–3.63 (m, 1H), 3.31 (dd, *J* = 17.2, 2.0 Hz, 1H), 3.04 (dd, *J* = 17.2, 11.6 Hz, 1H), 2.70–2.64 (m, 1H), 2.57–2.48 (m, 1H), 1.93–1.84 (m, 2H), 1.78–1.70 (m, 2H), 1.22 (s, 6H), 1.20 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.2, 164.1, 144.7, 137.4, 132.8, 128.5, 128.0, 126.4, 125.7, 123.8, 83.6, 44.9, 41.2, 33.7, 31.8, 24.8, 24.6, 23.4; HRMS [(FAB), $M^+$]: 408.1930 (calcd for $C_{24}H_{29}BO_3S$ 408.1930); IR (KBr): 2977, 2877, 1689, 1596, 1450, 1349, 1303, 1141, 964, 786, 763 $cm^{-1}$.

***(E)*-1-(2-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)cyclopentyl)propan-2-one (3g)**



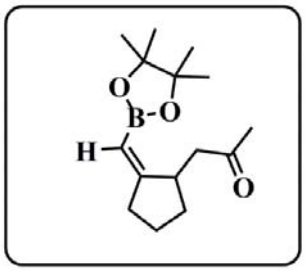
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 3.44–3.41 (m, 1H), 2.58 (dd, *J* = 15.2, 2.8 Hz, 1H), 2.37–2.28 (m,1H), 2.26–2.18 (m, 2H), 2.13 (s, 3H), 1.71–1.57 (m, 6H), 1.56–1.49 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 209.0, 165.6, 82.8, 50.1, 39.9, 31.5, 31.3, 29.2, 24.9, 24.8, 22.4, 17.4; HRMS [(FAB), $M^+$]: 278.2056 (calcd for $C_{16}H_{27}BO_3$ 278.2053); IR (KBr): 2977, 2869, 1712, 1635, 1357, 1303, 1234, 1149, 1087, 964, 848, 809, 755, 701 $cm^{-1}$.

***(E)*-1-Phenyl-2-(2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)cyclopentyl)ethan-1-one (3h)**



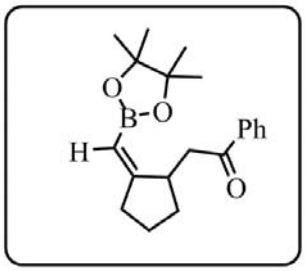
Colorless solid, m.p.: 83–84 °C.; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55–7.50 (m, 1H), 7.45–7.41 (m, 2H), 3.61–3.58 (m, 1H), 3.26 (dd, *J* = 16.0, 3.6 Hz, 1H), 2.73 (dd, *J* = 16.0, 11.2 Hz, 1H), 2.44–2.38 (m, 1H), 2.28–2.19 (m, 1H), 1.73–1.64 (m, 5H), 1.60–1.54 (m, 2H), 1.22 (s, 6H), 1.16 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.9, 165.8, 137.3, 132.6, 128.4, 128.3, 82.8, 44.9, 40.2, 31.8, 31.6, 24.8, 22.5, 17.5; HRMS [(FAB), $(M+H)^+$]: 341.2291 (calcd for $C_{21}H_{30}BO_3$ 341.2288); IR (KBr): 2977, 2869, 1681, 1627, 1450, 1357, 1295, 1141, 1087, 964, 809, 786 $cm^{-1}$.

***(Z)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3i)**



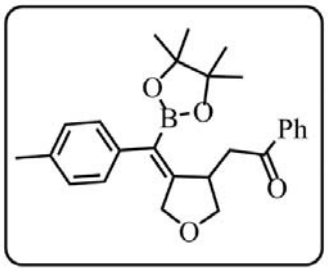
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 5.30 (s, 1H), 3.35–3.30 (m, 1H), 2.76 (dd, *J* = 15.2, 2.8 Hz, 1H), 2.48–2.41 (m, 1H), 2.35–2.23 (m, 2H), 2.15 (s, 3H), 1.85–2.23 (m, 1H), 1.70–1.59 (m, 2H), 1.51–1.38 (m, 1H), 1.23 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 208.6, 174.8, 82.7, 50.5, 39.4, 36.5, 31.8, 29.2, 24.8, 24.7, 23.3; HRMS [(FAB), $M^+$]: 264.1895 (calcd for $C_{15}H_{25}BO_3$ 264.1897); IR (KBr): 2977, 2877, 1712, 1643, 1365, 1319, 1257, 1149, 971, 840, 809, 709 $cm^{-1}$.

***(Z)*-1-Phenyl-2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)ethan-1-one (3j)**



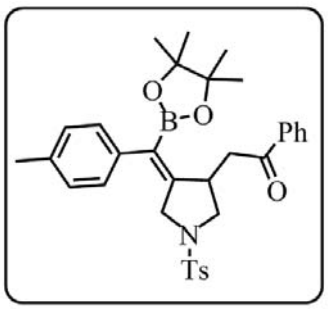
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 5.34 (s, 1H), 3.54–3.46 (m, 2H), 2.71 (dd, *J* = 15.2, 10.8 Hz, 1H), 2.54–2.48 (m, 1H), 2.39–2.31 (m, 1H), 1.86–1.51 (m, 4H), 1.23 (s, 6H), 1.18 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.7, 174.9, 137.1, 132.8, 128.4, 128.3, 82.8, 45.5, 39.9, 36.9, 32.1, 24.9, 24.8, 23.5; HRMS [(FAB), $M^+$]: 326.2052 (calcd for $C_{20}H_{27}BO_3$ 326.2053); IR (KBr): 2969, 2877, 1681, 1643, 1596, 1450, 1365, 1319, 1257, 1141, 971, 802, 755 $cm^{-1}$.

***(Z)*-1-Phenyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methylene)tetrahydrofuran-3-yl)ethan-1-one (3k)**



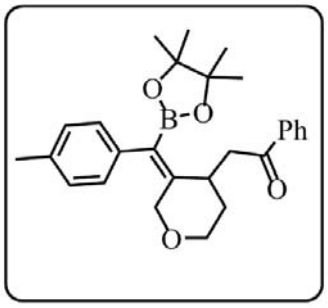
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.57–7.53 (m, 1H), 7.47–7.43 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.47 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.97–3.93 (m, 1H), 3.86–3.81(m, 2H), 3.40–3.24 (m, 2H), 2.31 (s, 3H), 1.24 (s, 6H), 1.16 (s, 3H), 1.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.9, 160.9, 138.5, 137.1, 135.6, 132.9, 128.8, 128.6, 128.0, 127.9, 83.5, 73.8, 70.9, 44.2, 40.2, 24.9, 24.7, 24.6, 21.1; HRMS [(FAB), $M^+$]: 418.2315 (calcd for $C_{26}H_{31}BO_4$ 418.2315); IR (KBr): 2977, 2923, 2854, 2360, 1681, 1511, 1450, 1357, 1311, 1141, 971, 809, 763, 609 $cm^{-1}$.

***(Z)*-1-Phenyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methylene)-1-tosylpyrrolidin-3-yl)ethan-1-one (3l)**



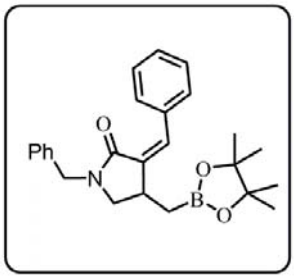
Brown solid, m.p.: 177–178 °C.; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.59–7.55 (m, 3H), 7.48–7.44 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.14 (d, *J* = 16.4 Hz, 1H), 3.86–3.81 (m, 1H), 3.47–3.40 (m, 2H), 3.23–3.21 (m, 2H), 3.12 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 1.10 (s, 6H), 1.06 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.2, 155.8, 143.6, 137.7, 136.8, 135.9, 133.2, 132.2, 129.6, 128.9, 128.6, 127.9, 127.8, 127.7, 86.3, 53.2, 51.6, 44.5, 39.1, 24.7, 24.5, 21.5, 21.2; HRMS [(FAB), $(M+H)^+$]: 572.2640 (calcd for $C_{33}H_{39}BNO_5S$ 572.2642); IR (KBr): 2977, 2923, 2854, 1681, 1511, 1450, 1349, 1157, 1095, 1033, 971, 809, 786, 763 $cm^{-1}$.

**(*Z*)-1-Phenyl-2-(3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methylene)tetrahydro-2*H*-pyran-4-yl)ethan-1-one (3m)**



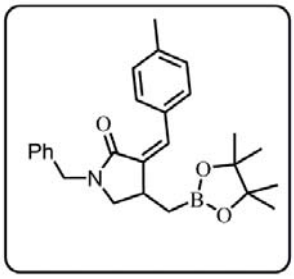
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.58–7.53 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.33 (d, *J* = 14.0 Hz, 1H), 3.96 (d, *J* = 13.6 Hz, 1H), 3.76–3.71 (m, 3H), 3.51 (dd, *J* = 16.0, 10.0 Hz, 1H), 3.23 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.30 (s, 3H), 2.16–2.08 (m, 1H), 1.73–1.69 (m, 1H), 1.16 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.8, 149.6, 137.4, 136.9, 135.6, 132.9, 128.7, 128.6, 128.5, 128.1, 83.5, 65.7, 63.2, 41.5, 34.8, 30.1, 24.7, 24.6, 21.1; HRMS [(FAB), $M^+$]: 432.2474 (calcd for $C_{27}H_{33}BO_4$ 432.2472); IR (KBr): 2977, 2931, 2854, 1681, 1604, 1511, 1450, 1349, 1303, 1141, 971, 809, 771, 755 $cm^{-1}$.

**(*Z*)-1-Benzyl-3-benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6a)**



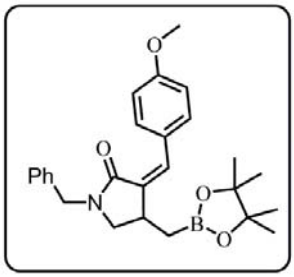
Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.34–7.23 (m, 8H), 6.69 (s, 1H), 4.52 (s, 2H), 3.47 (t, *J* = 6.0 Hz, 1H), 3.12–3.11 (m, 1H), 2.98–2.94 (m, 1H), 1.24–1.18 (m + s, 13H), 1.10–1.04 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.9, 137.1, 136.5, 134.8, 133.3, 130.5, 128.6, 128.1, 128.0, 127.7, 127.4, 83.4, 51.6, 46.9, 34.6, 24.9, 24.7; HRMS [(FAB), $M^+$]: 403.2318 (calcd for $C_{25}H_{30}BNO_3$ 403.2319); IR (KBr): 3081, 2940, 2879, 1697, 1640, 1493, 1346, 1225, 1056, 990 $cm^{-1}$.

**(*Z*)-1-Benzyl-3-(4-methylbenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6b)**



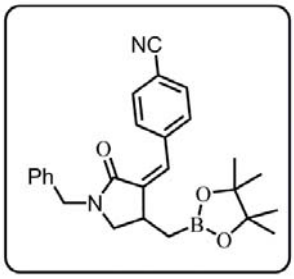
Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 5.6 Hz, 2H), 7.25–7.18 (m, 5H), 7.70 (d, *J* = 6.0 Hz, 2H), 6.60 (s, 1H), 4.46 (s, 2H), 3.41 (m, 1H), 3.05 (m, 1H), 2.92–2.89 (m, 1H), 2.27 (s, 3H), 1.12 (s + m, 13H), 1.02–0.98 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.1, 138.1, 136.7, 136.2, 133.4, 132.0, 130.6, 128.6, 128.6, 127.4, 83.4, 51.7, 46.9, 34.7, 24.9, 24.7, 21.4; HRMS [(FAB), $M^+$]: 417.2474 (calcd for $C_{26}H_{32}BNO_3$ 417.2475); IR (KBr): 3087, 2953, 2861, 1696, 1625, 1485, 1321, 1276, 1032, 997 $cm^{-1}$.

**(*Z*)-1-Benzyl-3-(4-methoxybenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl)pyrrolidin-2-one (6c)**



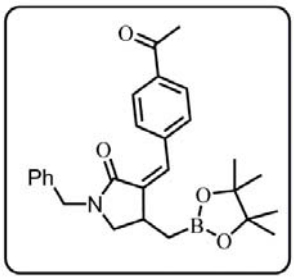
Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.31–7.23 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.60 (s, 1H), 4.15 (s, 2H), 3.79 (s, 3H), 3.48–3.43 (m, 1H), 3.10–3.07 (m, 1H), 2.96–2.92 (m, 1H), 1.23–1.16 (m + 2s, 13H), 1.21–1.01 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.3, 159.5, 136.7, 134.9, 133.1, 132.4, 128.6, 128.1, 127.7, 127.4, 113.1, 83.3, 55.2, 51.7, 46.9, 34.7, 24.9, 24.7; HRMS [(FAB), $M^+$]: 433.2423 (calcd for $C_{26}H_{32}BNO_4$ 433.2424); IR (KBr): 3067, 2931, 2842, 1697, 1641, 1454, 1353, 1291, 1041 $cm^{-1}$.

**(*Z*)-4-((1-Benzyl-2-oxo-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin -3-ylidene)methyl)benzonitrile (6d)**



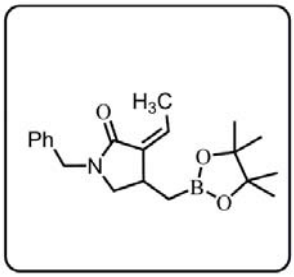
Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.32–7.23 (m, 5H), 6.65 (s, 1H), 4.50 (s, 2H), 3.49 (dd, *J* = 10.0 Hz, *J* = 7.6 Hz, 1H), 3.15 (m, 1H), 3.01–2.98 (m, 1H), 1.24–1.21 (m, 1H), 1.17 (s, 12H), 1.12–1.10 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.3, 140.7, 139.3, 136.1, 131.4, 130.9, 130.9, 128.7, 128.2, 127.6, 119.1, 111.0, 83.5, 51.6, 47.0, 34.6, 24.9, 24.7; HRMS [(FAB), $M^+$]: 428.2269 (calcd for $C_{26}H_{29}BN_2O_3$ 428.2271); IR (KBr): 3091, 2964, 2890, 1695, 1663, 1472, 1355, 1270, 1081, 971 $cm^{-1}$.

**(*Z*)-3-(4-Acetylbenzylidene)-1-benzyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)me thyl)pyrrolidin-2-one (6e)**



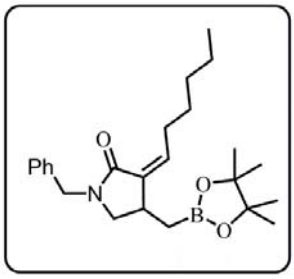
Pale yellow oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.90–7.86 (m, 4H), 7.31–7.22 (m, 5H), 6.69 (s, 1H), 4.50 (s, 2H), 3.47 (t, *J* = 9.6 Hz,1H), 3.14–3.11 (m, 1H), 3.00–2.96 (m, 1H), 2.56 (s, 3H), 1.21–1.16 (m + 2s, 13H), 1.12–1.06 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.8, 166.5, 139.7, 139.5, 136.3, 136.0, 131.7, 130.5, 128.6, 128.2, 127.7, 127.5, 83.4, 51.5, 47.0, 34.6, 26.6, 24.9, 24.7; HRMS [(FAB), $M^+$]: 445.2419 (calcd for $C_{27}H_{32}BNO_4$ 445.2424); IR (KBr): 3071, 2936, 2842, 1699, 1705, 1642, 1460, 1333, 1287, 1057, 986 $cm^{-1}$.

**(*Z*)-1-Benzyl-3-ethylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6f)**



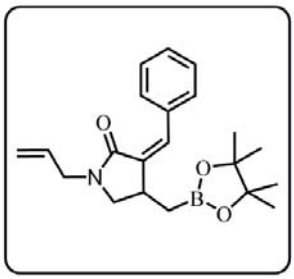

Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.25–7.22 (m, 3H), 5.91 (q, *J* = 7.2 Hz, 1H), 4.47 (dd, *J* = 19.6, 14.8 Hz, 2H), 3.34 (t, *J* = 8.8 Hz, 1H), 3.34–2.83 (m, 2H), 2.18 (d, *J* = 6.0 Hz, 3H), 1.17–1.16 (2s, 12H), 0.91–0.87 (m, 1H), 0.86–0.81 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.9, 136.8, 136.3, 128.6, 128.1, 127.3, 83.3, 51.7, 46.5, 32.9, 24.8, 24.7, 13.0; HRMS [(FAB), $M^+$]: 341.2151 (calcd for $C_{20}H_{28}BNO_3$ 341.2162); IR (KBr): 3032, 2912, 2862, 1701, 1640, 1457, 1302, 1275, 1098, 976 $cm^{-1}$.

**(*Z*)-1-Benzyl-3-hexylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6g)**



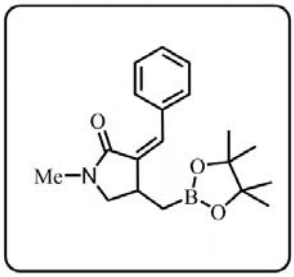

Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.27–7.21 (m, 3H), 5.81 (t, *J* = 7.2 Hz, 1H), 4.46 (dd, *J* = 14.8, 6.0 Hz, 2H), 3.35 (t, *J* = 8.8 Hz, 1H), 2.91–2.89 (m, 1H), 2.85–2.71 (m, 3H), 1.40–1.27 (m, 6H), 1.17 (s, 6H), 1.16 (s, 6H), 1.08–1.04 (m, 1H), 0.94–0.90 (m, 1H), 0.88–0.85 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.6, 136.8, 136.7, 135.4, 128.5, 128.1, 127.3, 83.3, 51.7, 46.5, 32.9, 31.5, 29.4, 26.5, 24.9, 24.7, 22.6, 14.0; HRMS [(FAB), $M^+$]: 397.2794 (calcd for $C_{24}H_{36}BNO_3$ 397.2788); IR (KBr): 3021, 2989, 2891, 1703, 1689, 1462, 1367, 1208, 1136, 976, 935 $cm^{-1}$.

**(*Z*)-1-Allyl-3-benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6h)**



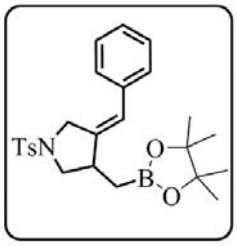

Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 6.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.65 (s, 1H), 5.76–5.70 (m, 1H), 5.21–5.14 (m, 2H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.54 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.15–3.11 (m, 1H), 3.04–3.00 (dd, *J* = 9.6, 4.8 Hz, 1H), 1.27–1.21 (m + s, 13H), 1.13–1.07 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.6, 137.1, 134.7, 133.1, 132.3, 130.4, 127.9, 127.6, 117.6, 83.4, 51.7, 44.5, 34.6, 24.9, 24.7; HRMS [(FAB), $M^+$]: 353.2162 (calcd for $C_{21}H_{28}BNO_3$ 353.2162); IR (KBr): 3030, 2934, 2821, 1695, 1634, 1472, 1346, 1056, 990, 934 $cm^{-1}$.

**(*Z*)-3-Benzylidene-1-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6i)**



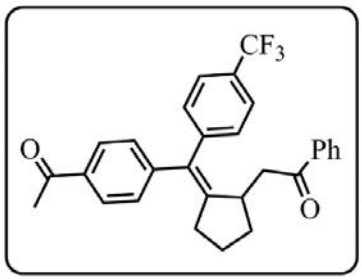

Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 3.59 (t, *J* = 8.0 Hz, 1H), 3.14–3.10 (m, 1H), 3.06–3.02 (m, 1H), 2.89 (s, 3H), 1.31–1.24 (m, 1H), 1.22 (s, 12H), 1.11–1.05 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.2, 137.1, 134.8, 132.7, 130.5, 127.9, 127.6, 83.4, 54.4, 34.6, 30.1, 24.9, 24.8; HRMS [(FAB), $M^+$]: 327.2001 (calcd for $C_{19}H_{26}BNO_3$ 327.2006); IR (KBr): 3015, 2856, 2821, 1699, 1656, 1443, 1346, 1372, 1044, 972, 943 $cm^{-1}$.

**(*Z*)-3-Benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine (6j)**



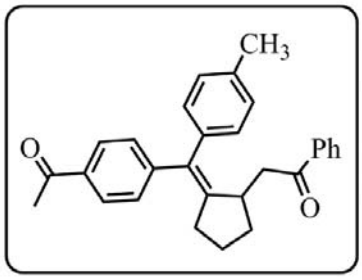

Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.32–7.26 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 4.23 (d, *J* = 14.8 Hz, 1H), 3.98 (d, *J* = 14.8 Hz, 1H), 3.61 (t, *J* = 7.6 Hz, 1H), 2.97–2.93 (m, 1H), 2.78 (t, *J* = 8.8 Hz, 1H), 2.38 (s, 3H), 1.17 (s, 6H), 1.15 (s, 6H), 1.14–1.09 (m, 1H), 0.94–0.88 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.4, 142.3, 136.6, 133.0, 129.6, 128.5, 128.0, 127.7, 126.8, 121.9, 83.3, 53.6, 50.8, 40.2, 24.8, 24.7, 21.4; HRMS [(FAB), $M^+$]: 453.2143 (calcd for $C_{25}H_{32}BNO_4S$ 453.2145).

***(Z)*-2-(2-((4-Acetylphenyl)(4-(trifluoromethyl)phenyl)methylene)cyclopentyl)-1-phenylethan-1-one (7a)**



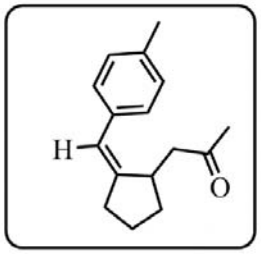

Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.49–7.43 (m, 3H), 7.32–7.27 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.46–3.36 (m, 1H), 2.85 (dd, *J* = 15.2, 3.6 Hz, 1H), 2.72–2.59 (m, 2H), 2.57 (s, 3H), 2.38–2.31 (m, 1H), 1.97–1.86 (m, 2H), 1.58–1.51 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 198.9, 197.6, 149.4, 147.3, 145.7, 136.4, 135.3, 133.0, 132.8, 129.9, 129.4, 129.0, 128.7, 128.4, 128.2, 127.2, 125.7, 47.2, 39.3, 33.2, 31.8, 26.6, 24.9; $^{19}$F NMR (470 MHz, $CDCl_3$): δ -62.77; HRMS [(FAB), $(M+H)^+$]: 463.1887 (calcd for $C_{29}H_{26}F_3O_2$ 463.1885); IR (KBr): 3062, 2954, 2931, 2869, 1681, 1604, 1326, 1265, 1164, 1126, 1064, 809, 786, 740, 655, 593, 570 $cm^{-1}$.

***(E)*-2-(2-((4-Acetylphenyl)(*p*-tolyl)methylene)cyclopentyl)-1-phenylethan-1-one (7b)**



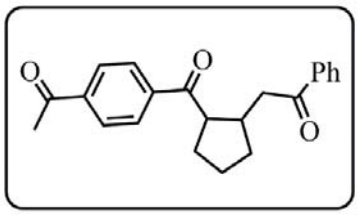

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.48–7.43 (m, 3H), 7.32–7.23 (m, 4H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 3.46–3.36 (m, 1H), 2.98 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.66–2.60 (m, 1H), 2.55 (s, 3H), 2.54–2.49 (m, 1H), 2.34 (s, 3H), 1.93–1.83 (m, 2H), 1.57–1.47 (m, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 199.6, 197.8, 148.4, 147.8, 139.1, 136.6, 134.9, 134.1, 132.7, 129.5, 129.4, 129.3, 128.3, 128.2, 128.0, 43.0,39.5, 33.2, 31.7, 26.6, 25.2, 21.2; HRMS [(FAB), $(M+H)^+$]: 409.2171 (calcd for $C_{29}H_{29}O_2$ 409.2167); IR (KBr): 2923, 2869, 1681, 1604, 1511, 1450, 1403, 1357, 1265, 1018, 956, 809, 786, 647 $cm^{-1}$.

***(Z)*-1-(2-(4-Methylbenzylidene)cyclopentyl)propan-2-one (7c)**



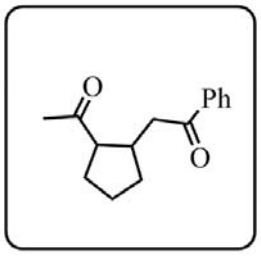

Colorless oil; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.31 (d, *J* = 2.0 Hz, 1H), 3.56–3.53 (m, 1H), 2.57 (dd, *J* = 17.0, 2.5 Hz, 1H), 2.52–2.39 (m, 2H), 2.30–2.24 (m, 4H), 2.02 (s, 3H), 1.99–1.95 (m, 1H), 1.66–1.59 (m, 2H), 1.48–1.42 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 208.4, 148.4, 135.7, 134.9, 129.1, 127.8, 121.2, 46.7, 36.0, 33.6, 30.1, 23.4, 21.1; HRMS [(FAB), $M^+$]: 228.1512 (calcd for $C_{16}H_{20}O$ 228.1514); IR (KBr): 2946, 2869, 1712, 1511, 1450, 1419, 1365, 1226, 1172, 1118, 1002, 809, 740, 678, 624 $cm^{-1}$.

**2-(2-(4-Acetylbenzoyl)cyclopentyl)-1-phenylethan-1-one (8a)**



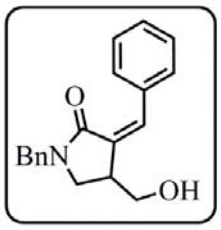

Colorless oil; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.94–7.92 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.53–7.50 (m, 1H), 7.44–7.41 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.49–3.44 (m, 1H), 3.18 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.99–2.91 (m, 1H), 2.81 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.39 (s, 3H), 2.15–2.09 (m, 1H), 2.07–2.00 (m, 1H), 1.79–1.66 (m, 2H), 1.43–1.36 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 201.9, 199.8, 143.7, 136.8, 134.6, 132.9, 129.3, 128.6, 128.3, 52.5, 43.8, 38.8, 32.3, 31.4, 24.6, 21.6; HRMS [(FAB), $(M+H)^+$]: 335.1650 (calcd for $C_{22}H_{23}O_3$ 335.1647); IR (KBr): 2946, 2923, 2869, 1673, 1604, 1450, 1411, 1373, 1280, 1211, 1180, 979, 833, 725, 678 $cm^{-1}$.

**2-(2-Acetylcyclopentyl)-1-phenylethan-1-one (8b)**



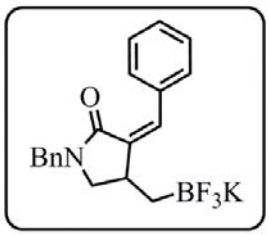

Colorless oil; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.55–7.43 (m, 1H), 7.46–7.431 (m, 2H), 3.10 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.89 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.75–2.67 (m, 1H), 2.64–2.59 (m, 1H), 2.18 (s, 3H), 2.03–1.94 (m, 2H), 1.73–1.64 (m, 2H), 1.35–1.27 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 201.9, 199.6, 136.8, 133.0, 128.5, 128.1, 58.3, 43.9, 38.1, 32.5, 29.6, 28.8, 24.5; HRMS [(FAB), $(M+H)^+$]: 231.1385 (calcd for $C_{15}H_{19}O_2$ 231.1385); IR (KBr): 2946, 2923, 2869, 1681, 1596, 1450, 1411, 1365, 1211, 979, 833, 817, 771, 609, 593 $cm^{-1}$.

***(Z)*-1-Benzyl-3-benzylidene-4-(hydroxymethyl)pyrrolidin-2-one (9)**



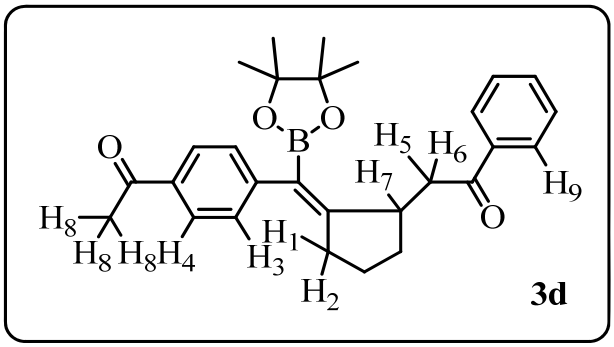

Light yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.34–7.22 (m, 8H), 6.71 (s, 1H), 4.49 (s, 2H), 3.61–3.58 (m, 2H), 3.40 (t, *J* = 8.0 Hz, 1H), 3.15–3.12 (m, 1H), 3.01–2.99 (m, 1H), 2.10 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.6, 136.2, 135.7, 134.3, 131.7, 130.7, 128.7, 128.5, 128.2, 127.8, 127.6, 65.7, 47.1, 46.8, 40.8; HRMS [(FAB), $M^+$]: 293.1415 (calcd for $C_{19}H_{19}NO_2$ 293.1416); IR (KBr): 3081, 1698, 1493, 1446, 1383, 1214, 1090, 1056, 1027, 997 $cm^{-1}$.

**Potassium (*Z*)-((1-benzyl-4-benzylidene-5-oxopyrrolidin-3-yl)methyl) trifluoroborate (10)**



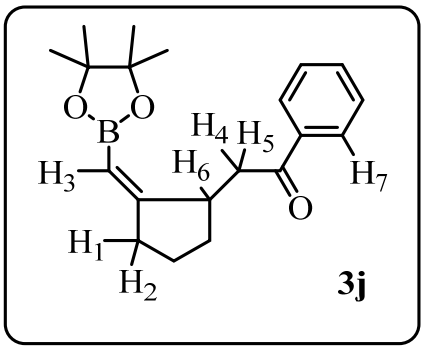

White solid, m.p.: 95–98 ℃. $^{1}$H NMR (400 MHz, d6-Acetone): δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.35–7.17 (m, 8H), 6.62 (s, 1H), 4.55 (d, *J* = 14.6 Hz, 1H), 4.42 (d, *J* = 14.6 Hz, 1H), 3.44 (t, *J* = 8.0 Hz, 1H), 3.07 (m, 1H), 2.92 (m, 1H), 0.72–0.68 (m, 1H), 0.25–0.22 (m, 1H); $^{13}$C NMR (100 MHz, $d_6$-Acetone): δ 168.3, 142.1, 138.7, 136.9, 131.6, 121.3, 128.9, 128.7, 128.2, 128.0, 127.9, 52.9, 47.2, 38.1; HRMS [(FAB), $M^+$]: 383.1074 (calcd for $C_{19}H_{18}BF_3KNO$ 383.1071); IR (KBr): 3076, 1695, 1483, 1432, 1375, 1210, 1085, 1043, 1031, 985 $cm^{-1}$.

## NOE data



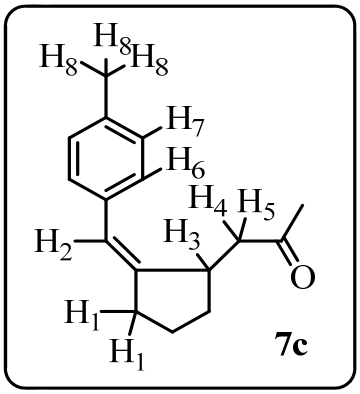

**3d**

| Irradiation | Intensity increase |
|---|---|
| $H_1$ (δ 2.16) | $H_2$ (δ 2.36, 9.20 %) |
| | $H_3$ (δ 7.20, 1.27 %) |
| $H_2$ (δ 2.36) | $H_1$ (δ 2.16, 10.26 %) |
| | $H_3$ (δ 7.20, 2.40 %) |
| $H_8$ (δ 2.57) | $H_4$ (δ 7.88, 1.84 %) |
| $H_5$ (δ 2.97) | $H_6$ (δ 3.40, 18.6 %) |
| | $H_9$ (δ 8.40, 2.84 %) |
| | No NOE for $H_3$ |
| $H_6$ (δ 3.40) | $H_5$ (δ 2.97, 17.4 %) |
| | $H_7$ (δ 3.74, 2.14 %) |
| | $H_9$ (δ 8.04, 3.44 %) |
| | No NOE for $H_3$ |




**3j**

| Irradiation | Intensity increase |
|---|---|
| $H_1$ (δ 2.35) | $H_3$ (δ 5.34, 1.39 %) |
| $H_2$ (δ 2.51) | $H_3$ (δ 5.34, 1.16 %) |
| $H_4$ (δ 2.71) | $H_5$ (δ 3.51, 11.64 %) |
| | $H_6$ (δ 3.46, 1.78 %) |
| | $H_7$ (δ 8.09, 1.25 %) |
| | No NOE for $H_3$ |
| $H_5$ (δ 3.51) | $H_4$ (δ 2.71, 11.27 %) |
| | $H_7$ (δ 8.09, 2.75 %) |



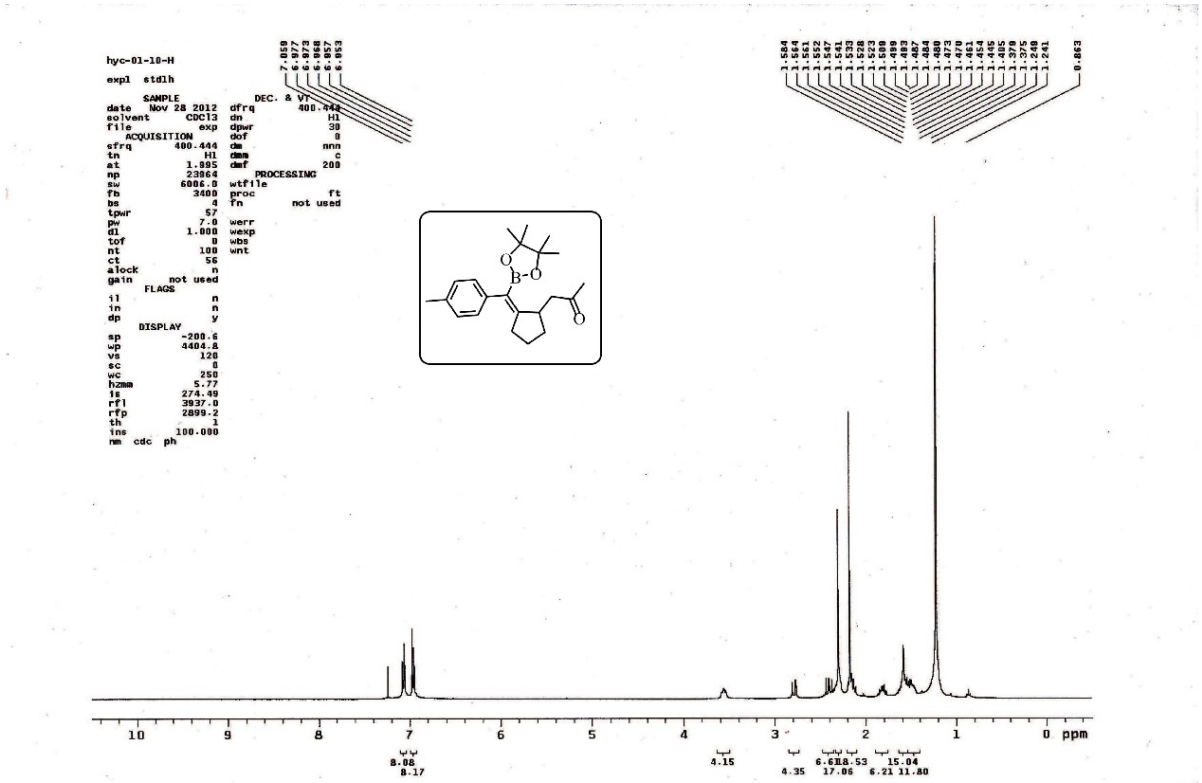

| Irradiation | Intensity increase |
|---|---|
| $H_3$ (δ 3.55) | $H_6$ (δ 7.14, 2.79 %) |
| | No NOE for $H_2$ |
| $H_2$ (δ 6.31) | $H_6$ (δ 7.14, 1.29 %) |
| | $H_1$ (δ 2.45, 1.86 %) |
| $H_7$ (δ 7.08) | $H_8$ (δ 2.29, 1.15 %) |
| $H_6$ (δ 7.14) | $H_2$ (δ 6.31, 0.62 %) |
| | $H_3$ (δ 3.55, 1.47 %) |

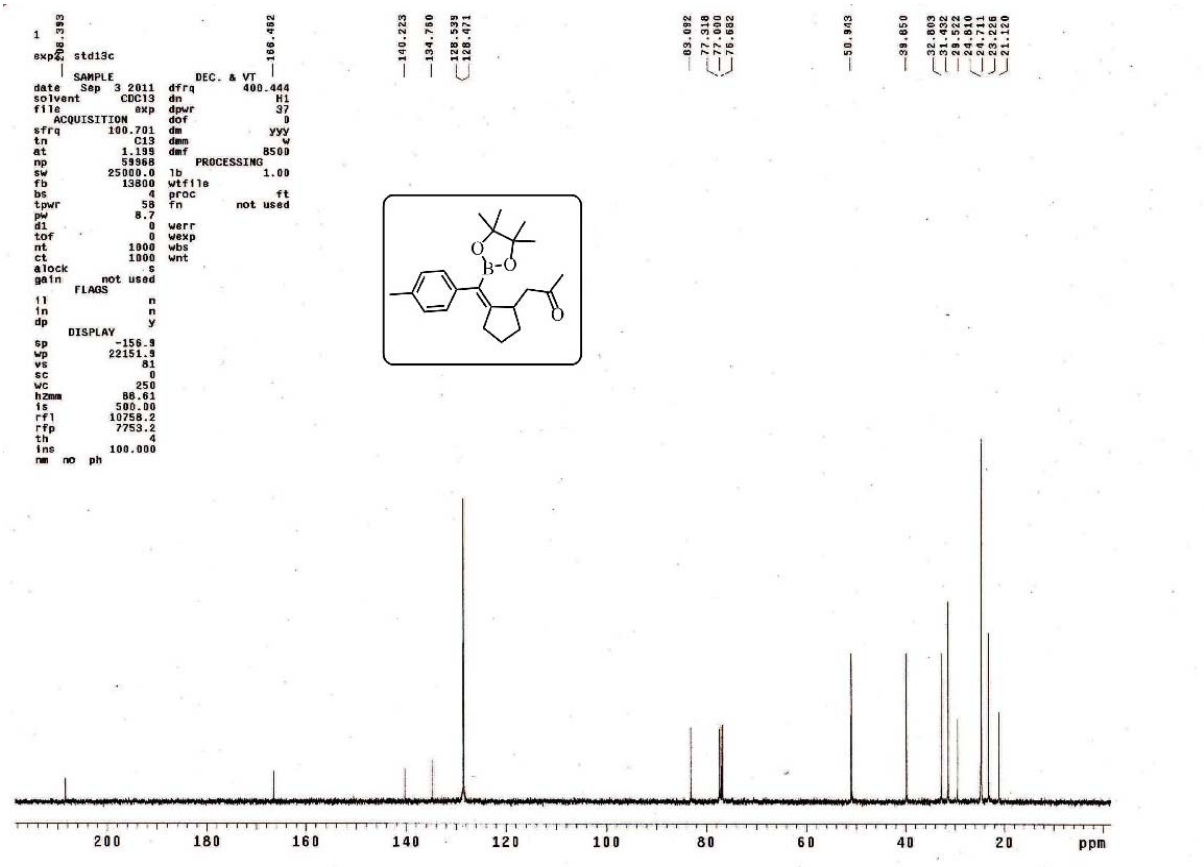
## References

1. C. Molinaro, T. F. Jamison, *J. Am. Chem. Soc*. **2003**, *125*, 8076.
2. L. Zhao, X. Lu, W. Xu, *J. Org. Chem.* **2005**, *70*, 4059.
3. H.-T. Chang, T. T. Jayanth, C.-H. Cheng, *J. Am. Chem. Soc.* **2007**, *129*, 4166.
4. S. Mannathan, M. Jeganmohan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2009**, **48**, 2192.

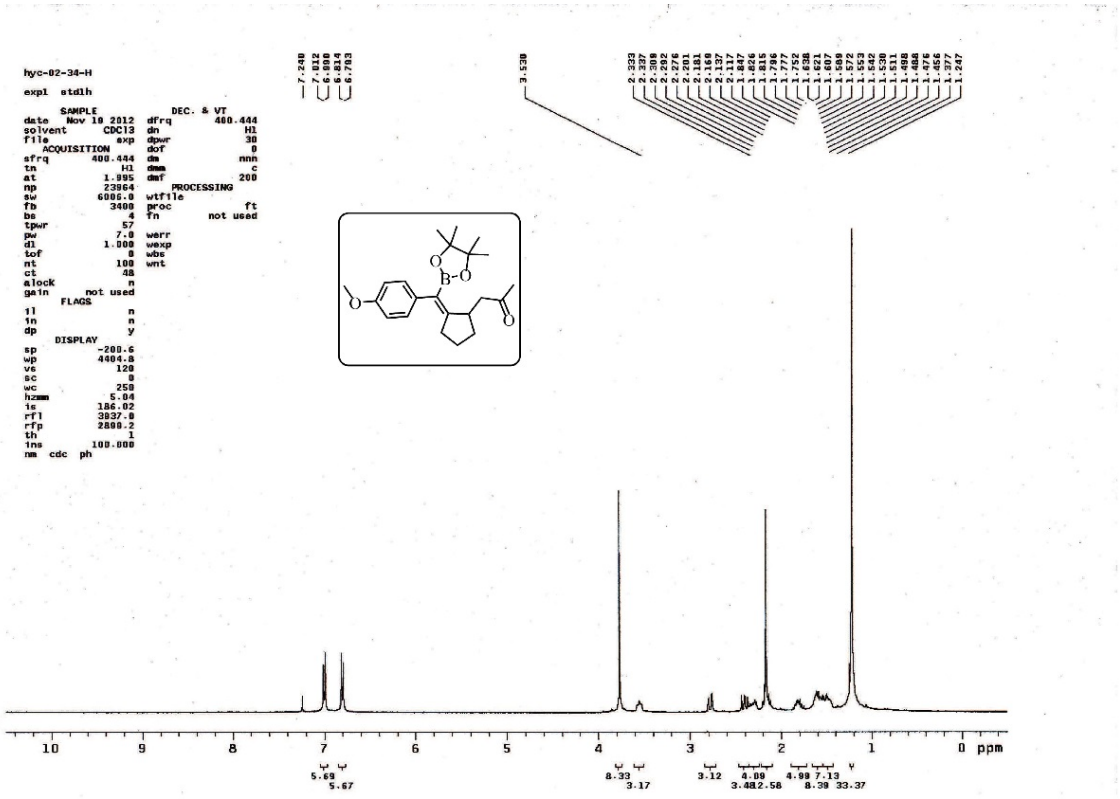
# $^{1}$H NMR and $^{13}$C NMR Spectra for Products (400 or 500 MHz)

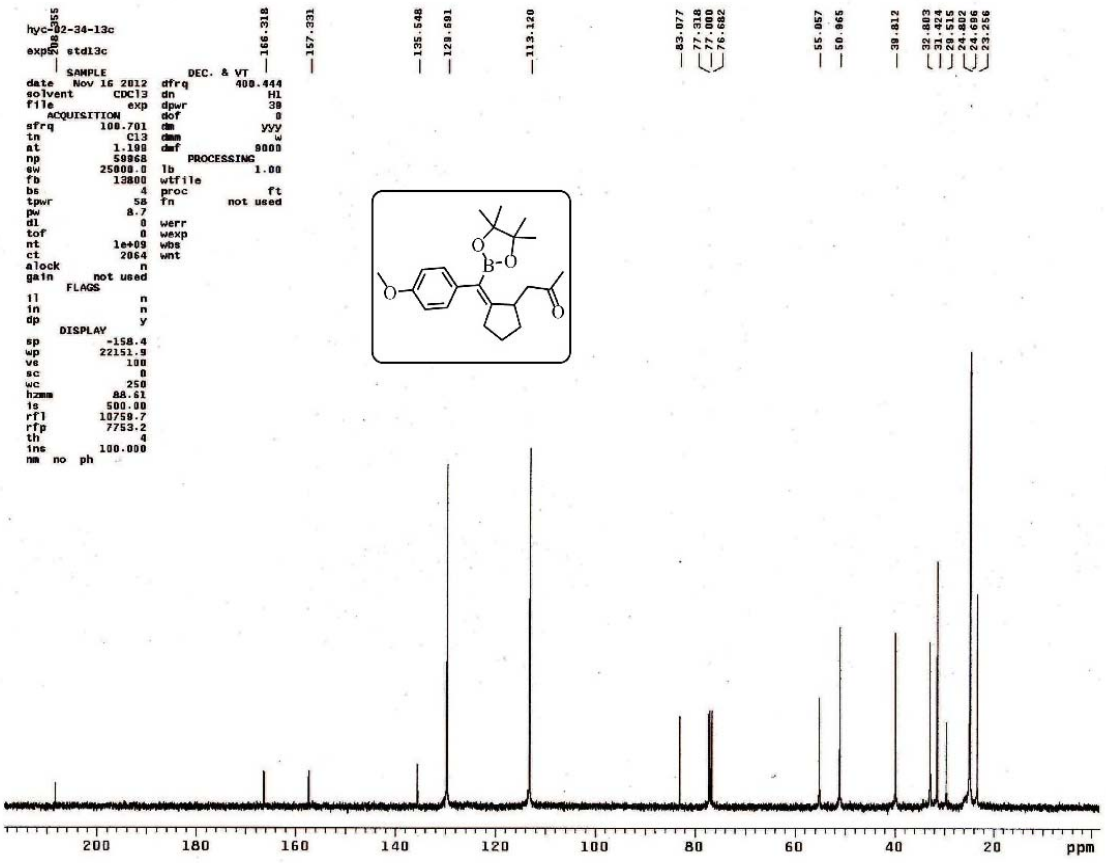
***(E)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methylene)cyclopentyl)propan-2-one (3a)**



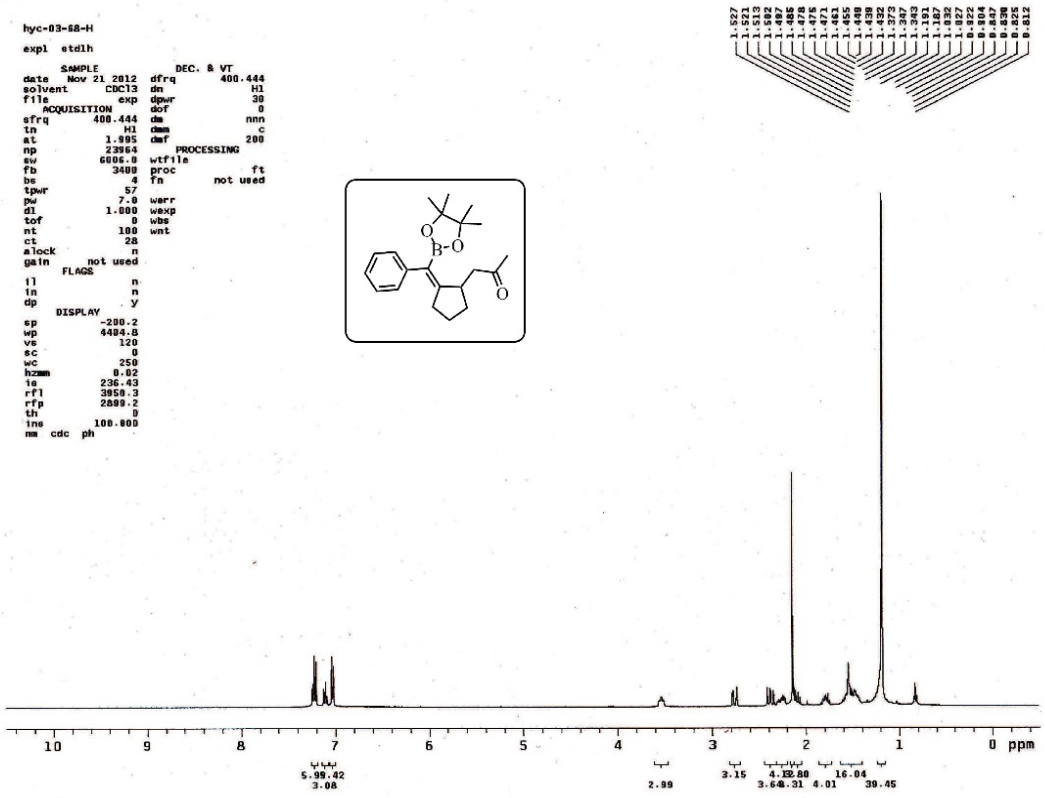



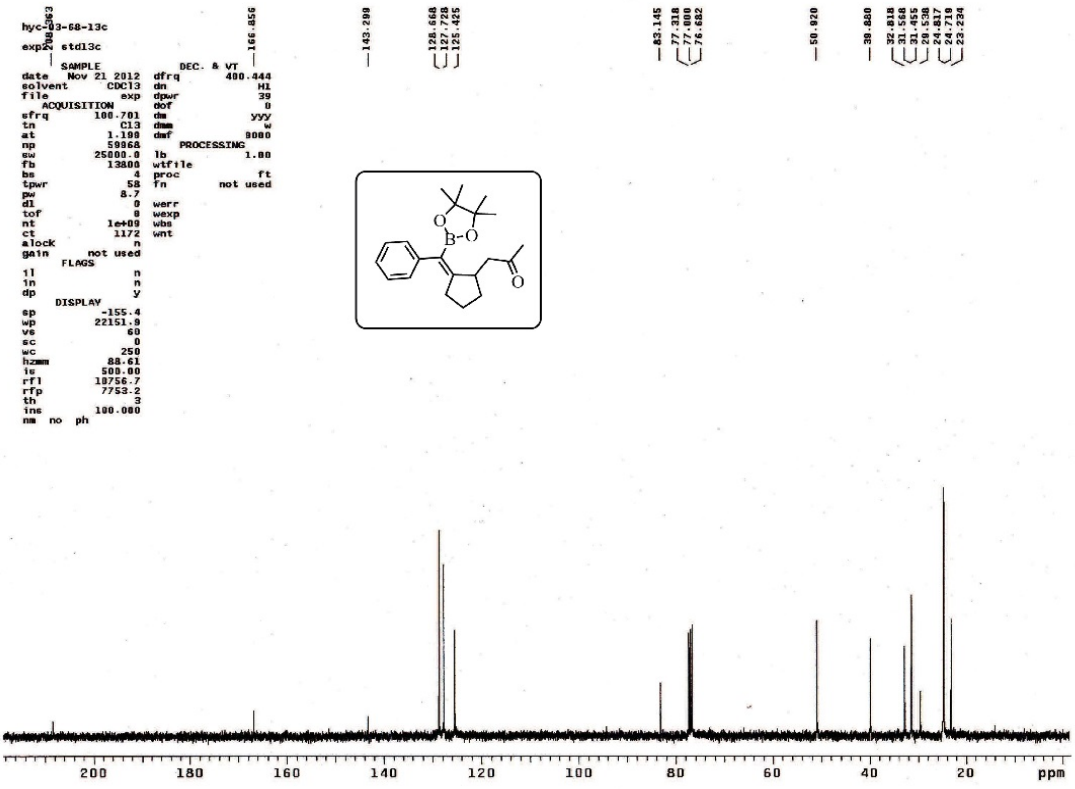
***(E)*-1-(2-((4-Methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3b)**



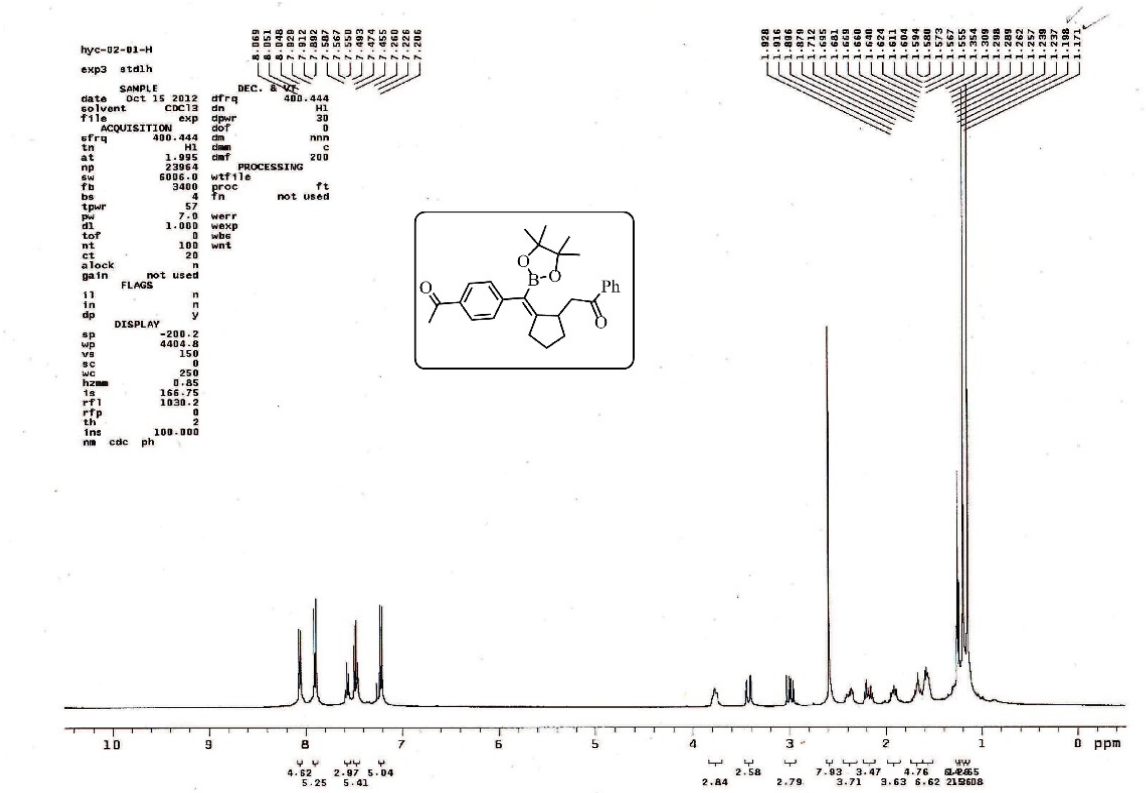



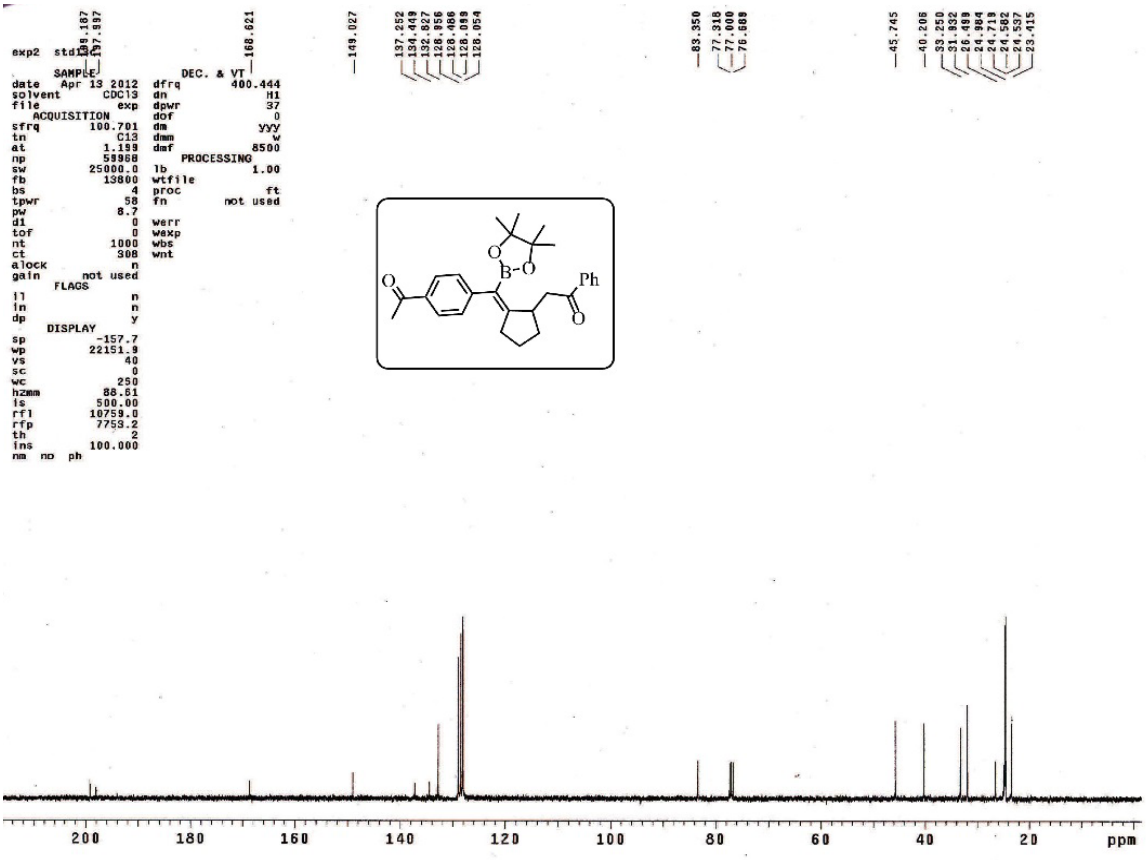
***(E)*-1-(2-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3c)**



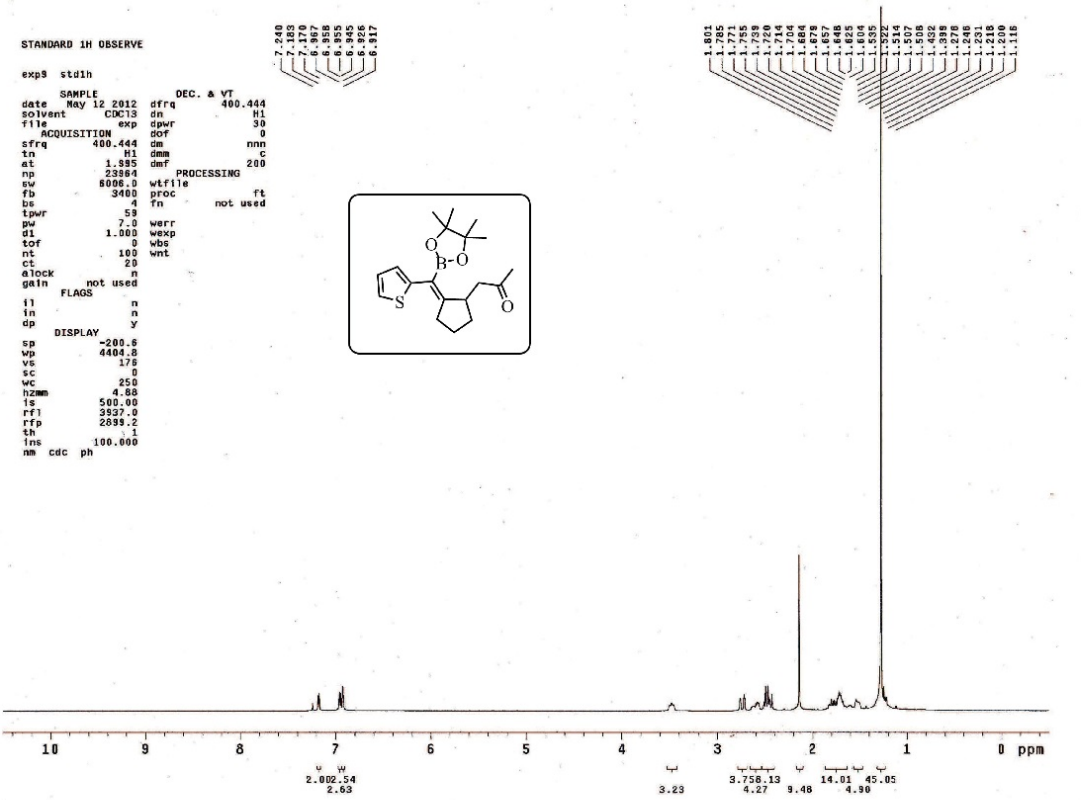



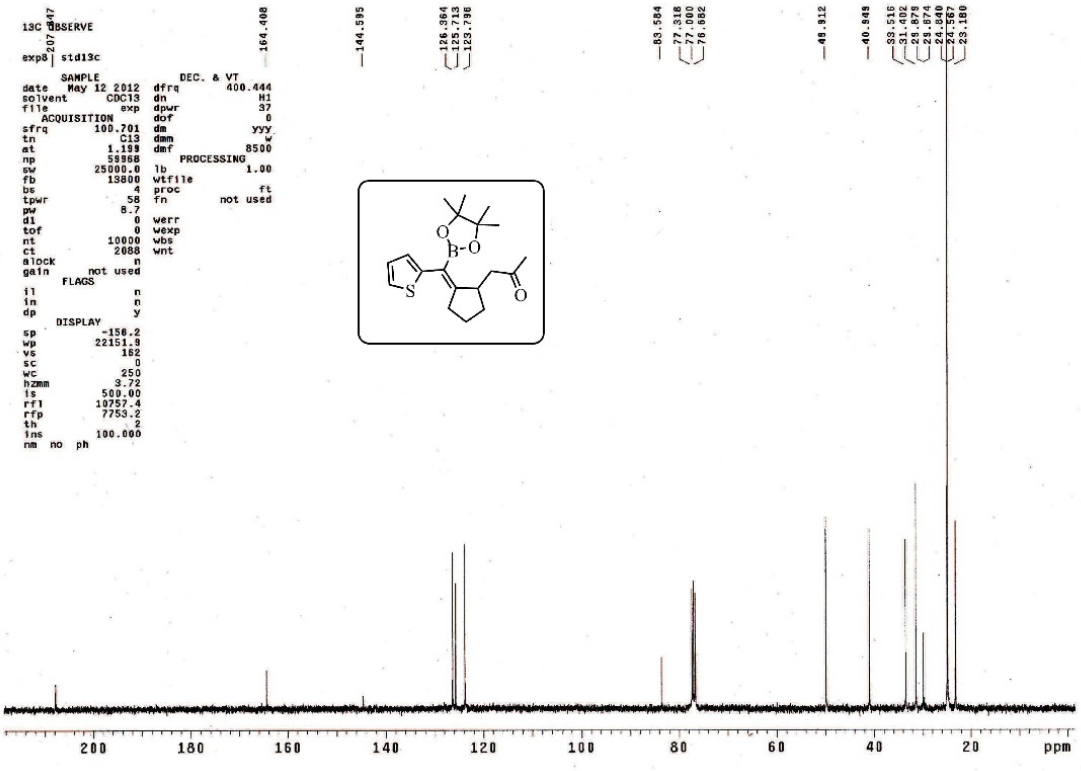
***(E)*-2-(2-((4-Acetylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)-1-phenylethan-1-one (3d)**



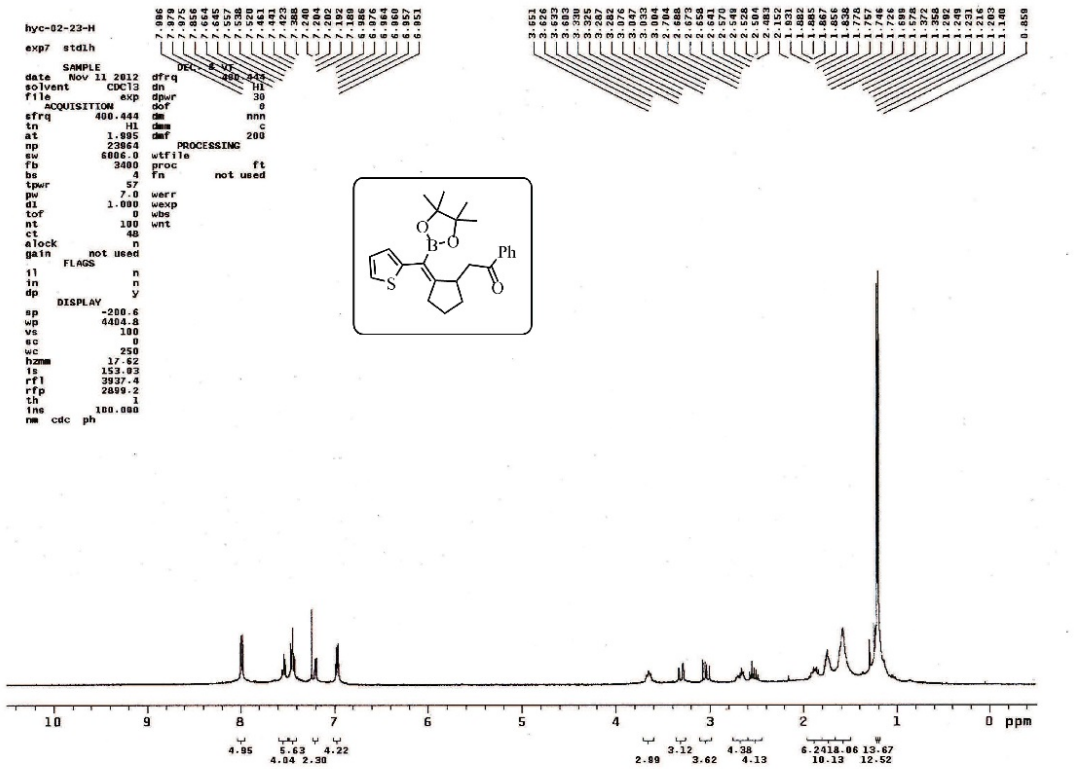


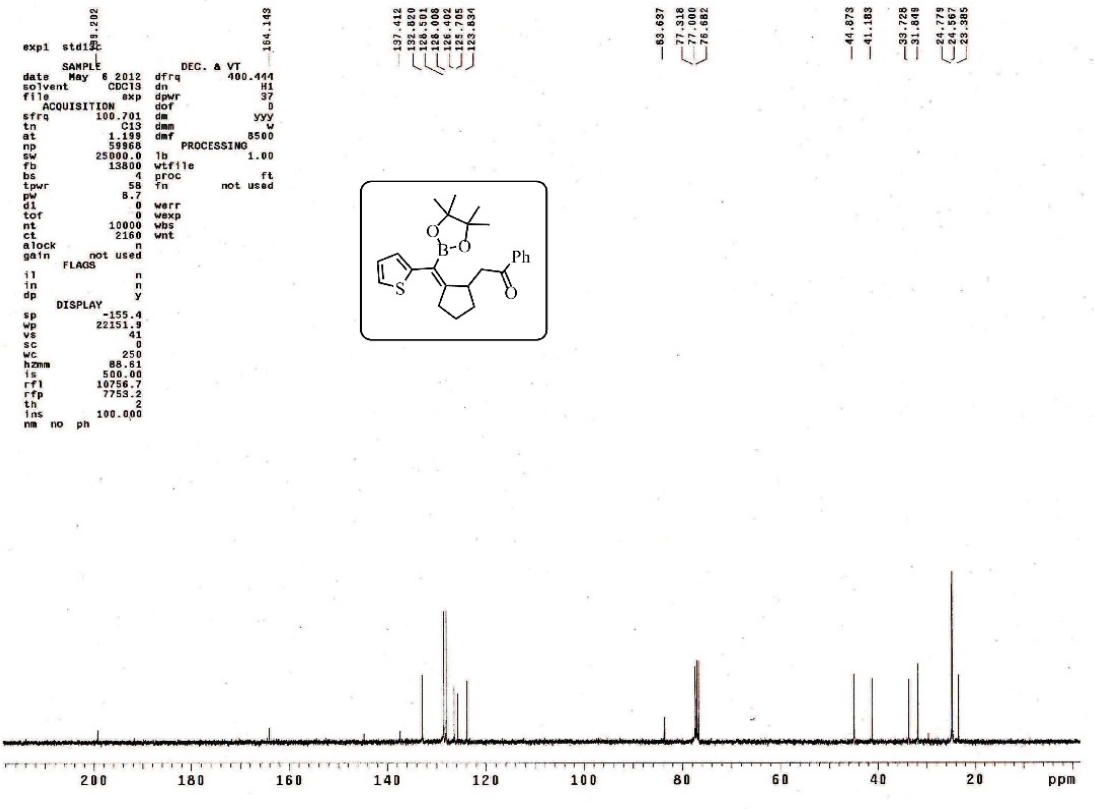
***(E)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methylene)cyclopentyl)propan-2-one (3e)**



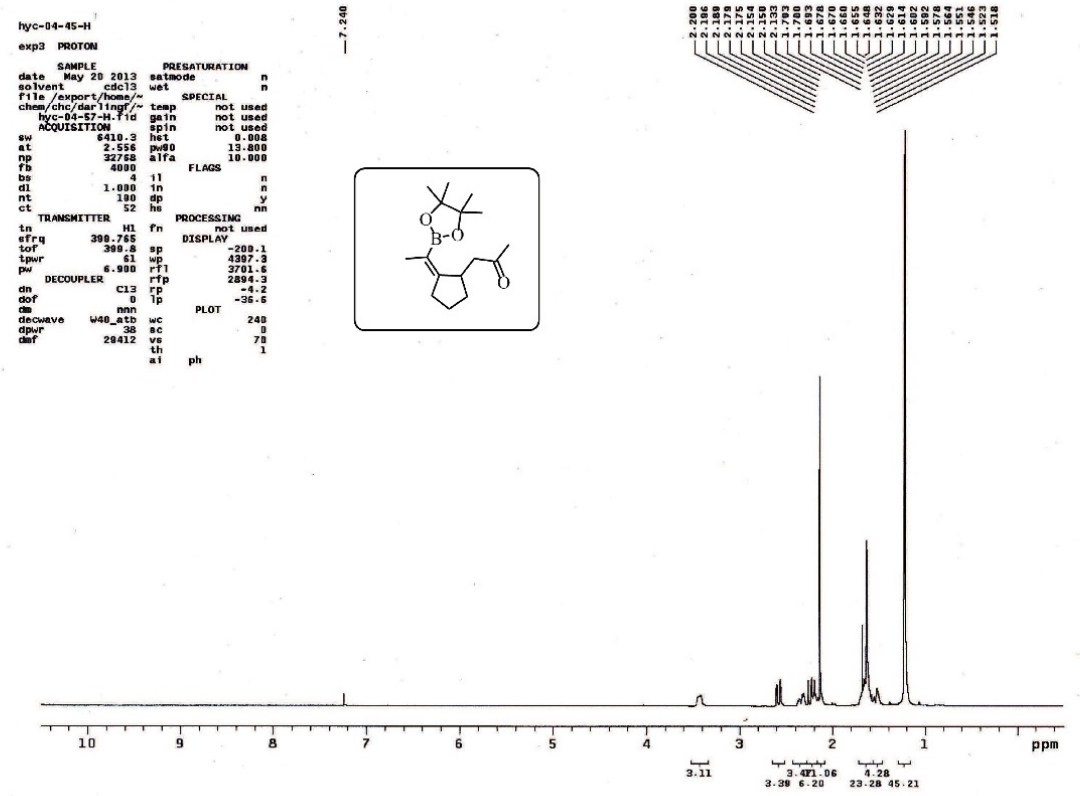



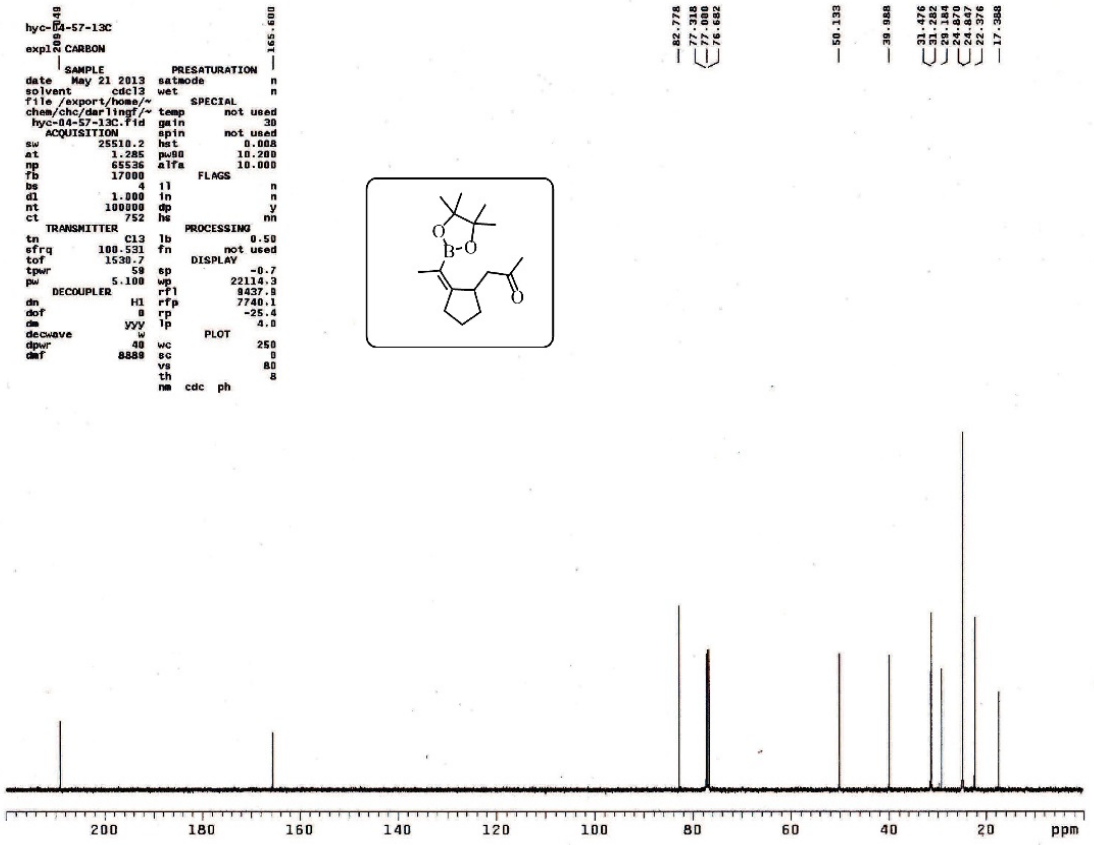
***(E)*-1-Phenyl-2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methylene)cyclopentyl)ethan-1-one (3f)**



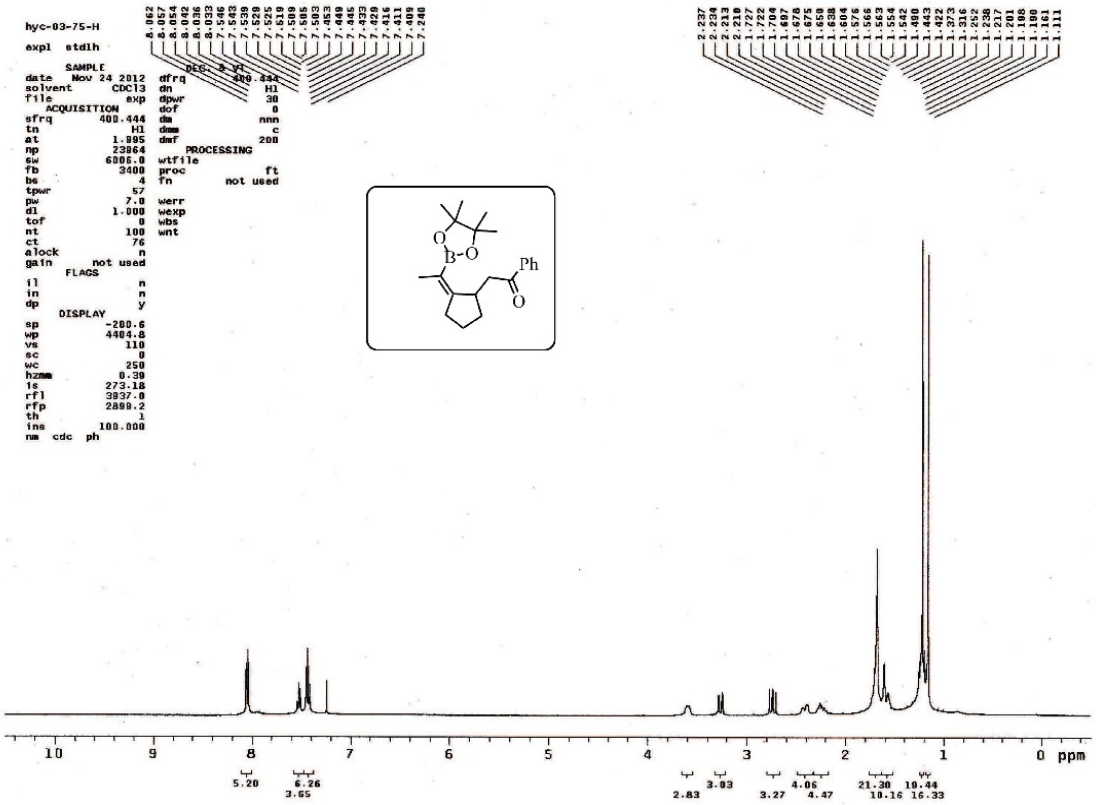


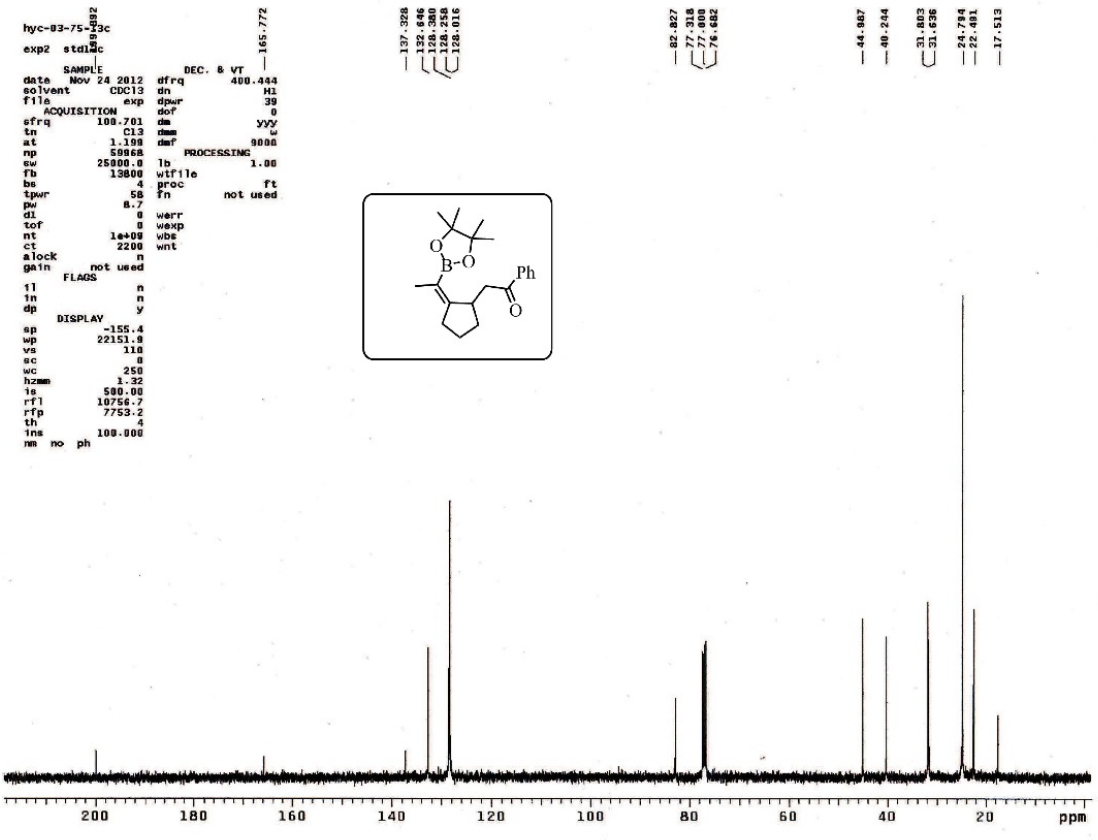
***(E)*-1-(2-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)cyclopentyl)propan-2-one (3g)**



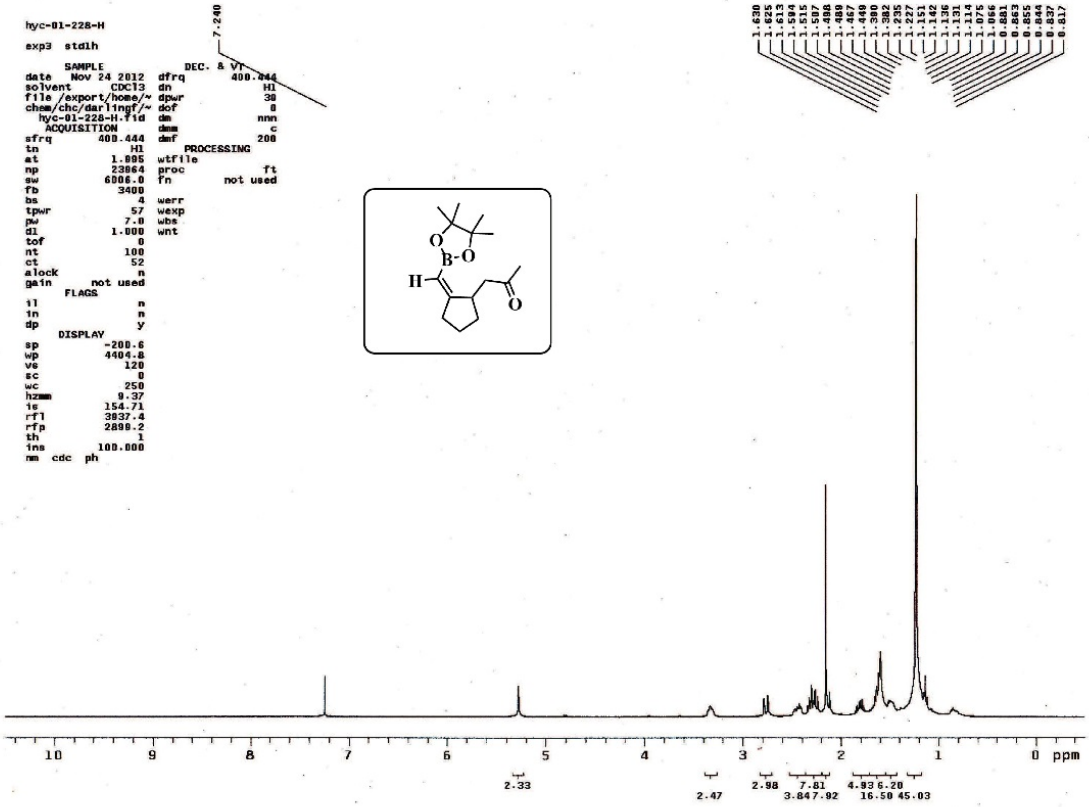



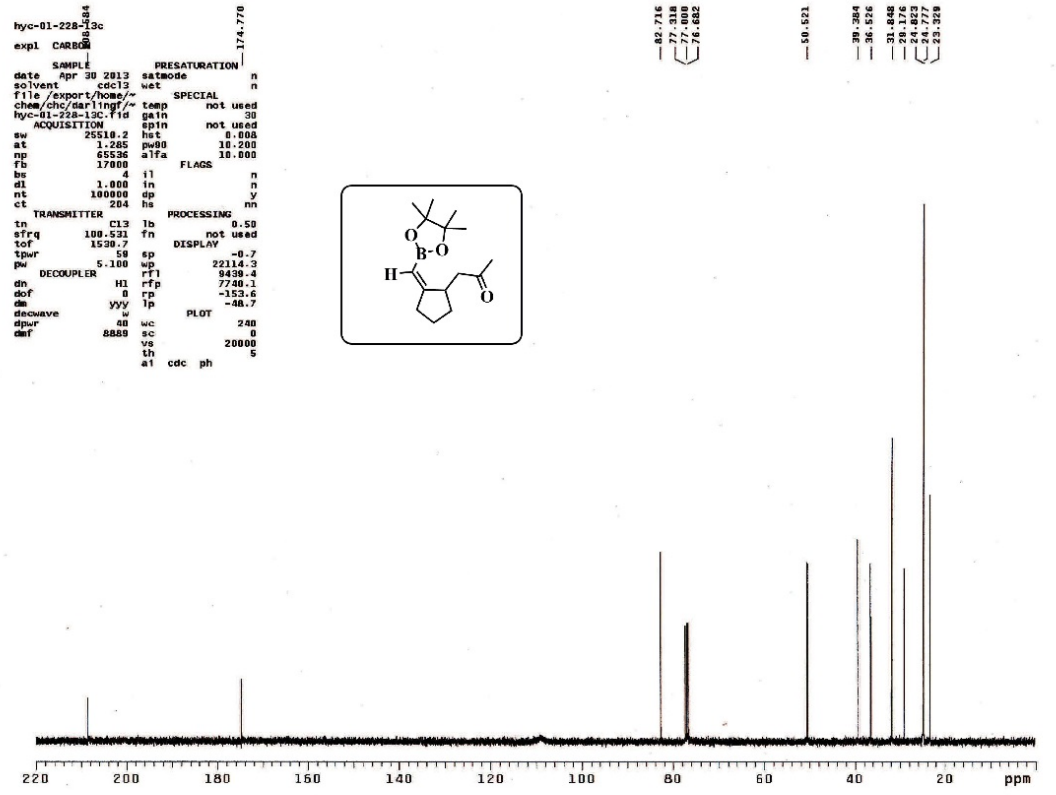
***(E)*-1-Phenyl-2-(2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)cyclopentyl)ethan-1-one (3h)**



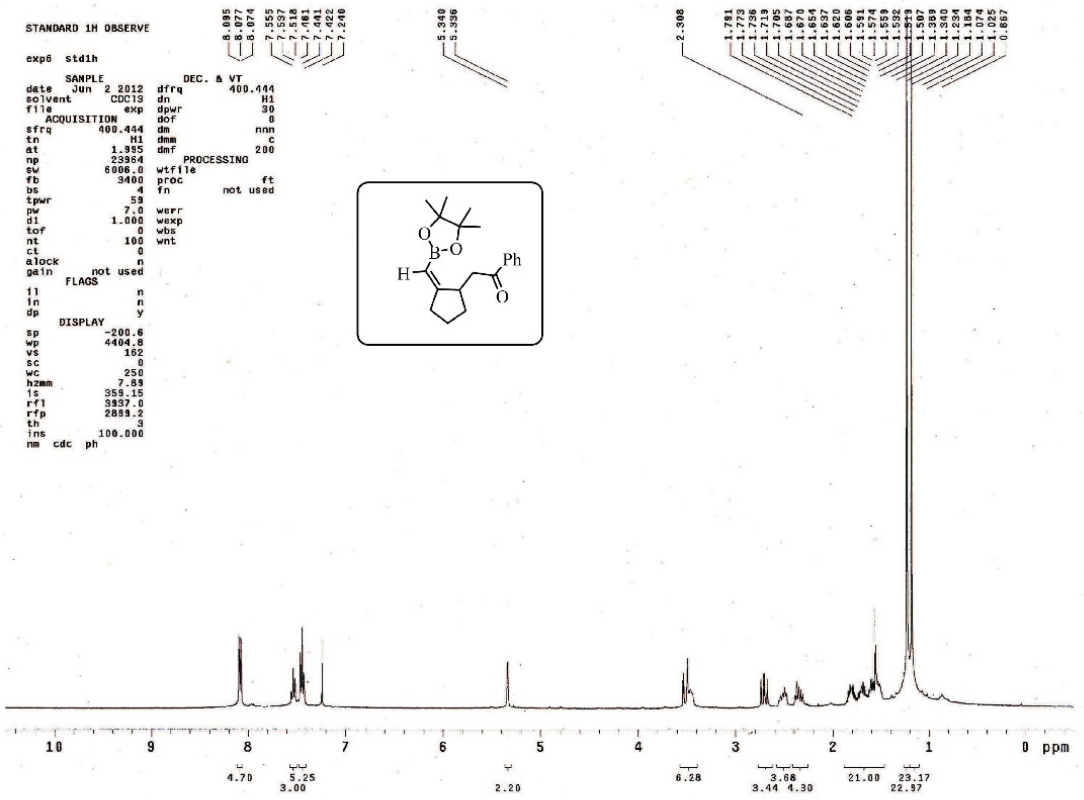



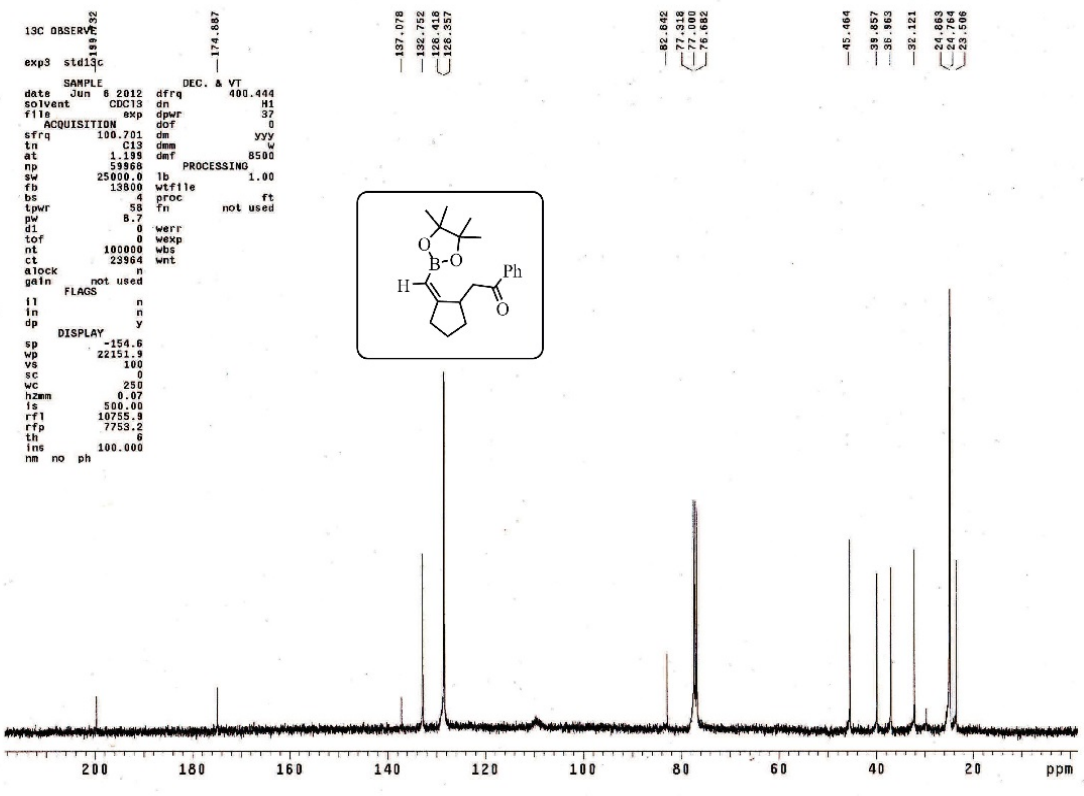
***(Z)*-1-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)propan-2-one (3i)**



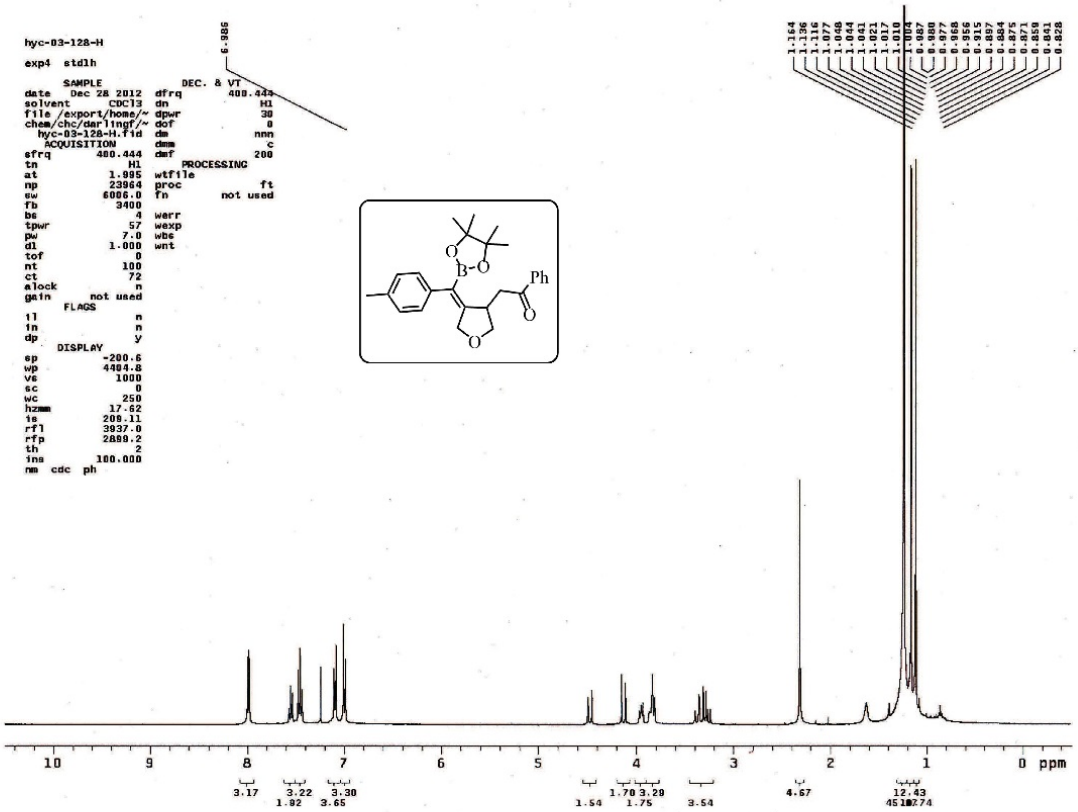



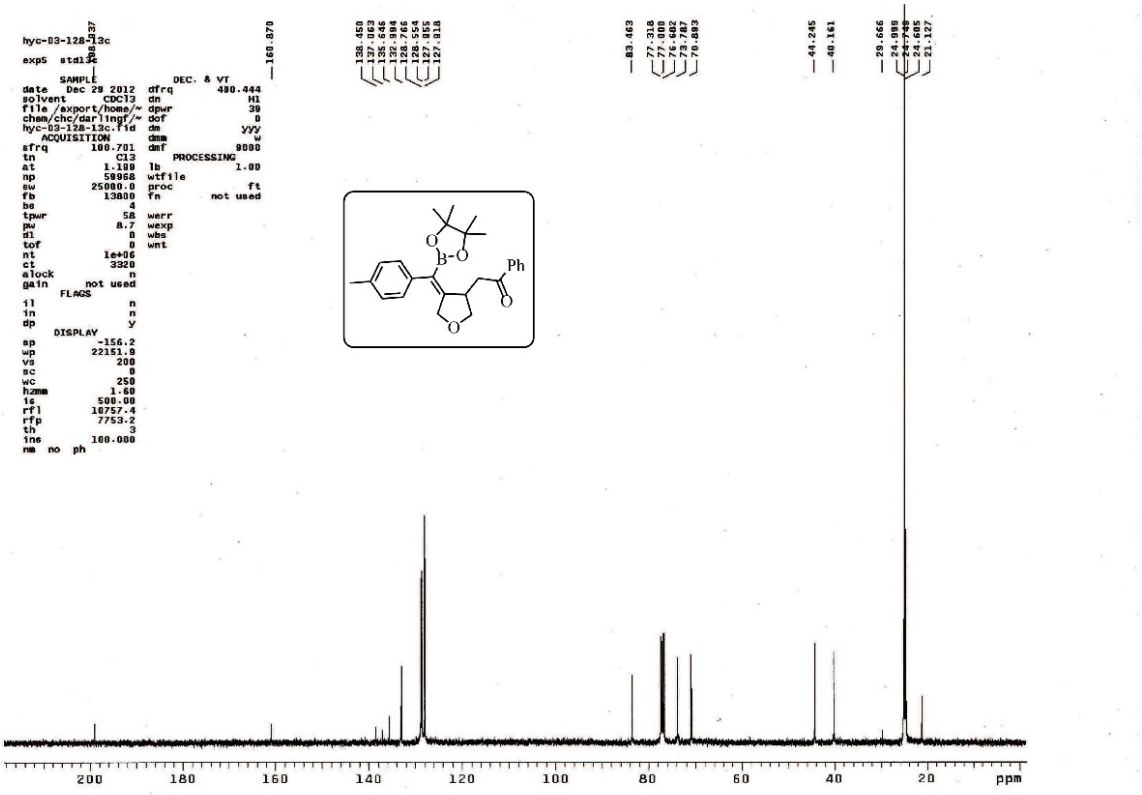
***(Z)*-1-Phenyl-2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclopentyl)ethan-1-one (3j)**



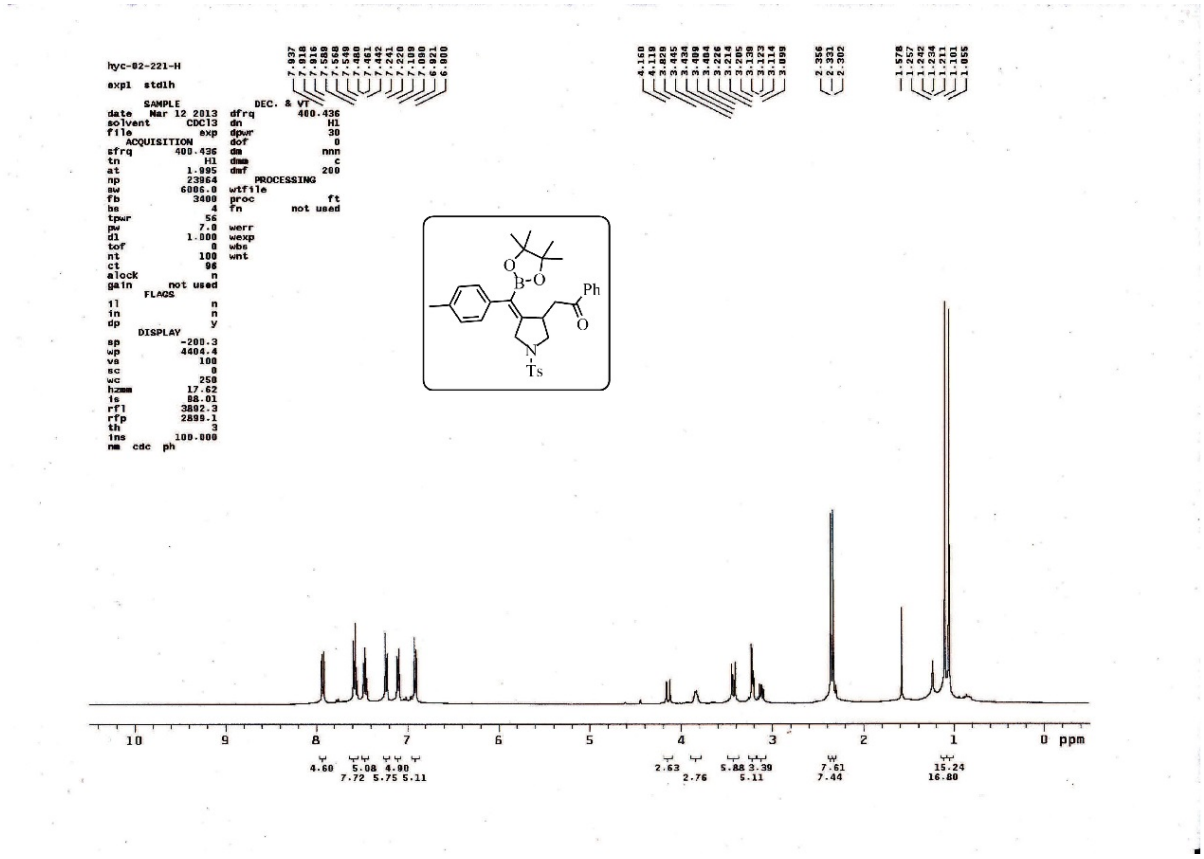



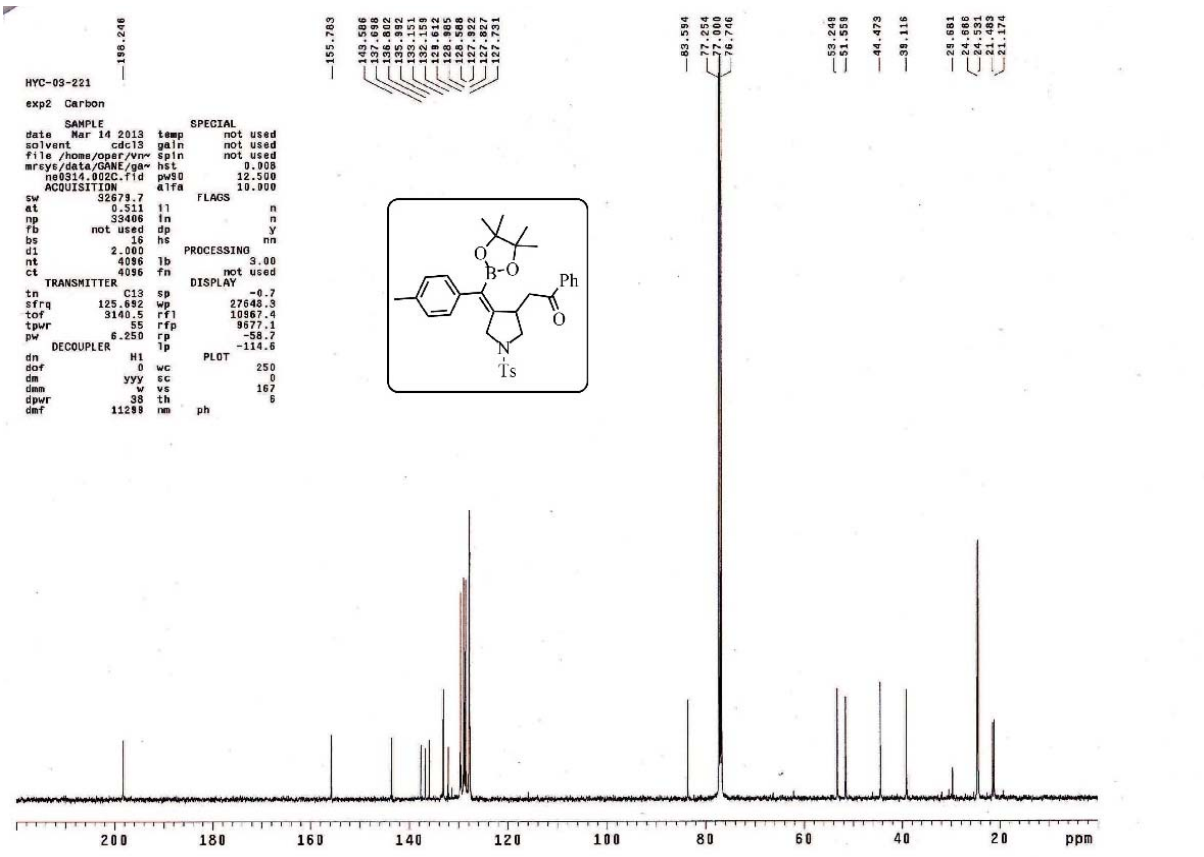
***(Z)*-1-Phenyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methylene)tetrahydrofuran-3-yl)ethan-1-one (3k)**



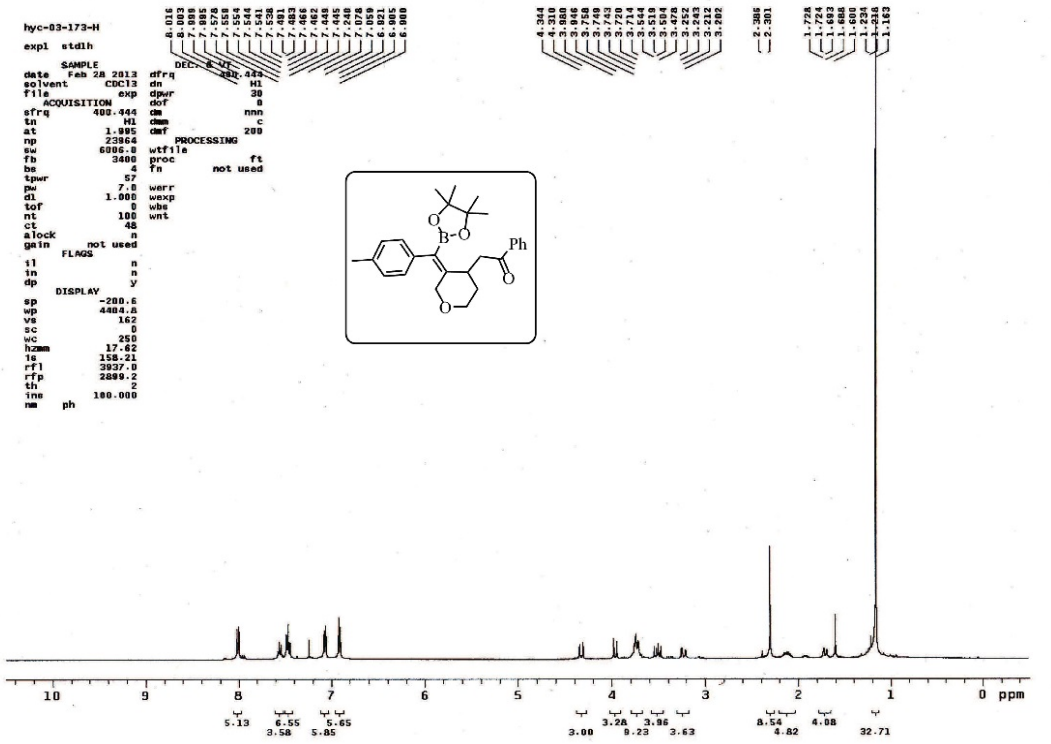



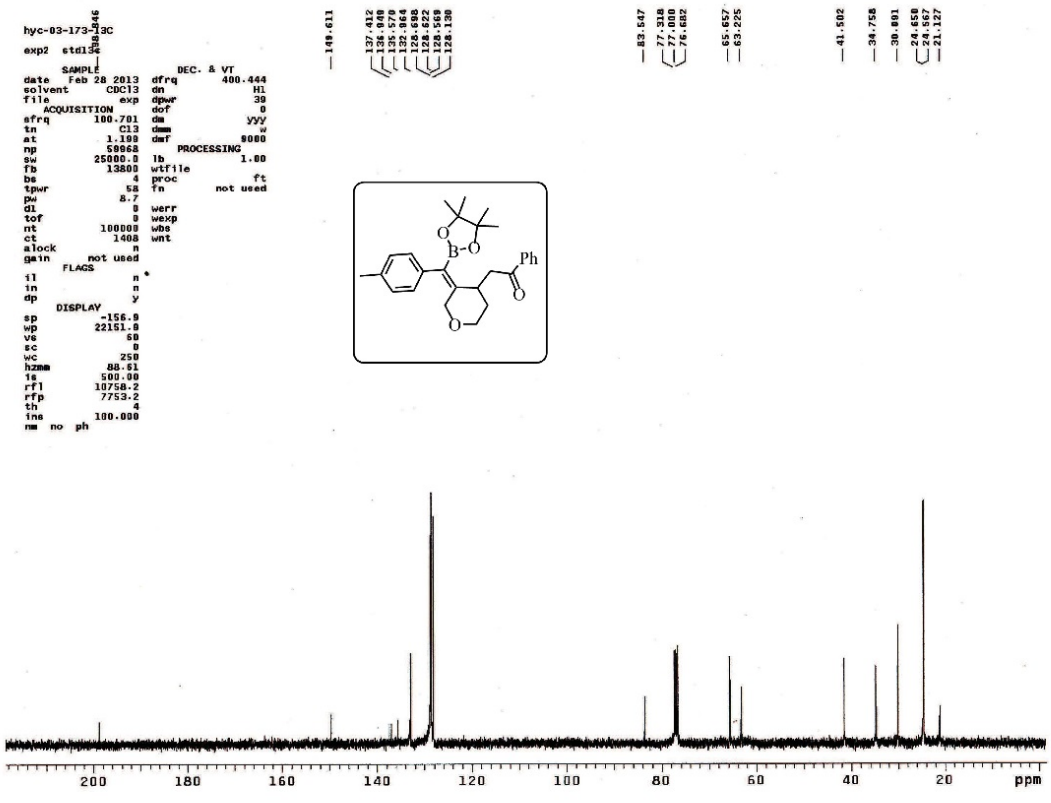
***(Z)*-1-Phenyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methylene)-1-tosylpyrrolidin-3-yl)ethan-1-one (3l)**



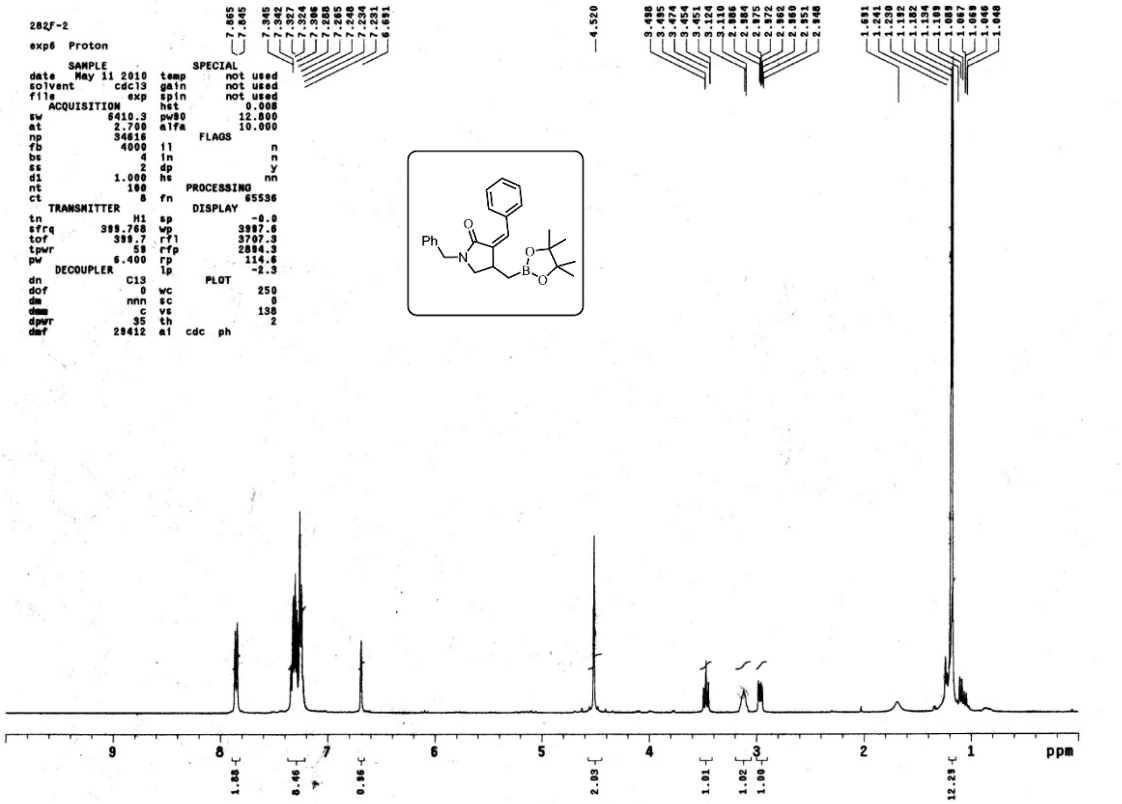



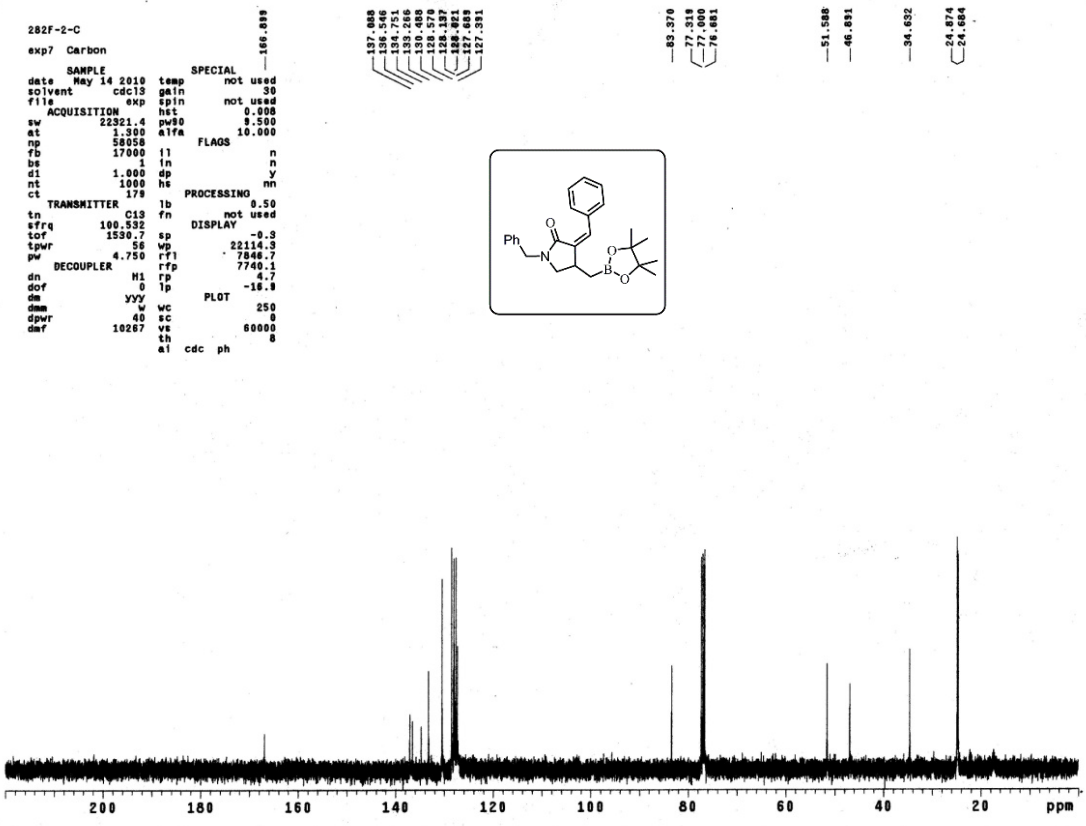
***(Z)*-1-Phenyl-2-(3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methylene)tetrahydro-2*H*-pyran-4-yl)ethan-1-one (3m)**



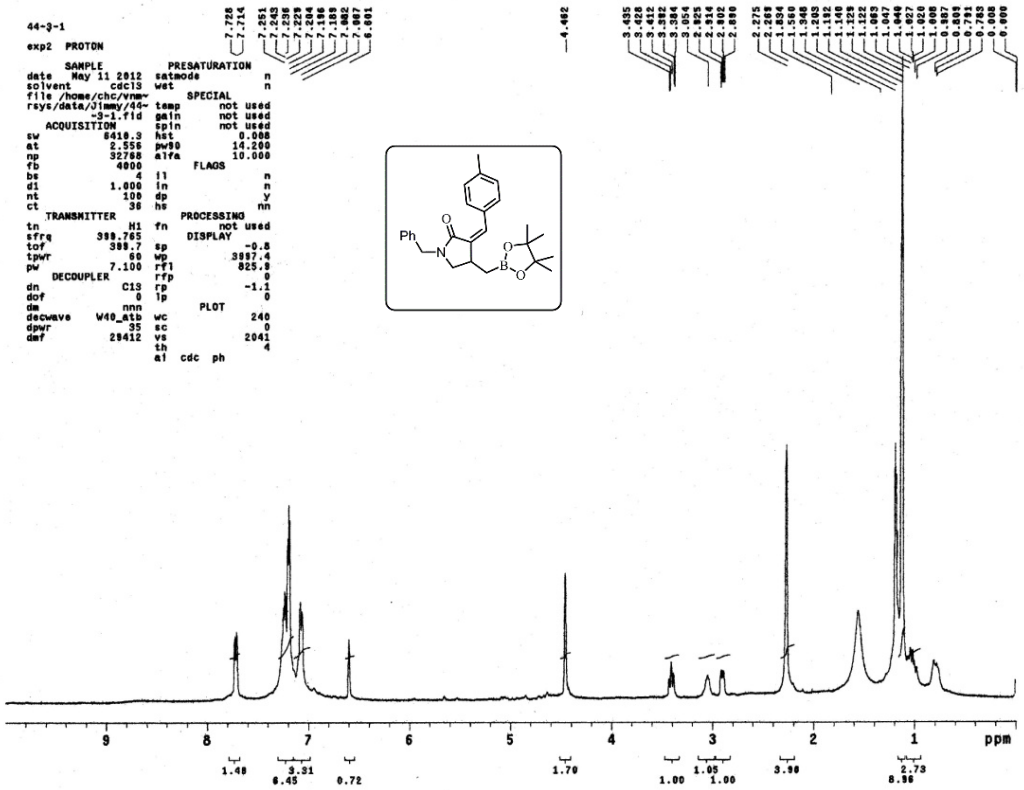



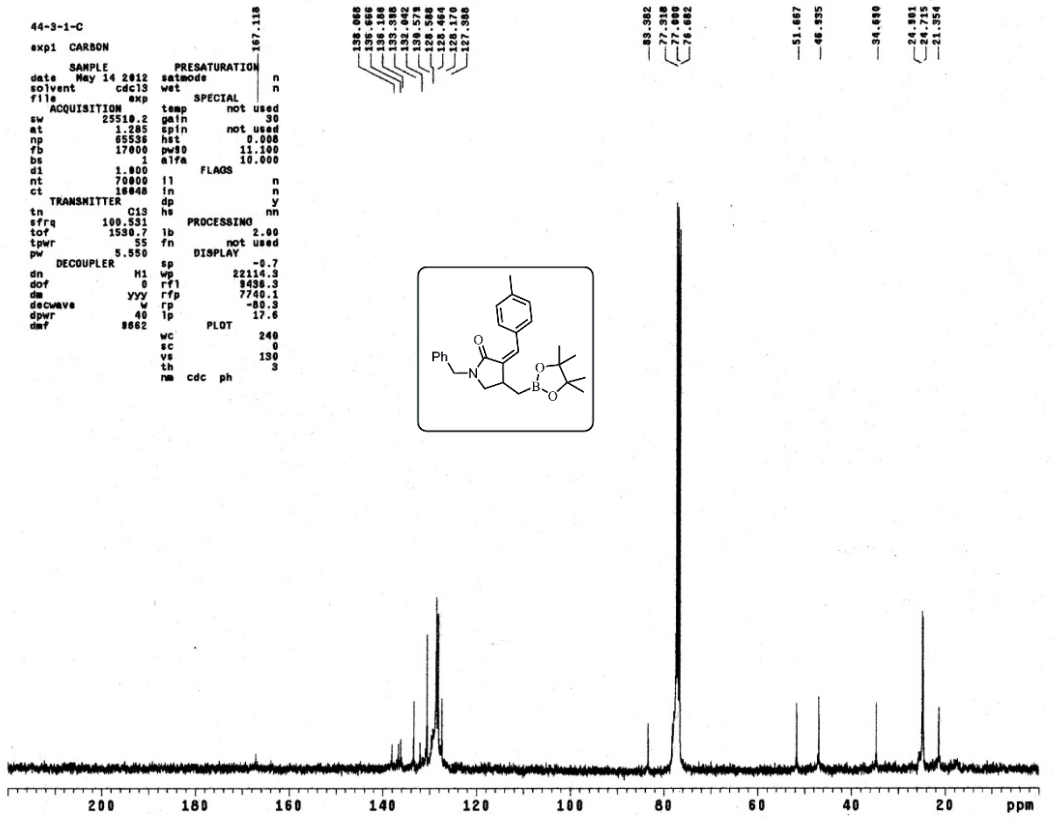
**(Z)-1-Benzyl-3-benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6a)**



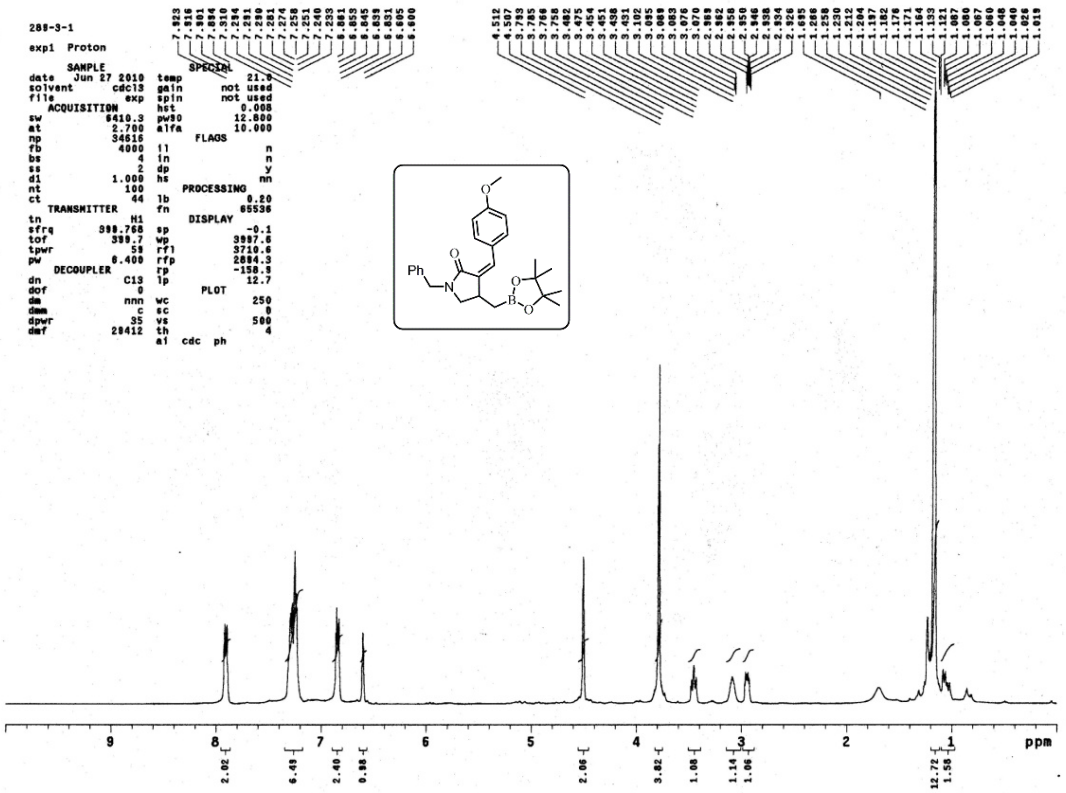



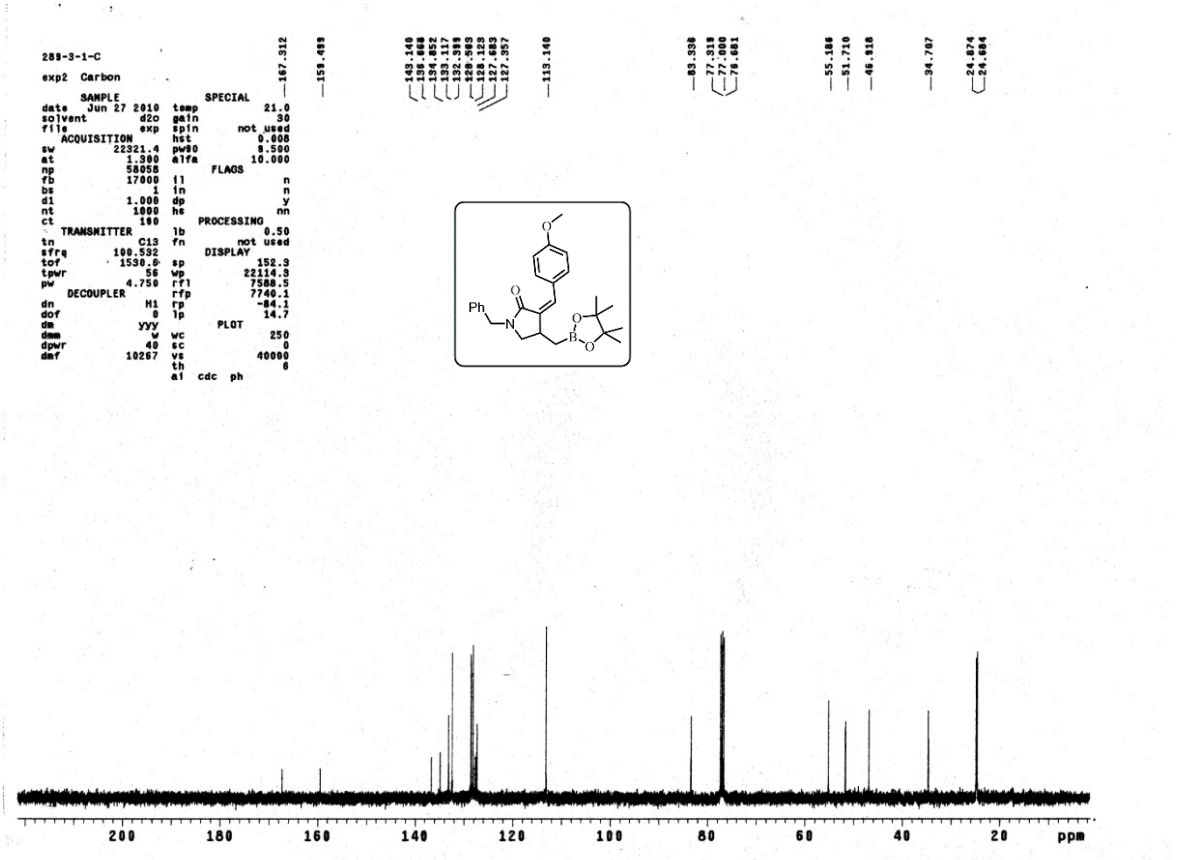
**(*Z*)-1-Benzyl-3-(4-methylbenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6b)**



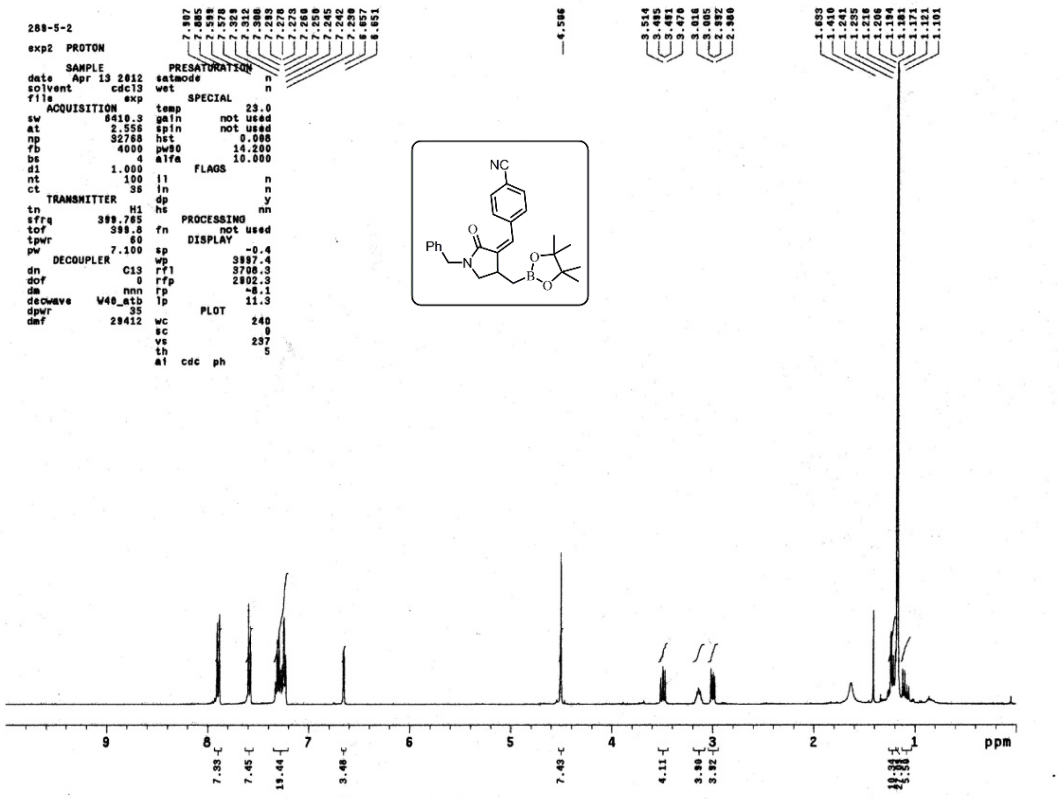


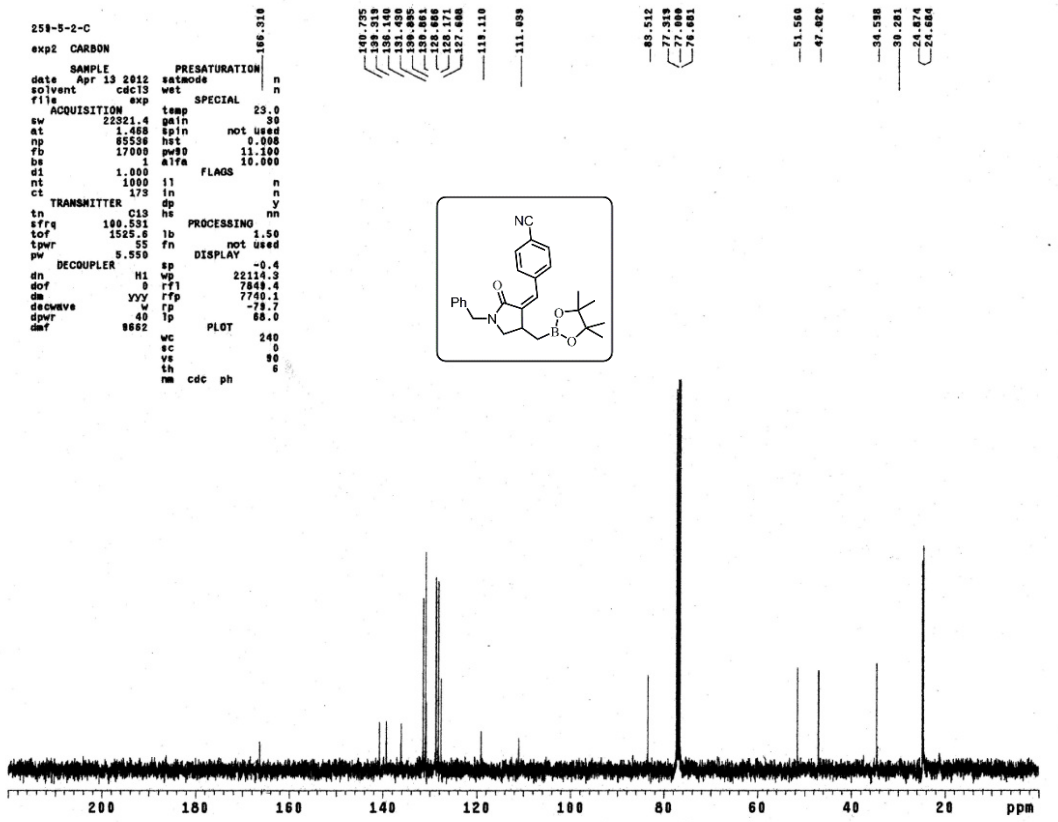
***(Z)*-1-Benzyl-3-(4-methoxybenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6c)**



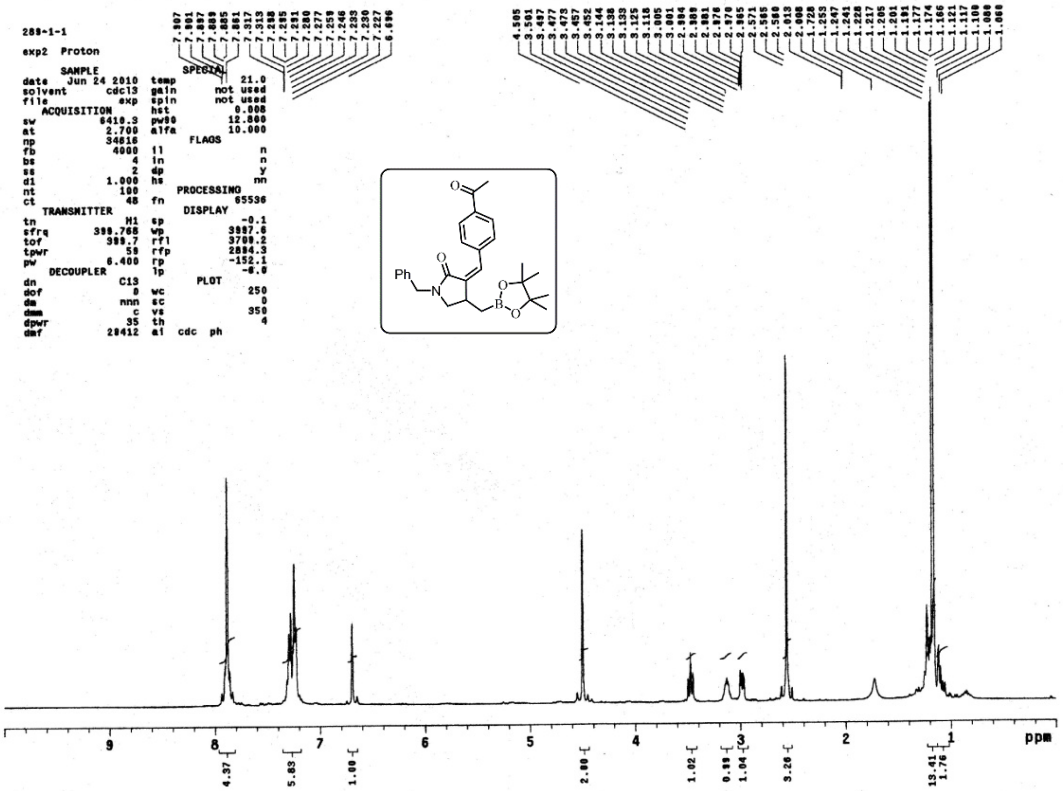


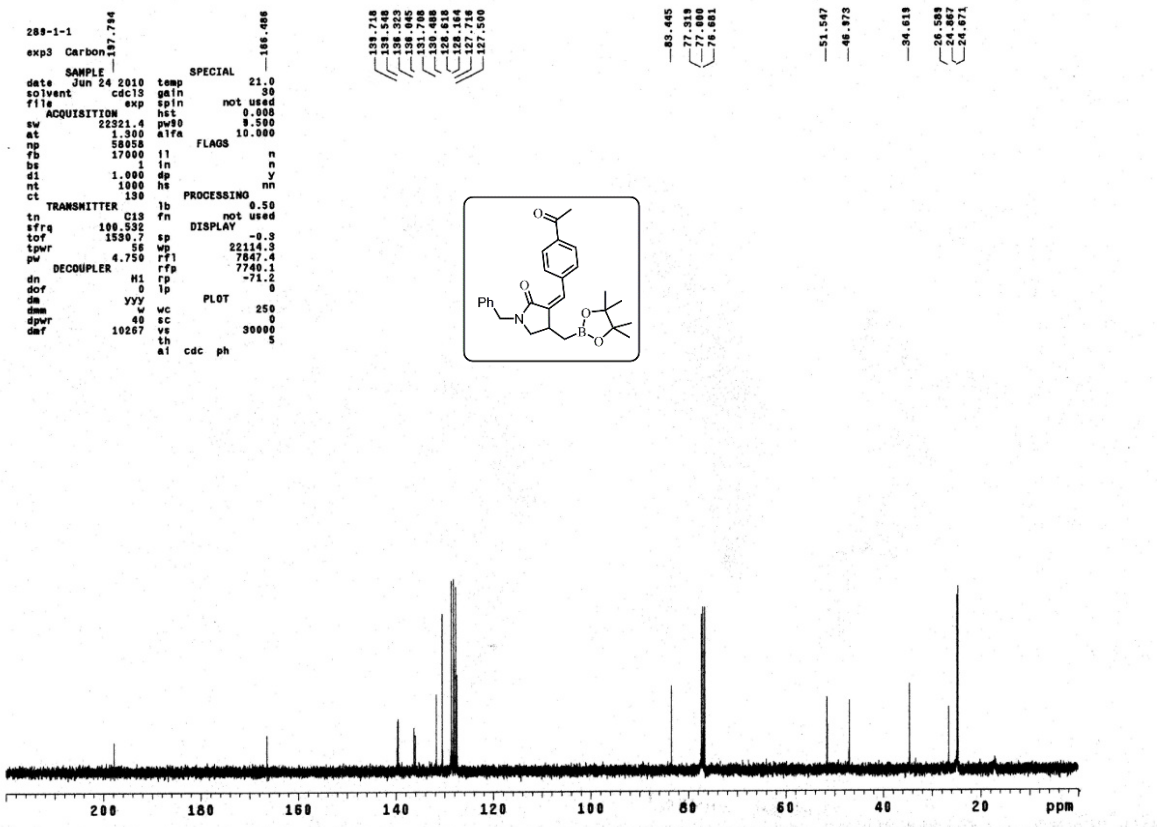
**(*Z*)-4-((1-Benzyl-2-oxo-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-3-ylidene)methyl)benzonitrile (6d)**



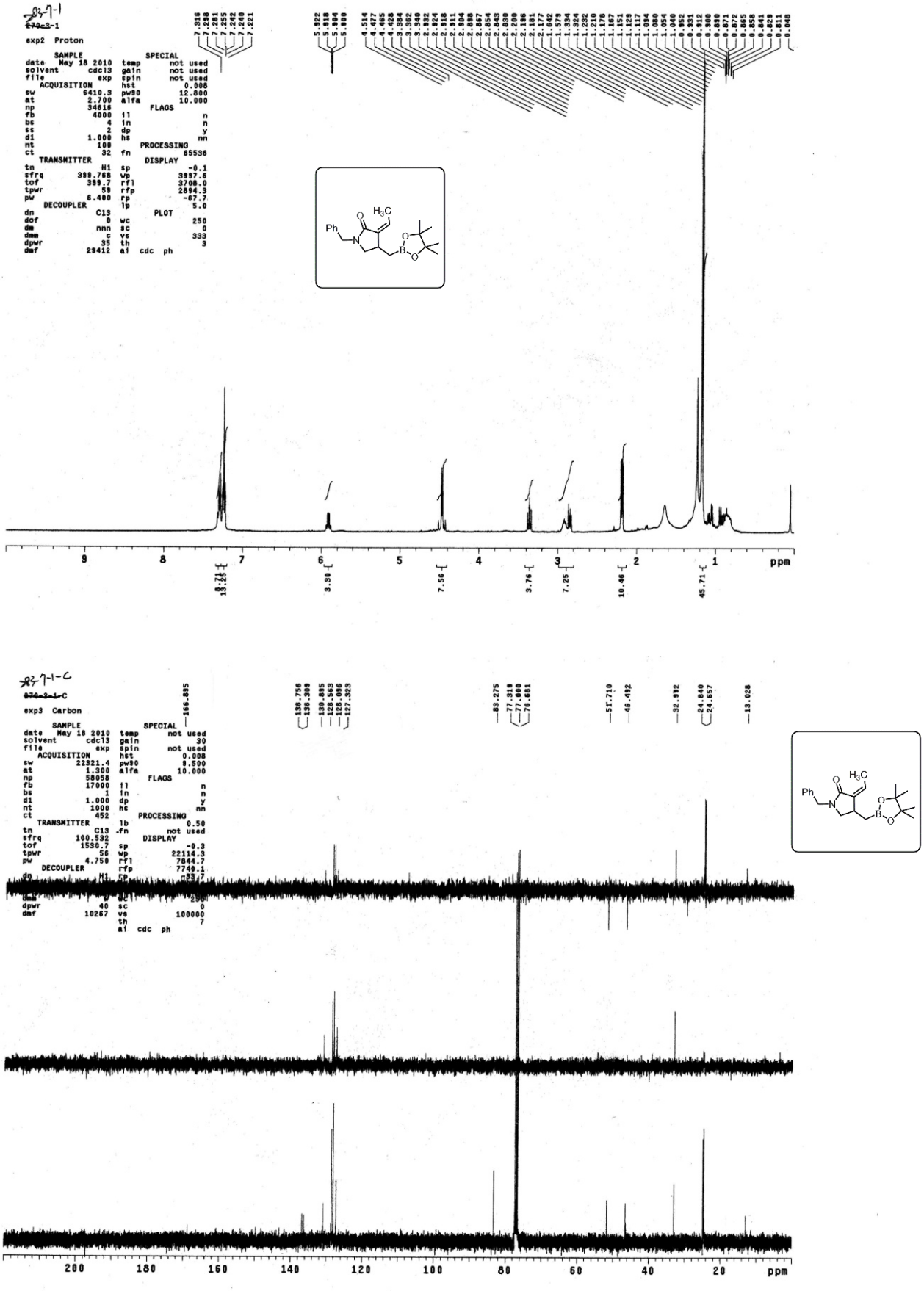


**(*Z*)-3-(4-Acetylbenzylidene)-1-benzyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6e)**

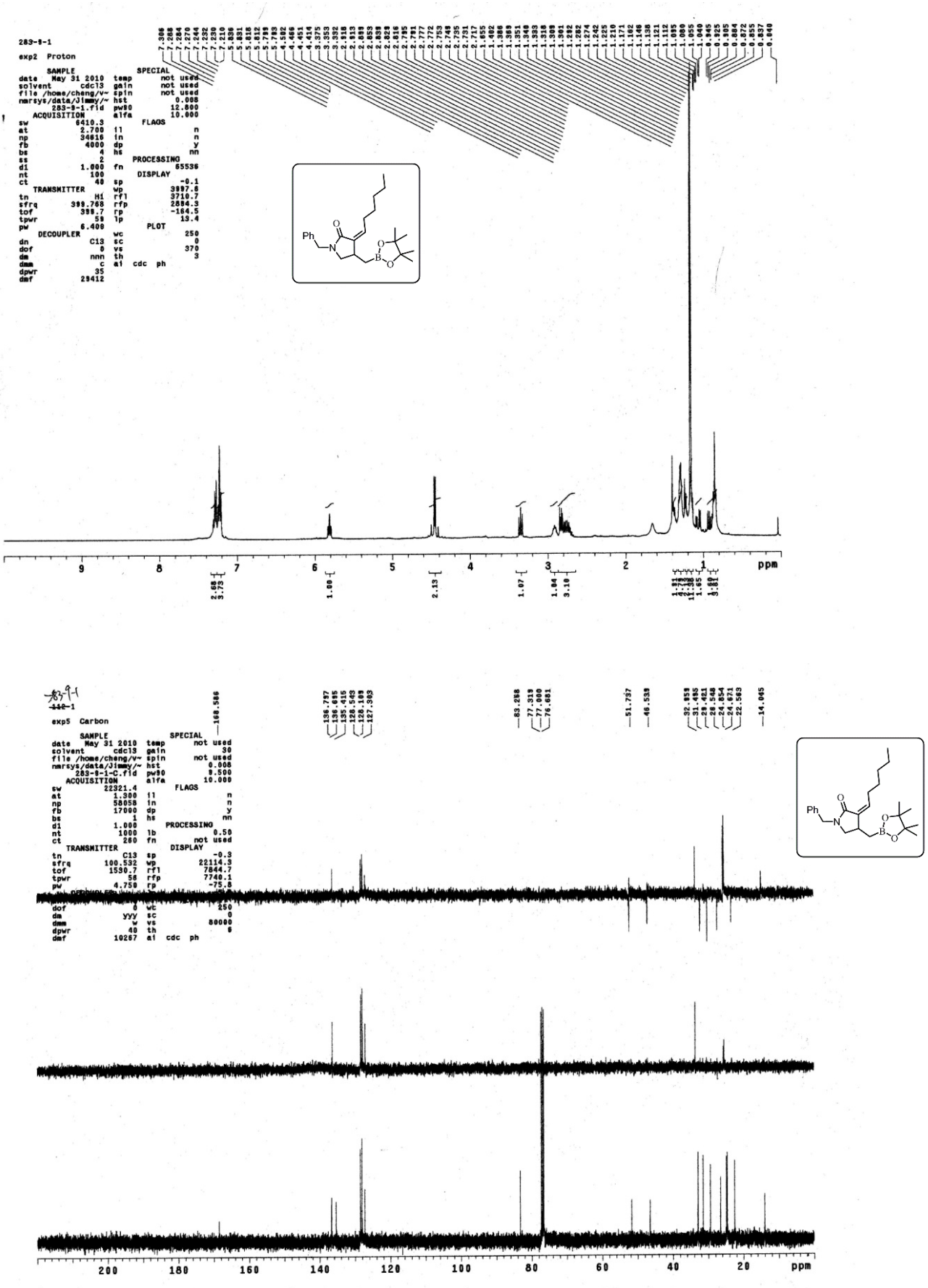




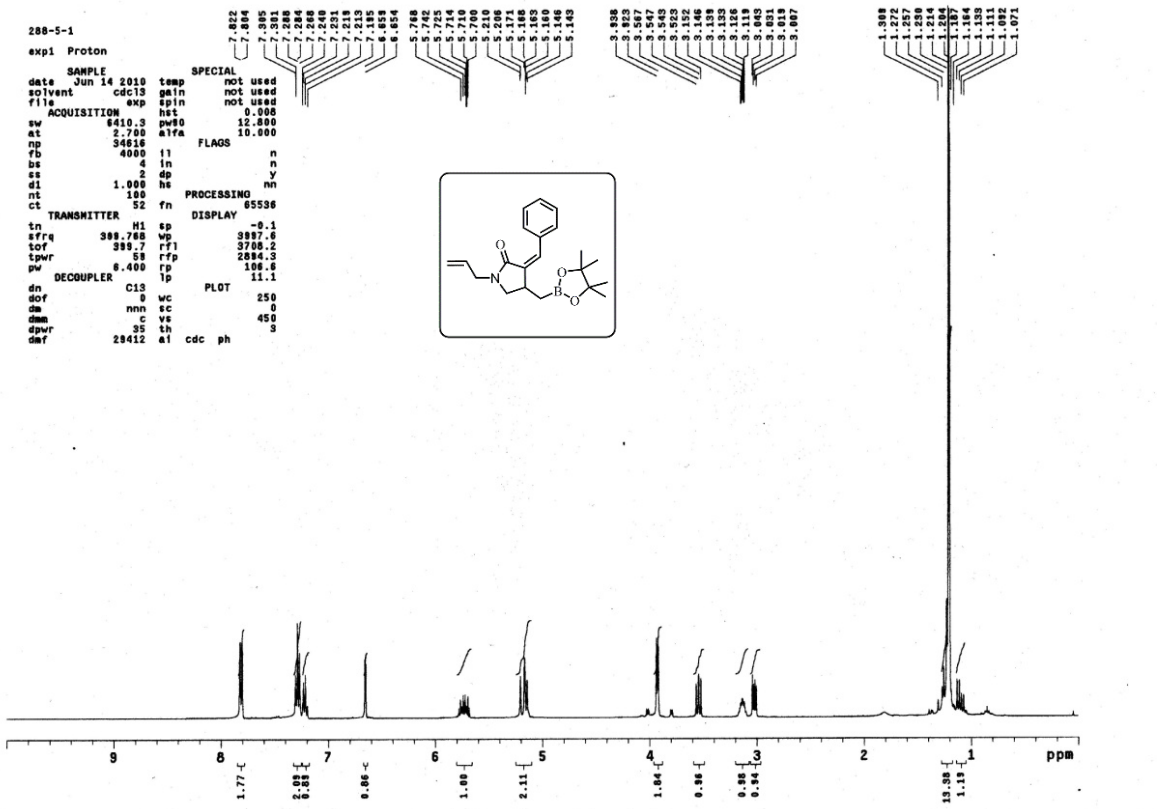
**(*Z*)-1-Benzyl-3-ethylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6f)**

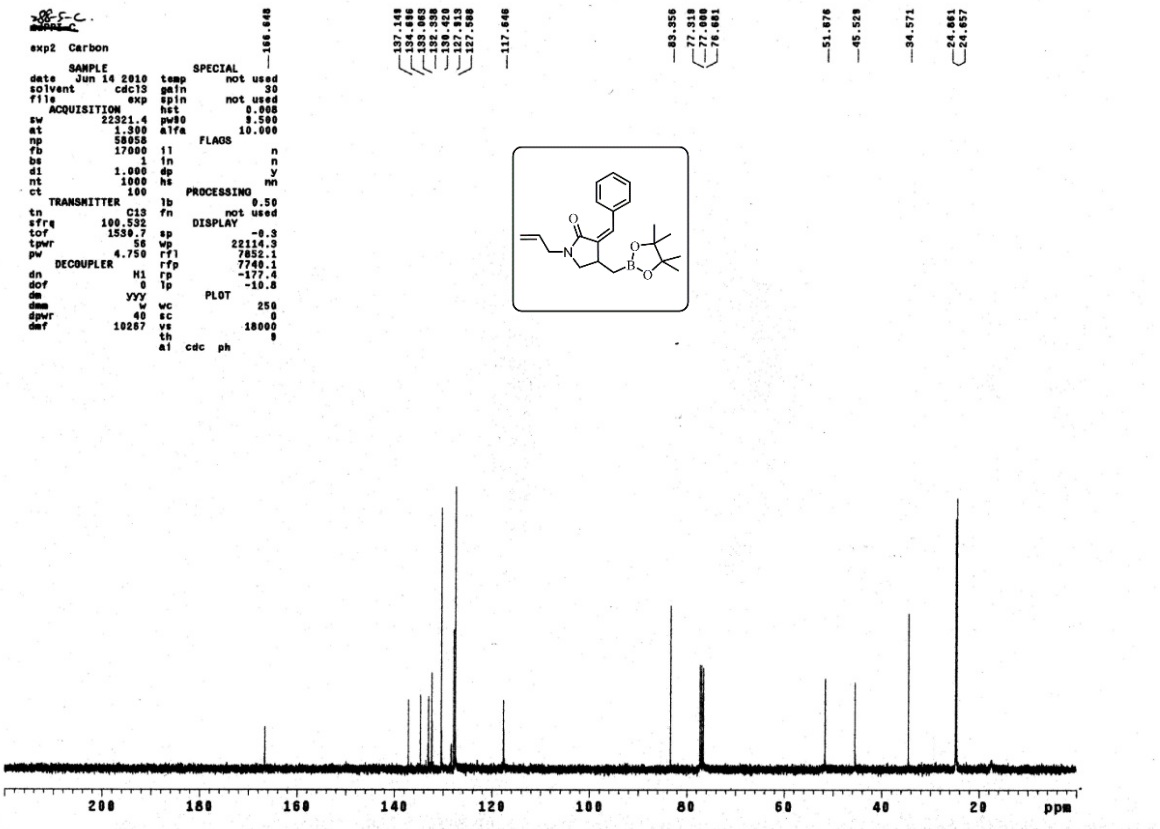


**(*Z*)-1-Benzyl-3-hexylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6g)**

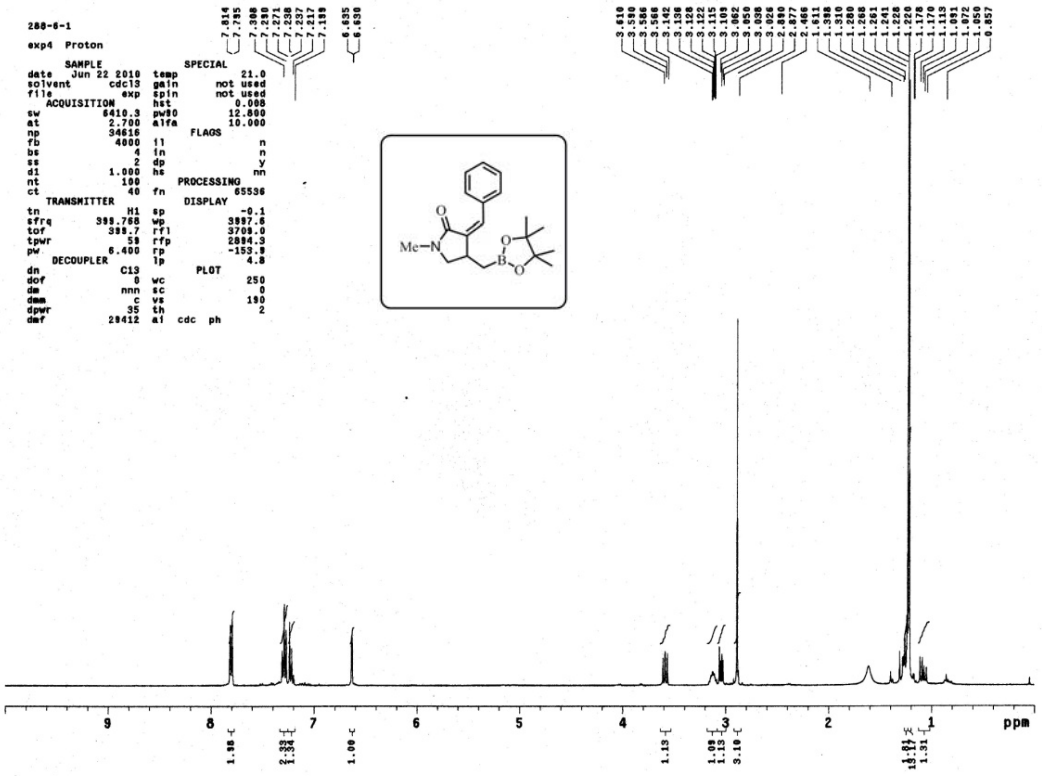


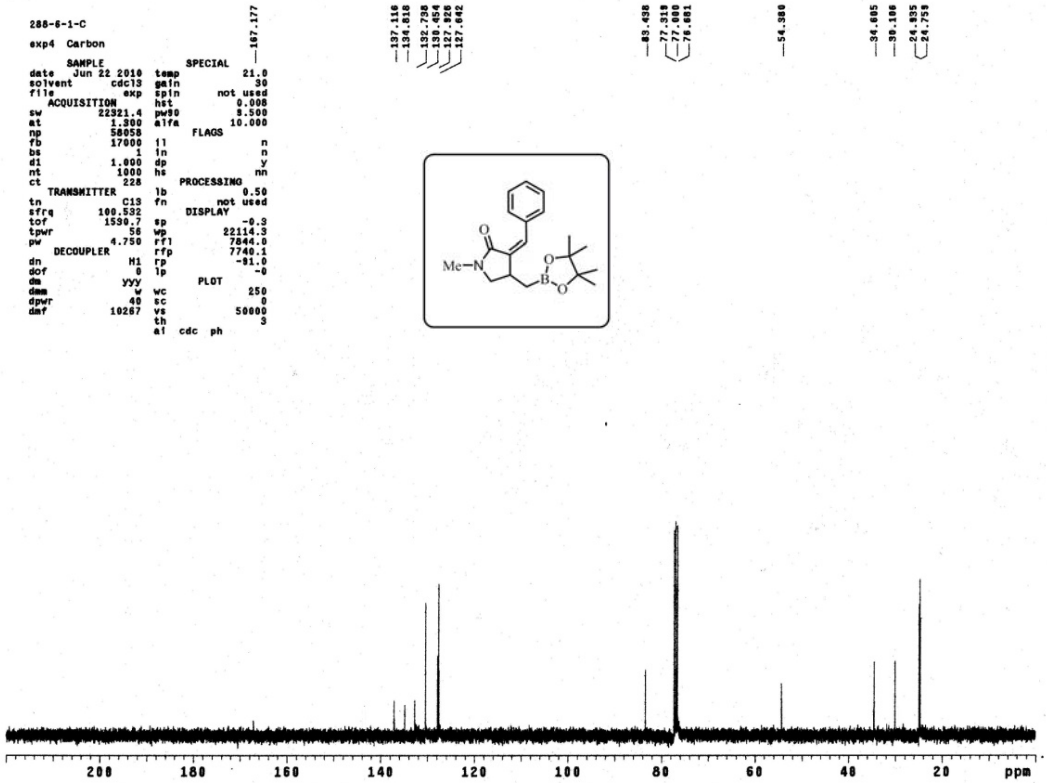
**(*Z*)-1-Allyl-3-benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6h)**



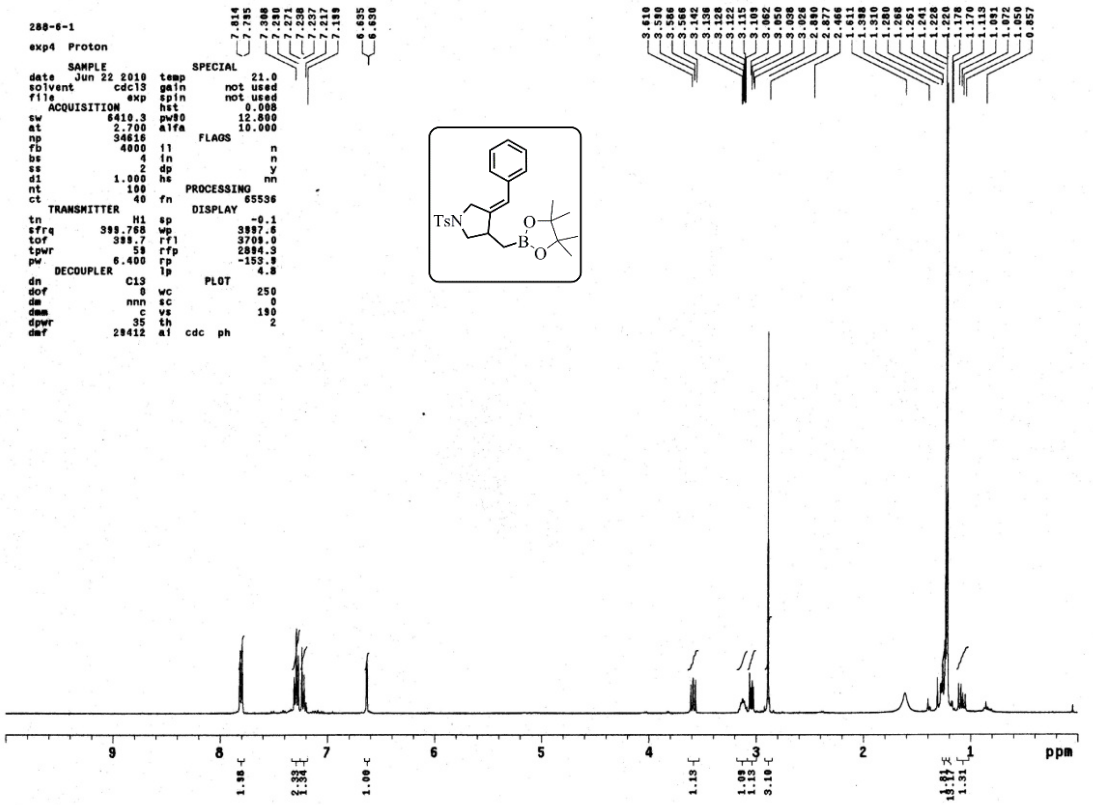



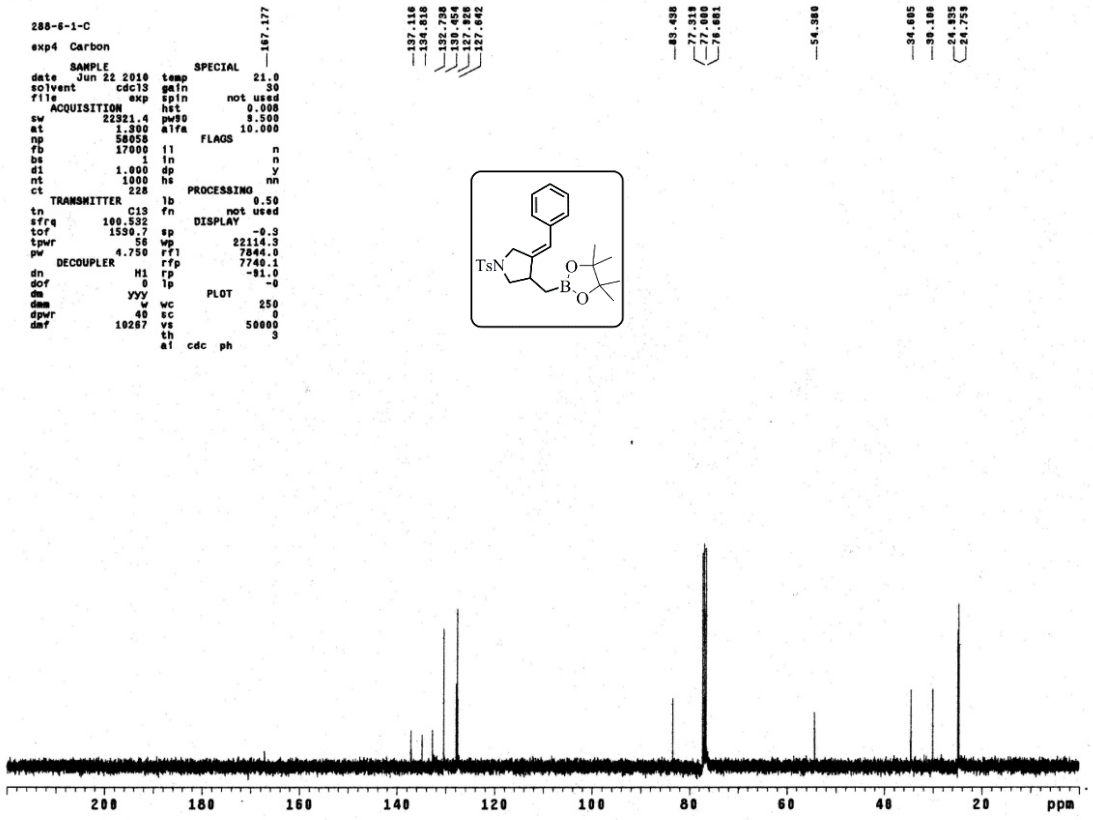
**(Z)-3-Benzylidene-1-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one (6i)**



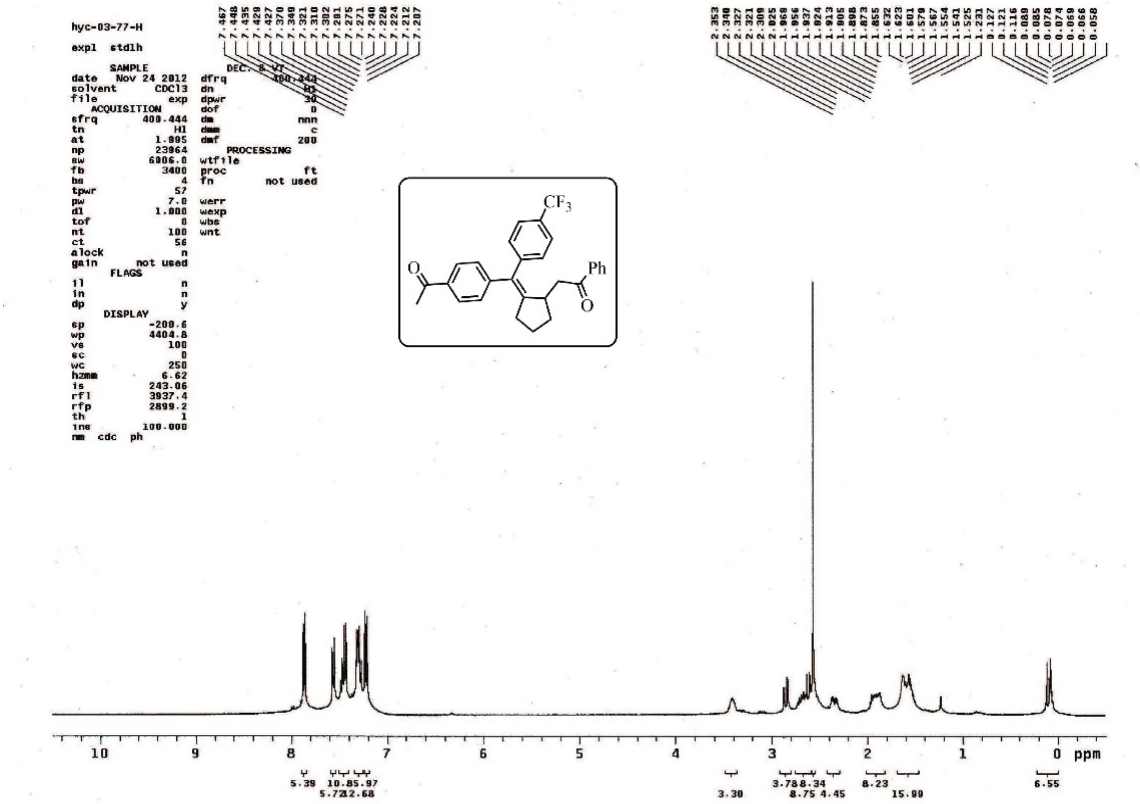



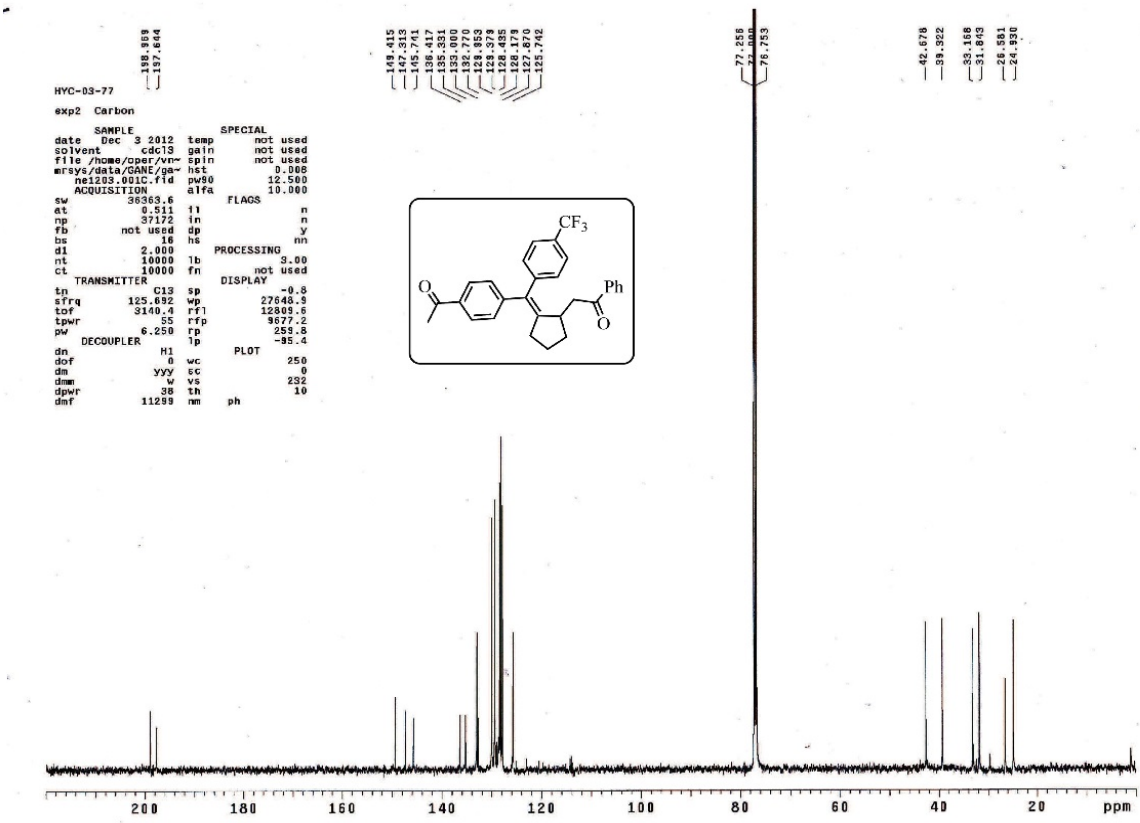
**(*Z*)-3-Benzylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpyrrolidine (6j)**



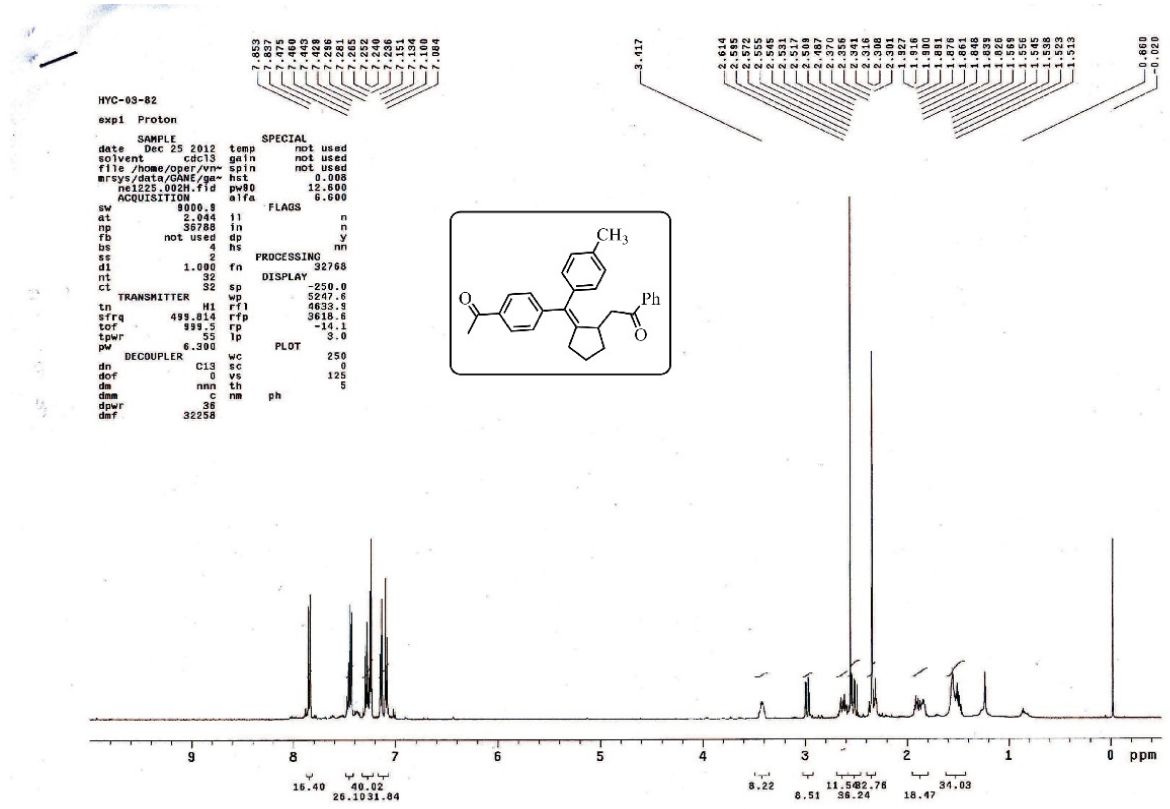


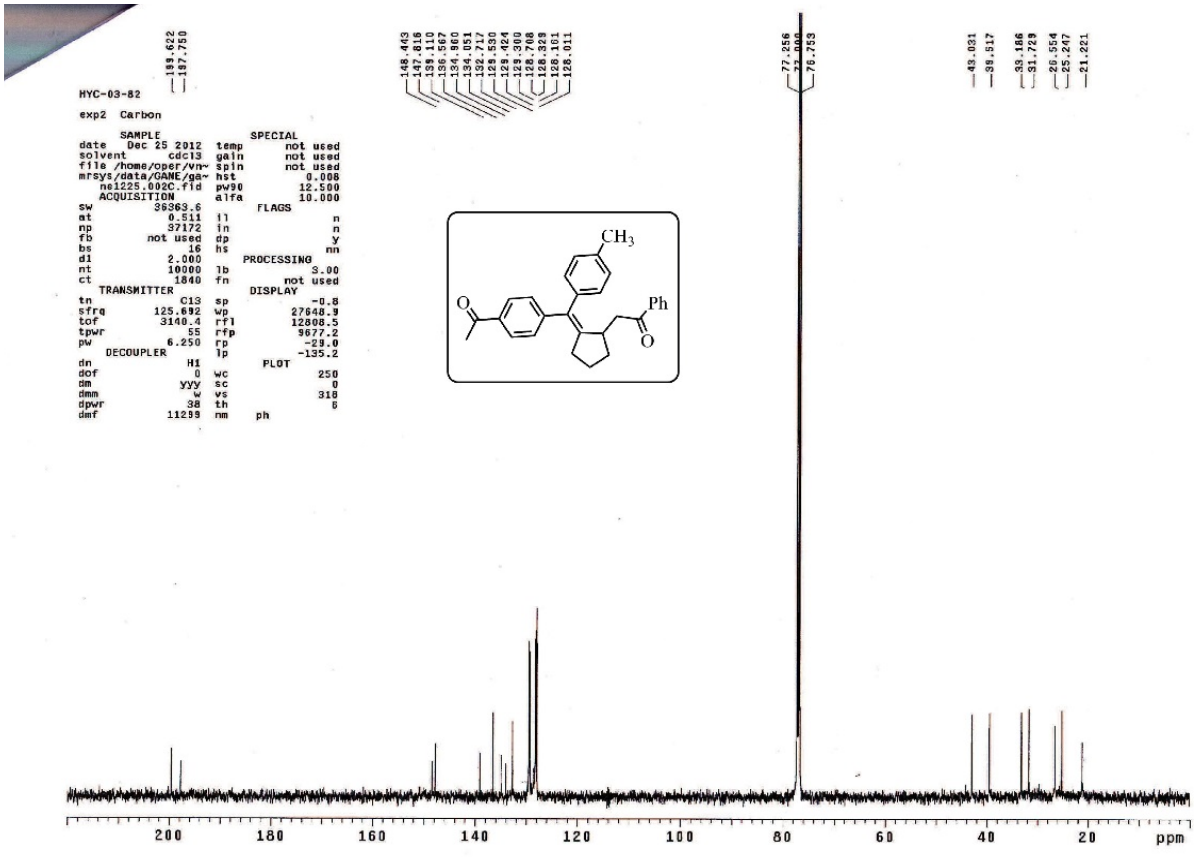
***(Z)*-2-(2-((4-Acetylphenyl)(4-(trifluoromethyl)phenyl)methylene)cyclopentyl)-1-phenylethan-1-one (7a)**



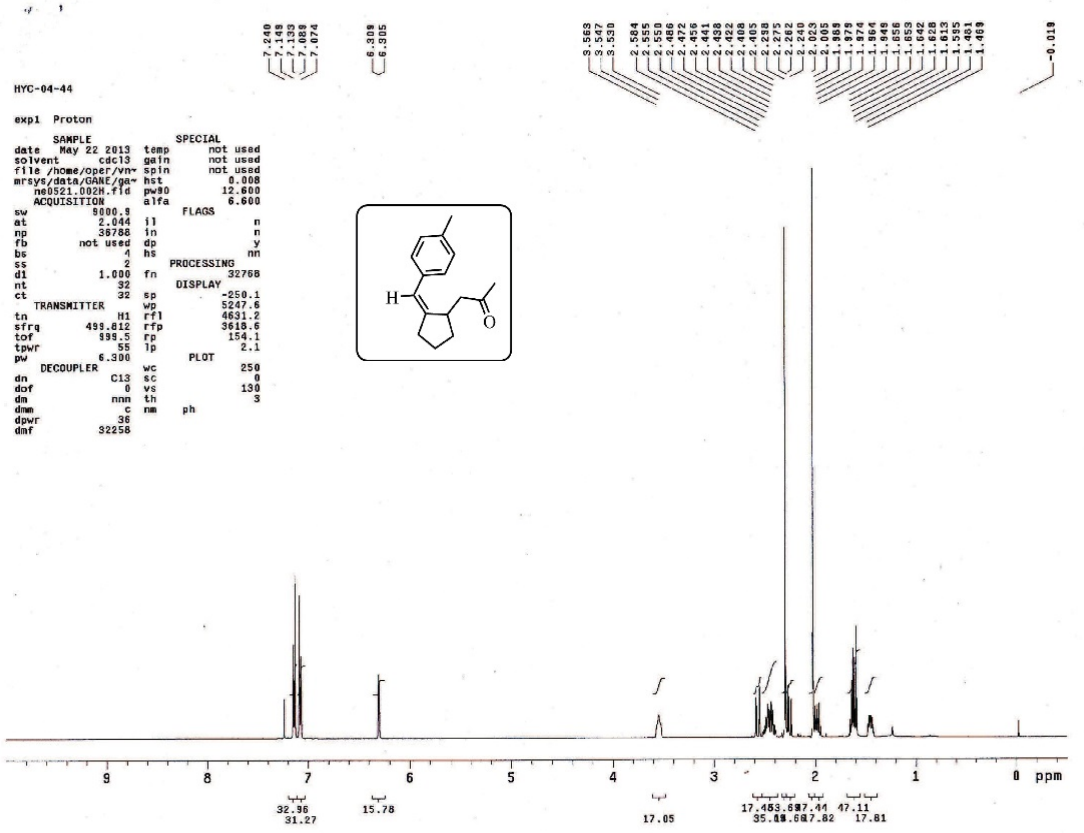



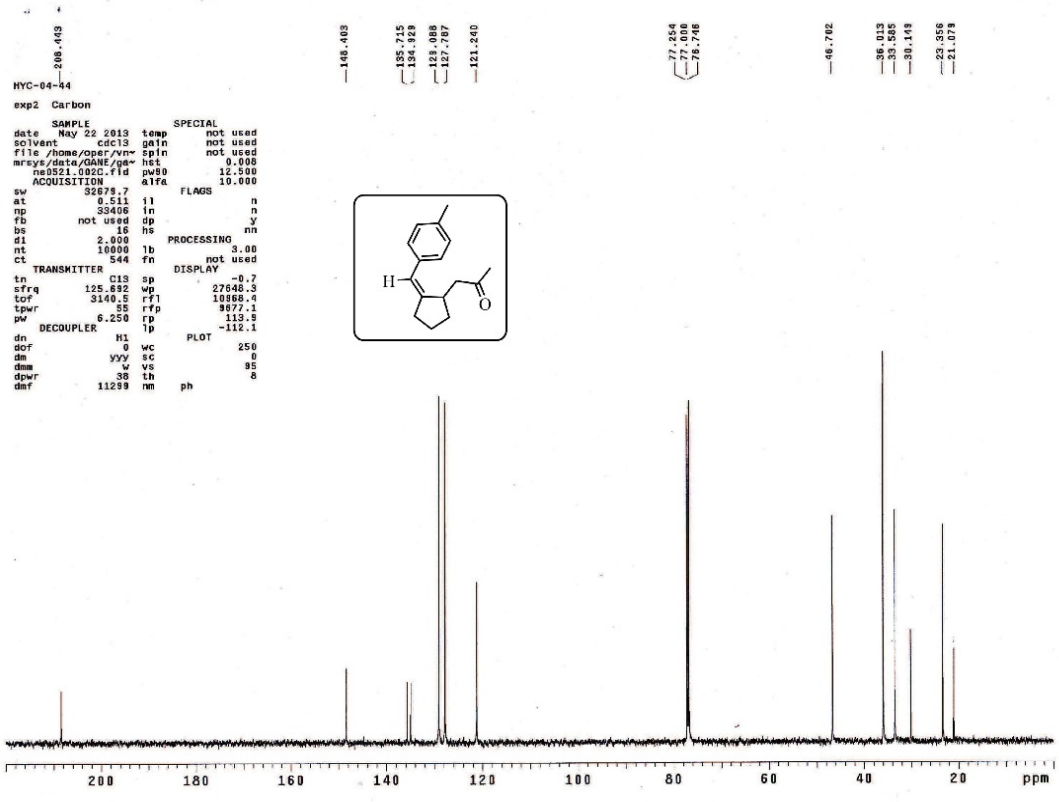
***(E)*-2-(2-((4-Acetylphenyl)(*p*-tolyl)methylene)cyclopentyl)-1-phenylethan-1-one (7b)**



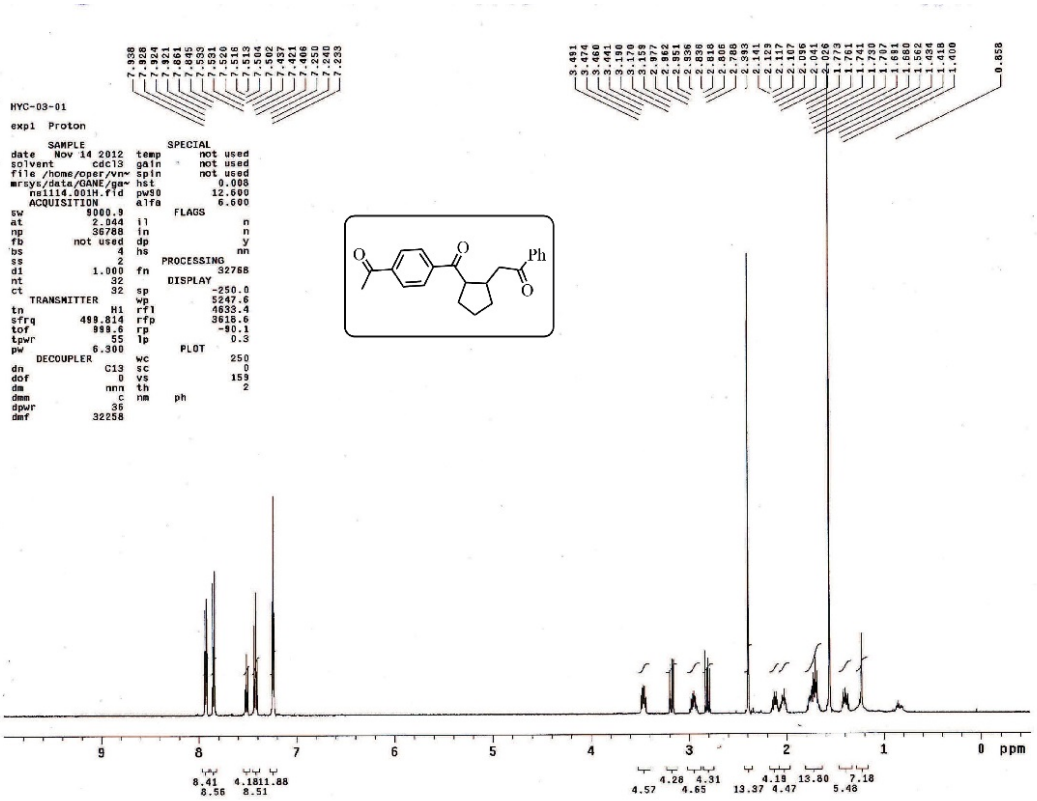



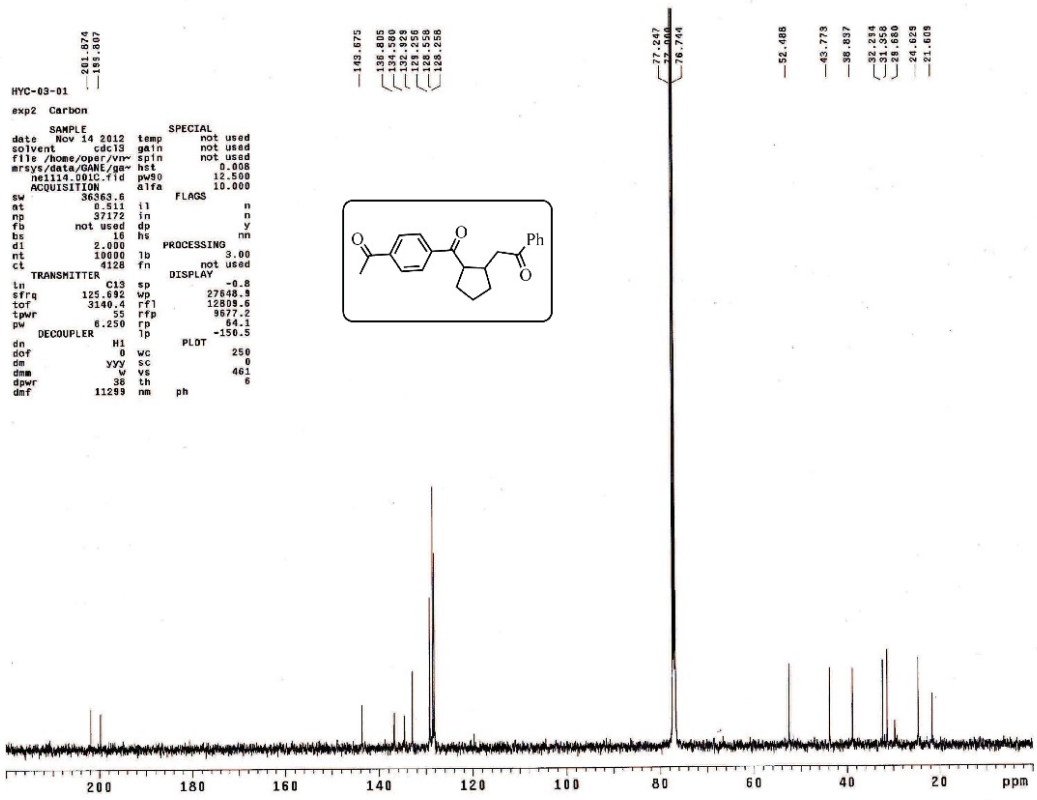
***(Z)*-1-(2-(4-Methylbenzylidene)cyclopentyl)propan-2-one (7c)**



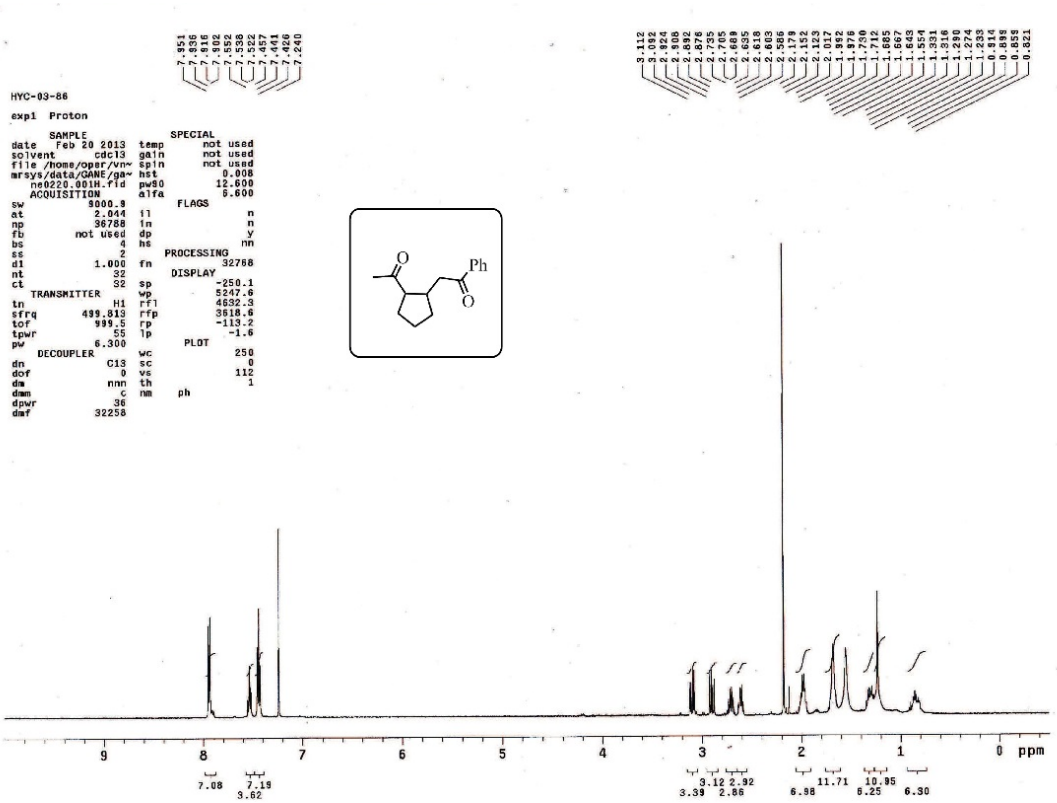



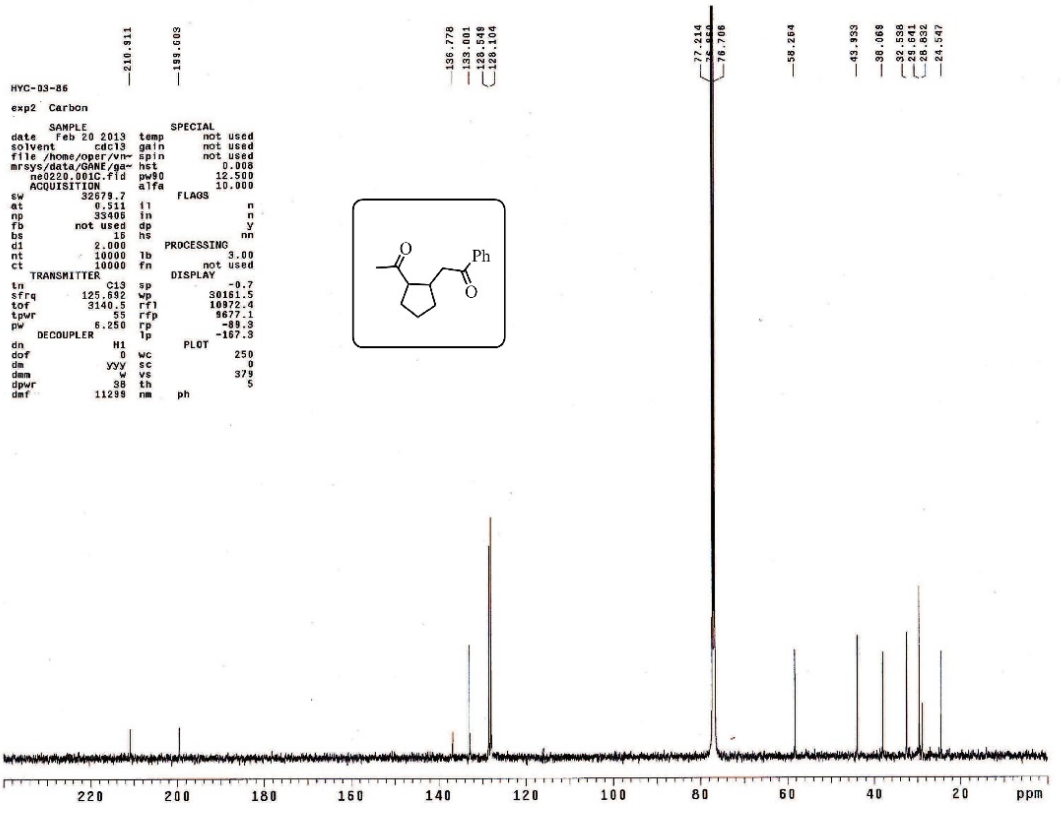
**2-(2-(4-Acetylbenzoyl)cyclopentyl)-1-phenylethan-1-one (8a)**



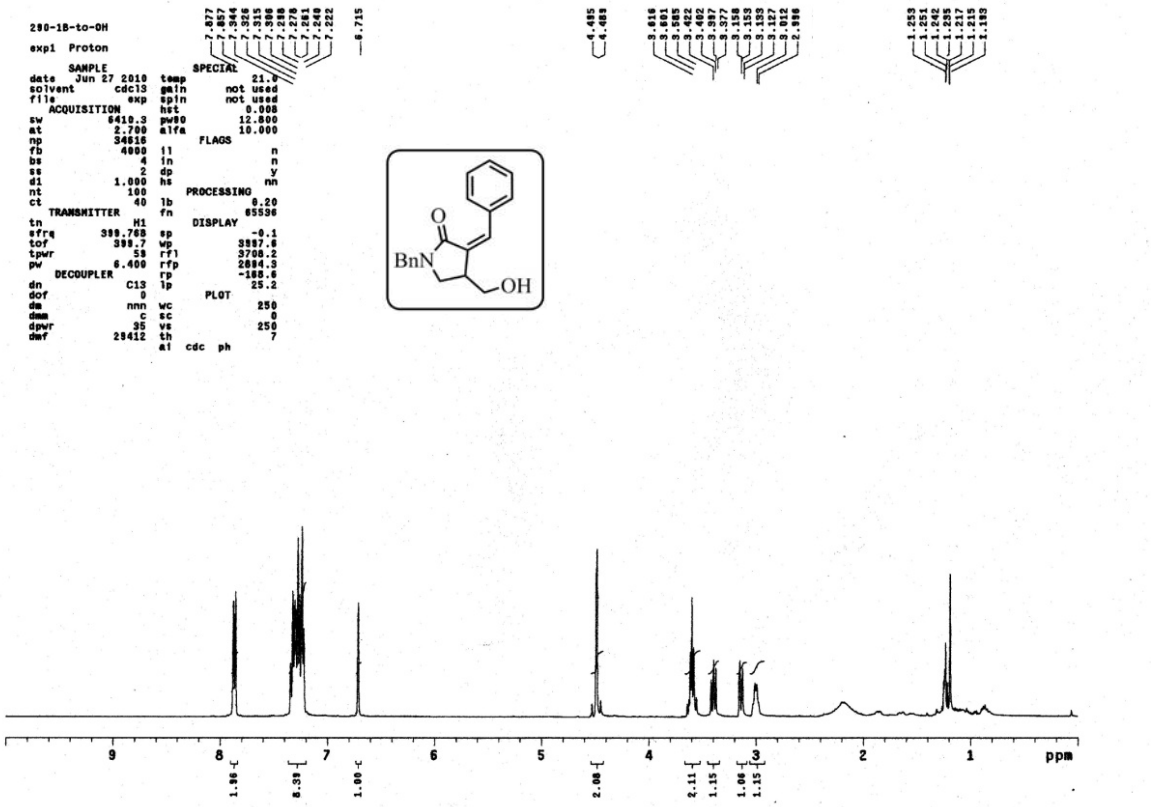



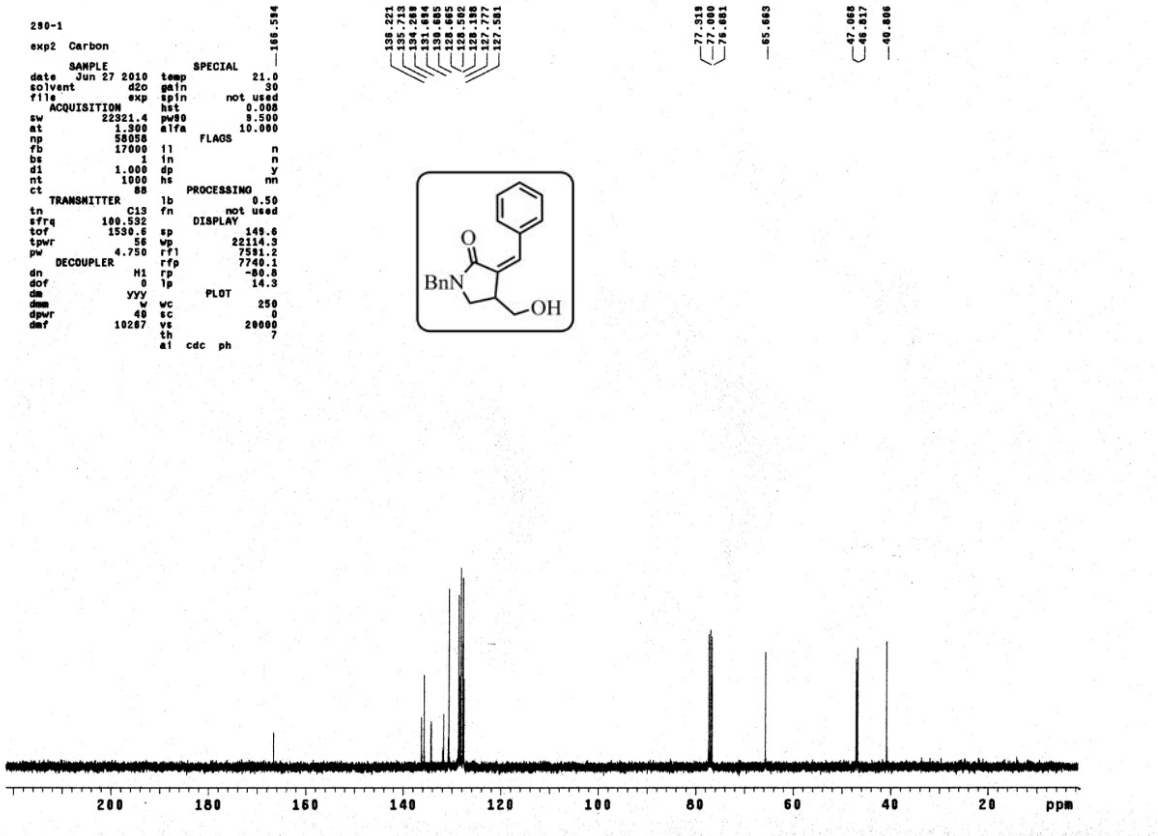
**2-(2-Acetylcyclopentyl)-1-phenylethan-1-one (8b)**



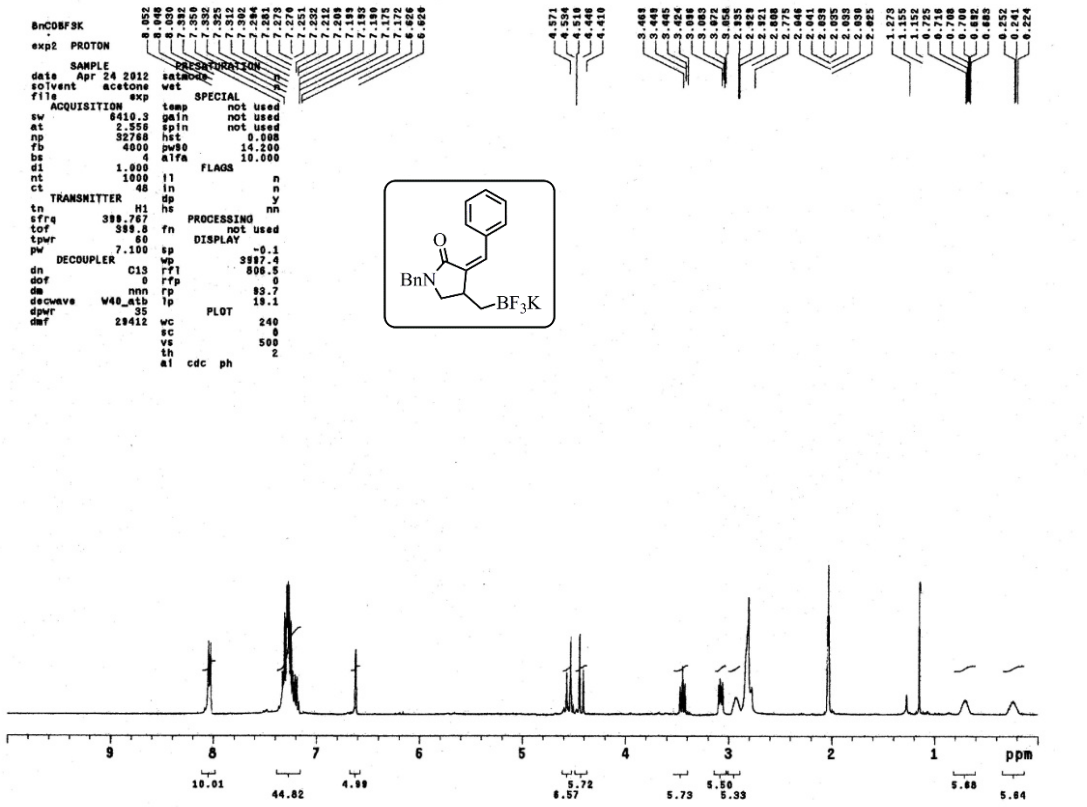



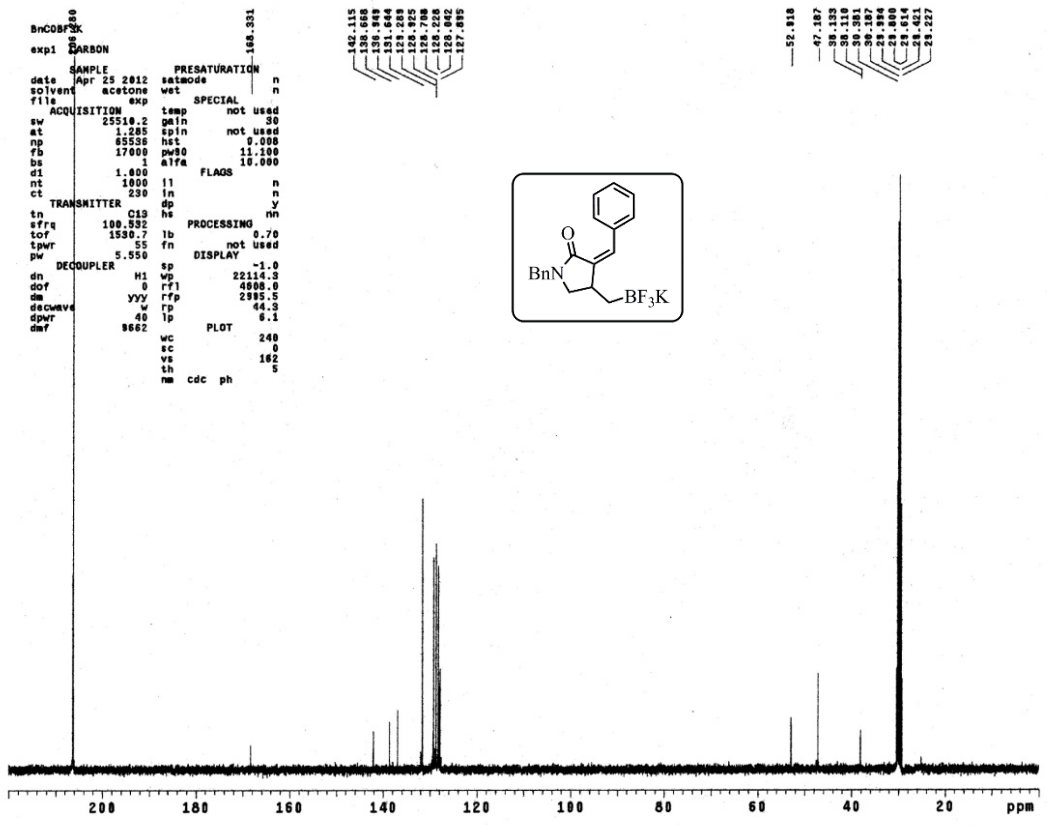
***(Z)*-1-Benzyl-3-benzylidene-4-(hydroxymethyl)pyrrolidin-2-one (9)**



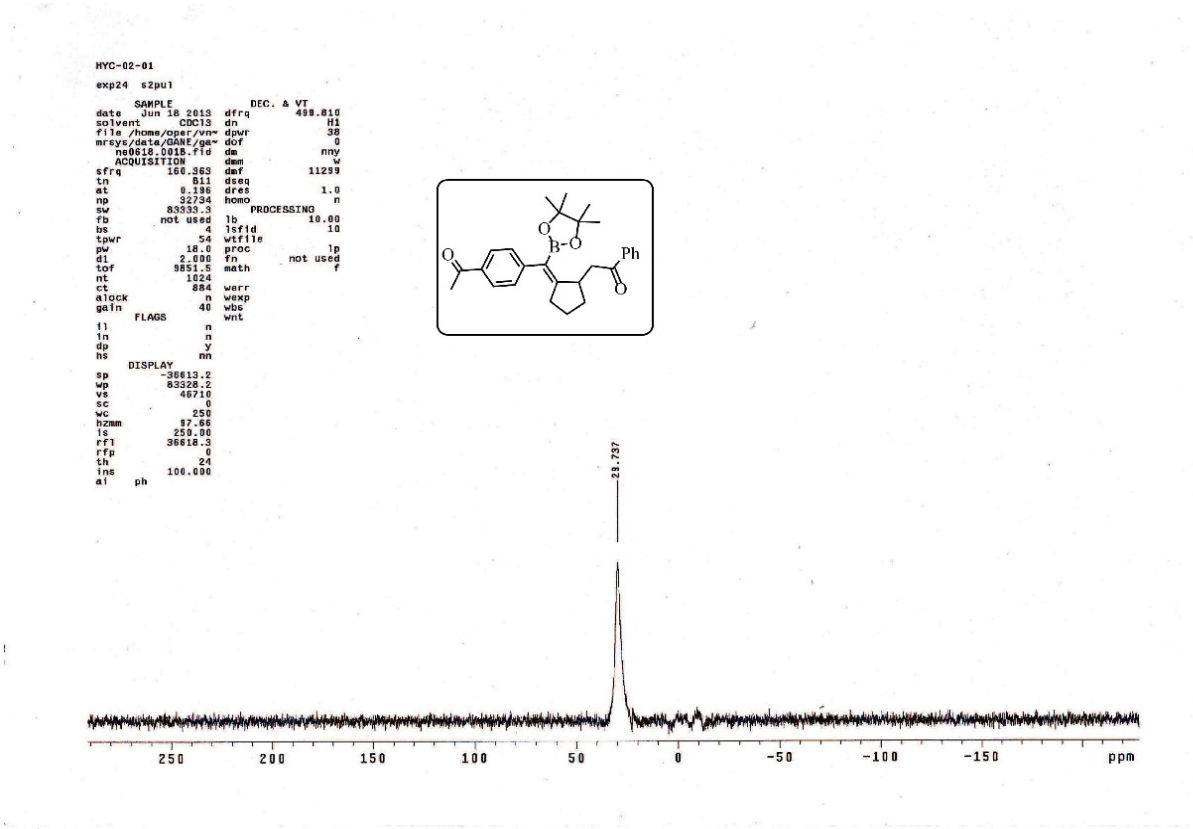



**Potassium (*Z*)-((1-benzyl-4-benzylidene-5-oxopyrrolidin-3-yl)methyl) trifluoroborate (10)**



$^{11}$B spectra of compound **3d**



## X-Ray Structure of Compound 3d:

(CCDC 1511606 (**3d)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif)

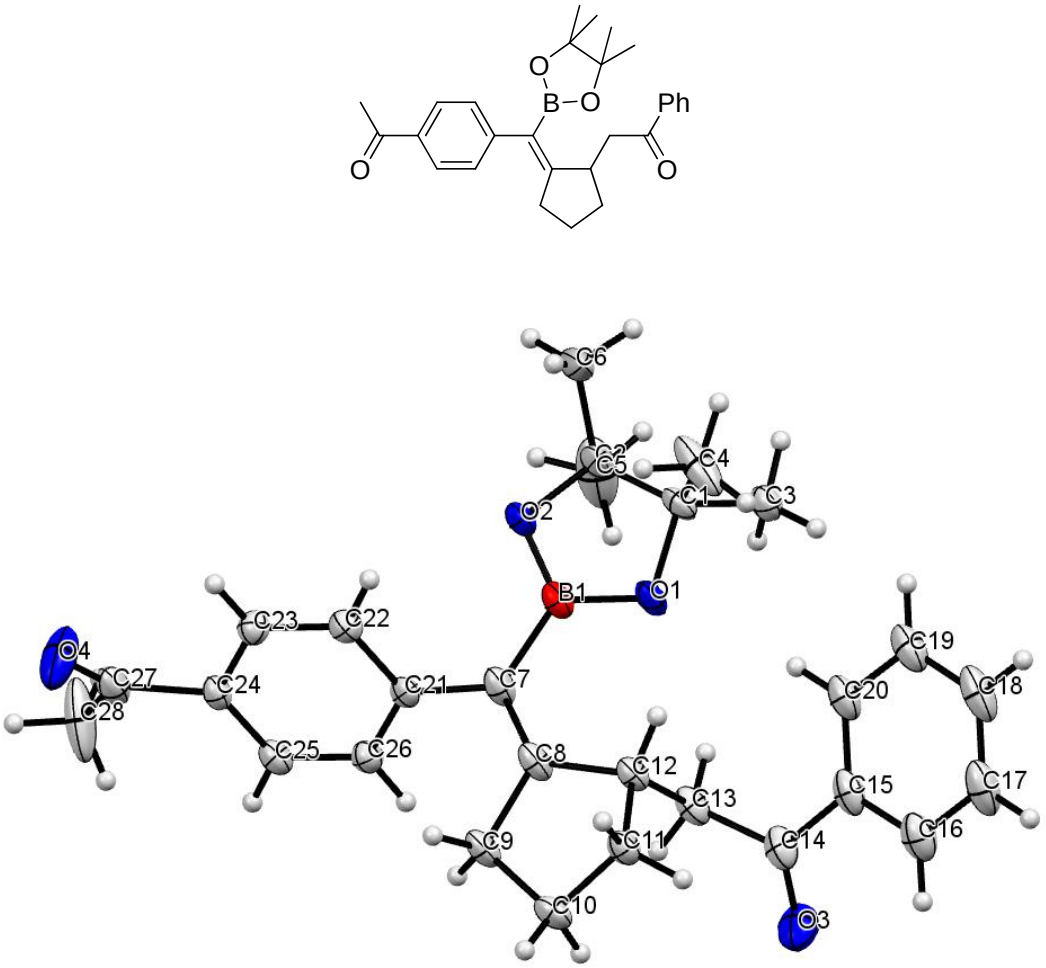



**Figure S1**. X-ray crystal structure of **3d**. Ellipsoids are drawn at the 50% probability level. The disorder phenyl ring (C21'–C26') have been omitted for clarity.

**Table S3**. Crystal data and structure refinement for **3d**.

| | | |
|---|---|---|
| Identification code | 120427lt_0m | |
| Empirical formula | C28 H33 B O4 | |
| Formula weight | 444.35 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 10.0442(4) Å | a= 84.471(2)°. |
| | b = 10.4197(4) Å | b= 84.954(2)°. |
| | c = 11.9542(5) Å | g = 75.059(2)°. |
| Volume | 1200.58(8) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.229 $Mg/m^3$ | |
| Absorption coefficient | 0.080 $mm^{-1}$ | |
| F(000) | 476 | |
| Crystal size | 0.15 x 0.12 x 0.12 $mm^3$ | |
| Theta range for data collection | 2.03 to 26.43°. | |
| Index ranges | -12<=h<=12, -13<=k<=13, -14<=l<=14 | |
| Reflections collected | 20192 | |
| Independent reflections | 4882 [R(int) = 0.0362] | |
| Completeness to theta = 26.43° | 98.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9486 and 0.8515 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4882 / 192 / 358 | |
| Goodness-of-fit on $F^2$ | 1.046 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0520, wR2 = 0.1247 | |
| R indices (all data) | R1 = 0.0726, wR2 = 0.1392 | |
| Largest diff. peak and hole | 0.465 and -0.410 $e.Å^{-3}$ | |