Supporting Information

Copper-catalyzed borylative multi-component synthesis of quaternary α-amino esters

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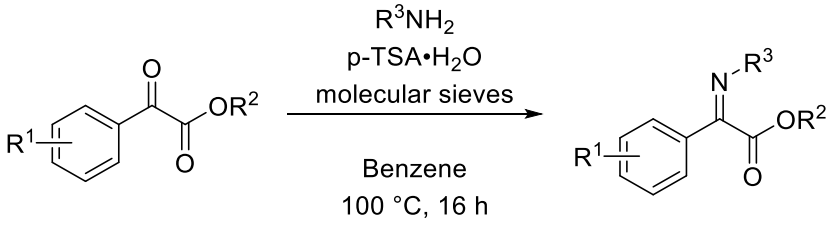
General Information

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium / benzophenone. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded using 400 and 500 MHz spectrometers, with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.27 or δ_C = 77.0) as internal standards. All coupling constants (J) are reported in Hertz (Hz). Mass spectra were obtained using positive and negative electrospray (ES±), atmospheric-pressure chemical ionization (APCI) or gas chromatography (GC) methodology. Infra-red spectra were recorded as evaporated films or neat using a FT/IR spectrometer. Column chromatography was carried out using 40 – 63 µm, 60 Å silica gel. Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness and plates were viewed using a 254 mm ultraviolet lamp and dipped in aqueous potassium permanganate or *p*-anisaldehyde. Melting points were measured on a melting point apparatus and are uncorrected.

Allene and Ketiminoester Starting Materials

Ketiminoesters were accessed from their corresponding ketoesters.

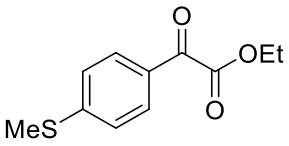


Scheme 1 : Synthesis of ketiminoesters

The following ketoesters were either purchased directly from commercial suppliers or prepared according to literature procedures.

Ethyl 2-oxo-2-phenylacetate (**S1**) (Aldrich), ethyl 2-oxo-2-(4-(trifluoromethyl)phenyl)acetate (**S2**)[1,2], ethyl 2-(4-bromophenyl)-2-oxoacetate (**S3**)[3], ethyl 2-(4-methoxyphenyl)-2-oxoacetate (**S5**)[4], ethyl 2-oxo-2-(*p*-tolyl)acetate (**S6**)[4], ethyl 2-(naphthalen-2-yl)-2-oxoacetate (**S7**)[4], ethyl 2-oxo-2-(thiophen-2-yl)acetate (**S8**)[4], ethyl 3,3,3-trifluoro-2-oxopropanoate (**S9**) (Aldrich), benzyl 2-oxo-2-phenylacetate (**S10**)[5], methyl 2-oxo-2-phenylacetate (**S11**) (Aldrich).

Ethyl 2-(4-(methylthio)phenyl)-2-oxoacetate (S4)



1,2-Dibromoethane (9 µL, 0.1 mmol, 1 mol%) and 4-bromophenyl methyl sulfide (2.03 g, 10.0 mmol, 1.0 equiv) were added to a suspension of magnesium turnings (255 mg, 10.5 mmol, 1.05 equiv) in THF (10 mL). The resulting mixture was heated at reflux for 1.5 hours then allowed to cool to room temperature. The remaining solid, if any, was allowed to settle down before the solution was titrated and used in further reaction.

To a solution of diethyl oxalate (1.09 mL, 8.00 mmol, 1.0 equiv) in anhydrous diethyl ether (12 mL) at -78 °C under N_2, was added dropwise the Grignard reagent solution (9.09 mL of a 0.88 M THF solution, 8.00 mmol, 1.0 equiv) over 1 hour. Once the addition was complete, the reaction mixture was stirred at -78 °C for 1 hour, then placed in an ice bath for 0.5 hour, followed by quenching with saturated aqueous NH_4Cl solution (15 mL) at 0 °C. The organic material was extracted with diethyl ether (3 x 20 mL). The organic layers were combined and washed with brine (20 mL). The resulting organic mixture was dried over $MgSO_4$, filtered and concentrated *in vacuo* before being purified by column chromatography (0 – 10% EtOAc in hexane) to afford the title product as a yellow oil (1.47 g, 6.54 mmol, 82%).

MS (ES^+) *m/z*: 247 ($[M+Na]^+$). HRMS calcd for $C_{11}H_{12}O_3SK$: 263.0139. Found: 263.0131; ν_{max} (thin film/cm^{-1}): 2981, 2923, 1731, 1672, 1584, 1206, 1175, 1093, 1018, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.42 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 2.53 (s, 3 H, SCH_3), 4.44 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 7.29 (d, *J* = 8.7 Hz, 2 H, ArCH), 7.92 (d, *J* = 8.7 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.3 ($CO_2CH_2CH_3$), 14.7 (SCH_3), 62.4 ($CO_2CH_2CH_3$), 125.1 (ArCH), 128.8 (ArC), 130.5 (ArCH), 149.1 (ArC), 164.0 ($CO_2CH_2CH_3$), 185.4 ($CCO_2CH_2CH_3$).

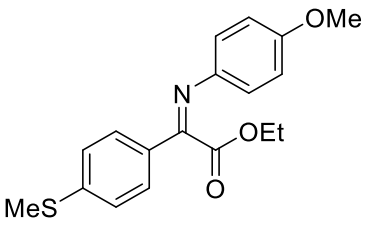
The following imines were prepared according to literature procedures.

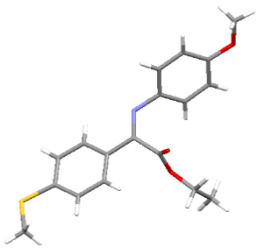
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-phenylacetate (**1a**)[6], ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(trifluoromethyl)phenyl)acetate (**1b**)[7], ethyl (*Z*)-2-(4-bromophenyl)-2-((4-methoxyphenyl)imino)acetate (**1c**)[7], ethyl (*Z*)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)acetate (**1e**)[6], ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(*p*-tolyl)acetate (**1f**)[6], benzyl (*Z*)-2-((4-methoxyphenyl)imino)-2-phenylacetate (**1n**)[8], methyl (*Z*)-2-((4-methoxyphenyl)imino)-2-phenylacetate (**1o**)[8], 3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**1p**)[9].

General Procedure A: Synthesis of Ketiminoesters

Ketoester (1.0 equiv), *p*-TSA monohydrate (0.05 equiv), and amine (1.05 equiv) were added to flame dried activated 4 Å molecular sieves in anhydrous benzene (0.67 M) under N_2. The mixture was stirred and heated at 100 °C in a sealed vial for 16 hours. The resulting mixture was allowed to cool to room temperature and was filtered, washed with CH_2Cl_2, and concentrated in vacuo, before being purified by column chromatography.

Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate (1d)



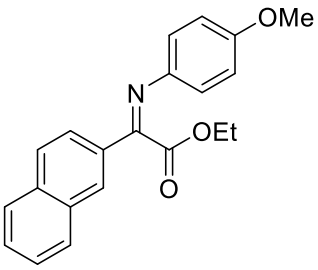


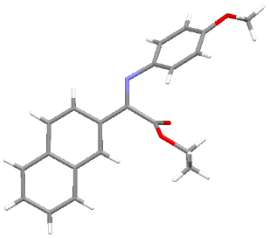
Prepared according to General Procedure A on a 2.00 mmol scale. Column chromatography (0 – 15% EtOAc in hexane) afforded the title compound as a yellow solid (634 mg, 1.92 mmol, 96%).

M.p.: 105-107 °C ($CHCl_3$); MS (ES^+) *m/z*: 352 ($[M+Na]^+$). HRMS calcd for $C_{18}H_{19}NO_3S$: 329.1080. Found: 329.1076; ν_{max} (thin film/cm^{-1}): 3066, 2997, 2969, 2930, 2837, 1731, 1225, 1186, 1179, 1165, 1090, 1019, 1010; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.07 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 2.52 (s, 3 H, SCH_3), 3.80 (s, 3 H, OCH_3), 4.17 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 6.86 (d, *J* = 8.9 Hz, 2 H, ArCH), 6.95 (d, *J* = 8.9 Hz, 2 H, ArCH), 7.28 (d, *J* = 8.7 Hz, 2 H, ArCH), 7.77 (d, *J* = 8.5 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 15.2 (SCH_3), 55.6 (OCH_3), 61.5 ($CO_2CH_2CH_3$), 114.2 (ArCH), 121.4 (ArCH), 125.7 (ArCH), 128.3 (ArCH), 130.7 (ArC), 143.5 (ArC), 143.8 (ArC), 157.4 (ArC), 159.1 (C=N), 165.6 (C=O).

1d was further characterized by X-ray crystallographic analysis.

Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate (1g)



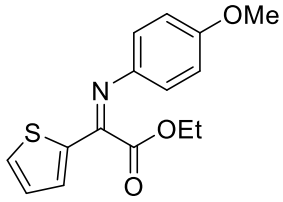


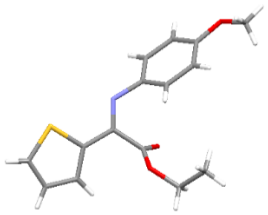
Prepared according to General Procedure A on a 2.00 mmol scale. Column chromatography (20% EtOAc in hexane) afforded the title compound as a yellow solid (601 mg, 1.80 mmol, 90%).

M.p.: 55-57 °C ($CHCl_3$); MS (ES^+) *m/z*: 356 ($[M+Na]^+$). HRMS calcd for $C_{21}H_{20}NO_3$: 334.1438. Found: 334.1432; ν_{max} (thin film/cm^{-1}): 3062, 2988, 2958, 2833, 1731, 1607, 1237, 1217, 1182, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.11 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.82 (s, 3 H, OCH_3), 4.24 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.90 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.01 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.50 – 7.60 (m, 2 H, ArCH), 7.85 – 7.94 (m, 3 H, ArCH), 8.13 (dd, *J* = 8.7, 1.8 Hz, 1 H, ArCH), 8.19 (s, 1 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 ($CO_2CH_2CH_3$), 55.6 (OCH_3), 61.7 ($CO_2CH_2CH_3$), 114.3 (ArCH), 121.4 (ArCH), 123.9 (ArCH), 126.8 (ArCH), 127.9 (ArCH), 128.0 (ArCH), 128.7 (ArCH), 129.2 (ArCH), 129.5 (ArCH), 131.7 (ArC), 133.0 (ArC), 135.0 (ArC), 143.5 (ArC), 157.5 (ArC), 159.8 (C=N), 165.8 (C=O).

1g was further characterized by X-ray crystallographic analysis.

Ethyl (*E*)-2-((4-methoxyphenyl)imino)-2-(thiophen-2-yl)acetate (1h)



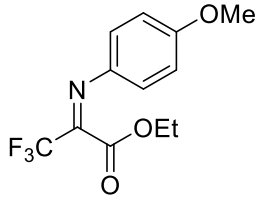


Prepared according to General Procedure A on a 1.50 mmol scale. Column chromatography (8% EtOAc in hexane) afforded the title compound as a yellow solid (311 mg, 1.08 mmol, 72%).

M.p.: 49-50 °C ($CHCl_3$); MS (ES^+) *m/z*: 312 ($[M+Na]^+$). HRMS calcd for $C_{15}H_{16}NO_3S$: 290.0845. Found: 290.0835; ν_{max} (thin film/cm^{-1}): 3074, 2981, 2904, 2835, 1727, 1606, 1499, 1424, 1289, 1242, 1188, 1031, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.08 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.79 (s, 3 H, OCH_3), 4.18 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.86 (d, *J* = 8.9 Hz, 2 H, ArCH), 6.95 (d, *J* = 8.9 Hz, 2 H, ArCH), 7.09 (dd, *J* = 5.1, 3.8 Hz, 1 H, ArCH), 7.41 (dd, *J* = 3.8, 1.1 Hz, 1 H, ArCH), 7.51 (dd, *J* = 5.0, 1.1 Hz, 1 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 55.5 (OCH_3), 61.8 ($CO_2CH_2CH_3$), 114.2 (ArCH), 121.6 (ArCH), 127.9 (ArCH), 131.1 (2 x ArCH), 141.1 (ArC), 142.8 (ArC), 153.6 (C=N), 157.5 (ArC), 164.5 (C=O).

1h was further characterized by X-ray crystallographic analysis.

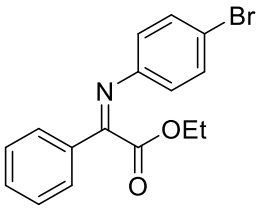
Ethyl (*E*)-3,3,3-trifluoro-2-((4-methoxyphenyl)imino)propanoate (1i)



Prepared according to General Procedure A on a 2.50 mmol scale. Column chromatography (10% EtOAc in hexane) afforded the title compound as a yellow oil (62.3 mg, 0.226 mmol, 9%).

MS (ES^+) *m/z*: 298 ($[M+Na]^+$). HRMS calcd for $C_{12}H_{13}NO_3F_3$: 276.0842. Found: 276.0840; ν_{max} (thin film/cm^{-1}): 2987, 2840, 2362, 1739, 1600, 1504, 1248, 1162, 1033; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.18 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.82 (s, 3 H, OCH_3), 4.25 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.89 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.01 (d, *J* = 9.0 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 55.6 (OCH_3), 62.9 ($CO_2CH_2CH_3$), 114.5 (ArCH), 118.6 (q, *J* = 278.5 Hz, CF_3), 122.4 (ArCH), 139.2 (ArC), 146.9 (q, *J* = 36.7 Hz, C=N), 159.6 (ArC), 160.5 (C=O); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -69.5.

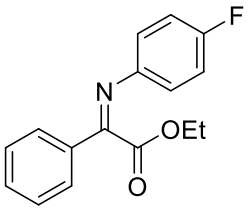
Ethyl (*Z*)-2-((4-bromophenyl)imino)-2-phenylacetate (1j)



Prepared according to General Procedure A on a 2.00 mmol scale. Column chromatography (3% EtOAc in hexane) afforded the title compound as a yellow oil (449 mg, 1.35 mmol, 68%).

MS (ES^+) *m/z*: 354 ($[M+Na]^+$). HRMS calcd for $C_{16}H_{15}NO_2Br$: 332.0281. Found: 332.0272; ν_{max} (thin film/cm^{-1}): 3062, 2980, 2935, 1728, 1623, 1476, 1224, 1187, 1069, 1008; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.06 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 4.17 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.84 – 6.90 (m, 2 H, ArCH), 7.42 – 7.56 (m, 5 H, ArCH), 7.87 – 7.93 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 61.6 ($CO_2CH_2CH_3$), 118.0 (ArC), 121.5 (ArCH), 128.1 (ArCH), 128.8 (ArCH), 131.8 (ArCH), 132.1 (ArCH), 133.6 (ArC), 149.2 (ArC), 160.8 (C=N), 164.6 (C=O).

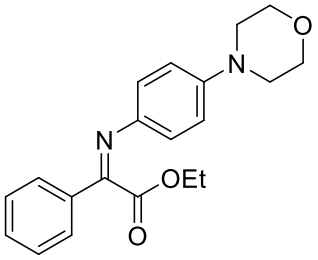
Ethyl (*Z*)-2-((4-fluorophenyl)imino)-2-phenylacetate (1k)



Prepared according to General Procedure A on a 2.00 mmol scale. Column chromatography (5% EtOAc in hexane) afforded the title compound as a yellow oil (297 mg, 1.09 mmol, 55%).

MS (ES^+) *m/z*: 294 ($[M+Na]^+$). HRMS calcd for $C_{16}H_{15}NO_2F$: 272.1081 Found: 272.1071; ν_{max} (thin film/cm^{-1}): 3066, 2982, 2937, 1728, 1628, 1500, 1448, 1305, 1228, 1177, 1093, 1017; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.06 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 4.16 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 6.91 – 6.98 (m, 2 H, ArCH), 6.98 – 7.07 (m, 2 H, ArCH), 7.43 – 7.57 (m, 3 H, ArCH), 7.84 – 7.92 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 61.7 ($CO_2CH_2CH_3$), 115.7 (d, *J* = 22.5 Hz, ArCH), 121.4 (d, *J* = 8.3 Hz, ArCH), 128.1 (ArCH), 128.9 (ArCH), 132.0 (ArCH), 133.8 (ArC), 146.3 (d, *J* = 2.8 Hz, ArC), 160.4 (d, *J* = 243.4 Hz, ArC), 160.9 (d, *J* = 1.2 Hz, C=N), 165.0 (C=O); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -118.7 (dddd, *J* = 13.5, 8.4, 5.0, 1.7 Hz).

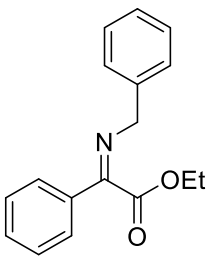
Ethyl (*Z*)-2-((4-morpholinophenyl)imino)-2-phenylacetate (1l)



Prepared according to General Procedure A on a 2.00 mmol scale. Column chromatography (30% EtOAc in hexane) afforded the title compound as a yellow solid (158 mg, 0.467 mmol, 23%).

M.p.: 125-127 °C ($CHCl_3$); MS (ES^+) *m/z*: 361 ($[M+Na]^+$). HRMS calcd for $C_{20}H_{23}N_2O_3$: 339.1703. Found: 339.1697; ν_{max} (thin film/cm^{-1}): 2962, 2854, 2821, 1726, 1613, 1506, 1448, 1227, 1120, 1017; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.09 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.11 – 3.16 (m, 4 H, NCH_2), 3.83 – 3.89 (m, 4 H, OCH_2), 4.19 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 6.88 (d, *J* = 8.9 Hz, 2 H, ArCH), 6.97 (d, *J* = 8.9 Hz, 2 H, ArCH), 7.41 – 7.54 (m, 3 H, ArCH), 7.82 – 7.92 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 49.7 (NCH_2), 61.5 ($CO_2CH_2CH_3$), 67.0 (OCH_2), 116.1 (ArCH), 121.3 (ArCH), 127.9 (ArCH), 128.8 (ArCH), 131.5 (ArCH), 134.4 (ArC), 142.8 (ArC), 149.2 (ArC), 159.1 (C=N), 165.8 (C=O).

Ethyl (*Z*)-2-(benzylimino)-2-phenylacetate (1m)



Prepared according to General Procedure A on a 5.00 mmol scale. Column chromatography (0 - 10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow liquid (600 mg, 2.25 mmol, 44%).

MS (ES^+) *m/z*: 290 ($M+Na^+$). HRMS calcd for $C_{17}H_{18}NO_2$: 268.1332. Found: 268.1323; ν_{max} (thin film/cm^{-1}): 3062, 3029, 2981, 1730, 1688, 1641, 1597, 1580, 1495, 1450, 1368, 1294, 1198, 1177, 1095, 1040, 1026, 1015; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.42 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 4.49 (q, *J* = 7.0 Hz, 2 H, $CO_2CH_2CH_3$), 4.78 (s, 2 H, CH_2Ph), 7.28 - 7.32 (m, 1 H, ArCH), 7.36 (m, 2 H, ArCH), 7.39 - 7.45 (m, 5 H, ArCH), 7.79 - 7.82 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.3 ($CO_2CH_2CH_3$), 58.4 (CH_2Ph), 61.5 ($CO_2CH_2CH_3$), 127.0 (ArCH), 127.3 (ArCH), 127.9 (ArCH), 128.4 (ArCH), 128.5 (ArCH), 131.0 (ArCH), 134.2 (ArC), 138.8 (ArC), 160.6 (C=N), 165.5 (C=O).

Allenes were either purchased directly from commercial suppliers or prepared according to literature procedures.

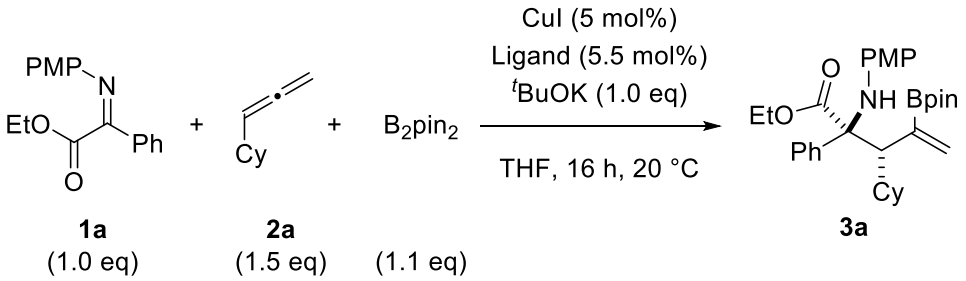
Propa-1,2-dien-1-ylcyclohexane (**2a**) (Aldrich), undeca-1,2-diene (**2b**)[10], penta-3,4-dien-1-ylbenzene (**2c**)[11], buta-2,3-dien-1-ylcyclohexane (**2d**)[12], *tert*-butyl(hepta-5,6-dien-1-yloxy)dimethylsilane (**2e**)[13,14], 7-bromohepta-1,2-diene (**2f**)[15], propa-1,2-dien-1-ylbenzene (**2g**)[11], 1-methyl-3-(propa-1,2-dien-1-yl)benzene (**2h**)[11], 1-fluoro-3-(propa-1,2-dien-1-yl)benzene (**2i**)[16], *N*,*N*-diethyl-3-(propa-1,2-dien-1-yl)benzamide (**2j**)[16], 1-chloro-4-(propa-1,2-dien-1-yl)benzene (**2k**)[11], 3-methylbuta-1,2-diene (**2l**) (Aldrich).

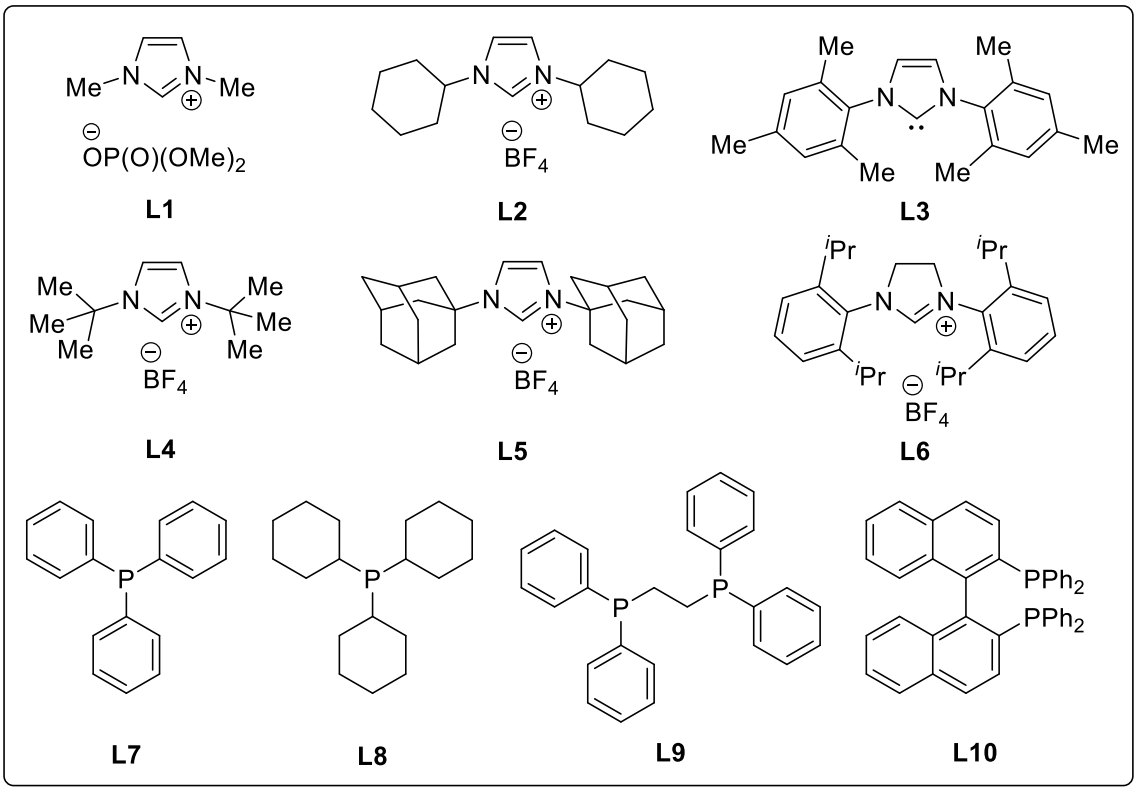
Diastereoselective Copper-Catalysed Coupling of Allenes, Ketiminoesters and B_2pin_2

General Procedure B: Diastereoselective Copper-Catalysed Coupling of Allenes, Ketiminoesters and B_2pin_2

To a solution of IPrCuCl (5 mol%) in anhydrous THF (0.05 M) at room temperature under N_2, was added ^{t}BuOK (1.0 equiv from a 1 M THF solution), and the reaction was stirred for 20 minutes at room temperature. B_2pin_2 (1.3 equiv) in anhydrous THF (0.325 M) was then added and the resulting mixture stirred for 30 minutes. A solution of propa-1,2-dien-1-ylcyclohexane (1.5 equiv) in anhydrous THF (0.625 M) and a solution of ketimine (1.0 equiv) in anhydrous THF (0.42 M) were then added dropwise simultaneously at room temperature. The reaction was stirred at room temperature for 16 hours then filtered through a silica plug, concentrated *in vacuo* and the crude product mixture was purified by silica chromatography to afford the product.

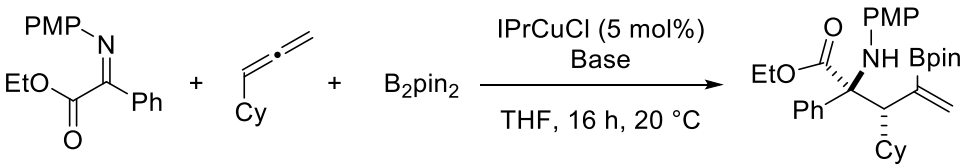
Further Optimization Studies





Entry	Ligand	Buried volume (%)[17]	NMR yield (%)	*dr*
1	**L1**	26.3	72	72:28
2	**L2**	27.5	55	62:38
3	**L3**	36.5	77	45:55
4	**L4**	39.6	21	84:16
5	**L5**	39.8	3	82:18
6	**L6**	47.0	0	-
Entry	Ligand	Cone/Bite angle (°)[18,19]	NMR yield (%)	*dr*
7	**L7**	145	24	63:37
8	**L8**	170	42	63:37
9	**L9**	85	36	60:40
10	**L10**	92	21	70:30

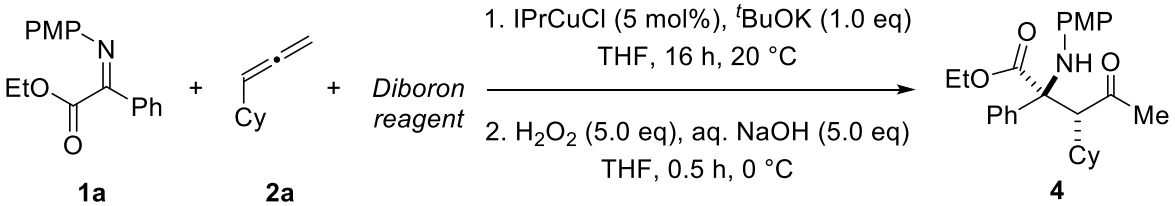
Table S1: Additional Ligand Screening



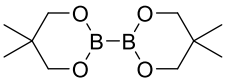
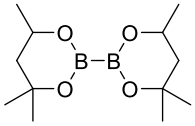
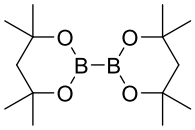
1a (1.0 eq) + **2a** (1.5 eq) + B_2pin_2 (1.1 eq) → **3a**

Entry	Base (x eq)	NMR yield (%)	*dr*
1	^{t}BuOK (0.2)	51	92:8
2	^{t}BuOK (0.5)	68	93:7
3	^{t}BuOK (0.8)	77	92:8
4	^{t}BuOK (1.0)	84	91:9
5	MeONa (1.0)	24	94:6
6	EtONa (1.0)	34	93:7
7	^{t}PentONa (1.0)	40	92:8
8	$Al(O^{t}Bu)_3$ (1.0)	0	-
9	$Ti(O^{i}Pr)_4$ (1.0)	0	-
10	K_3PO_4 (1.0)	22	87:13
11	K_2CO_3 (1.0)	21	92:8
12	CsF (1.0)	19	91:9
13	Cs_2CO_3 (1.0)	49	90:10
14	Ag_2CO_3 (1.0)	0	-
15	$BaCO_3$ (1.0)	0	-
16	Li_2CO_3 (1.0)	0	-

Table S2 : Additional Base Screening



1a (1.0 eq) + **2a** (1.5 eq) + *Diboron reagent* (1.3 eq) → **4**

Entry	Diboron reagent	NMR yield (%)	*dr*
1		0	-
2		12	90:10
3		20	90:10

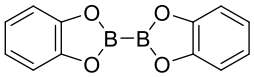
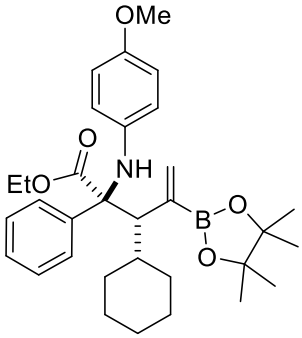
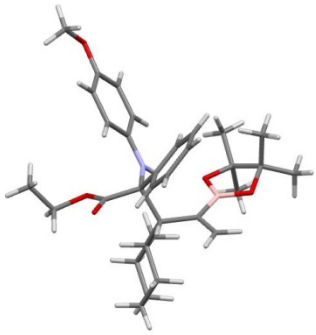
4		3	-

Table S3: Additional Diboron Screening

***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3a)**



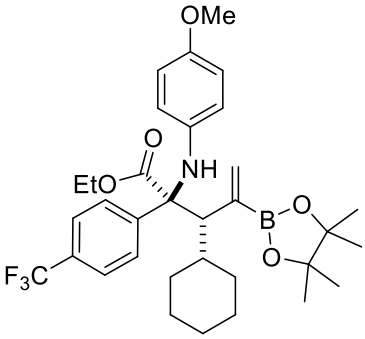


Prepared according to General Procedure B on a 0.250 mmol scale (92:8 d.r. of crude material). Column chromatography (5 - 8% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow solid (114 mg, 0.214 mmol, 85%).

M.p.: 145-148 °C ($CHCl_3$); MS (ES^-) *m/z*: 532 ($[M-H]^-$). HRMS calcd for $C_{32}H_{44}NBO_5Na$: 556.3205. Found: 556.3196; ν_{max} (thin film/cm^{-1}): 3402, 2976, 2923, 2850, 1718, 1618, 1510, 1464, 1446, 1372, 1362, 1300, 1238, 1177, 1141, 1039; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.88 (q, *J* = 11.4 Hz, 1 H, CH_2), 0.95 - 1.06 (m, 1 H, CH_2), 1.06 - 1.14 (m, 1 H, CH_2), 1.19 (t, *J* = 7.0 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.27 - 1.31 (m, 7 H, 2 x CH_3 + 1 H from CH_2), 1.33 (s, 6 H, 2 x CH_3), 1.62 (d, *J* = 12.4 Hz, 1 H, CH_2), 1.70 (d, *J* = 12.7 Hz, 2 H, CH_2), 1.82 (t, *J* = 13.3 Hz, 2 H, CH_2), 1.92 - 2.03 (m, 1 H, $CHCHC{=}CH_2$), 2.92 (d, *J* = 7.6 Hz, 1 H, $CHC{=}CH_2$), 3.69 (s, 3 H, OCH_3), 4.10 - 4.21 (m, 1 H, $CO_2CH_2CH_3$), 4.22 - 4.33 (m, 1 H, $CO_2CH_2CH_3$), 4.96 (apparent s, 1 H, $C{=}CH_2$), 5.51 (d, *J* = 2.7 Hz, 1 H, $C{=}CH_2$), 5.96 (br. s, 1 H, NH), 6.30 (d, *J* = 8.4 Hz, 2 H, ArCH), 6.61 (d, *J* = 8.4 Hz, 2 H, ArCH), 7.07 - 7.18 (m, 3 H, ArCH), 7.35 - 7.45 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 24.2 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.3 (CH_2), 32.9 (CH_2), 38.3 ($CHCHC{=}CH_2$), 55.6 (OCH_3), 61.1 ($CO_2CH_2CH_3$), 66.0 ($CHC{=}CH_2$), 70.4 ($CCO_2CH_2CH_3$), 83.7 ($OC(CH_3)_2$), 113.5 (ArCH), 116.5 (ArCH), 126.5 (ArCH), 127.4 (ArCH), 128.4 (ArCH), 136.6 ($C{=}CH_2$), 139.3 (ArC), 140.7 (ArC), 150.9 (ArC), 174.1 (C=O), ($BC{=}CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 30.3.

3a was further characterized by X-ray crystallographic analysis.

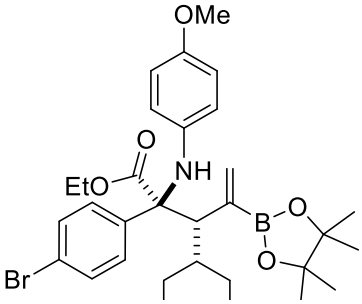
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)pent-4-enoate (3b)**

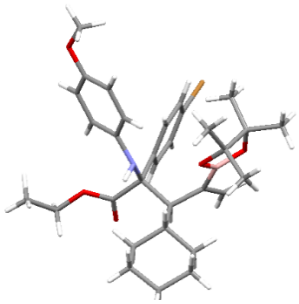


Prepared according to General Procedure B on a 0.250 mmol scale (80:20 d.r. of crude material). Column chromatography (5 - 8% Et_2O in hexane + 1% NEt_3, then 5% Et_2O and 10% toluene in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (69%) was determined by ^1H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^-) *m/z*: 600 ($[M-H]^-$). HRMS calcd for $C_{33}H_{43}NBO_5F_3K$: 640.2818. Found: 640.2822; ν_{max} (thin film/cm^{-1}): 3403, 2978, 2931, 2851, 1720, 1617, 1511, 1422, 1362, 1326, 1240, 1165, 1141, 1124, 1071, 1038, 1018; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.84 - 0.98 (m, 2 H, CH_2), 0.98 - 1.05 (m, 1 H, CH_2), 1.05 - 1.12 (m, 1 H, CH_2), 1.17 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.20 - 1.26 (m, 1 H, CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.63 (d, *J* = 12.5 Hz, 1 H, CH_2), 1.71 (dd, *J* = 12.7, 2.1 Hz, 2 H, CH_2), 1.81 (t, *J* = 12.9 Hz, 2 H, CH_2), 1.92 - 2.03 (m, 1 H, $CHCHC=CH_2$), 2.88 (d, *J* = 7.5 Hz, 1 H, $CHC=CH_2$), 3.70 (s, 3 H, OCH_3), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.20 - 4.30 (m, 1 H, $CO_2CH_2CH_3$), 4.95 (d, *J* = 3.0 Hz, 1 H, $C=CH_2$), 5.54 (d, *J* = 3.3 Hz, 1 H, $C=CH_2$), 5.99 (br. s, 1 H, NH), 6.24 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.62 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.41 (d, *J* = 8.5 Hz, 2 H, ArCH), 7.58 (d, *J* = 7.8 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.8 ($CO_2CH_2CH_3$), 24.3 (CH_3), 25.0 (CH_3), 26.2 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.6 (CH_2), 32.7 (CH_2), 38.4 ($CHCHC=CH_2$), 55.6 (OCH_3), 61.4 ($CO_2CH_2CH_3$), 66.1 ($CHC=CH_2$), 70.4 ($CCO_2CH_2CH_3$), 83.9 ($OC(CH_3)_2$), 113.7 (ArCH), 116.2 (ArCH), 124.3 (q, *J* = 272.6 Hz, $ArCCF_3$), 124.3 (q, *J* = 4.0 Hz, ArCH), 128.9 (q, *J* = 33.2 Hz, $ArCCF_3$), 129.0 (ArCH), 137.2 ($C=CH_2$), 140.2 (ArC), 143.7 (ArC), 151.2 (ArC), 173.7 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.4.

***rac*-Ethyl (2*S*,3*S*)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3c)**



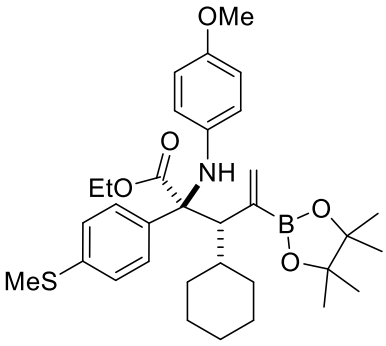


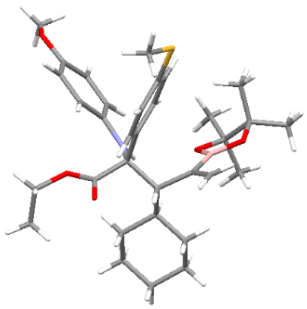
Prepared according to General Procedure B on a 0.250 mmol scale (89:11 d.r. of crude material). Column chromatography (10 - 15% Et_2O in hexane + 1% NEt_3) afforded the title compound as a light brown solid (87.8 mg, 0.143 mmol, 57%).

M.p.: 135-137 °C (Et_2O); MS (ES^+) *m/z*: 634 ($[M+Na]^+$). HRMS calcd for $C_{32}H_{43}NBBrO_5Na$: 634.2310. Found: 634.2290; ν_{max} (thin film/cm^{-1}): 3391, 2921, 2849, 1715, 1510, 1238, 1138; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.81 – 0.89 (m, 1 H, CH_2), 0.89 – 1.11 (m, 3 H, CH_2), 1.15 (t, *J* = 7.1 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.27 (s, 6 H, 2 x CH_3), 1.31 (s, 6 H, 2 x CH_3), 1.57 – 1.65 (m, 1 H, CH_2), 1.65 – 1.73 (m, 2 H, CH_2), 1.73 – 1.87 (m, 2 H, CH_2), 1.87 – 2.04 (m, 1 H, $CHCHC=CH_2$), 2.84 (d, *J* = 7.5 Hz, 1 H, $CHC=CH_2$), 3.69 (s, 3 H, OCH_3), 4.12 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.23 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.98 (d, *J* = 3.4 Hz, 1 H, $C=CH_2$), 5.57 (d, *J* = 3.4 Hz, 1 H, $C=CH_2$), 5.92 (br. s, 1 H, NH), 6.25 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.61 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.23 – 7.35 (m, 4 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 24.4 (CH_3), 25.2 (CH_3), 26.4 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 32.6 (CH_2), 33.0 (CH_2), 38.5 ($CHCHC=CH_2$), 55.8 (OCH_3), 61.5 ($CO_2CH_2CH_3$), 66.2 ($CHC=CH_2$), 70.3 ($CCO_2CH_2CH_3$), 84.0 ($OC(CH_3)_2$), 113.8 (ArCH), 116.5 (ArCH), 120.9 (ArC), 130.6 (2 x ArCH), 137.4 ($C=CH_2$), 138.8 (ArC), 140.4 (ArC), 151.3 (ArC), 174.0 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.2.

3c was further characterized by X-ray crystallographic analysis.

***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3d)**





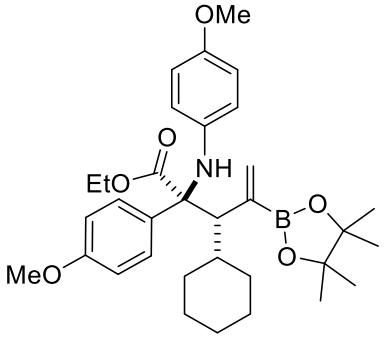
Prepared according to General Procedure B on a 0.250 mmol scale (93:7 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a white solid (106 mg, 0.183 mmol, 73%).

M.p.: 125-127 °C (Et_2O); MS (ES^+) *m/z*: 618 ($[M+K]^+$). HRMS calcd for $C_{33}H_{46}NBO_5S$: 579.3184. Found: 579.3196; ν_{max} (thin film/cm^{-1}): 3423, 2977, 2921, 2853, 1713, 1509, 1295, 1252, 1234, 1141; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.87 (q, *J* = 12.4 Hz, 1 H, CH_2), 0.99 (q, *J* = 12.4 Hz, 1 H, CH_2), 1.09 (tt, *J* = 12.3,

3.3 Hz, 1 H, CH_2), 1.16 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.19 – 1.26 (m, 2 H, CH_2), 1.28 (s, 6 H, 2 x CH_3), 1.32 (s, 6 H, 2 x CH_3), 1.61 (d, *J* = 12.4 Hz, 1 H, CH_2), 1.69 (d, *J* = 12.4 Hz, 2 H, CH_2), 1.80 (d, *J* = 12.4 Hz, 2 H, CH_2), 1.90 – 2.03 (m, 1 H, $CHCHC=CH_2$), 2.41 (s, 3 H, SCH_3), 2.87 (d, *J* = 7.5 Hz, 1 H, $CHC=CH_2$), 3.69 (s, 3 H, OCH_3), 4.12 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.24 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.98 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 5.55 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 5.92 (br. s, 1 H, NH), 6.28 (d, *J* = 9.1 Hz, 2 H, ArCH), 6.61 (d, *J* = 9.1 Hz, 2 H, ArCH), 7.02 (d, *J* = 8.9 Hz, 2 H, ArCH), 7.32 (m, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 15.7 (SCH_3), 24.4 (CH_3), 25.1 (CH_3), 26.4 (CH_2), 27.1 (CH_2), 27.1 (CH_2), 32.5 (CH_2), 33.0 (CH_2), 38.5 ($CHCHC=CH_2$), 55.8 (OCH_3), 61.3 ($CO_2CH_2CH_3$), 66.1 ($CHC=CH_2$), 70.3 ($CCO_2CH_2CH_3$), 83.9 ($OC(CH_3)_2$), 113.7 (ArCH), 116.5 (ArCH), 125.5 (ArCH), 129.2 (ArCH), 136.4 (ArC), 136.4 (ArC), 137.2 ($C=CH_2$), 140.7 (ArC), 151.1 (ArC), 174.2 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 30.3.

3d was further characterized by X-ray crystallographic analysis.

***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3e)**

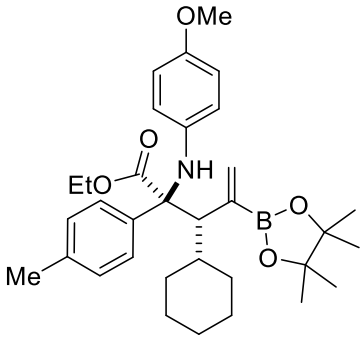


Prepared according to General Procedure B on a 0.250 mmol scale (90:10 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a pale yellow gum (119 mg, 0.211 mmol, 85%).

MS (ES^-) *m/z*: 562 ($[M-H]^-$). HRMS calcd for $C_{33}H_{45}NBO_6$: 562.3345. Found: 562.3342; ν_{max} (thin film/cm^{-1}): 3404, 2977, 2928, 2850, 1718, 1608, 1510, 1464, 1362, 1300, 1239, 1177, 1141, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.85 - 0.92 (m, 1 H, CH_2), 0.96 - 1.04 (m, 1 H, CH_2), 1.05 - 1.14 (m, 1 H, CH_2), 1.18 (t, *J* = 7.0 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.21 - 1.25 (m, 1 H, CH_2), 1.28 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.61 (d, *J* = 12.3 Hz, 1 H, CH_2), 1.70 (d, *J* = 13.1 Hz, 2 H, CH_2), 1.81 (d, *J* = 11.8 Hz, 2 H, CH_2), 1.88 - 2.02 (m, 1 H, $CHCHC=CH_2$), 2.89 (d, *J* = 7.5 Hz, 1 H, $CHC=CH_2$), 3.69 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 4.10 - 4.18 (m, 1 H, $CO_2CH_2CH_3$), 4.20 - 4.31 (m, 1 H, $CO_2CH_2CH_3$), 4.99 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 5.56 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 5.91 (br. s, 1 H, NH), 6.30 (d, *J* = 8.8 Hz, 2 H, ArCH), 6.61 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.68 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArCH); ^{13}C

NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 24.3 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.4 (CH_2), 32.9 (CH_2), 38.3 (*C*HCHC=CH_2), 55.0 (OCH_3), 55.6 (OCH_3), 61.1 ($CO_2CH_2CH_3$), 66.1 (*C*HC=CH_2), 70.0 (*C*$CO_2CH_2CH_3$), 83.7 (O*C*$(CH_3)_2$), 112.7 (ArCH), 113.5 (ArCH), 116.4 (ArCH), 129.7 (ArCH), 131.3 (ArC), 136.8 (C=*C*H_2), 140.7 (ArC), 150.9 (ArC), 158.0 (ArC), 174.3 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.8.

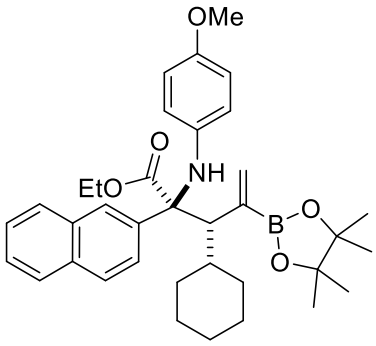
rac-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)pent-4-enoate (3f)



Prepared according to General Procedure B on a 0.250 mmol scale (89:11 d.r. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a pale yellow gum. The yield (74%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^-) *m/z*: 546 ($[M-H]^-$). HRMS calcd for $C_{33}H_{46}NBO_5K$: 586.3101. Found: 586.3105; ν_{max} (thin film/cm^{-1}): 3404, 2976, 2923, 2851, 1718, 1511, 1446, 1362, 1301, 1238, 1176, 1142, 1039; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.87 (qd, *J* = 12.3, 3.2 Hz, 1 H, CH_2), 0.96 - 1.06 (m, 1 H, CH_2), 1.06 - 1.14 (m, 1 H, CH_2), 1.18 (t, *J* = 7.1 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.21 - 1.25 (m, 1 H, CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.61 (d, *J* = 12.5 Hz, 1 H, CH_2), 1.70 (d, *J* = 13.0 Hz, 2 H, CH_2), 1.81 (t, *J* = 12.7 Hz, 2 H, CH_2), 1.91 - 2.01 (m, 1 H, C*H*CHC=CH_2), 2.24 (s, 3 H, ArCCH_3), 2.90 (d, *J* = 7.6 Hz, 1 H, C*H*C=CH_2), 3.69 (s, 3 H, OCH_3), 4.14 (dq, *J* = 10.7, 7.2 Hz, 1 H, $CO_2CH_2CH_3$), 4.26 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.98 (d, *J* = 3.4 Hz, 1 H, C=CH_2), 5.52 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 5.91 (br. s, 1 H, NH), 6.30 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.61 (d, *J* = 8.9 Hz, 2 H, ArCH), 6.95 (d, *J* = 8.2 Hz, 2 H, ArCH), 7.21 - 7.27 (m, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 20.9 (Ar*C*CH_3), 24.3 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.3 (CH_2), 32.9 (CH_2), 38.3 (*C*HCHC=CH_2), 55.6 (OCH_3), 61.1 ($CO_2CH_2CH_3$), 65.9 (*C*HC=CH_2), 70.2 (*C*$CO_2CH_2CH_3$), 83.7 (O*C*$(CH_3)_2$), 113.4 (ArCH), 116.5 (ArCH), 128.2 (ArCH), 128.3 (ArCH), 135.9 (ArC), 136.2 (ArC), 136.6 (C=*C*H_2), 140.8 (ArC), 150.8 (ArC), 174.2 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 27.8.

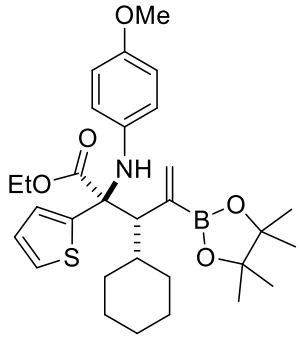
rac-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3g)



Prepared according to General Procedure B on a 0.250 mmol scale (88:12 d.r. of crude material). Column chromatography (20% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum (132 mg, 0.226 mmol, 90%).

MS (ES^+) *m/z*: 622 ($[M+K]^+$). HRMS calcd for $C_{36}H_{47}NBO_5$: 584.3542. Found: 584.3530; ν_{max} (thin film/cm^{-1}): 3403, 2976, 2923, 2849, 1716, 1509, 1237, 1139; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.82 – 0.95 (m, 1 H, CH_2), 0.99 – 1.16 (m, 3 H, CH_2), 1.20 (t, *J* = 7.2 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.28 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.57 – 1.66 (m, 1 H, CH_2), 1.66 – 1.76 (m, 2 H, CH_2), 1.77 – 1.92 (m, 2 H, CH_2), 1.96 – 2.08 (m, 1 H, C*H*CHC=CH_2), 3.02 (d, *J* = 7.8 Hz, 1 H, C*H*C=CH_2), 3.66 (s, 3 H, OCH_3), 4.20 (dq, *J* = 10.7, 7.2 Hz, 1 H, $CO_2CH_2CH_3$), 4.29 (dq, *J* = 10.7, 7.2 Hz, 1 H, $CO_2CH_2CH_3$), 4.91 (d, *J* = 3.4 Hz, 1 H, C=CH_2), 5.40 (d, *J* = 3.4 Hz, 1 H, C=CH_2), 6.02 (br. s, 1 H, NH), 6.31 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.56 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.35 – 7.46 (m, 3 H, ArCH), 7.56 (d, *J* = 8.8 Hz, 1 H, ArCH), 7.67 – 7.74 (m, 2 H, ArCH), 8.00 (s, 1 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 ($CO_2CH_2CH_3$), 24.5 (CH_3), 25.2 (CH_3), 26.5 (CH_2), 27.1 (CH_2), 27.2 (CH_2), 32.4 (CH_2), 33.1 (CH_2), 38.6 (*C*HCHC=CH_2), 55.8 (OCH_3), 61.4 ($CO_2CH_2CH_3$), 66.1 (C*H*C=CH_2), 70.8 (*C*$CO_2CH_2CH_3$), 83.9 (O*C*$(CH_3)_2$), 113.7 (ArCH), 116.6 (ArCH), 125.5 (ArCH), 125.7 (ArCH), 126.6 (ArCH), 127.2 (ArCH), 127.3 (ArCH), 127.5 (ArCH), 128.6 (ArCH), 131.0 (ArC) 132.4 (ArC), 133.2 (ArC), 137.2 (C=*C*H_2), 140.8 (ArC), 151.1 (ArC), 174.3 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.7.

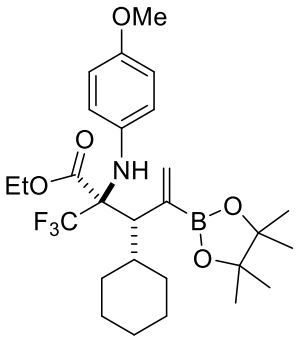
***rac*-Ethyl (2*R*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)pent-4-enoate (3h)**



Prepared according to General Procedure B on a 0.250 mmol scale (75:25 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow foam (103 mg, 0.190 mmol, 76%).

MS (ES^-) *m/z*: 538 ($[M-H]^-$). HRMS calcd for $C_{30}H_{42}NBO_5SNa$: 562.2769. Found: 562.2770; ν_{max} (thin film/cm^{-1}): 3383, 2975, 2922, 2851, 1744, 1721, 1509, 1463, 1423, 1390, 1380, 1362, 1299, 1234, 1169, 1141, 1096, 1039 ; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.85 - 0.94 (m, 1 H, CH_2), 0.95 - 1.03 (m, 1 H, CH_2), 1.04 - 1.12 (m, 1 H, CH_2), 1.16 - 1.23 (m, 1 H, CH_2), 1.26 (t, *J* = 7.0 Hz, 3 H, $CO_2CH_2CH_3$), 1.31 (s, 6 H, 2 x CH_3), 1.35 (s, 6 H, 2 x CH_3), 1.56 - 1.63 (m, 2 H, CH_2), 1.65 - 1.76 (m, 3 H, CH_2), 1.89 (d, *J* = 12.8 Hz, 1 H, CH_2), 1.92 - 1.99 (m, 1 H, $CHCHC=CH_2$), 2.82 (d, *J* = 6.3 Hz, 1 H, $CHC=CH_2$), 3.70 (s, 3 H, OCH_3), 4.20 - 4.27 (m, 1 H, $CO_2CH_2CH_3$), 4.27 - 4.34 (m, 1 H, $CO_2CH_2CH_3$), 5.23 (d, *J* = 2.7 Hz, 1 H, $C=CH_2$), 5.63 (d, *J* = 2.1 Hz, 1 H, $C=CH_2$), 6.24 (br. s, 1 H, NH), 6.36 (d, *J* = 7.8 Hz, 2 H, ArCH), 6.65 (d, *J* = 7.9 Hz, 2 H, ArCH), 6.71 - 6.76 (m, 2 H, ArCH), 7.09 (d, *J* = 4.4 Hz, 1 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 24.3 (CH_3), 25.0 (CH_3), 26.2 (CH_2), 26.8 (CH_2), 26.8 (CH_2), 32.5 (CH_2), 32.9 (CH_2), 38.1 ($CHCHC=CH_2$), 55.6 (OCH_3), 61.6 ($CO_2CH_2CH_3$), 67.7 ($CHC=CH_2$), 69.4 ($CCO_2CH_2CH_3$), 83.9 ($OC(CH_3)_2$), 113.6 (ArCH), 116.2 (ArCH), 125.4 (ArCH), 125.7 (ArCH), 126.9 (ArCH), 136.3 ($C=CH_2$), 140.0 (ArC), 144.3 (ArC), 151.2 (ArC), 173.8 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 31.2.

rac-Ethyl (2*R*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trifluoromethyl)pent-4-enoate (3i)

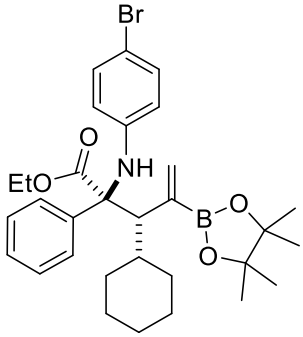


Prepared according to General Procedure B on a 0.162 mmol scale (61:39 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum (58 mg, 0.110 mmol, 68%).

MS (ES^-) *m/z*: 524 ($[M-H]^-$). HRMS calcd for $C_{27}H_{39}NBO_5F_3Na$: 548.2766. Found: 548.2767; ν_{max} (thin film/cm^{-1}): 3370, 2979, 2927, 2852, 1739, 1512, 1445, 1381, 1373, 1362, 1305, 1244, 1163, 1138, 1036; major and minor diastereoisomers ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.79 - 0.90 (m, 1 H, CH_2 **major**), 0.91 - 0.99 (m, 1 H, CH_2 **major**), 1.00 - 1.11 (m, 4 H, 1 H from CH_2 **major** + 3 H from CH_2 **minor**), 1.15 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$ **major**), 1.21 - 1.26 (m, 2 H, 1 H from CH_2 **major** + 1 H from

CH_2 **minor**), 1.27 (s, 6 H, 2 x CH_3 **major**), 1.28 (s, 6 H, 2 x CH_3 **major**), 1.33 (s, 7 H, 1 H from CH_2 **major** + 2 x CH_3 **minor**), 1.34 - 1.37 (m, 9 H, 2 x CH_3 **minor** + $CO_2CH_2CH_3$ **minor**), 1.45 - 1.51 (m, 1 H, CH_2 **minor**), 1.56 - 1.65 (m, 2 H, 1 H from CH_2 **major** + 1 H from CH_2 **minor**), 1.65 - 1.75 (m, 6 H, 3 H from CH_2 **major** + 3 H from CH_2 **minor**), 1.83 - 1.91 (m, 1 H, C*H*CHC=CH_2 **minor**), 2.01 - 2.13 (m, 3 H, C*H*CHC=CH_2 **major** + 1 H from CH_2 **major** + 1 H from CH_2 **minor**), 2.88 (d, *J* = 4.0 Hz, 1 H, C*H*C=CH_2 **major**), 2.90 (d, *J* = 3.7 Hz, 1 H, C*H*C=CH_2 **minor**), 3.75 (s, 6 H, OCH_3 **major** + OCH_3 **minor**), 4.05 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$ **major**), 4.29 - 4.44 (m, 2 H, $CO_2CH_2CH_3$ **minor**), 5.42 (br. s, 1 H, NH **major**), 5.68 (d, *J* = 2.6 Hz, 1 H, C=CH_2 **major**), 5.81 (d, *J* = 2.0 Hz, 1 H, C=CH_2 **minor**), 6.05 (d, *J* = 3.1 Hz, 1 H, C=CH_2 **major**), 6.14 (br. s, 1 H, NH **minor**), 6.19 (d, *J* = 2.7 Hz, 1 H, C=CH_2 **minor**), 6.73 (d, *J* = 8.5 Hz, 4 H, ArCH **major** + ArCH **minor**), 6.79 (d, *J* = 8.1 Hz, 4 H, ArCH **major** + ArCH **minor**); major and minor diastereoisomers ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$ **major**), 14.0 ($CO_2CH_2CH_3$ **minor**), 24.2 (CH_3 **minor**), 24.4 (CH_3 **major**), 24.8 (CH_3 **major**), 24.9 (CH_3 **minor**), 26.0 (CH_2 **minor**), 26.2 (CH_2 **major**), 26.6 (CH_2 **minor**), 26.7 (CH_2 **minor**), 26.8 (CH_2 **major**), 26.9 (CH_2 **major**), 31.5 (CH_2 **minor**), 32.1 (CH_2 **major**), 33.2 (CH_2 **major**), 33.5 (CH_2 **minor**), 37.5 (*C*HCHC=CH_2 **minor**), 37.5 (*C*HCHC=CH_2 **major**), 55.5 (OCH_3 **major**), 55.6 (OCH_3 **minor**), 59.4 (*C*HC=CH_2 **minor**), 59.6 (*C*HC=CH_2 **major**), 61.4 ($CO_2CH_2CH_3$ **major**), 62.0 ($CO_2CH_2CH_3$ **minor**), 84.0 (O*C*$(CH_3)_2$ **major**), 84.4 (O*C*$(CH_3)_2$ **minor**), 113.7 (ArCH **major**), 113.8 (ArCH **minor**), 118.2 (ArCH **minor**), 119.5 (ArCH **major**), 137.2 (C=*C*H_2 **major**), 138.5 (ArC **major**), 138.7 (C=*C*H_2 **minor**), 139.0 (ArC **minor**), 152.9 (ArC **minor**), 153.4 (ArC **major**), 168.4 (C=O **major**), 169.0 (C=O **minor**), (both **major** and **minor** B*C*=CH_2 + *C*CF_3 + CF_3 not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 30.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ ppm -62.7 (**minor**), -61.9 (**major**).

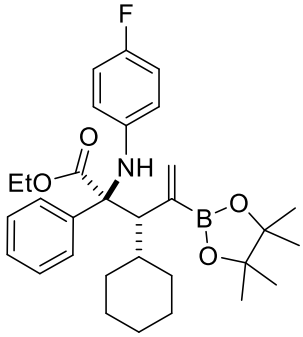
***rac*-Ethyl (2*S*,3*S*)-2-((4-bromophenyl)amino)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3j)**



Prepared according to General Procedure B on a 0.250 mmol scale (89:11 d.r. of crude material). Column chromatography (1.5 - 2% Et_2O in hexane + 1% NEt_3) afforded the title compound as a colourless gum. The yield (68%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^-) *m/z*: 580 ($[M-H]^-$). HRMS calcd for $C_{31}H_{41}NBO_4BrK$: 620.1944. Found: 620.1937; ν_{max} (thin film/cm^{-1}): 3411, 2976, 2927, 2851, 1721, 1592, 1519, 1490, 1446, 1423, 1363, 1307, 1260, 1219, 1167, 1141, 1108, 1073, 1033; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.84 - 0.93 (m, 1 H, CH_2), 0.96 - 1.06 (m, 1 H, CH_2), 1.07 - 1.15 (m, 1 H, CH_2), 1.20 (t, *J* = 7.2 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.23 - 1.27 (m, 1 H, CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.63 (d, *J* = 12.4 Hz, 1 H, CH_2), 1.71 (d, *J* = 12.7 Hz, 2 H, CH_2), 1.80 (t, *J* = 10.6 Hz, 2 H, CH_2), 1.88 - 1.99 (m, 1 H, $CHCHC=CH_2$), 2.92 (d, *J* = 7.8 Hz, 1 H, $CHC=CH_2$), 4.12 - 4.22 (m, 1 H, $CO_2CH_2CH_3$), 4.22 - 4.30 (m, 1 H, $CO_2CH_2CH_3$), 4.95 (d, *J* = 1.5 Hz, 1 H, $C=CH_2$), 5.52 (d, *J* = 2.7 Hz, 1 H, $C=CH_2$), 6.23 (d, *J* = 7.8 Hz, 3 H, 2 x ArCH + NH), 7.07 (d, *J* = 8.4 Hz, 2 H, ArCH), 7.10 - 7.19 (m, 3 H, ArCH), 7.30 - 7.41 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 24.2 (CH_3), 25.0 (CH_3), 26.2 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.1 (CH_2), 32.9 (CH_2), 38.4 ($CHCHC=CH_2$), 61.4 ($CO_2CH_2CH_3$), 65.9 ($CHC=CH_2$), 70.2 ($CCO_2CH_2CH_3$), 83.8 ($OC(CH_3)_2$), 107.9 (ArC), 117.4 (ArCH), 126.8 (ArCH), 127.7 (ArCH), 128.1 (ArCH), 130.4 (ArCH), 137.2 ($C=CH_2$), 138.4 (ArC), 145.6 (ArC), 173.5 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.1.

rac-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-fluorophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3k)

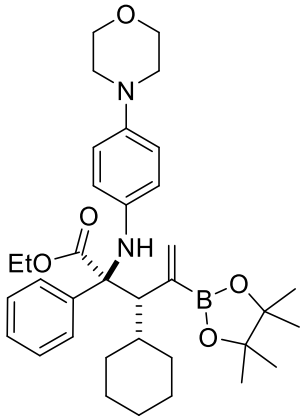


Prepared according to General Procedure B on a 0.250 mmol scale (88:12 d.r. of crude material) Column chromatography (1% Et_2O in hexane + 1% NEt_3) afforded the title compound as a colourless gum (98.2 mg, 0.188 mmol, 75%).

MS (ES^+) *m/z*: 560 ($[M+K]^+$). HRMS calcd for $C_{31}H_{41}NBO_4FK$: 560.2744. Found: 560.2734; ν_{max} (thin film/cm^{-1}): 3407, 2976, 2927, 2852, 1720, 1613, 1508, 1446, 1422, 1363, 1307, 1261, 1223, 1167, 1142, 1110, 1033; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.82 - 0.94 (m, 1 H, CH_2), 0.96 - 1.05 (m, 1 H, CH_2), 1.07 - 1.15 (m, 1 H, CH_2), 1.20 (t, *J* = 7.2 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.23 - 1.26 (m, 1 H, CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.62 (d, *J* = 12.3 Hz, 1 H, CH_2), 1.71 (d, *J* = 12.8 Hz, 2 H, CH_2), 1.81 (t, *J* = 11.9 Hz, 2 H, CH_2), 1.89 - 2.01 (m, 1 H, $CHCHC=CH_2$), 2.92 (d, *J* = 7.8 Hz, 1 H, $CHC=CH_2$), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.27 (dq, *J* = 10.8, 7.0 Hz, 1 H, $CO_2CH_2CH_3$), 4.95 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 5.52 (d, *J* = 3.5 Hz, 1 H, $C=CH_2$), 6.11 (s, 1 H, NH), 6.27 (dd, *J* = 9.0, 4.5 Hz, 2 H, ArCH), 6.71 (t, *J* = 8.8 Hz, 2 H, ArCH), 7.08 - 7.20 (m, 3 H, ArCH), 7.37 (d, *J* = 6.3 Hz, 2 H, ArCH); ^{13}C

NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 24.2 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.2 (CH_2), 32.9 (CH_2), 38.4 (*C*HCHC=CH_2), 61.3 ($CO_2CH_2CH_3$), 65.9 (*C*HC=CH_2), 70.4 (*C*$CO_2CH_2CH_3$), 83.8 (O*C*$(CH_3)_2$), 114.1 (d, *J* = 22.5 Hz, ArCH), 116.2 (d, *J* = 6.9 Hz, ArCH), 126.7 (ArCH), 127.6 (ArCH), 128.3 (ArCH), 137.0 (C=*C*H_2), 138.8 (ArC), 142.8 (ArC), 155.0 (d, *J* = 233.8 Hz, ArCF), 173.8 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -130.0 (td, *J* = 8.7, 4.4 Hz).

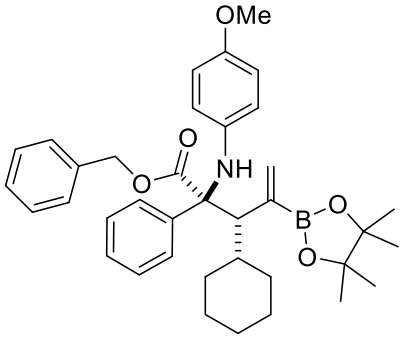
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-morpholinophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3l)**



Prepared according to General Procedure B on a 0.250 mmol scale (90:10 d.r. of crude material) Column chromatography (30% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (74%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^+) *m/z*: 627 ($[M+H]^+$). HRMS calcd for $C_{35}H_{49}N_2BO_5Na$: 611.3627. Found: 611.3617; ν_{max} (thin film/cm^{-1}): 3406, 2975, 2926, 2851, 1718, 1514, 1447, 1362, 1300, 1268, 1226, 1167, 1142, 1121, 1031; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.84 - 0.90 (m, 1 H, CH_2), 0.97 - 1.04 (m, 1 H, CH_2), 1.04 - 1.11 (m, 1 H, CH_2), 1.20 (t, *J* = 7.2 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.22 - 1.26 (m, 1 H, CH_2), 1.28 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.61 - 1.65 (m, 1 H, CH_2), 1.70 (d, *J* = 12.8 Hz, 2 H, CH_2), 1.82 (t, *J* = 13.7 Hz, 2 H, CH_2), 1.92 - 2.03 (m, 1 H, C*H*CHC=CH_2), 2.92 (d, *J* = 7.8 Hz, 1 H, C*H*C=CH_2), 2.95 - 3.00 (m, 4 H, 2 x NCH_2), 3.82 (t, *J* = 4.6 Hz, 4 H, 2 x OCH_2), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.27 (dq, *J* = 11.0, 7.0 Hz, 1 H, $CO_2CH_2CH_3$), 4.95 (d, *J* = 3.3 Hz, 1 H, C=CH_2), 5.50 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 5.99 (s, 1 H, NH), 6.32 (d, *J* = 8.8 Hz, 2 H, ArCH), 6.66 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.07 - 7.19 (m, 3 H, ArCH), 7.40 (d, *J* = 6.8 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 24.2 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 32.3 (CH_2), 32.9 (CH_2), 38.3 (*C*HCHC=CH_2), 51.2 (NCH_2), 61.2 ($CO_2CH_2CH_3$), 65.9 (*C*HC=CH_2), 67.2 (OCH_2), 70.3 (*C*$CO_2CH_2CH_3$), 83.7 (O*C*$(CH_3)_2$), 116.4 (ArCH), 116.9 (ArCH), 126.5 (ArCH), 127.4 (ArCH), 128.4 (ArCH), 136.7 (C=*C*H_2), 139.2 (ArC), 141.0 (ArC), 142.1 (ArC), 174.1 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.7.

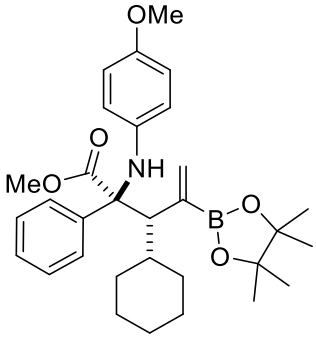
***rac*-Benzyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3n)**

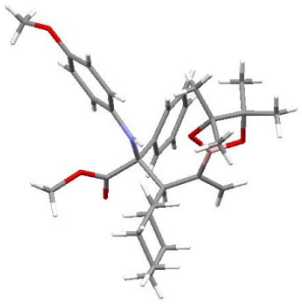


Prepared according to General Procedure B on a 0.250 mmol scale (94:6 d.r. of crude material). Column chromatography (4% Et_2O in hexane + 1% NEt_3 then recolumned in 1 - 2% EtOAc in hexane + 1% NEt_3) afforded the title compound as a yellow gum (99.6 mg, 0.167 mmol, 67%).

MS (ES^+) *m/z*: 634 ($[M+K]^+$). HRMS calcd for $C_{37}H_{46}NBO_5K$: 634.3101. Found: 634.3093; ν_{max} (thin film/cm^{-1}): 3410, 2977, 2925, 2851, 1721, 1510, 1446, 1422, 1372, 1362, 1301, 1238, 1215, 1176, 1141, 1077, 1038; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.83 (m, 1 H, CH_2), 0.88 - 0.98 (m, 1 H, CH_2), 0.99 - 1.06 (m, 1 H, CH_2), 1.06 - 1.09 (m, 1 H, CH_2), 1.12 - 1.15 (m, 1 H, CH_2), 1.25 (d, *J* = 5.3 Hz, 1 H, CH_2), 1.27 (s, 6 H, 2 x CH_3), 1.32 (s, 6 H, 2 x CH_3), 1.57 - 1.61 (m, 1 H, CH_2), 1.62 - 1.68 (m, 1 H, CH_2), 1.73 (d, *J* = 12.5 Hz, 1 H, CH_2), 1.79 (d, *J* = 12.8 Hz, 1 H, CH_2), 1.85 - 1.99 (m, 1 H, C*H*CHC=CH_2), 2.89 (d, *J* = 7.5 Hz, 1 H, C*H*C=CH_2), 3.69 (s, 3 H, OCH_3), 4.94 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 5.10 (d, *J* = 12.3 Hz, 1 H, CO_2CH_2Ph), 5.23 (d, *J* = 12.3 Hz, 1 H, CO_2CH_2Ph), 5.51 (d, *J* = 3.8 Hz, 1 H, C=CH_2), 5.96 (br. s, 1 H, NH), 6.27 (d, *J* = 8.8 Hz, 2 H, ArCH), 6.58 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.08 - 7.13 (m, 1 H, ArCH), 7.14 (d, *J* = 8.3 Hz, 2 H, ArCH), 7.16 - 7.20 (m, 2 H, ArCH), 7.24 -7.27 (m, 3 H, ArCH), 7.43 (d, *J* = 7.0 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.2 (CH_3), 25.0 (CH_3), 26.2 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 32.4 (CH_2), 32.8 (CH_2), 38.2 (*C*HCHC=CH_2), 55.6 (OCH_3), 66.2 (*C*HC=CH_2), 67.1 (CO_2CH_2Ph), 70.5 (*C*CO_2CH_2Ph), 83.7 (O*C*$(CH_3)_2$), 113.6 (ArCH), 116.4 (ArCH), 126.6 (ArCH), 127.4 (ArCH), 127.9 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 128.6 (ArCH), 135.4 (ArC), 136.7 (C=*C*H_2), 139.2 (ArC), 140.6 (ArC), 151.0 (ArC), 174.0 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 27.4.

***rac*-Methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3o)**

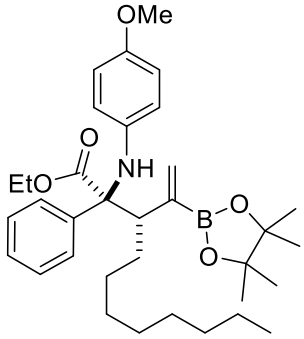




Prepared according to General Procedure B on a 0.250 mmol scale (91:9 d.r. of crude material). Column chromatography (4 - 8% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (76%) was determined by ^1H NMR analysis using $MeNO_2$ as an internal standard. A sample of the product was recrystallized with $CHCl_3$ to afford the title compound as a yellow crystal. M.p.: 161-164 °C ($CHCl_3$); MS (ES^+) *m/z*: 558 ($[M+K]^+$). HRMS calcd for $C_{31}H_{42}NBO_5K$: 558.2788. Found: 558.2785; ν_{max} (thin film/cm^{-1}): 3406, 2976, 2925, 2850, 1722, 1510, 1446, 1431, 1380, 1372, 1362, 1301, 1238, 1167, 1141, 1076, 1038; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.86 (qd, *J* = 12.3, 3.4 Hz, 1 H, CH_2), 1.00 (qd, *J* = 12.3, 3.4 Hz, 1 H, CH_2), 1.09 (qt, *J* = 12.5, 3.3 Hz, 1 H, CH_2), 1.15 - 1.28 (m, 2 H, CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.33 (s, 6 H, 2 x CH_3), 1.62 (d, *J* = 12.7 Hz, 1 H, CH_2), 1.70 (d, *J* = 13.0 Hz, 2 H, CH_2), 1.77 (d, *J* = 12.8 Hz, 1 H, CH_2), 1.83 (d, *J* = 12.4 Hz, 1 H, CH_2), 1.97 (m, *J* = 11.4, 3.3 Hz, 1 H, C*H*CHC=CH_2), 2.93 (d, *J* = 7.9 Hz, 1 H, C*H*C=CH_2), 3.69 (s, 3 H, ArCOCH_3), 3.73 (s, 3 H, CO_2CH_3), 4.95 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 5.51 (d, *J* = 3.7 Hz, 1 H, C=CH_2), 5.99 (br. s, 1 H, NH), 6.29 (d, *J* = 8.9 Hz, 2 H, ArCH), 6.62 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.08 - 7.12 (m, 1 H, ArCH), 7.15 (m, *J* = 8.1 Hz, 2 H, ArCH), 7.38 (d, *J* = 6.7 Hz, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.2 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (CH_2), 27.1 (CH_2), 31.9 (CH_2), 33.0 (CH_2), 38.3 (*C*HCHC=CH_2), 52.0 (CO_2CH_3), 55.6 (ArCO*C*H_3), 66.0 (*C*HC=CH_2), 70.3 (*C*CO_2CH_3), 83.8 (O*C*(CH_3)$_2$), 113.6 (ArCH), 116.4 (ArCH), 126.6 (ArCH), 127.5 (ArCH), 128.4 (ArCH), 136.7 (C=*C*H_2), 139.0 (ArC), 140.5 (ArC), 150.9 (ArC), 174.8 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 30.7.

3o was further characterized by X-ray crystallographic analysis.

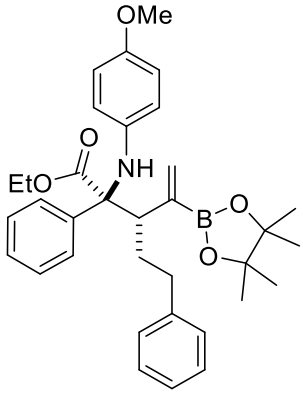
***rac*-Ethyl (2*S*,3*S*)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,2-oxaborolan-2-yl)vinyl)undecanoate (3p)**



Prepared according to General Procedure B on a 0.250 mmol scale (77:23 d.r. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a pale yellow gum (91.6 mg, 0.163 mmol, 65%).

MS (ES^-) *m/z*: 562 ($[M-H]^-$). HRMS calcd for $C_{34}H_{50}NBO_5K$: 602.3414. Found: 602.3418; ν_{max} (thin film/cm^{-1}): 3421, 2976, 2926, 2854, 1722, 1512, 1464, 1445, 1370, 1303, 1238, 1180, 1142, 1110, 1039; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (t, *J* = 6.9 Hz, 4 H, CH_2CH_3 + 1 H from CH_2), 1.13 (t, *J* = 7.0 Hz, 4 H, $CO_2CH_2CH_3$ + 1 H from CH_2), 1.21 - 1.27 (m, 10 H, 5 x CH_2), 1.29 (s, 6 H, 2 x CH_3), 1.35 (s, 6 H, 2 x CH_3), 1.43 - 1.52 (m, 1 H, $CH_2CHC{=}CH_2$), 1.97 - 2.11 (m, 1 H $CH_2CHC{=}CH_2$), 2.85 (dd, *J* = 12.0, 2.8 Hz, 1 H, $CHC{=}CH_2$), 3.68 (s, 3 H, OCH_3), 4.12 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.24 (dq, *J* = 10.8, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.96 (d, *J* = 3.3 Hz, 1 H, $C{=}CH_2$), 5.59 (br. s, 1 H, NH), 5.65 (d, *J* = 3.5 Hz, 1 H, $C{=}CH_2$), 6.26 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.60 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.13 - 7.19 (m, 1 H, ArCH), 7.19 - 7.25 (m, 2 H, ArCH), 7.61 (d, *J* = 7.3 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 ($CO_2CH_2CH_3$), 14.1($CH_2CH_2CH_3$), 22.6 (CH_2), 24.3 (CH_3), 25.1 (CH_3), 28.4 (CH_2), 28.7 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 55.6 (OCH_3), 60.0 ($CHC{=}CH_2$), 61.0 ($CO_2CH_2CH_3$), 71.4 ($CCO_2CH_2CH_3$), 83.6 ($OC(CH_3)_2$), 113.7 (ArCH), 115.8 (ArCH), 126.6 (ArCH), 127.4 (ArCH), 128.6 (ArCH), 136.3 ($C{=}CH_2$), 139.3 (ArC), 140.9 (ArC), 151.1 (ArC), 173.6 (C=O), ($BC{=}CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 27.9.

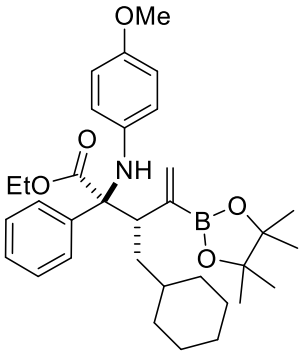
rac-Ethyl (2*S*,3*S*)-2-((4-methoxyphenyl)amino)-3-phenethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3q)



Prepared according to General Procedure B on a 0.200 mmol scale (66:34 d.r. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a pale yellow gum (67.7 mg, 0.122 mmol, 61%).

MS (ES^-) *m/z*: 554 ($[M-H]^-$). HRMS calcd for $C_{34}H_{42}NBO_5K$: 594.2788. Found: 594.2788; ν_{max} (thin film/cm^{-1}): 3389, 2976, 2351, 1724, 1602, 1512, 1445, 1366, 1305, 1238, 1181, 1138, 1031; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.90 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$ **minor**), 1.07 (t, *J* = 7.0 Hz, 3 H, $CO_2CH_2CH_3$ **major**), 1.33 (s, 6 H, $OC(CH_3)_2$ **major**), 1.36 (s, 12 H, $OC(CH_3)_2$ **major** + $OC(CH_3)_2$ **minor**), 1.40 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.43 - 1.50 (m, 1 H, 1 H from $CH_2CHC=CH_2$ **minor**), 1.81 - 1.90 (m, 1 H, 1 H from $CH_2CHC=CH_2$ **major**), 2.04 - 2.16 (m, 2 H, 1 H from CH_2Ph **minor** + 1 H from $CH_2CHC=CH_2$ **minor**), 2.30 - 2.38 (m, 2 H, 1 H from CH_2Ph **major** + 1 H from $CH_2CHC=CH_2$ **major**), 2.44 - 2.52 (m, 1 H, 1 H from CH_2Ph **minor**), 2.52 - 2.61 (m, 1 H, 1 H from CH_2Ph **major**), 2.79 (d, *J* = 10.0 Hz, 1 H, 1 H from $CHC=CH_2$ **minor**), 2.88 - 2.97 (m, 1 H, 1 H from $CHC=CH_2$ **major**), 3.67 (s, 3 H, OCH_3 **major**), 3.68 (s, 3 H, OCH_3 **minor**), 3.77 - 3.87 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 3.90 - 4.00 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 4.02 - 4.12 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 4.12 - 4.22 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 5.06 (d, *J* = 3.3 Hz, 1 H, 1 H from $C=CH_2$ **major**), 5.46 (s, 1 H, NH **major**), 5.52 (s, 1 H, 1 H from $C=CH_2$ **minor**), 5.75 (d, *J* = 3.5 Hz, 1 H, 1 H from $C=CH_2$ **major**), 5.93 (br. s, 1 H, NH **minor**), 6.01 (d, *J* = 3.3 Hz, 1 H, 1 H from $C=CH_2$ **minor**), 6.25 (m, *J* = 8.0 Hz, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 6.59 (dd, *J* = 8.9, 5.9 Hz, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 6.86 (d, *J* = 6.8 Hz, 2 H, ArCH **major** + ArCH **minor**), 7.13 (m, *J* = 6.8 Hz, 3 H, 2 x ArCH **major** + 2 x ArCH **minor**), 7.16 - 7.21 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 7.21 - 7.26 (m, 4 H, 2 x ArCH **major** + 3 x ArCH **minor**), 7.27 - 7.30 (m, 1 H, ArCH **major**), 7.59 (d, *J* = 7.5 Hz, 2 H, ArCH **major**), 7.76 (d, *J* = 6.3 Hz, 2 H, ArCH **minor**); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.8 ($CO_2CH_2CH_3$ **minor**), 13.9 ($CO_2CH_2CH_3$ **major**), 24.4 ($OC(CH_3)_2$ **major**), 24.5 ($OC(CH_3)_2$ **minor**), 25.1 ($OC(CH_3)_2$ **minor**), 25.2 ($OC(CH_3)_2$ **major**), 29.0 (CH_2 **minor**), 30.7 (CH_2 **major**), 33.8 (CH_2 **minor**), 34.6 (CH_2 **major**), 55.5 (OCH_3 **major** + OCH_3 **minor**), 59.3 ($CHC=CH_2$ **major** + $CHC=CH_2$ **minor**), 60.3 ($CO_2CH_2CH_3$ **minor**), 61.0 ($CO_2CH_2CH_3$ **major**), 71.3 ($CCO_2CH_2CH_3$ **major**), 71.5 ($CCO_2CH_2CH_3$ **minor**), 83.7 ($OC(CH_3)_2$ **major**), 84.0 ($OC(CH_3)_2$ **minor**), 113.7 (PMP ArCH **major**), 113.8 (PMP ArCH **minor**), 115.5 (PMP ArCH **minor**), 115.9 (PMP ArCH **major**), 125.6 (ArCH **minor**), 125.7 (ArCH **major**), 126.7 (ArCH **major** + ArCH **minor**), 127.2 (ArCH **minor**), 127.5 (ArCH **major**), 128.1 (ArCH **minor**), 128.2 (ArCH **major**), 128.3 (ArCH **minor**), 128.4 (ArCH **major**), 128.5 (ArCH **major**), 129.5 (ArCH **minor**), 135.2 ($C=CH_2$ **minor**), 136.7 ($C=CH_2$ **major**), 139.1 (ArC **minor**), 140.7 (ArC **major** + ArC **minor**), 141.4 (ArC **major**), 141.6 (ArC **minor**), 142.2 (ArC **major**), 151.2 (ArC **minor**), 151.4 (ArC **major**), 173.4 (C=O **major**), 173.6 (C=O **minor**), ($BC=CH_2$ **major** and $BC=CH_2$ **minor** not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.9.

***rac*-Ethyl (2*S*,3*S*)-3-(cyclohexylmethyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3r)**

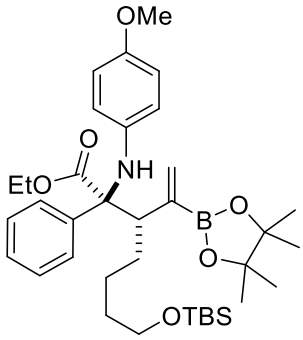


Prepared according to General Procedure B on a 0.250 mmol scale (70:30 d.r. of crude material). Column chromatography (4% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum (124.9 mg, 0.228 mmol, 91%).

MS (ES^+) *m/z*: 586 ($[M+K]^+$). HRMS calcd for $C_{33}H_{46}NBO_5K$: 586.3101. Found: 586.3099; ν_{max} (thin film/cm^{-1}): 3416, 2977, 2922, 2850, 1723, 1602, 1511, 1446, 1370, 1302, 1237, 1215, 1198, 1178, 1142, 1036; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.70 (d, *J* = 10.8 Hz, 1 H, 1 H from CH_2 **major**), 0.77 - 0.87 (m, 2 H, CH_2 **minor**), 0.91 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$ **minor**), 0.96 - 1.03 (m, 3 H, $CHCH_2CHC{=}CH_2$ **major** + $CHCH_2CHC{=}CH_2$ **minor** + 1 H from CH_2 **major**), 1.08 - 1.13 (m, 3 H, CH_2 **major** + 1 H from CH_2 **minor**), 1.16 (t, *J* = 7.2 Hz, 5 H, $CO_2CH_2CH_3$ **major** + CH_2 **minor**), 1.24 (dd, *J* = 9.9, 2.9 Hz, 2 H, 1 H from $CH_2CHC{=}CH_2$ major + 1 H from CH_2 **minor**), 1.29 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.34 (s, 6 H, $OC(CH_3)_2$ **major**), 1.35 (s, 6 H, $OC(CH_3)_2$ **major**), 1.39 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.45 - 1.55 (m, 4 H, CH_2 **minor**), 1.55 - 1.68 (m, 5 H, CH_2 **major**), 1.69 - 1.79 (m, 3 H, $CH_2CHC{=}CH_2$ **minor** + 1 H from CH_2 **major**), 2.06 (td, *J* = 12.9, 2.4 Hz, 1 H, 1 H from $CH_2CHC{=}CH_2$ **major**), 2.91 (d, *J* = 11.8 Hz, 1 H, $CHC{=}CH_2$ **major**), 2.99 (dd, *J* = 12.3, 2.8 Hz, 1 H, $CHC{=}CH_2$ **minor**), 3.68 (s, 3 H, OCH_3 **major**), 3.68 (s, 3 H, OCH_3 **minor**), 3.78 - 3.88 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 3.89 - 4.00 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 4.09 - 4.19 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 4.19 - 4.31 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 4.93 (d, *J* = 3.3 Hz, 1 H, 1 H from $C{=}CH_2$ **major**), 5.53 (s, 1 H, 1 H from $C{=}CH_2$ **minor**), 5.64 (d, *J* = 3.0 Hz, 2 H, 1 H from $C{=}CH_2$ **major** + NH **major**), 5.93 (d, *J* = 3.3 Hz, 1 H, 1 H from $C{=}CH_2$ **minor**), 5.98 (br. s, 1 H, NH **minor**), 6.22 - 6.30 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 6.57 - 6.63 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 7.13 - 7.24 (m, 4 H, 3 x ArCH **major** + ArCH **minor**), 7.27 - 7.33 (m, 2 H, ArCH **minor**), 7.60 (d, *J* = 6.3 Hz, 2 H, ArCH **major**), 7.82 (d, *J* = 7.3 Hz, 2 H, ArCH **minor**); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.8 ($CO_2CH_2CH_3$ **minor**), 14.0 ($CO_2CH_2CH_3$ **major**), 24.3 ($OC(CH_3)_2$ **major**), 24.3 ($OC(CH_3)_2$ **minor**), 25.1 ($OC(CH_3)_2$ **minor**), 25.1 ($OC(CH_3)_2$ **major**), 25.8 (CH_2 **minor**), 25.9, (CH_2 **major**), 26.3 (CH_2 **minor**), 26.4 (CH_2 **major**), 26.5 (CH_2 **minor**), 26.6 (CH_2 **major**), 30.7 (CH_2 **minor**), 31.1 (CH_2 **major**), 34.6 ($CHCH_2CHC{=}CH_2$ **minor**), 34.7 (CH_2 **minor**), 34.8 (CH_2 **major +** $CH_2CHC{=}CH_2$ **minor**), 35.4 ($CHCH_2CHC{=}CH_2$ **major**), 36.2 ($CH_2CHC{=}CH_2$ **major**), 55.6 (OCH_3 **major** + OCH_3 **minor**), 57.0 ($CHC{=}CH_2$

major + *C*HC=CH_2 **minor**), 60.2 ($CO_2CH_2CH_3$ **minor**), 61.0 ($CO_2CH_2CH_3$ **major**), 71.4 ($CCO_2CH_2CH_3$ **major**), 71.7 ($CCO_2CH_2CH_3$ **minor**), 83.7 ($OC(CH_3)_2$ **major**), 83.9 ($OC(CH_3)_2$ **minor**), 113.7 (PMP ArCH **major**), 113.8 (PMP ArCH **minor**), 115.4 (PMP ArCH **minor**), 115.8 (PMP ArCH **major**), 126.6 (ArCH **major**), 126.7 (ArCH **minor**), 127.1 (ArCH **minor**), 127.4 (ArCH **major**), 128.6 (ArCH **major**), 129.5 (ArCH **minor**), 134.5 (C=CH_2 **minor**), 136.4 (C=CH_2 **major**), 139.2 (ArC **major** + ArC **minor**), 140.8 (ArC **major**), 141.7 (ArC **minor**), 151.0 (ArC **major**), 151.3 (ArC **minor**), 173.5 (C=O **major**), 173.8 (C=O **minor**), (B*C*=CH_2 **major** and B*C*=CH_2 **minor** not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 30.0.

***rac*-Ethyl (2*S*,3*S*)-7-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3s)**

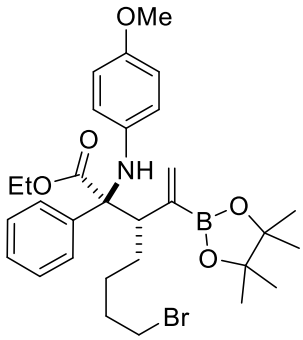


Prepared according to General Procedure B on a 0.250 mmol scale (80:20 d.r. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a pale yellow gum (87.2 mg, 0.137 mmol, 55%).

MS (ES^+) *m/z*: 660 ($[M+Na]^+$). HRMS calcd for $C_{36}H_{57}NBO_6Si$: 638.4043. Found: 638.4042; ν_{max} (thin film/cm^{-1}): 3417, 2929, 2857, 2354, 1724, 1603, 1511, 1463, 1445, 1366, 1303, 1238, 1181, 1141, 1097, 1039; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm -0.03 (s, 6 H, $Si(CH_3)_2$ **minor**), 0.03 (s, 6 H, $Si(CH_3)_2$ **major**), 0.84 (s, 9 H, $SiC(CH_3)_3$ **minor**), 0.88 (s, 9 H, $SiC(CH_3)_3$ **major**), 0.92 (t, *J* = 7.1 Hz, 4 H, $CO_2CH_2CH_3$ **minor** + 1 H from $CH_2CH_2CH_2OTBS$ **minor**), 1.12 (t, *J* = 7.1 Hz, 5 H, $CO_2CH_2CH_3$ **major** + 1 H from CH_2CH_2OTBS **minor** + 1 H from $CH_2CH_2CH_2OTBS$ **minor**), 1.19 - 1.27 (m, 4 H, $CH_2CH_2CH_2OTBS$ **major** + 1 H from $CH_2CHC=CH_2$ **minor** + 1 H from CH_2CH_2OTBS **minor**), 1.28 (s, 6 H, $OC(CH_3)_2$ **major**), 1.34 (s, 12 H, $OC(CH_3)_2$ **major** + $OC(CH_3)_2$ **minor**), 1.38 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.41 - 1.54 (m, 3 H, 1 H from $CH_2CHC=CH_2$ **major** + CH_2CH_2OTBS **major**), 1.72 - 1.83 (m, 1 H, 1 H from $CH_2CHC=CH_2$ **minor**), 2.00 - 2.11 (m, 1 H, 1 H from $CH_2CHC=CH_2$ **major**), 2.77 (d, *J* = 11.3 Hz, 1 H, $CHC=CH_2$ **minor**), 2.85 (dd, *J* = 12.0, 2.4 Hz, 1 H, $CHC=CH_2$ **major**), 3.36 - 3.43 (m, 2 H, CH_2OSi **minor**), 3.55 (t, *J* = 6.6 Hz, 2 H, CH_2OSi **major**), 3.68 (s, 6 H, OCH_3 **major** + OCH_3 **minor**), 3.80 - 3.88 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 3.91 - 4.01 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **minor**), 4.06 - 4.15 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 4.19 - 4.28 (m, 1 H, 1 H from $CO_2CH_2CH_3$ **major**), 4.97 (d, *J* = 3.2 Hz, 1 H, 1 H from C=CH_2 **major**), 5.50 (s, 1 H, 1 H from C=CH_2 **minor**), 5.55 (s, 1 H, NH **major**), 5.66 (d, *J* = 3.4 Hz, 1 H, 1 H from C=CH_2 **major**), 5.94

(d, *J* = 3.2 Hz, 1 H, 1 H from C=CH_2 **minor**), 5.98 (br. s, 1 H, NH **minor**), 6.22 - 6.29 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 6.57 - 6.63 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 7.17 (d, *J* = 7.0 Hz, 1 H, ArCH **major**), 7.19 - 7.26 (m, 3 H, 2 x ArCH **major** + ArCH **minor**), 7.27 - 7.31 (m, 2 H, ArCH **minor**), 7.61 (d, *J* = 6.9 Hz, 2 H, ArCH **major**), 7.83 (d, *J* = 7.3 Hz, 2 H, ArCH **minor**); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm -5.3 (Si(CH_3)$_2$ **minor**), -5.3 (Si(CH_3)$_2$ **major**), 13.8 (CO_2CH_2*C*H_3 **minor**), 14.0 (CO_2CH_2*C*H_3 **major**), 18.3 (Si*C*(CH_3)$_3$ **minor**), 18.4 (Si*C*(CH_3)$_3$ **major**), 24.0 (*C*$H_2CH_2CH_2$OTBS **minor**), 24.3 (OC(*C*H_3)$_2$ **major**), 24.4 (OC(*C*H_3)$_2$ **minor**), 24.7 (*C*$H_2CH_2CH_2$OTBS **major**), 25.1 (OC(*C*H_3)$_2$ **minor**), 25.1 (OC(*C*H_3)$_2$ **major**), 25.9 (SiC(*C*H_3)$_3$ **minor**), 26.0 (SiC(*C*H_3)$_3$ **major**), 28.5 (*C*H_2CHC=CH_2 **major** + *C*H_2CHC=CH_2 **minor**), 32.3 (*C*H_2CH_2OTBS **minor**), 32.7 (*C*H_2CH_2OTBS **major**), 55.6 (OCH_3 **major** + OCH_3 **minor**), 59.8 (*C*HC=CH_2 **major** + *C*HC=CH_2 **minor**), 60.3 (CO_2*C*H_2CH_3 **minor**), 61.0 (CO_2*C*H_2CH_3 **major**), 63.0 (CH_2OTBS **minor**), 63.2 (CH_2OTBS **major**), 71.3 (*C*$CO_2CH_2CH_3$ **major**), 71.6 (*C*$CO_2CH_2CH_3$ **minor**), 83.6 (O*C*(CH_3)$_2$ **major**), 83.9 (O*C*(CH_3)$_2$ **minor**), 113.7 (PMP ArCH **major**), 113.8 (PMP ArCH **minor**), 115.5 (PMP ArCH **minor**), 115.8 (PMP ArCH **major**), 126.7 (ArCH **major**), 126.8 (ArCH **minor**), 127.2 (ArCH **minor**), 127.4 (ArCH **major**), 128.6 (ArCH **major**), 129.5 (ArCH **minor**), 134.7 (C=*C*H_2 **minor**), 136.4 (C=*C*H_2 **major**), 139.2 (ArC **major** + ArC **minor**), 140.8 (ArC **major**), 141.6 (ArC **minor**), 151.1 (ArC **major**), 151.3 (ArC **minor**), 173.6 (C=O **minor**), 173.7 (C=O **major**); (B*C*=CH_2 **major** and B*C*=CH_2 **minor** not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 27.4.

***rac*-Ethyl (2*S*,3*S*)-7-bromo-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3t)**

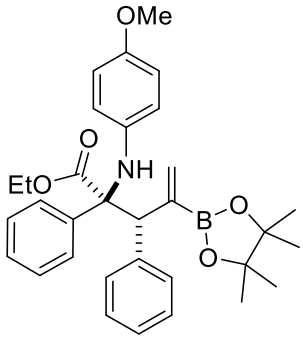


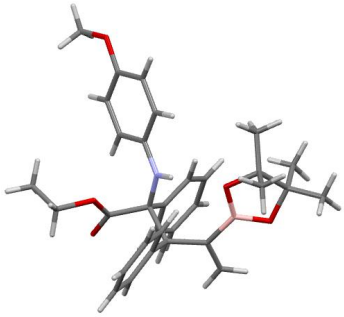
Prepared according to General Procedure B on a 0.250 mmol scale (63:37 d.r. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (66%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^+) *m/z*: 624 ($[M+K]^+$). HRMS calcd for $C_{30}H_{41}NBO_5BrK$: 624.1893. Found: 624.1885; ν_{max} (thin film/cm^{-1}): 3380, 2978, 2934, 2832, 2352, 2328, 1726, 1603, 1511, 1463, 1444, 1380, 1365, 1339, 1304, 1237, 1200, 1181, 1141, 1076, 1033; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.92 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 0.95 - 1.02 (m, 1 H, C*H*$_2CH_2CH_2$Br), 1.12 - 1.19 (m, 1 H, C*H*$_2$CHC=CH_2), 1.21 - 1.27 (m, 1 H, C*H*$_2CH_2CH_2$Br), 1.34 (s, 6 H, 2 x CH_3), 1.39 (s, 6 H, 2 x CH_3), 1.52 - 1.57 (m, 1 H, C*H*$_2CH_2$Br), 1.67 (dq, *J* =

14.1, 7.1 Hz, 1 H, CH_2CH$_2$Br), 1.75 - 1.87 (m, 1 H, CH_2CHC=CH$_2$), 2.75 (d, *J* = 11.3 Hz, 1 H, C*H*C=CH$_2$), 3.18 (td, *J* = 6.8, 2.1 Hz, 2 H, CH$_2$Br), 3.68 (s, 3 H, OCH$_3$), 3.82 - 3.89 (m, 1 H, CO$_2$CH_2CH$_3$), 3.91 - 4.02 (m, 1 H, CO$_2$CH_2CH$_3$), 5.56 (s, 1 H, C=CH$_2$), 5.97 (d, *J* = 3.3 Hz, 2 H, C=CH$_2$ + NH), 6.27 (d, *J* = 8.8 Hz, 2 H, ArCH), 6.61 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.21 - 7.27 (m, 1 H, ArCH), 7.28 - 7.34 (m, 2 H, ArCH), 7.84 (d, *J* = 7.5 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, CDCl$_3$) δ ppm 13.8 (CO$_2$CH$_2$*C*H$_3$), 24.5 (CH$_3$), 25.1 (CH$_3$), 25.8 (*C*H$_2$CHC=CH$_2$), 26.3 (*C*H$_2$CH$_2$CH$_2$Br), 32.1 (*C*H$_2$CH$_2$Br), 33.5 (CH$_2$Br), 55.6 (OCH$_3$), 60.3 (CO$_2$*C*H$_2$CH$_3$), 71.5 (*C*CO$_2$CH$_2$CH$_3$), 84.0 (O*C*(CH$_3$)$_2$), 113.8 (ArCH), 115.6 (ArCH), 126.9 (ArCH), 127.3 (ArCH), 129.4 (ArCH), 135.0 (C=*C*H$_2$), 138.8 (ArC), 141.4 (ArC), 151.4 (ArC), 173.6 (C=O), (*C*HC=CH$_2$ and B*C*=CH$_2$ not observed); ^{11}B NMR (128 MHz, CDCl$_3$) δ ppm 33.2.

rac-Ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3u)



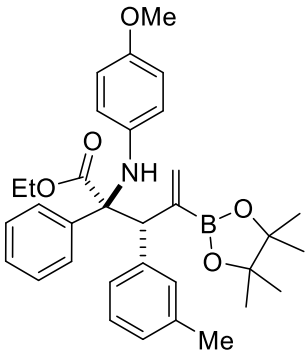


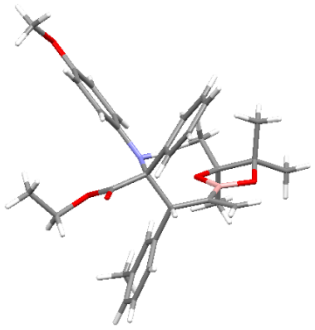
Prepared according to General Procedure B on a 0.250 mmol scale (92:8 d.r. of crude material). Column chromatography (5 - 10% Et$_2$O in hexane + 1% NEt$_3$) afforded the title compound as a yellow solid. The yield (75%) was determined by ^{1}H NMR analysis using MeNO$_2$ as an internal standard.

M.p.: 135-137 °C (CHCl$_3$); MS (ES$^-$) *m/z*: 526 (M-H$^-$). HRMS calcd for $C_{32}H_{38}BNO_5Na$: 550.2735. Found: 550.2726; ν_{max} (thin film/cm^{-1}): 3410, 2976, 1722, 1601, 1511, 1463, 1446, 1380, 1360, 1307, 1238, 1168, 1139, 1034; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 0.82 (t, *J* = 7.2 Hz, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.14 (s, 6 H, 2 x CH$_3$), 1.23 (s, 6 H, 2 x CH$_3$), 3.69 (s, 3 H, OCH$_3$), 3.82 (dq, *J* = 10.7, 7.1 Hz, 1 H, CO$_2$CH_2CH$_3$), 3.95 (dq, *J* = 10.8, 7.1 Hz, 1 H, CO$_2$CH_2CH$_3$), 4.32 (s, 1 H, C*H*C=CH$_2$), 5.18 (d, *J* = 2.8 Hz, 1 H, C=CH$_2$), 5.71 (d, *J* = 3.0 Hz, 1 H, C=CH$_2$), 6.15 (br. s, 1 H, NH), 6.31 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.61 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.15 - 7.22 (m, 2 H, ArCH), 7.22 - 7.26 (m, 4 H, ArCH), 7.52 (d, *J* = 7.3 Hz, 2 H, ArCH), 7.67 (d, *J* = 7.0 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, CDCl$_3$) δ ppm 13.5 (CO$_2$CH$_2$*C*H$_3$), 24.3 (CH$_3$), 24.8 (CH$_3$), 55.7 (OCH$_3$), 60.9 (CO$_2$*C*H$_2$CH$_3$), 64.7 (*C*HC=CH$_2$), 70.7 (*C*CO$_2$CH$_2$CH$_3$), 84.0 (O*C*(CH$_3$)$_2$), 113.7 (ArCH), 116.0 (ArCH), 126.5 (ArCH), 127.0 (ArCH), 127.5 (ArCH), 127.9 (ArCH), 128.8 (ArCH), 129.3 (ArCH), 135.3 (C=*C*H$_2$), 138.9 (ArC), 140.5 (ArC), 140.5 (ArC), 151.1 (ArC), 172.9 (C=O), (B*C*=CH$_2$ not observed); ^{11}B NMR (128 MHz, CDCl$_3$) δ ppm 29.7.

3u was further characterized by X-ray crystallographic analysis.

***rac*-Ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate (3v)**





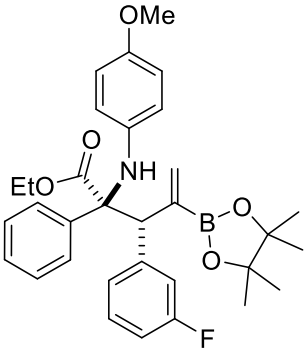
Prepared according to General Procedure B on a 0.250 mmol scale (78:22 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a white solid (571 mg, 0.105 mmol, 43%).

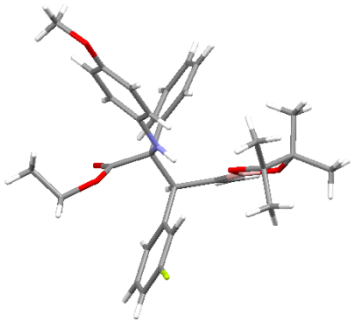
M.p.: 127-130 °C (Et_2O); MS (ES^+) *m/z*: 564 ($[M+Na]^+$). HRMS calcd for $C_{33}H_{41}NBO_5Na$: 542.3072. Found: 542.3062; ν_{max} (thin film/cm^{-1}): 3410, 3055, 2977, 2930, 2830, 1721, 1605, 1510, 1305, 1236, 1138, 1037; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.84 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$ **major**), 1.05 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$ **minor**), 1.18 (s, 6 H, 2 x CH_3 **major**), 1.25 (s, 6 H, 2 x CH_3 **major**), 1.34 (s, 6 H, 2 x CH_3 **minor**), 1.37 (s, 6 H, 2 x CH_3 **minor**), 2.16 (s, 3 H, $ArCCH_3$ **minor**), 2.32 (s, 3 H, $ArCCH_3$ **major**), 3.67 (s, 3 H, OCH_3 **minor**), 3.69 (s, 3 H, OCH_3 **major**), 3.78 – 3.87 (m, 1 H, $CO_2CH_2CH_3$ **major**), 3.91 – 3.98 (m, 1 H, $CO_2CH_2CH_3$ **major**), 3.98 – 4.04 (m, 1 H, $CO_2CH_2CH_3$ **minor**), 4.08 – 4.15 (m, 1 H, $CO_2CH_2CH_3$ **minor**), 4.16 (s, 1 H, $CHC=CH_2$ **minor**), 4.29 (s, 1 H, $CHC=CH_2$ **major**), 5.20 (apparent s, 1 H, $C=CH_2$ **major**), 5.71 (d, *J* = 2.9 Hz, 1 H, $C=CH_2$ **major**), 5.87 (d, *J* = 2.7 Hz, 1 H, $C=CH_2$ **minor**), 6.02 (d, *J* = 2.7 Hz, 1 H, $C=CH_2$ **minor**), 6.14 (br. s, 1 H, NH **major**), 6.28 – 6.34 (m, 5 H, 2 H from ArCH **major** + 2 H from ArCH **minor** + NH **minor**), 6.57 – 6.64 (m, 4 H, 2 H from ArCH **major** + 2 H from ArCH **minor**), 6.83 – 6.91 (m, 3 H, ArCH **minor**), 6.91 – 6.96 (m, 1 H, ArCH **minor**), 7.01 (d, *J* = 7.5 Hz, 1 H, ArCH **major**), 7.12 – 7.19 (m, 2 H, ArCH **major**), 7.20 – 7.32 (m, 6 H, 3 H from ArCH **major** + 3 H from ArCH **minor**), 7.39 (d, *J* = 7.5 Hz, 1 H, ArCH **major**), 7.63 (apparent s, 2 H, ArCH **minor**), 7.69 (d, *J* = 7.8 Hz, 2 H, ArCH **major**); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.6 ($CO_2CH_2CH_3$ **major**), 14.1 ($CO_2CH_2CH_3$ **minor**), 21.4 ($ArCCH_3$ **minor**), 21.6 ($ArCCH_3$ **major**), 24.5 (CH_3 **major**), 24.8 (CH_3 **minor**), 24.9 (CH_3 **minor**), 25.0 (CH_3 **major**), 55.7 (OCH_3 **minor**), 55.8 (OCH_3 **major**), 60.8 ($CO_2CH_2CH_3$ **minor**), 60.9 ($CO_2CH_2CH_3$ **major**), 65.0 ($CHC=CH_2$ **major**), 66.4 ($CHC=CH_2$ **minor**), 70.9 ($CCO_2CH_2CH_3$ **major**), 71.5 ($CCO_2CH_2CH_3$ **minor**), 84.1 ($OC(CH_3)_2$ **major**), 84.3 ($OC(CH_3)_2$ **minor**), 113.8 (ArCH **major** + ArCH **minor**), 116.1 (ArCH **major**), 116.2 (ArCH **minor**), 126.4 (ArCH **major**), 126.9 (ArCH **minor**), 127.1 (ArCH **major**), 127.2

(ArCH **minor**), 127.2 (ArCH **minor**), 127.2 (ArCH **minor**), 127.3 (ArCH **minor**), 127.4 (ArCH **major**), 127.6 (ArCH **major**), 128.0 (ArCH **major**), 129.0 (ArCH **major**), 129.3 (ArCH **minor**), 130.4 (ArCH **major**), 131.2 (ArCH **minor**), 134.8 (C=*C*H_2 **minor**), 135.4 (C=*C*H_2 **major**), 136.7 (ArC **minor**), 137.4 (ArC **major**), 138.8 (2 x ArC **minor**), 139.1 (ArC **major**), 140.5 (ArC **major**), 140.7 (ArC **major**), 141.3 (ArC **minor**), 151.2 (ArC **major**), 151.5 (ArC **minor**), 173.1 (C=O **major**), 173.5 (C=O **minor**), (B*C*=CH_2 **major** and B*C*=CH_2 **minor** not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 30.5.

3v was further characterized by X-ray crystallographic analysis.

***rac*-Ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3w)**



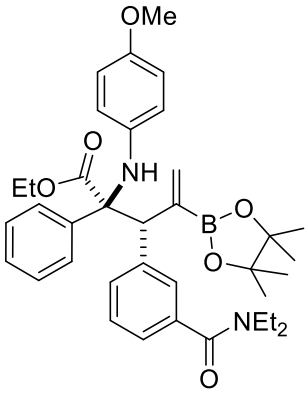


Prepared according to General Procedure B on a 0.250 mmol scale (86:14 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a white solid (50.7 mg, 0.093 mmol, 37%).

M.p.: 126-128 °C (Et_2O); MS (ES^+) *m/z*: 584 ($[M+K]^+$). HRMS calcd for $C_{32}H_{38}NBO_5F$: 546.2822. Found: 546.2811; ν_{max} (thin film/cm^{-1}): 3405, 3060, 2978, 2937, 2832, 1720, 1510, 1309, 1236, 1138, 1036; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.87 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.15 (s, 6 H, 2 x CH_3), 1.24 (s, 6 H, 2 x CH_3), 3.68 (s, 3 H, OCH_3), 3.87 (dq, *J* = 10.6, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 3.98 (dq, *J* = 10.7, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.29 (s, 1 H, C*H*C=CH_2), 5.14 (d, *J* = 2.9 Hz, 1 H, C=CH_2), 5.72 (d, *J* = 2.9 Hz, 1 H, C=CH_2), 6.13 (br. s, 1 H, NH), 6.30 (d, *J* = 8.5 Hz, 2 H, ArCH), 6.60 (d, *J* = 8.6 Hz, 2 H, ArCH), 6.88 (t, *J* = 8.0 Hz, 1 H, ArCH), 7.16 – 7.28 (m, 5 H, ArCH), 7.36 (d, *J* = 10.7 Hz, 1 H, ArCH), 7.63 (d, *J* = 7.5 Hz, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.7 ($CO_2CH_2CH_3$), 24.4 (CH_3), 25.0 (CH_3), 55.8 (OCH_3), 61.2 ($CO_2CH_2CH_3$), 64.6 (*C*HC=CH_2), 70.8 (*C*$CO_2CH_2CH_3$), 84.3 (O*C*$(CH_3)_2$), 113.5 (d, *J* = 21.0 Hz, ArCH), 113.9 (ArCH), 116.2 (ArCH), 116.5 (d, *J* = 22.4 Hz, ArCH), 125.4 (d, *J* = 2.8 Hz, ArCH), 127.3 (ArCH), 127.8 (ArCH), 128.9 (ArCH), 129.4 (d, *J* = 8.3 Hz, ArCH), 136.2 (C=*C*H_2), 138.7 (ArC), 140.4 (ArC), 143.4 (d, *J* = 7.2 Hz, ArC), 151.4 (ArC), 162.6 (d, *J* = 244.5 Hz, ArC), 172.9 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 30.0; ^{19}F NMR (471 MHz) δ ppm -113.65 (ddd, *J* = 10.7, 8.5, 6.1 Hz).

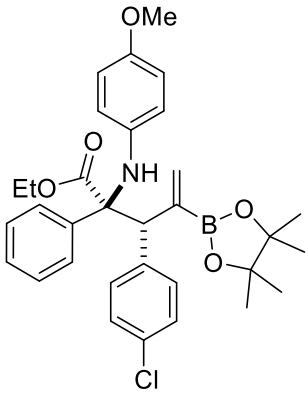
3w was further characterized by X-ray crystallographic analysis.

***rac*-Ethyl (2*S*,3*R*)-3-(3-(diethylcarbamoyl)phenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3x)**



Prepared according to General Procedure B on a 0.250 mmol scale (85:15 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (61%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard.
MS (ES^+) *m/z*: 649 ($[M+Na]^+$). HRMS calcd for $C_{37}H_{47}N_2BO_6Na$: 649.3419. Found: 649.3408; ν_{max} (thin film/cm^{-1}): 3410, 3061, 2977, 2933, 2831, 2241, 1721, 1622, 1510, 1307, 1236, 1137, 1033; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.84 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.08 (br. s, 3 H, NCH_2CH_3), 1.16 (s, 6 H, 2 x CH_3), 1.23 (s, 9 H, 2 x CH_3 + 3 H from NCH_2CH_3), 3.23 (br. s, 2 H, NCH_2CH_3), 3.52 (br. s, 2 H, NCH_2CH_3), 3.67 (s, 3 H, OCH_3), 3.81 (dq, *J* = 10.5, 7.2 Hz, 1 H, $CO_2CH_2CH_3$), 3.95 (dq, *J* = 10.5, 7.2 Hz, 1 H, $CO_2CH_2CH_3$), 4.32 (s, 1 H, $CHC=CH_2$), 5.21 (d, *J* = 2.9 Hz, 1 H, $C=CH_2$), 5.73 (d, *J* = 2.9 Hz, 1 H, $C=CH_2$), 6.12 (s, 1 H, NH), 6.25 – 6.32 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.59 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.16 – 7.32 (m, 5 H, ArCH), 7.50 (s, 1 H, ArCH), 7.58 (d, *J* = 7.8 Hz, 1 H, ArCH), 7.64 (d, *J* = 7.0 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.2 (NCH_2CH_3), 13.7 ($CO_2CH_2CH_3$), 14.5 (NCH_2CH_3), 24.5 (CH_3), 25.0 (CH_3), 39.4 (NCH_2CH_3), 43.5 (NCH_2CH_3), 55.8 (OCH_3), 61.1 ($CO_2CH_2CH_3$), 64.9 ($CH=CH_2$), 70.9 ($CCO_2CH_2CH_3$), 84.3 ($OC(CH_3)_2$), 113.9 (ArCH), 116.2 (ArCH), 124.9 (ArCH), 127.2 (ArCH), 127.7 (ArCH), 127.7 (ArCH), 128.2 (ArCH), 128.9 (ArCH), 130.3 (ArCH), 136.2 ($C=CH_2$), 137.1 (ArC), 139.0 (ArC), 140.5 (ArC), 140.8 (ArC), 151.4 (ArC), 171.3 (NC=O), 172.9 (OC=O), ($BC=CH_2$ not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 30.0.

***rac*-Ethyl (2*S*,3*R*)-3-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate 3y**

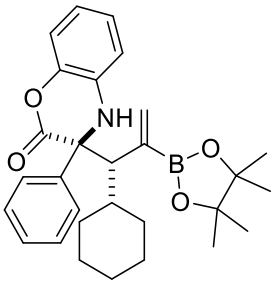


Prepared according to General Procedure B on a 0.250 mmol scale (80:20 d.r. of crude material). Column chromatography (10% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum (43 mg, 0.076 mmol, 30%).

MS (ES^-) *m/z*: 584 ($[M+Na]^+$). HRMS calcd for $C_{32}H_{38}NBO_5Cl$: 562.2526. Found: 562.2518; ν_{max} (thin film/cm^{-1}): 3410, 2977, 2931, 2830, 1721, 1510, 1309, 1237, 1138, 1037; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.91 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.18 (s, 6 H, 2 x CH_3), 1.27 (s, 6 H, 2 x CH_3), 3.71 (s, 3 H, OCH_3), 3.90 (dq, *J* = 10.7, 7.1 Hz, 1 H, $CO_2CH_2CH_3$), 4.02 (dq, *J* = 10.7, 7.1, 6.5 Hz, 1 H, $CO_2CH_2CH_3$), 4.32 (s, 1 H, $CHC=CH_2$), 5.19 (d, *J* = 2.9 Hz, 1 H, $C=CH_2$), 5.76 (d, *J* = 2.9 Hz, 1 H, $C=CH_2$), 6.13 (s, 1 H, NH), 6.32 (d, *J* = 9.1 Hz, 2 H, ArCH), 6.64 (d, *J* = 9.1 Hz, 2 H, ArCH), 7.21 – 7.32 (m, 5 H), 7.50 (d, *J* = 8.5 Hz, 2 H, ArCH), 7.64 (d, *J* = 7.1 Hz, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.7 ($CO_2CH_2CH_3$), 24.4 (CH_3), 25.0 (CH_3), 55.8 (OCH_3), 61.2 ($CO_2CH_2CH_3$), 64.2 ($CHC=CH_2$), 70.8 ($CCO_2CH_2CH_3$), 84.3 ($OC(CH_3)_2$), 113.9 (ArCH), 116.3 (ArCH), 127.3 (ArCH), 127.8 (ArCH), 128.1 (ArCH), 128.9 (ArCH), 131.0 (ArCH), 132.5 (ArC), 136.0 ($C=CH_2$), 138.8 (ArC), 139.3 (ArC), 140.3 (ArC), 151.4 (ArC), 172.9 (C=O), ($BC=CH_2$ not observed); ^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 30.1.

Use of Cyclic Ketimines

rac-(_S_)-3-((_S_)-1-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-3-phenyl-3,4-dihydro-2H-benzo[_b_][1,4]oxazin-2-one (3z)



Prepared according to General Procedure B on a 0.250 mmol scale (>95:5 d.r. of crude material). Column chromatography (3 - 8% Et_2O in hexane + 1% NEt_3) afforded the title compound as a colourless oil (13 mg, 0.027 mmol, 11%).

MS (ES^-) *m/z*: 472 ($[M-H]^-$). HRMS calcd for $C_{29}H_{36}NBO_4$: 473.2732. Found: 473.2725; ν_{max} (thin film/cm^{-1}): 3335, 2976, 2924, 2851, 1760, 1620, 1600, 1503, 1446, 1424, 1391, 1381, 1372, 1334, 1306, 1275, 1220, 1211, 1186, 1168, 1140, 1112, 1077, 1029; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (t, *J* = 11.5 Hz, 1 H, CH_2), 1.10 - 1.23 (m, 4 H, CH_2), 1.30 (s, 6 H, 2 x CH_3), 1.39 (s, 6 H, 2 x CH_3), 1.62 (d, *J* = 7.0 Hz, 1 H, CH_2), 1.66 - 1.74 (m, 3 H, CH_2), 1.77 - 1.89 (m, 1 H, C*H*CHC=CH_2), 1.99 (d, *J* = 11.5 Hz, 1 H, CH_2), 3.40 (d, *J* = 8.0 Hz, 1 H, C*H*C=CH_2), 5.24 (d, *J* = 3.3 Hz, 1 H, C=CH_2), 5.59 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 6.67 (t, *J* = 8.0 Hz, 1 H, ArCH), 6.78 - 6.86 (m, 2 H, ArCH), 7.00 (t, *J* = 7.3 Hz, 1 H, ArCH), 7.06 - 7.12 (m, 2 H, ArCH + NH), 7.16 (t, *J* = 7.5 Hz, 2 H, ArCH), 7.19 - 7.25 (m, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.3 (CH_3), 25.0 (CH_3), 26.3 (CH_2), 26.9 (2 x CH_2), 32.3 (CH_2), 32.7 (CH_2), 38.7 (*C*HCHC=CH_2), 61.0 (*C*HC=CH_2), 66.5 (*C*CO_2), 84.1 (O*C*(CH_3)$_2$), 113.9 (ArCH), 116.4 (ArCH), 118.3 (ArCH), 124.9 (ArCH), 126.6 (ArCH), 127.3 (ArCH), 128.3 (ArCH), 133.4 (ArC), 137.3 (C=*C*H_2), 139.3 (ArC), 140.0 (ArC), 167.5 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 30.3.

Unsuccessful couplings using cyclic ketimines

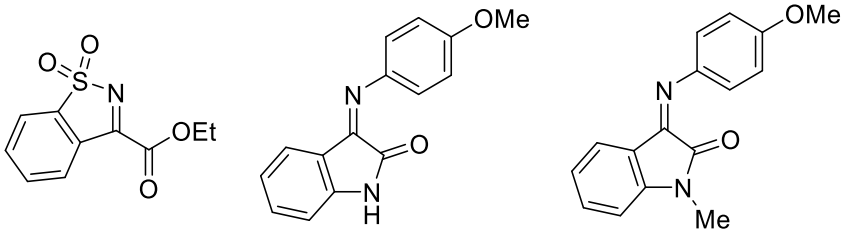
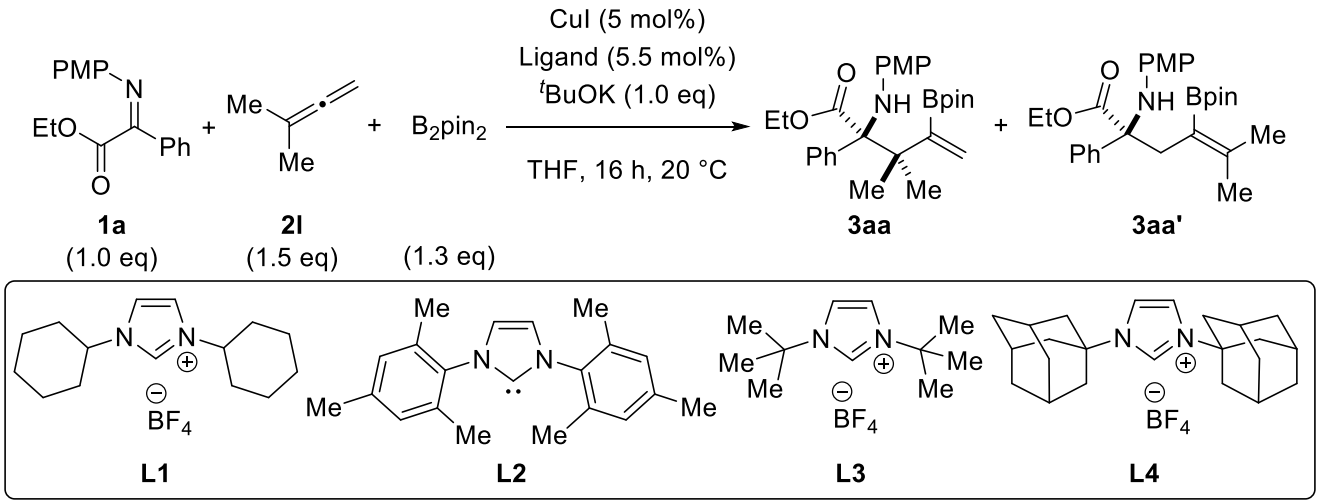


Figure S1: Additional cyclic ketimine substrates whose use in the three-component coupling was investigated

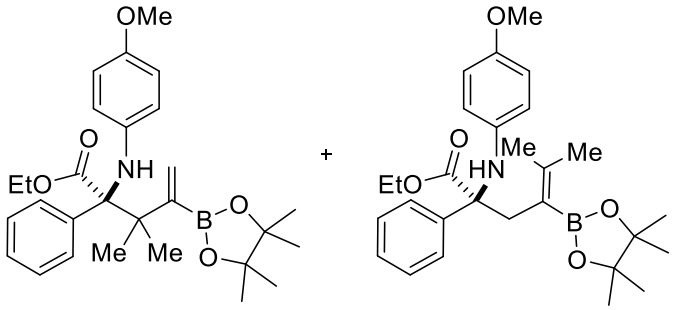
Use of 1,1-Disubstituted Allene



Entry	Ligand	Buried volume (%)[17]	NMR yield (%)	*rs* (3aa:3aa')
1	**L1**	27.5	14	62:38
2	**L2**	36.5	16	68:32
3	**L3**	39.6	2	50:50
4	**L4**	39.8	6	57:43

Table S4: Additional Ligand Screening

***rac*-Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3aa) and *rac*-Ethyl 2-((4-methoxyphenyl)amino)-5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (3aa')**



3aa
minor

3aa'
major

Prepared according to General Procedure B on a 0.250 mmol scale (17:83 r.s. of crude material). Column chromatography (5% Et_2O in hexane + 1% NEt_3) afforded the title compound as a yellow gum. The yield (73%) was determined by ^1H NMR analysis using $MeNO_2$ as an internal standard.

MS (ES^-) *m/z*: 478 ($[M-H]^-$). HRMS calcd for $C_{28}H_{38}NBO_5K$: 518.2475. Found: 518.2475; ν_{max} (thin film/cm^{-1}): 3379, 2978, 2932, 1726, 1620, 1511, 1445, 1372, 1353, 1292, 1237, 1218, 1175, 1145, 1110, 1075, 1039; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.93 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$ **minor**), 1.00 (t, *J* = 7.2 Hz, 3 H $CO_2CH_2CH_3$ **major**), 1.17 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.19 (s, 6 H, $OC(CH_3)_2$ **minor**), 1.20 (s, 6 H, $OC(CH_3)_2$ **major**), 1.26 (s, 6 H, $OC(CH_3)_2$ **major**), 1.36 (s, 6 H, $C(CH_3)_2C=CH_2$ **minor**), 1.37 (s, 3 H, $C=C(CH_3)_2$ **major**), 1.89 (s, 3 H, $C=C(CH_3)_2$ **major**), 3.00 (d, *J* = 13.8 Hz, 1 H, $CH_2C=C(CH_3)_2$ **major**), 3.26 (d, *J* = 13.8 Hz, 1 H, $CH_2C=C(CH_3)_2$ **major**), 3.65 (s, 3 H, OCH_3 **minor**), 3.66 (s, 3 H, OCH_3 **major**), 3.78 - 3.91 (m, 1 H, $CO_2CH_2CH_3$ **minor**), 3.92 - 4.01 (m, 1 H, $CO_2CH_2CH_3$ **minor**), 4.06 (m, *J* = 1.0 Hz, 2 H, $CO_2CH_2CH_3$ **major**), 5.26 (br. s, 1 H, NH **major**), 5.52 (d, *J* = 1.8 Hz, 1 H, $C=CH_2$ **minor**), 5.95 (d, *J* = 2.3 Hz, 1 H, $C=CH_2$ **minor**), 6.13 (s, 1 H, NH **minor**), 6.14 - 6.19 (m, 2 H, ArCH **minor**), 6.37 (d, *J* = 9.0 Hz, 2 H, ArCH **major**), 6.53 (d, *J* = 9.0 Hz, 2 H, ArCH **minor**), 6.57 (d, *J* = 9.0 Hz, 2 H, ArCH **major**), 7.16 - 7.23 (m, 2 H, ArCH **major** + ArCH **minor**), 7.23 - 7.27 (m, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**), 7.54 (d, *J* = 7.0 Hz, 4 H, 2 x ArCH **major** + 2 x ArCH **minor**); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.7 ($CO_2CH_2CH_3$ **minor**), 13.8 ($CO_2CH_2CH_3$ **major**), 21.4 ($C=C(CH_3)_2$ **major**), 23.6 ($OC(CH_3)_2$ **minor**), 24.6 ($C=C(CH_3)_2$

major), 25.0 (OC(CH$_3$)$_2$ **major**), 25.1 (OC(CH$_3$)$_2$ **major**), 25.8 (OC(CH$_3$)$_2$ **minor**), 41.6 (CH$_2$C=C(CH$_3$)$_2$ **major**), 46.1 (C(CH$_3$)$_2$C=CH$_2$ **minor**), 55.5 (OCH$_3$ **major** + OCH$_3$ **minor**), 60.0 (CO$_2$$CH_2CH_3$ **minor**), 61.1 (CO$_2$$CH_2CH_3$ **major**), 68.7 (CCO$_2$CH$_2$CH$_3$ **major**), 72.8 (CCO$_2$CH$_2$CH$_3$ **minor**), 83.0 (OC(CH$_3$)$_2$ **major**), 83.9 (OC(CH$_3$)$_2$ **minor**), 113.7 (ArCH **minor**), 113.8 (ArCH **major**), 115.6 (ArCH **minor**), 117.1 (ArCH **major**), 123.8 (ArCH **minor**), 126.8 (ArCH **major**), 127.1 (ArCH **minor**), 127.7 (ArCH **major**), 128.0 (ArCH **major**), 130.1 (ArCH **minor**), 131.4 (C=CH$_2$ **minor**), 137.8 (ArC **minor**), 140.2 (ArC **major**), 140.3 (ArC **major**), 141.5 (ArC **minor**), 150.7 (C=C(CH$_3$)$_2$ **major**), 151.1 (ArC **minor**), 151.9 (ArC **major**), 172.9 (C=O **minor**), 174.1 (C=O **major**), (BC=C(CH$_3$)$_2$ **major** and BC=CH$_2$ **minor** not observed); ^{11}B NMR (128 MHz, CDCl$_3$) δ ppm 30.5.

Alternative procedure for the synthesis of *rac*-ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3aa) and *rac*-Ethyl 2-((4-methoxyphenyl)amino)-5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (3aa') using (β-ICyD)-CuCl

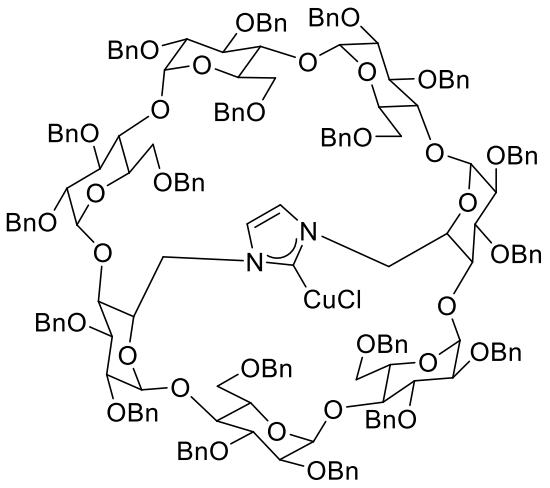
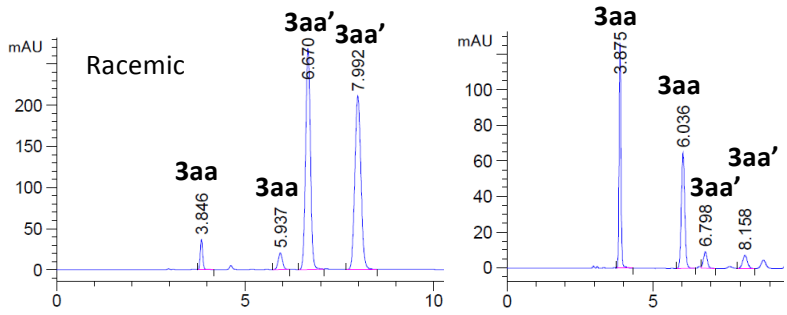


Figure S2: Structure of (β-ICyD)-CuCl

To a solution of (β-ICyD)-CuCl (14.9 mg, 0.005 mmol, 5 mol%) in THF (0.4 mL) at room temperature under N_2, was added *t*-BuOK (0.1 mL of a 1 M THF solution, 0.100 mmol, 1.0 equiv), and the reaction was stirred for 25 minutes at room temperature. B_2pin_2 (1.3 equiv) in THF (0.4 mL) was then added and the resulting mixture stirred for 40 minutes. 3-Methylbuta-1,2-diene (14.7 µL, 0.150 mmol, 1.5 equiv) and a solution of ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-phenylacetate (28.3 mg, 0.100 mmol, 1.0 equiv) in THF (0.5 mL) were then added dropwise simultaneously at room temperature. The reaction mixture was then heated to 60 °C. The reaction mixture was stirred at 60 °C for 24 hours then filtered through a Celite plug, concentrated *in vacuo* to afford the crude product mixture (87:13

r.s. of crude material). The yield (43%) was determined by ^{1}H NMR analysis using $MeNO_2$ as an internal standard. A sample was taken and purified by column chromatography (5% Et_2O in hexane).

Enantiomeric purities of **3aa** and **3aa'** were determined by HPLC analysis in comparison with authentic racemic material (52:48 e.r. and 51:49 e.r. respectively shown; Lux 5 µm Amylose-1 column, 98:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 230 nm).

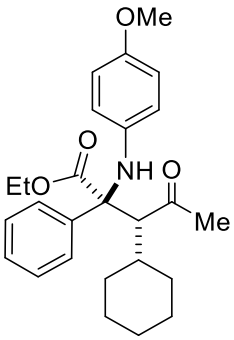


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.846	BB	0.0703	164.59941	36.72825	3.2767
2	5.937	BB	0.1255	164.51022	20.53767	3.2749
3	6.670	BB	0.1360	2349.33740	268.72800	46.7687
4	7.992	BB	0.1719	2344.86426	210.62708	46.6797

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.875	BB	0.0707	572.89362	126.85855	44.9694
2	6.036	BB	0.1274	532.00476	65.02781	41.7598
3	6.798	VB	0.1408	85.52240	9.33983	6.7131
4	8.158	BB	0.1758	83.54187	7.39510	6.5576

Derivatisations of 3a

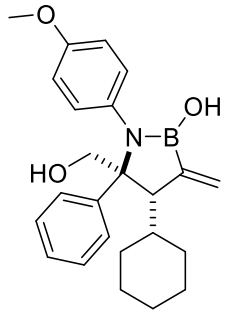
***rac*-Ethyl (2*S*,3*R*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-oxo-2-phenylpentanoate (4)**



To a solution of *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (40.0 mg, 0.075 mmol, 1.0 equiv, >95:5 d.r.) in THF (0.38 mL) at 0 °C, were added H_2O_2 (0.04 mL of a 30% w:w aqueous solution, 0.375 mmol, 5.0 equiv) and NaOH (0.19 mL of a 2 M aqueous solution, 0.375 mmol, 5.0 equiv). The reaction mixture was stirred at 0 °C for 30 minutes then extracted with Et_2O (3 x 1 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product mixture (>95:5 d.r.) was purified by column chromatography (8% Et_2O in hexane) to afford the title compound as a yellow gum (32.1 mg, 0.075 mmol, 99%).

MS (ES^+) *m/z*: 462 ($[M+H]^+$). HRMS calcd for $C_{26}H_{33}NO_4Na$: 446.2302. Found: 446.2303; ν_{max} (thin film/cm^{-1}): 3387, 2928, 2851, 1703, 1511, 1446, 1355, 1298, 1240, 1179, 1131, 1036; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 1.04 - 1.17 (m, 4 H, CH_2), 1.19 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.23 - 1.30 (m, 1 H, CH_2), 1.50 (s, 3 H, $C(O)CH_3$), 1.60 - 1.66 (m, 1 H, CH_2), 1.67 - 1.76 (m, 2 H, CH_2), 1.80 (t, *J* = 11.9 Hz, 2 H, CH_2), 1.91 - 2.01 (m, 1 H, $CHCHC(O)CH_3$), 3.49 (d, *J* = 6.3 Hz, 1 H, $CHC(O)CH_3$), 3.69 (s, 3 H, OCH_3), 4.22 (m, 2 H, $CO_2CH_2CH_3$), 5.40 (br. s, 1 H, NH), 6.31 (d, *J* = 9.0 Hz, 2 H, ArCH), 6.61 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.21 - 7.26 (m, 3 H, ArCH), 7.57 (dd, *J* = 8.2, 1.4 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2CH_3$), 26.0 (CH_2), 26.5 (CH_2), 27.0 (CH_2), 30.9 (CH_2), 32.3 (CH_2), 35.2 ($C(O)CH_3$), 39.2 ($CHCHC(O)CH_3$), 55.6 (OCH_3), 61.6 ($CO_2CH_2CH_3$), 65.7 ($CHC(O)CH_3$), 68.4 ($CCO_2CH_2CH_3$), 113.7 (ArCH), 117.0 (ArCH), 127.4 (ArCH), 128.2 (ArCH), 128.5 (ArCH), 137.7 (ArC), 139.3 (ArC), 151.7 (ArC), 172.3 ($CO_2CH_2CH_3$), 212.2 ($C(O)CH_3$).

rac-(4*S*,5*S*)-4-Cyclohexyl-5-(hydroxymethyl)-1-(4-methoxyphenyl)-3-methylene-5-phenyl-1,2-azaborolidin-2-ol (5)

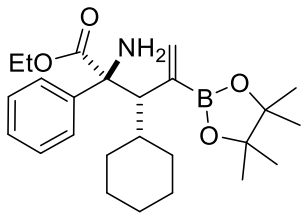


To a solution of lithium aluminium hydride (0.075 mL of a 1 M Et_2O solution, 0.075 mmol, 1.0 equiv) in THF (0.35 mL) at 0 °C, was added a solution of *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (40.0 mg, 0.075 mmol, 1.0 equiv, >95:5 d.r.) in THF (0.40 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 4 hours then NaOH (2 M aqueous solution, 0.2 mL) and H_2O (0.3 mL) were added dropwise at 0 °C. The reaction mixture was filtered, washed with Et_2O and concentrated *in vacuo*. The crude product mixture (>95:5 d.r.) was purified by column chromatography (30 - 70% Et_2O in hexane) to afford the title compound as a yellow gum (14.9 mg, 0.038 mmol, 51%).

MS ($APCI^-$) HRMS calcd for $C_{24}H_{29}NBO_3$: 390.2246. Found: 390.2258; ν_{max} (thin film/cm^{-1}): 3403, 2924, 2851, 1618, 1509, 1481, 1447, 1422, 1373, 1303, 1235, 1179, 1110, 1035; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 0.91 - 1.00 (m, 3 H, CH_2), 1.04 - 1.12 (m, 2 H, CH_2), 1.18 - 1.23 (m, 1 H, $CHCHC=CH_2$), 1.45 - 1.54 (m, 3 H, CH_2), 1.54 - 1.59 (m, 1 H, CH_2), 1.65 (d, *J* = 12.7 Hz, 1 H, CH_2), 2.25 (apparent s, 1 H, $CHC=CH_2$), 3.65 (s, 3 H, OCH_3), 3.80 (br. s, 1 H, OH), 4.06 (br. s, 1 H, OH), 4.57 (dd, *J* = 11.7, 2.0 Hz, 1 H, CH_2OH), 4.71 (d, *J* = 11.7 Hz, 1 H, CH_2OH), 5.71 (d, *J* = 3.2 Hz, 1 H, $C=CH_2$), 6.14 (d, *J* = 3.2 Hz, 1 H, $C=CH_2$), 6.20

(d, *J* = 9.0 Hz, 2 H, ArCH), 6.55 (d, *J* = 9.0 Hz, 2 H, ArCH), 7.30 (t, *J* = 7.3 Hz, 1 H, ArCH), 7.38 (t, *J* = 7.7 Hz, 2 H, ArCH), 7.45 (d, *J* = 7.3 Hz, 2 H, ArCH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 26.1 (CH_2), 26.6 (CH_2), 26.7 (CH_2), 29.8 (CH_2), 34.6 (CH_2), 37.2 (*C*HCHC=CH_2), 55.5 (OCH_3), 60.9 (*C*HC=CH_2), 62.0 (*C*CH_2OH), 62.8 (CH_2OH), 114.3 (ArCH), 118.0 (ArCH), 126.5 (ArCH), 127.1 (ArCH), 128.6 (ArCH), 130.8 (C=*C*H_2), 138.3 (ArC), 143.0 (ArC), 152.8 (ArC), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.6.

rac-Ethyl (2*S*,3*S*)-2-amino-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (6)

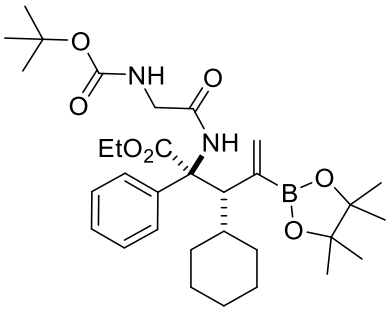


To a solution of *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (40.0 mg, 0.075 mmol, 1.0 equiv, >95:5 d.r.) in MeCN (0.5 mL) at -10 °C, was added a solution of $(NH_4)_2Ce(NO_3)_6$ (0.123 g, 0.225 mmol, 3.0 equiv) in H_2O (1.5 mL). The reaction mixture was stirred at -10 °C for 75 minutes then H_2O (1 mL) was added. The reaction mixture was then extracted with EtOAc (4 x 2 mL). The organic layers were combined, washed with saturated aqueous $NaHCO_3$ solution (2 mL), saturated aqueous Na_2SO_3 solution (2 mL), saturated aqueous $NaHCO_3$ solution (2 mL) and saturated brine solution (2 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was dissolved in MeCN (0.5 mL) at 20 °C and HCl (0.2 mL of a 1 M aqueous solution, 0.2 mmol, 2.7 equiv) was added. The reaction mixture was stirred at 20 °C for 15 minutes then concentrated *in vacuo*. Saturated aqueous Na_2CO_3 solution (1 mL) was added to the reaction mixture. The reaction mixture was then extracted with EtOAc (3 x 1 mL). The organic layers were combined, washed with saturated brine solution (1 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (30 - 100% Et_2O in hexane + 1% NEt_3) to afford the title compound as a yellow-orange gum (12.4 mg, 0.029 mmol, 39%, >95:5 d.r.).

MS (ES^+) *m/z*: 450 ($[M+Na]^+$). HRMS calcd for $C_{25}H_{38}NBO_4Na$: 450.2786. Found: 450.2778; ν_{max} (thin film/cm^{-1}): 3412, 2976, 2925, 2851, 1726, 1599, 1446, 1423, 1379, 1371, 1301, 1275, 1214, 1167, 1142, 1111, 1079, 1031; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.81 - 0.92 (m, 1 H, CH_2), 1.08 (dd, *J* = 12.7, 2.7 Hz, 1 H, CH_2), 1.11 - 1.16 (m, 1 H, CH_2), 1.18 (s, 6 H, 2 x CH_3), 1.21 (s, 6 H, 2 x CH_3), 1.24 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.27 - 1.31 (m, 1 H, CH_2), 1.57 - 1.64 (m, 1 H, CH_2), 1.64 - 1.73 (m, 3 H, CH_2), 1.73 - 1.85 (m, 3 H, 2 H from CH_2 + C*H*CHC=CH_2), 2.65 (br. s, 2 H, NH_2), 3.26 (d, *J* = 7.8 Hz, 1 H, C*H*C=CH_2), 4.06 - 4.16 (m, 1 H, $CO_2CH_2CH_3$), 4.16 - 4.26 (m, 1 H, $CO_2CH_2CH_3$), 5.34 (d, *J* = 3.2 Hz, 1 H, C=CH_2), 5.56

(d, *J* = 3.7 Hz, 1 H, C=CH_2), 7.15 (t, *J* = 7.3 Hz, 1 H, ArCH), 7.23 (t, *J* = 7.1 Hz, 2 H, ArCH), 7.48 (d, *J* = 7.3 Hz, 2 H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2\mathit{C}H_3$), 24.4 (CH_3), 24.7 (CH_3), 26.4 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 32.2 (CH_2), 32.6 (CH_2), 39.0 (*C*HCHC=CH_2), 59.5 (*C*HC=CH_2), 61.4 ($CO_2\mathit{C}H_2CH_3$), 66.7 (*C*$CO_2CH_2CH_3$), 83.0 (O*C*(CH_3)$_2$), 126.2 (ArCH), 126.7 (ArCH), 127.8 (ArCH), 133.3 (C=*C*H_2), 143.6 (ArC), 175.1 (C=O), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.9.

rac-Ethyl (2*S*,3*S*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (7)



To a solution of (*tert*-butoxycarbonyl)glycine (5.3 mg, 0.0304 mmol, 1.0 equiv) and *N*-methylmorpholine (3.5 µL, 0.0319 mmol, 1.05 equiv) in THF (0.5 mL) at -15 °C, was added isobutyl chloroformate (4.0 µL, 0.0304 mmol, 1.0 equiv). The reaction mixture was stirred for 15 minutes at -15 °C. A solution of *rac*-ethyl (2*S*,3*S*)-2-amino-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (13.0 mg, 0.0304 mmol, 1.0 equiv, >95:5 d.r.) in THF (0.5 mL) was then added. The reaction mixture was stirred at 20 °C for 17 hours then concentrated *in vacuo*. The crude product was purified by column chromatography (20 - 100% Et_2O in hexane + 1% NEt_3) to afford the title compound as a colourless gum (10.0 mg, 0.0171 mmol, 56%, >95:5 d.r.).

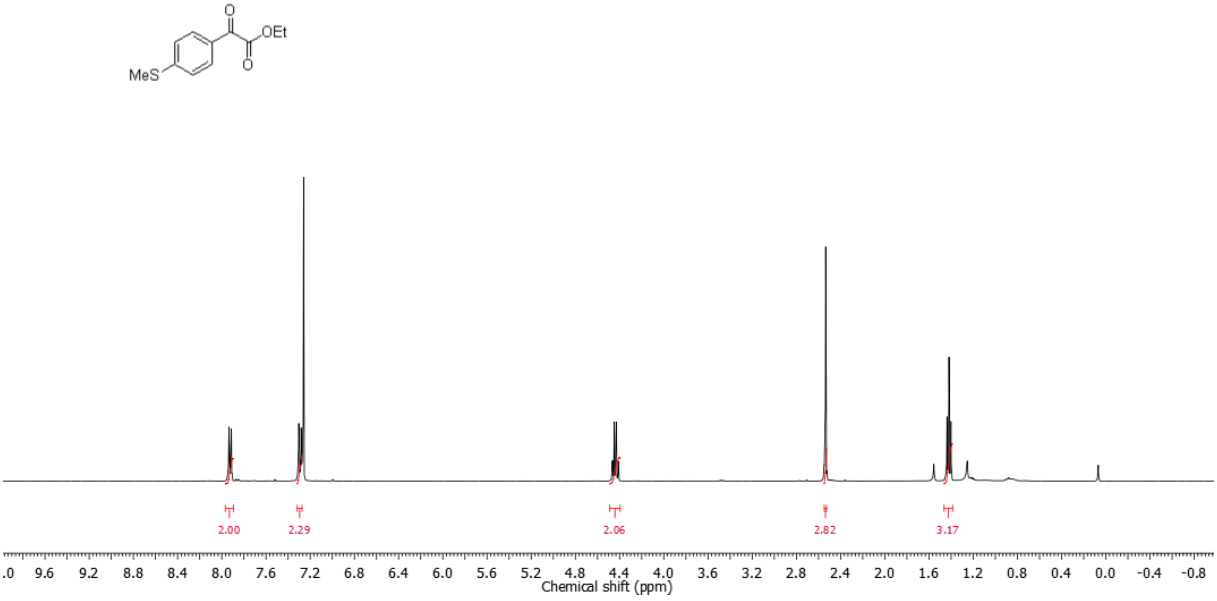
MS (ES^+) *m/z*: 607 ([M+Na]$^+$). HRMS calcd for $C_{32}H_{49}N_2BO_7Na$: 607.3525. Found: 607.3527; ν_{max} (thin film/cm^{-1}): 3339, 2978, 2927, 2852, 1720, 1699, 1498, 1447, 1422, 1391, 1366, 1329, 1297, 1243, 1217, 1167, 1141, 1108, 1059, 1043; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.81 (qd, *J* = 12.3, 2.9 Hz, 1 H, CH_2), 0.98 - 1.12 (m, 2 H, CH_2), 1.15 (t, *J* = 7.2 Hz, 4 H, $CO_2CH_2C\mathit{H}_3$ + 1 H from CH_2), 1.22 (s, 6 H, OC(CH_3)$_2$), 1.27 (s, 6 H, OC(CH_3)$_2$), 1.35 (m, *J* = 2.5 Hz, 1 H, CH_2), 1.47 (s, 9 H, C(CH_3)$_3$), 1.61 - 1.78 (m, 5 H, CH_2), 2.13 (td, *J* = 11.9, 2.6 Hz, 1 H, C*H*CHC=CH_2), 3.19 (br. s, 1 H, C*H*C=CH_2), 3.99 (m, 2 H, CH_2CONH), 4.15 (qd, *J* = 7.2, 2.1 Hz, 2 H, $CO_2C\mathit{H}_2CH_3$), 5.27 (br. s, 1 H, $CH_2N\mathit{H}$), 5.31 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 5.75 (d, *J* = 3.5 Hz, 1 H, C=CH_2), 7.12 - 7.18 (m, 1 H, ArCH), 7.22 (t, *J* = 7.5 Hz, 2 H, ArCH), 7.31 (d, *J* = 7.8 Hz, 2 H, ArCH), 8.32 (br. s, 1 H, $CH_2CON\mathit{H}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 ($CO_2CH_2\mathit{C}H_3$), 24.3 (OC(*C*H_3)$_2$), 24.7 (OC(*C*H_3)$_2$), 26.3 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 28.4 (C(*C*H_3)$_3$), 31.2 (CH_2), 33.6 (CH_2), 38.5 (*C*HCHC=CH_2), 44.1 (*C*H_2CONH), 61.4 ($CO_2\mathit{C}H_2CH_3$), 62.6 (*C*HC=CH_2), 67.9 (*C*$CO_2CH_2CH_3$), 79.6 (*C*(CH_3)$_3$), 84.1 (O*C*(CH_3)$_2$), 126.7 (ArCH), 126.9 (ArCH), 127.6 (ArCH), 137.7

(C=*C*H_2), 139.4 (ArC), 155.7 (*C*$O_2C(CH_3)_3$), 167.9 (CH_2*C*ONH), 171.3 (*C*$O_2CH_2CH_3$), (B*C*=CH_2 not observed); ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 31.9.

^{1}H and ^{13}C NMR spectra

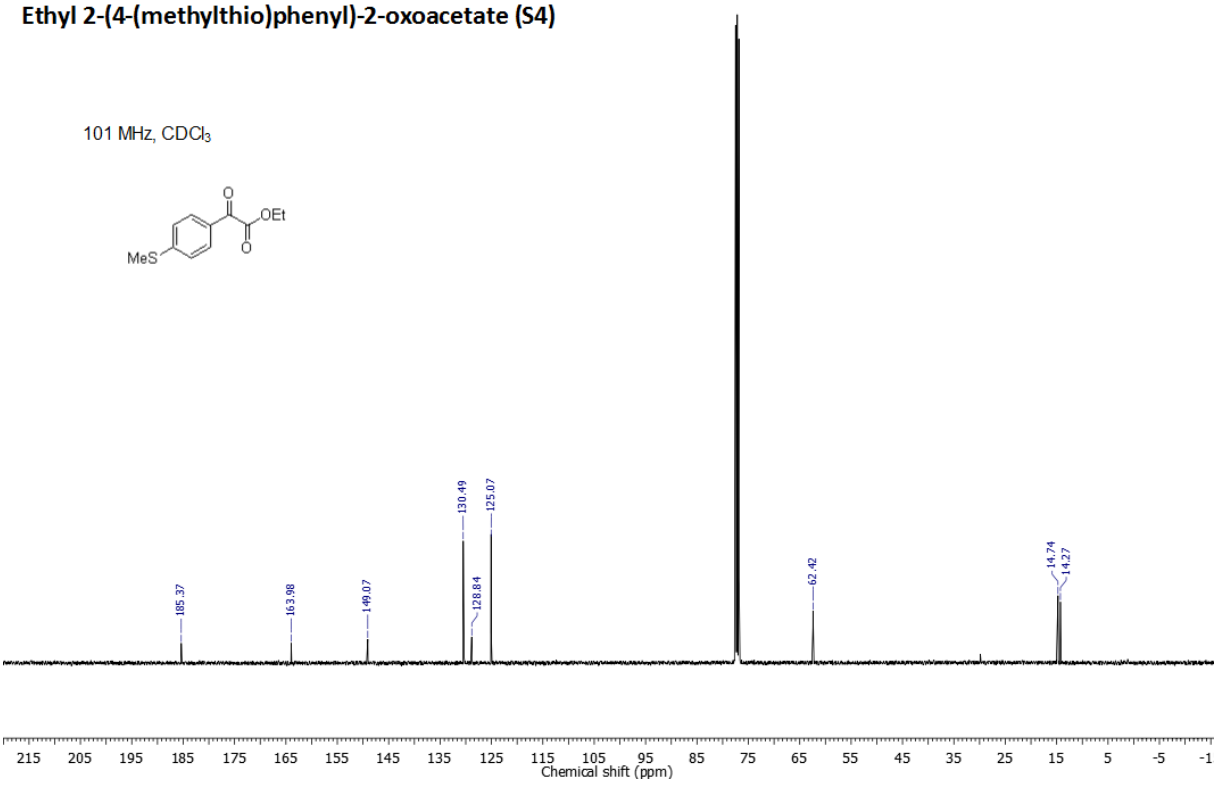
Ethyl 2-(4-(methylthio)phenyl)-2-oxoacetate (S4)

400 MHz, $CDCl_3$



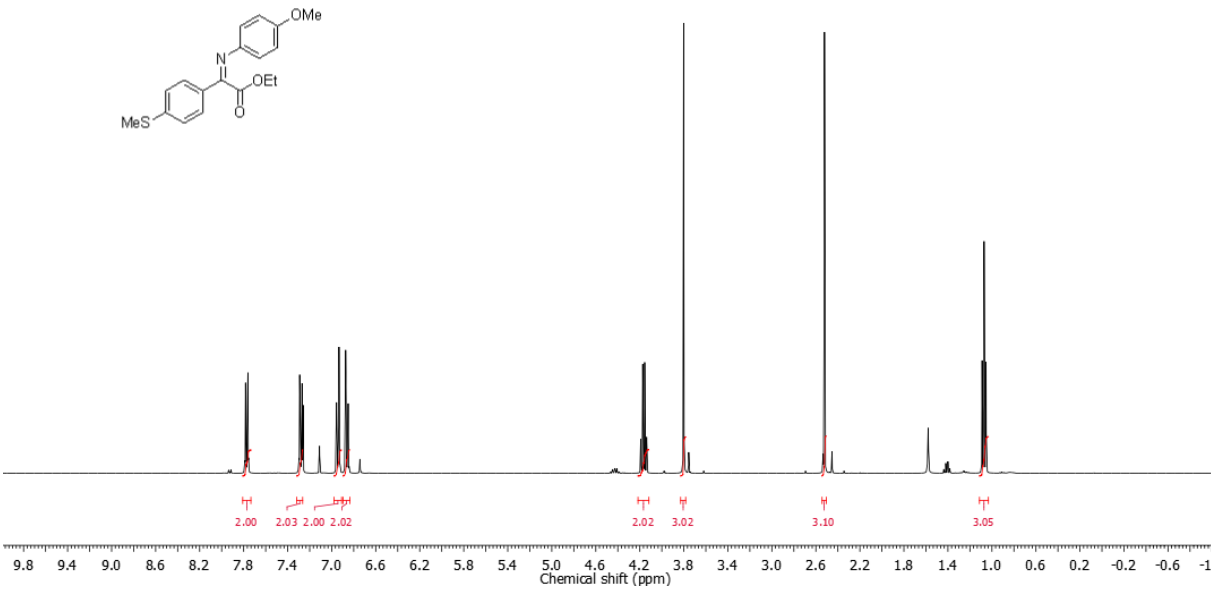
Ethyl 2-(4-(methylthio)phenyl)-2-oxoacetate (S4)

101 MHz, $CDCl_3$



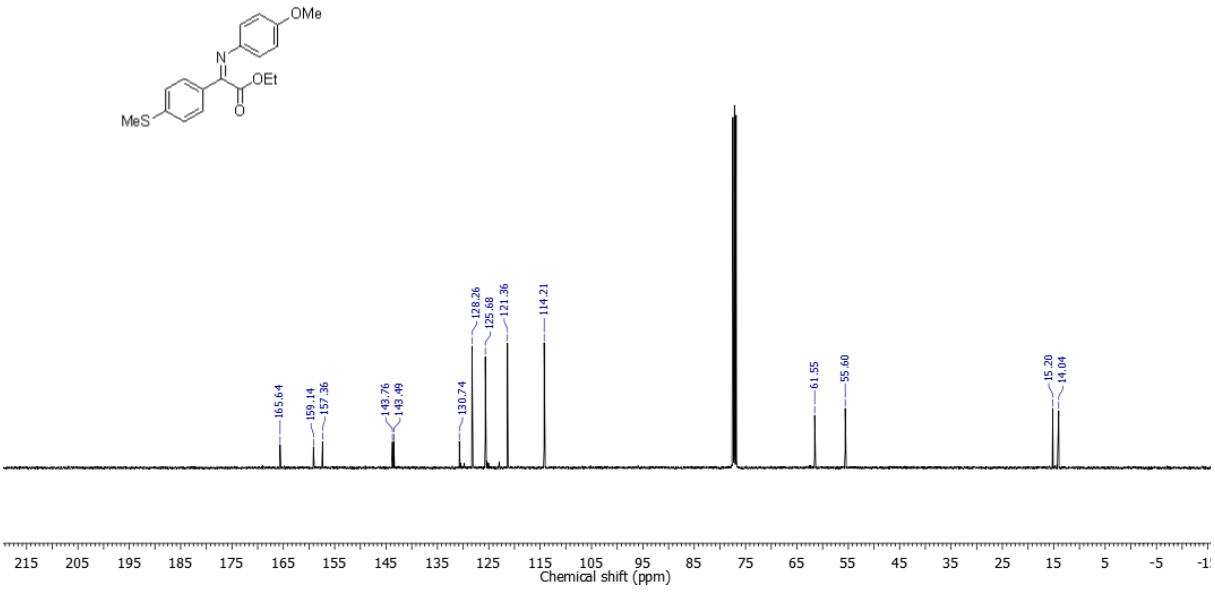
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate (1d)

400 MHz, $CDCl_3$



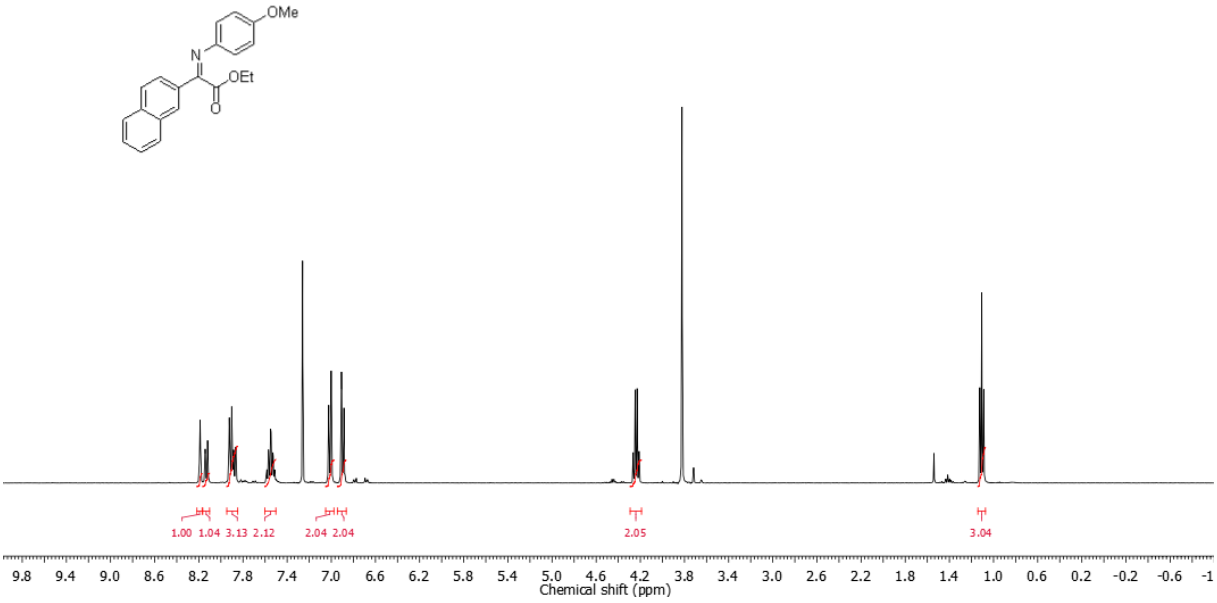
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate (1d)

101 MHz, $CDCl_3$



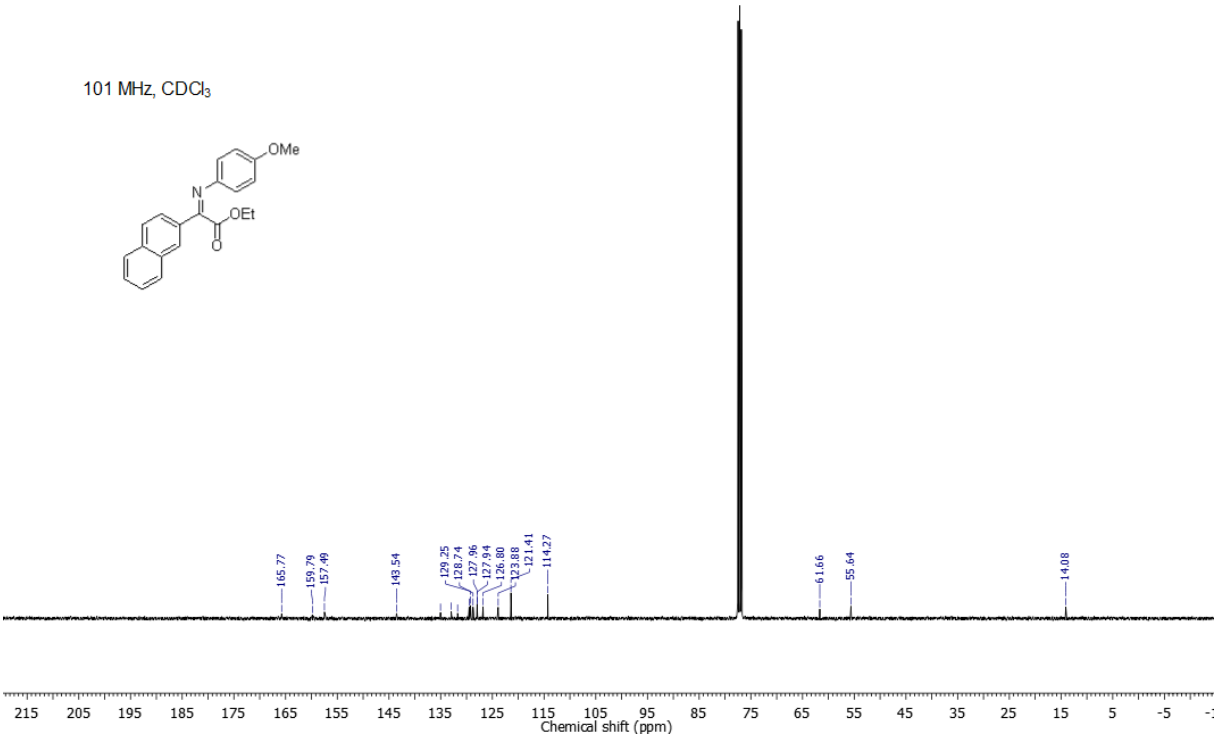
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate (1g)

400 MHz, $CDCl_3$



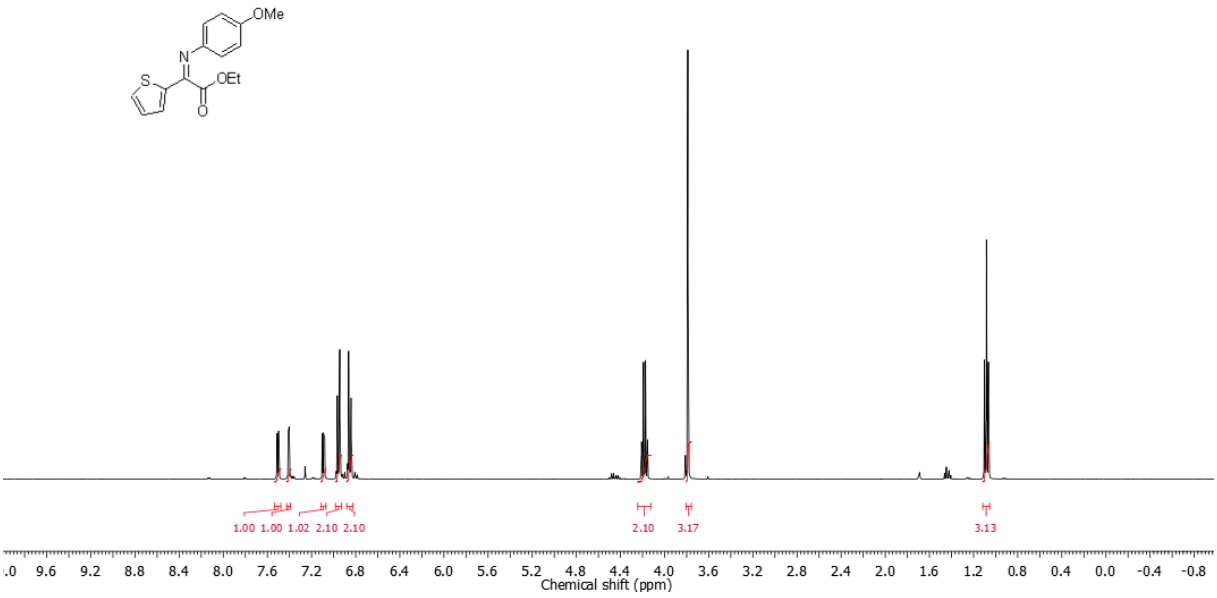
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate (1g)

101 MHz, $CDCl_3$



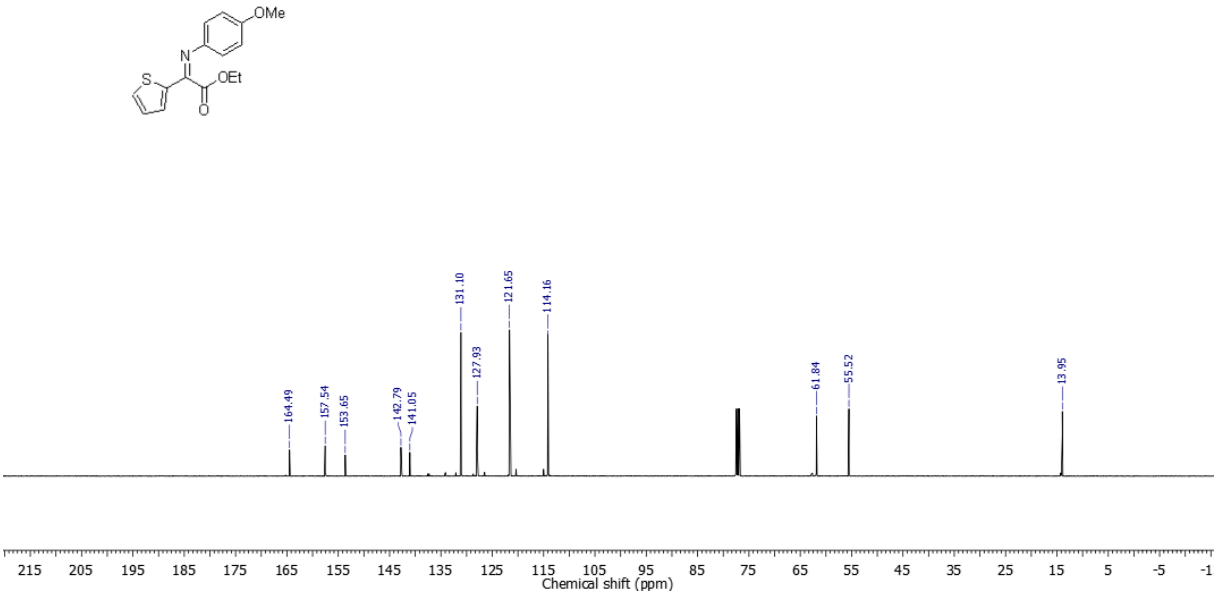
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate (1h)

400 MHz, $CDCl_3$



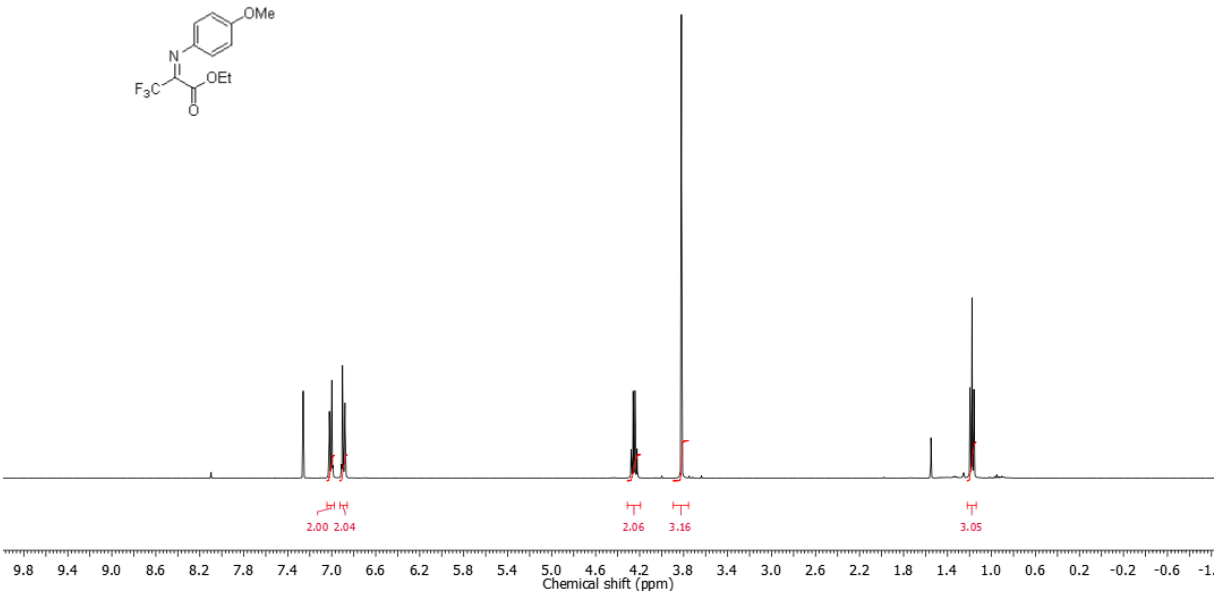
Ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate (1h)

101 MHz, $CDCl_3$



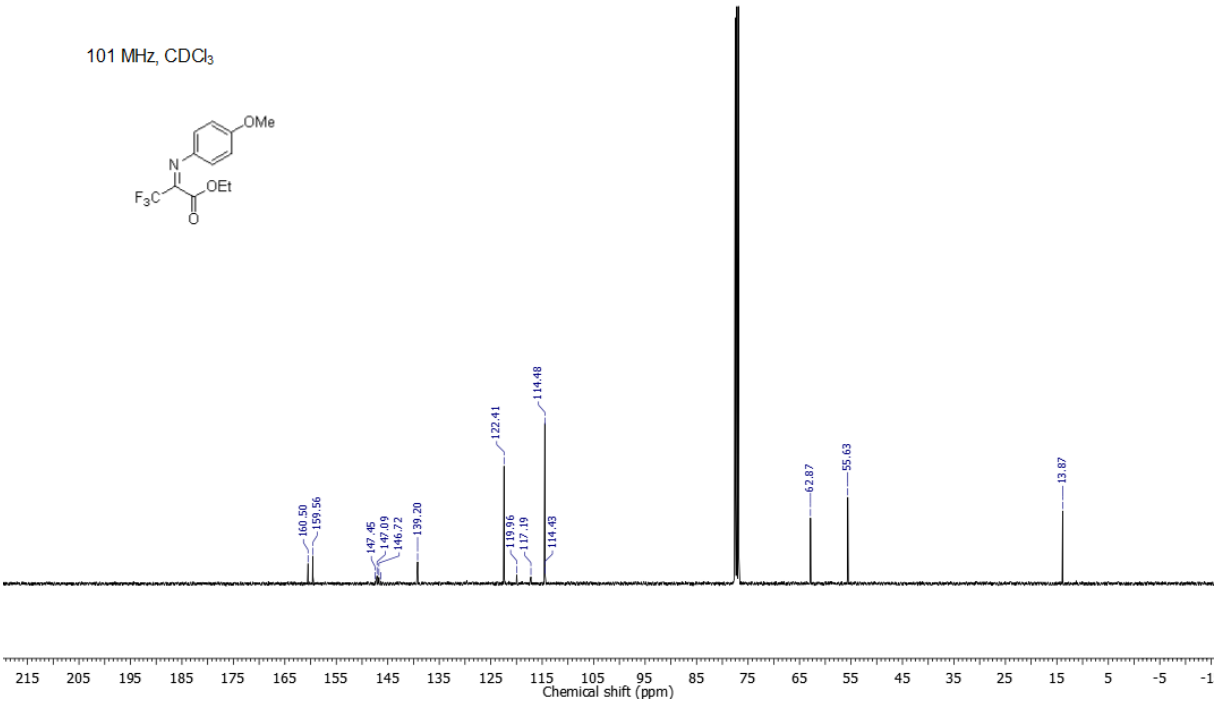
Ethyl (*E*)-3,3,3-trifluoro-2-((4-methoxyphenyl)imino)propanoate (1i)

400 MHz, $CDCl_3$



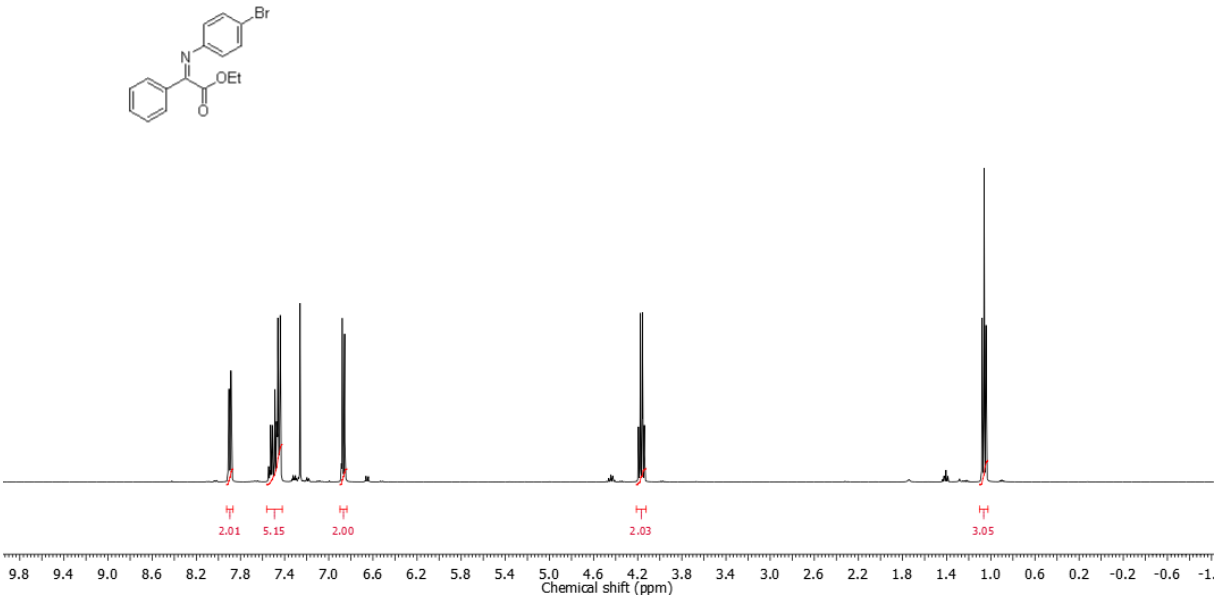
Ethyl (*E*)-3,3,3-trifluoro-2-((4-methoxyphenyl)imino)propanoate (1i)

101 MHz, $CDCl_3$



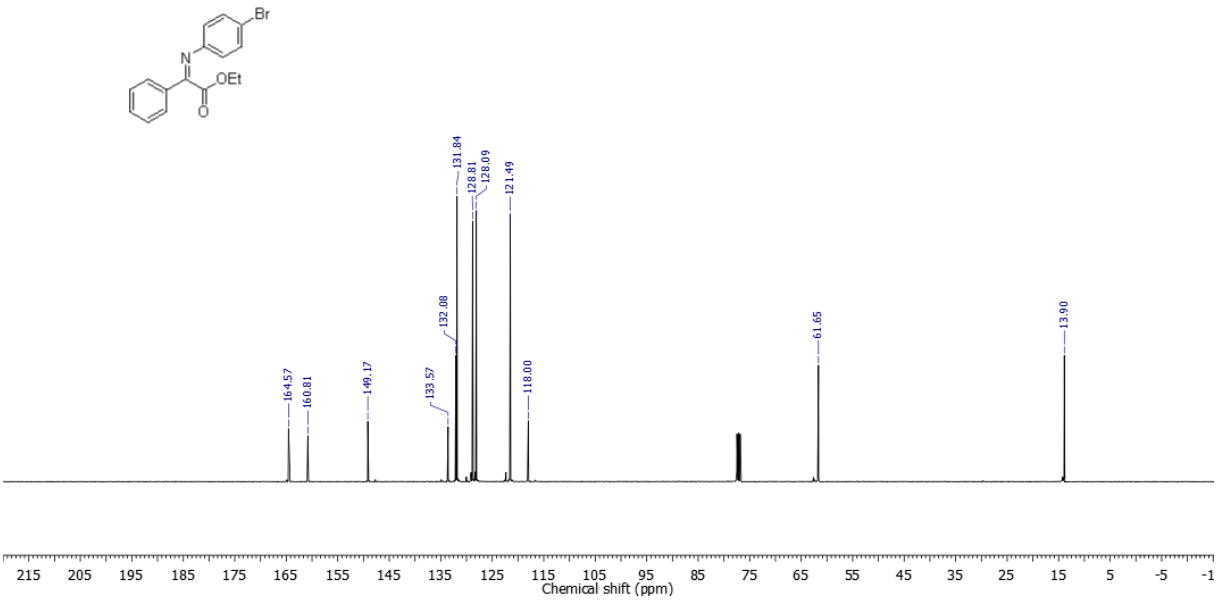
Ethyl (*Z*)-2-((4-bromophenyl)imino)-2-phenylacetate (1j)

400 MHz, $CDCl_3$



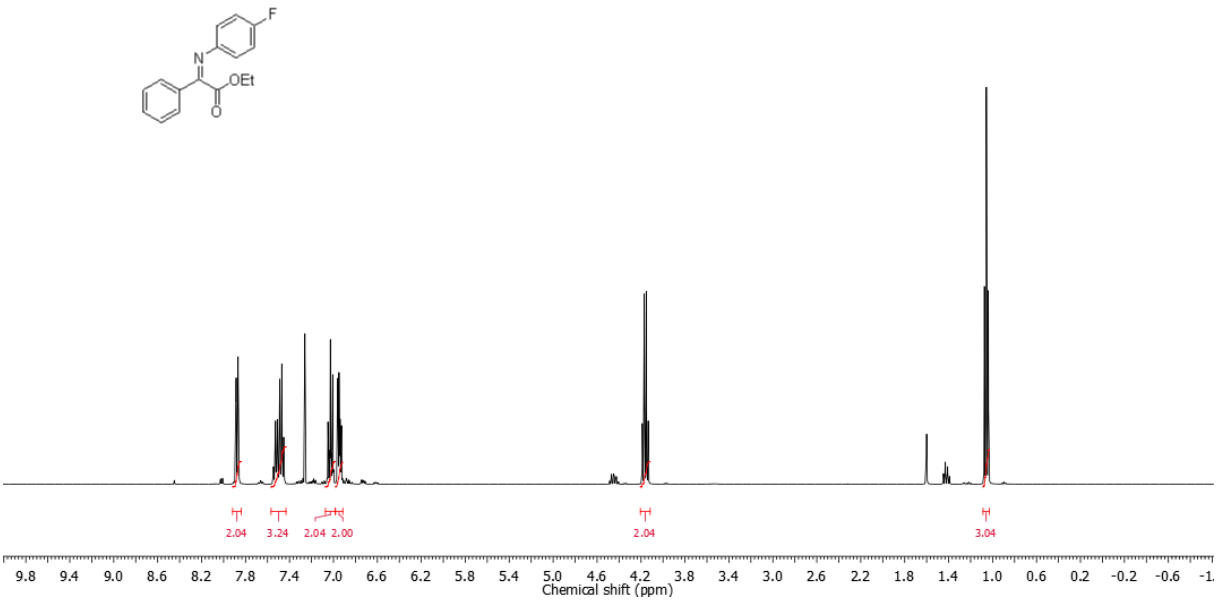
Ethyl (*Z*)-2-((4-bromophenyl)imino)-2-phenylacetate (1j)

101 MHz, $CDCl_3$



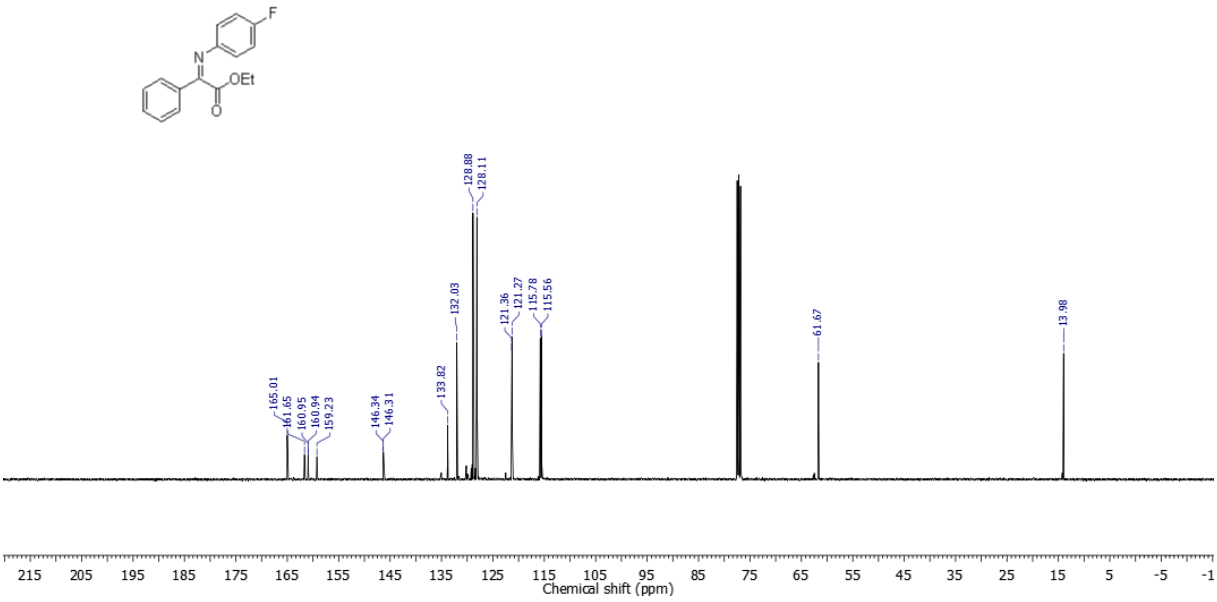
Ethyl (*Z*)-2-((4-fluorophenyl)imino)-2-phenylacetate (1k)

400 MHz, $CDCl_3$



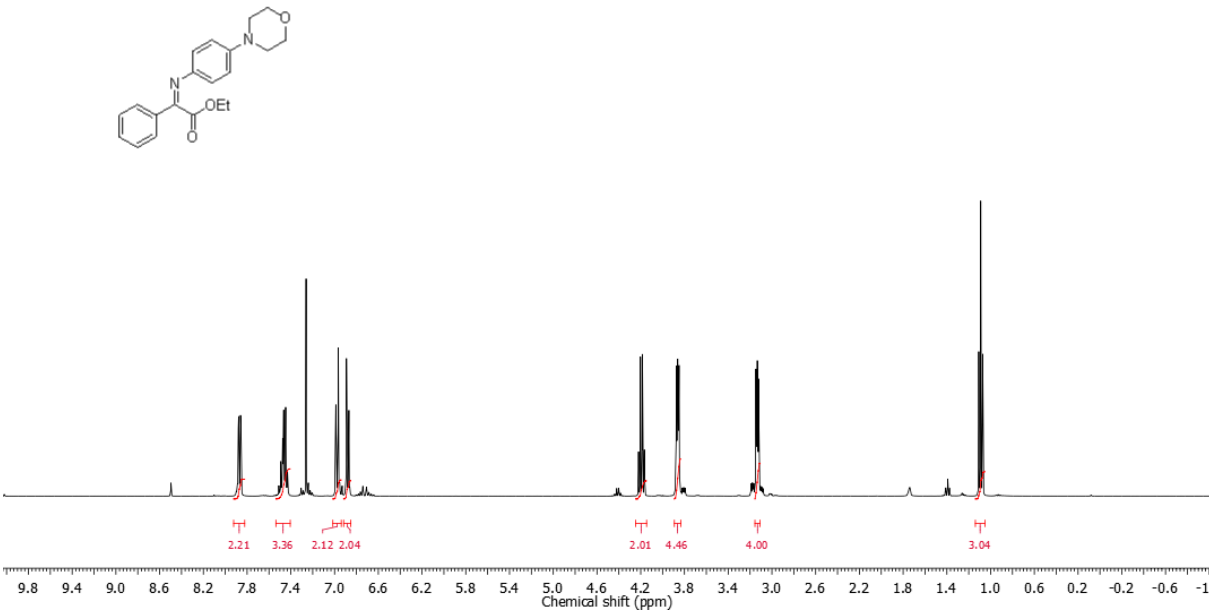
Ethyl (*Z*)-2-((4-fluorophenyl)imino)-2-phenylacetate (1k)

101 MHz, $CDCl_3$



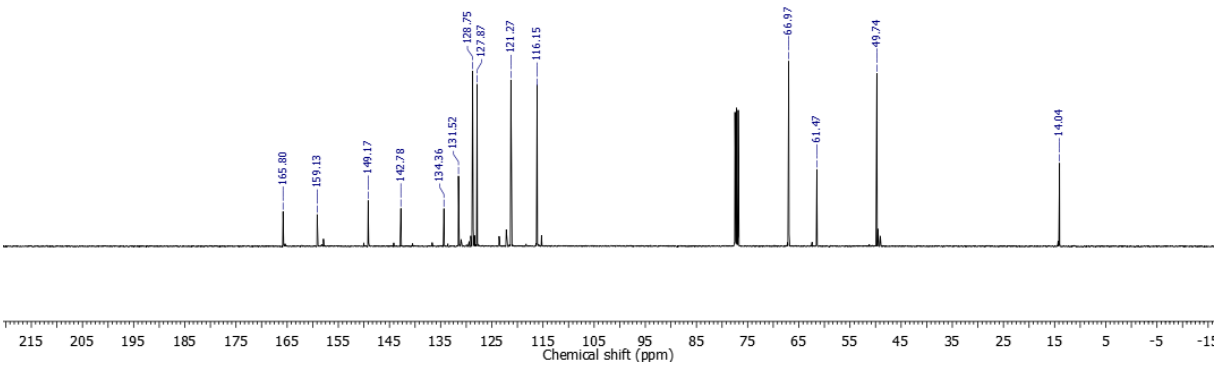
Ethyl (*Z*)-2-((4-morpholinophenyl)imino)-2-phenylacetate (1l)

400 MHz, $CDCl_3$

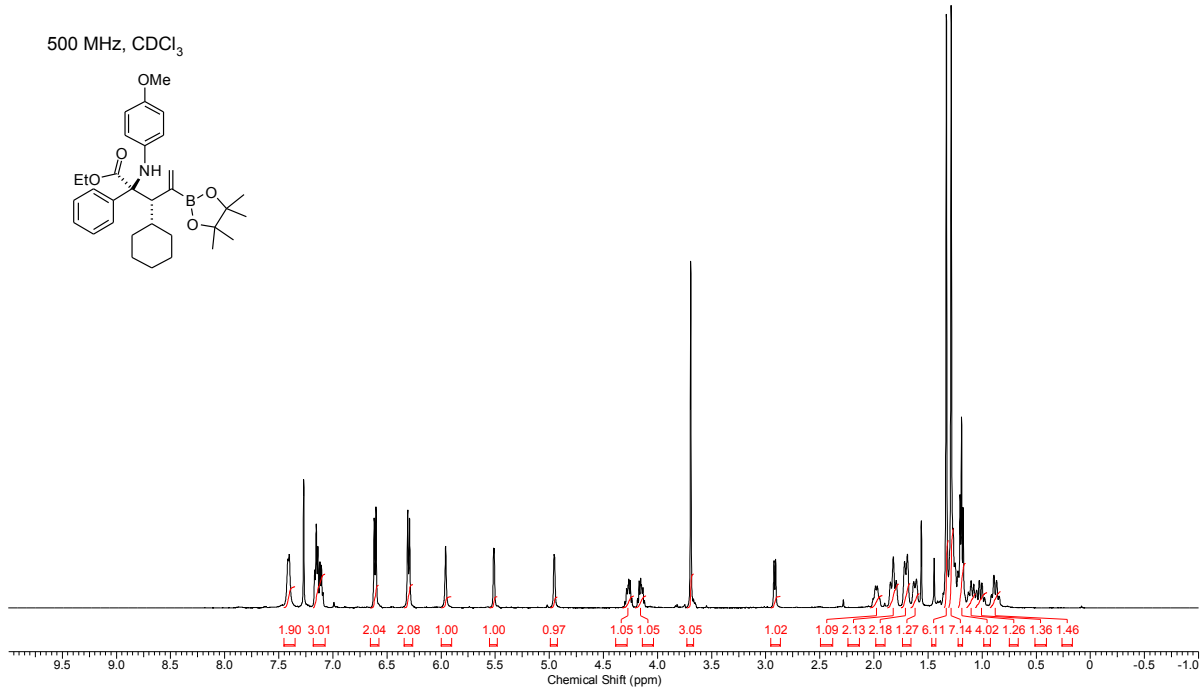


Ethyl (*Z*)-2-((4-morpholinophenyl)imino)-2-phenylacetate (1l)

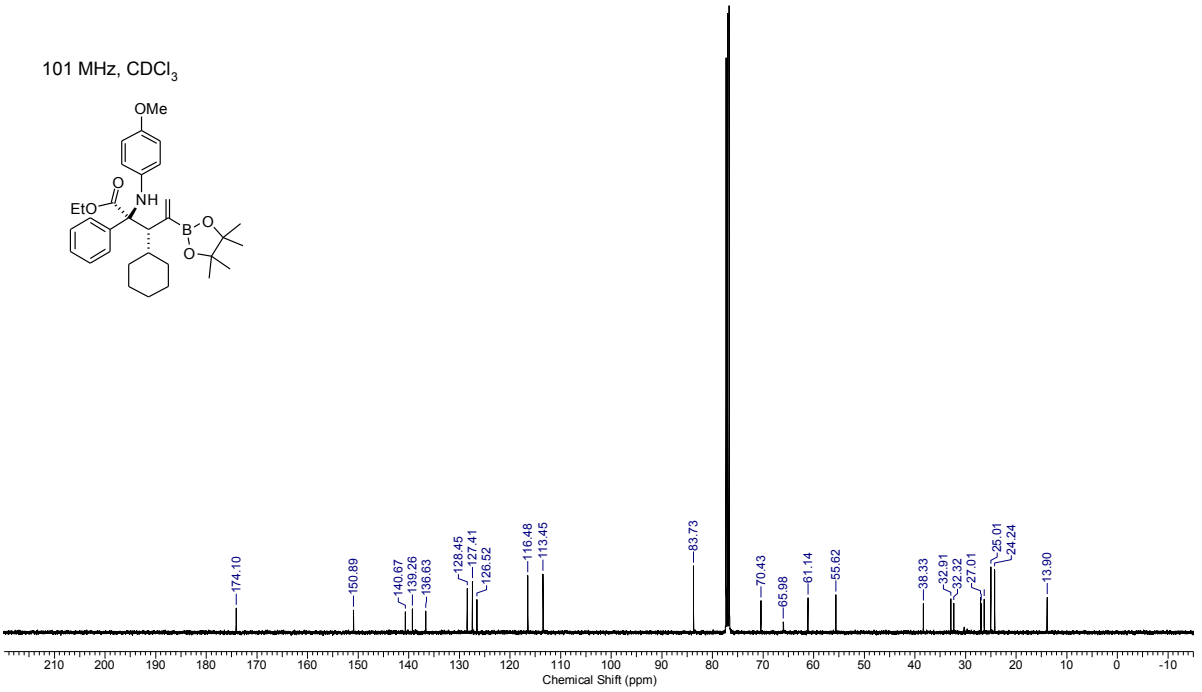
101 MHz, $CDCl_3$



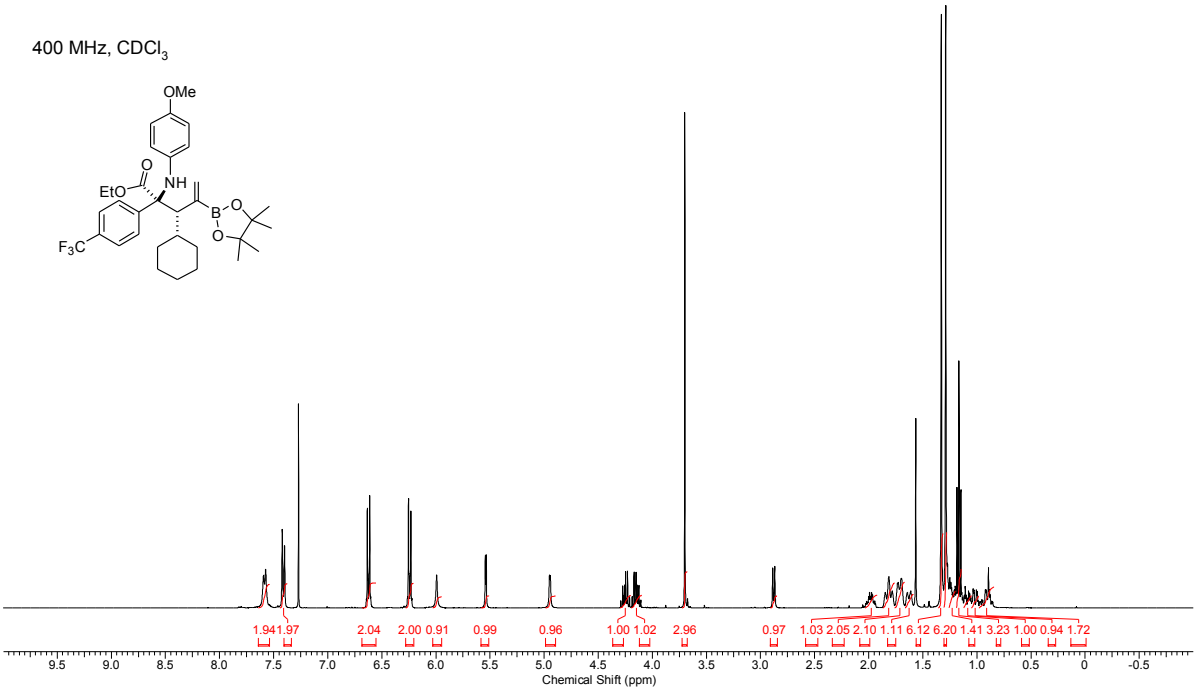
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3a)**



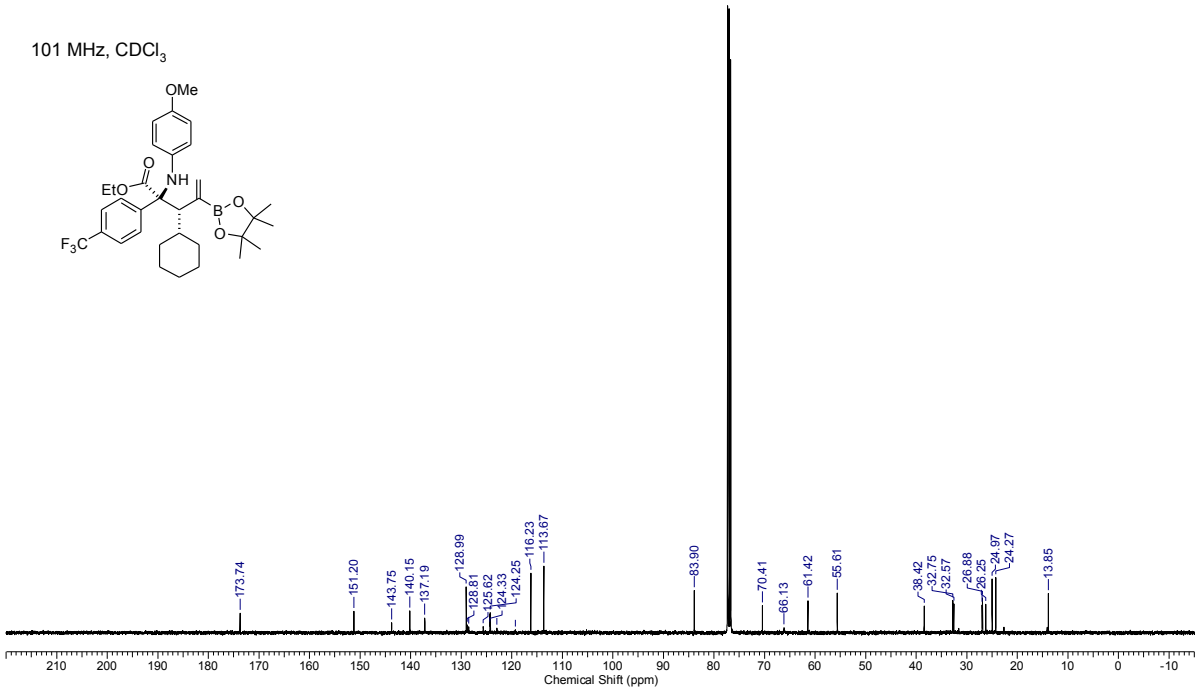
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3a)**



***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)pent-4-enoate (3b)**

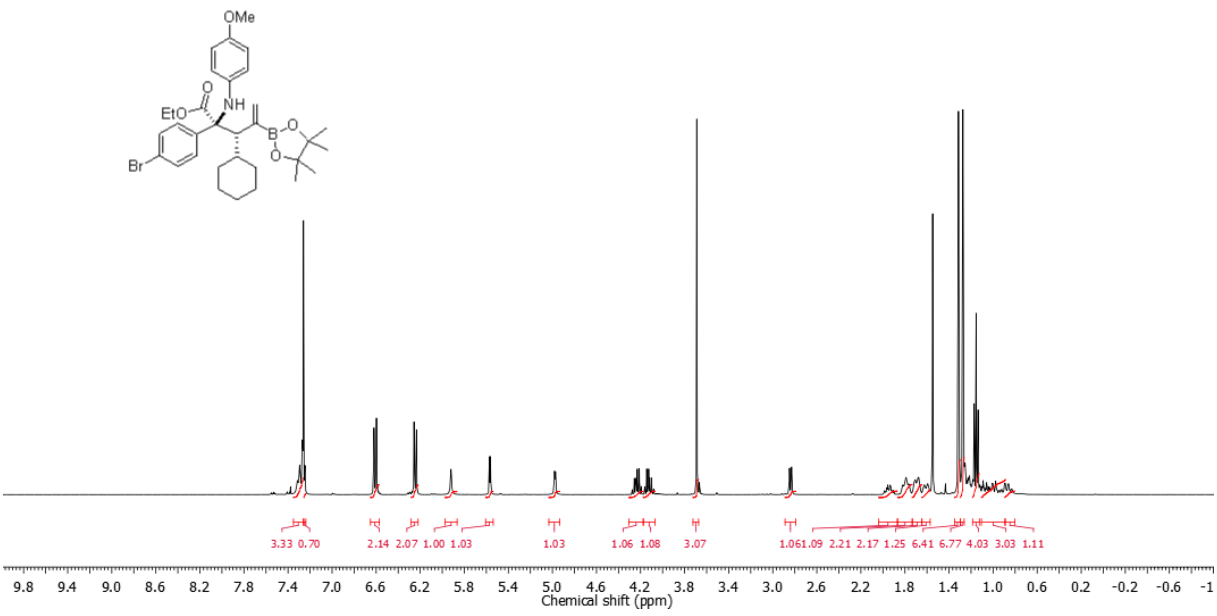


***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)pent-4-enoate (3b)**



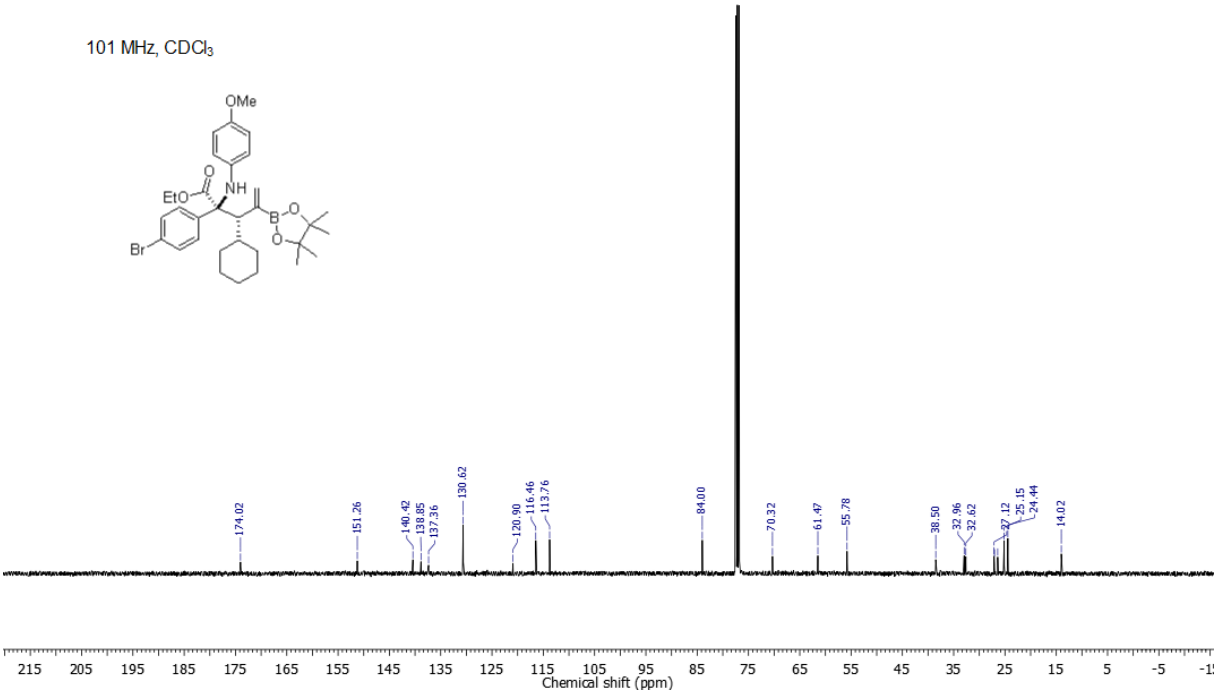
***rac*-Ethyl (2S,3S)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3c)**

400 MHz, $CDCl_3$

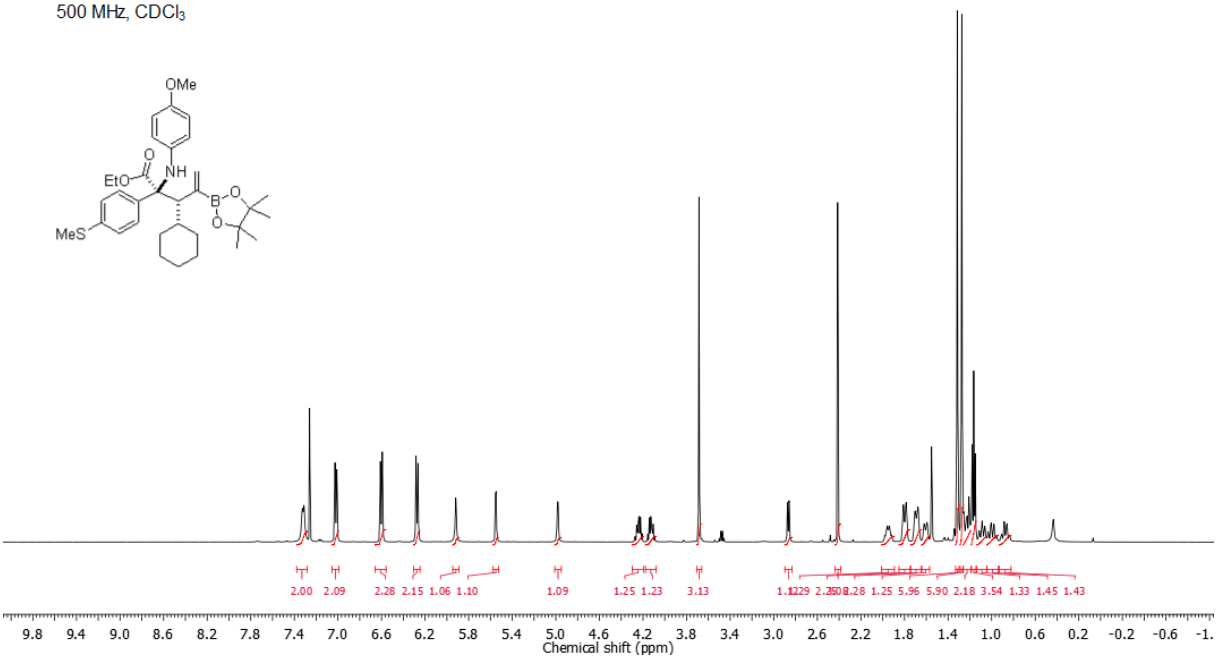


***rac*-Ethyl (2S,3S)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3c)**

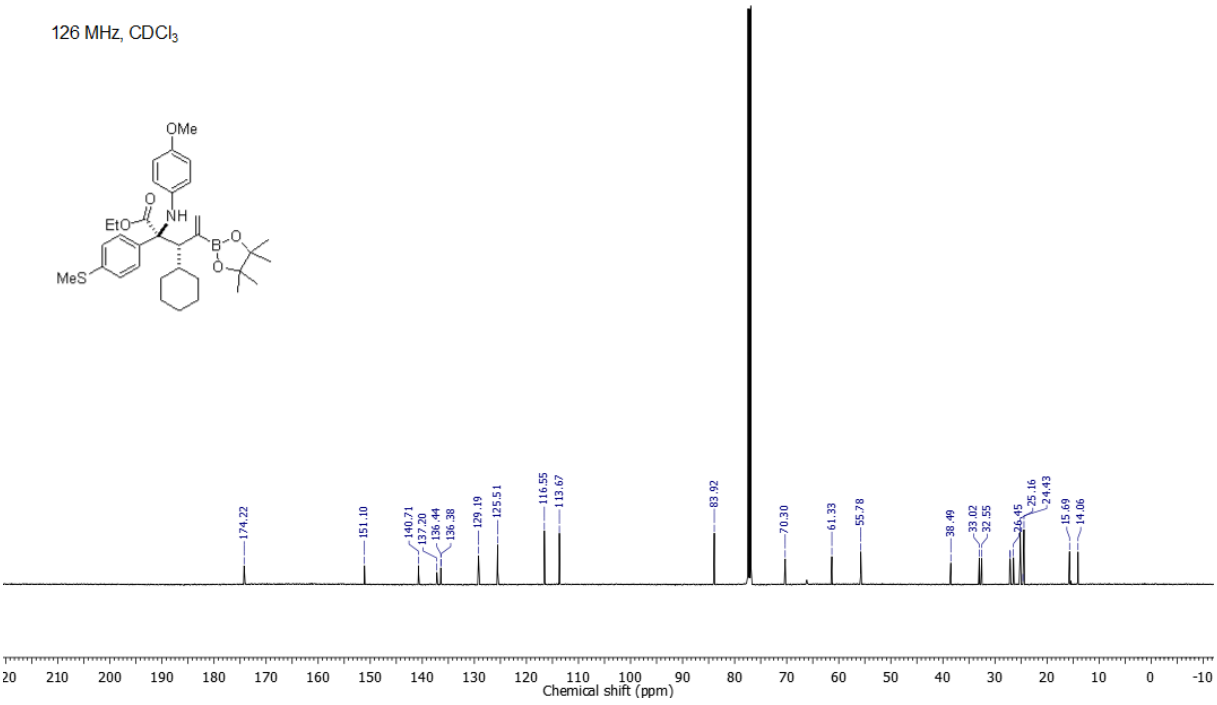
101 MHz, $CDCl_3$



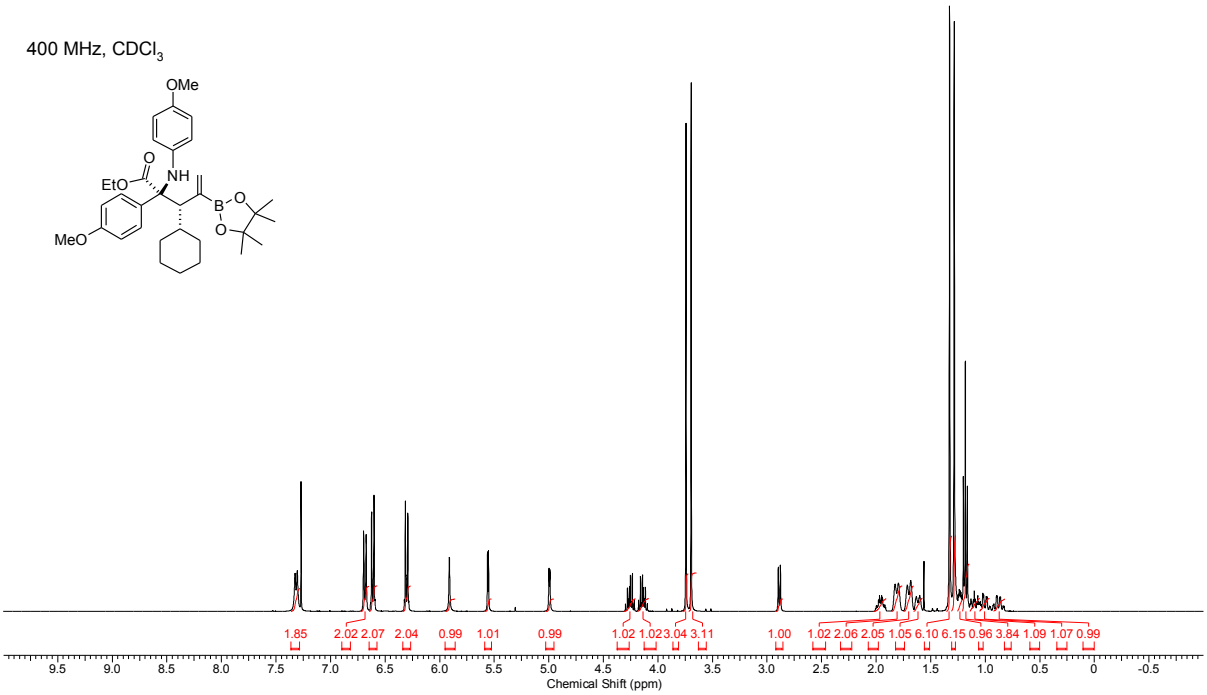
***rac*-Ethyl (2S,3S)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3d)**



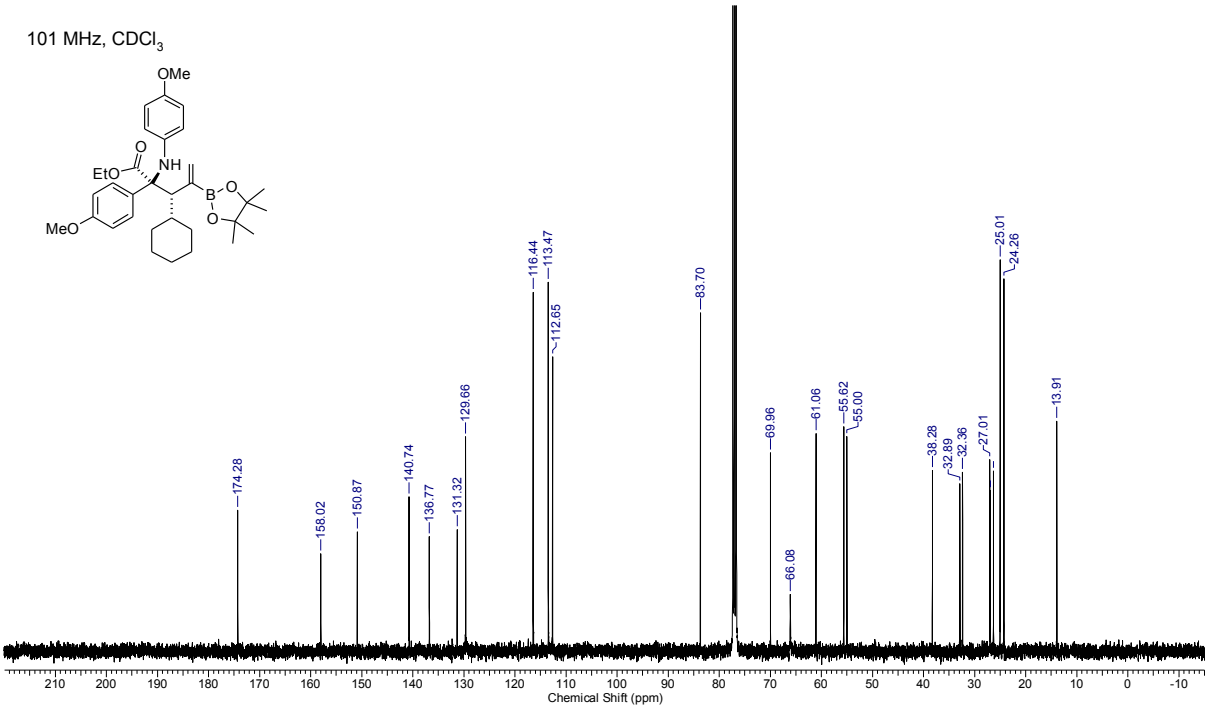
***rac*-Ethyl (2S,3S)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3d)**



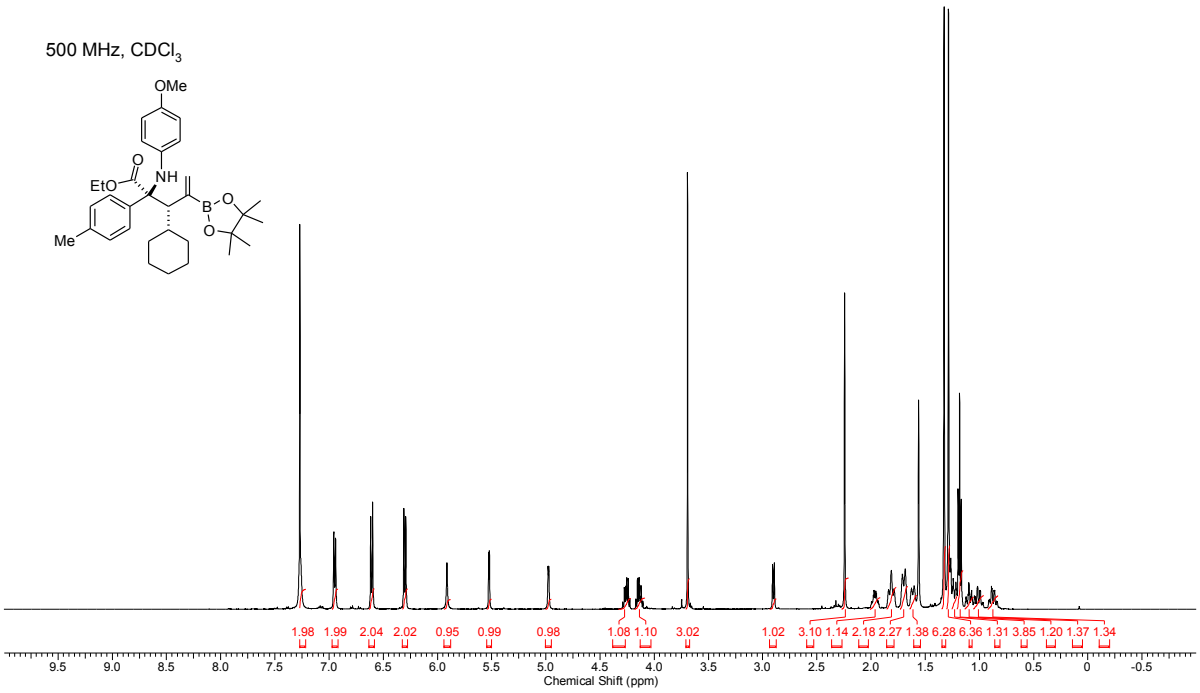
rac-Ethyl (2_S_,3_S_)-3-cyclohexyl-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3e)



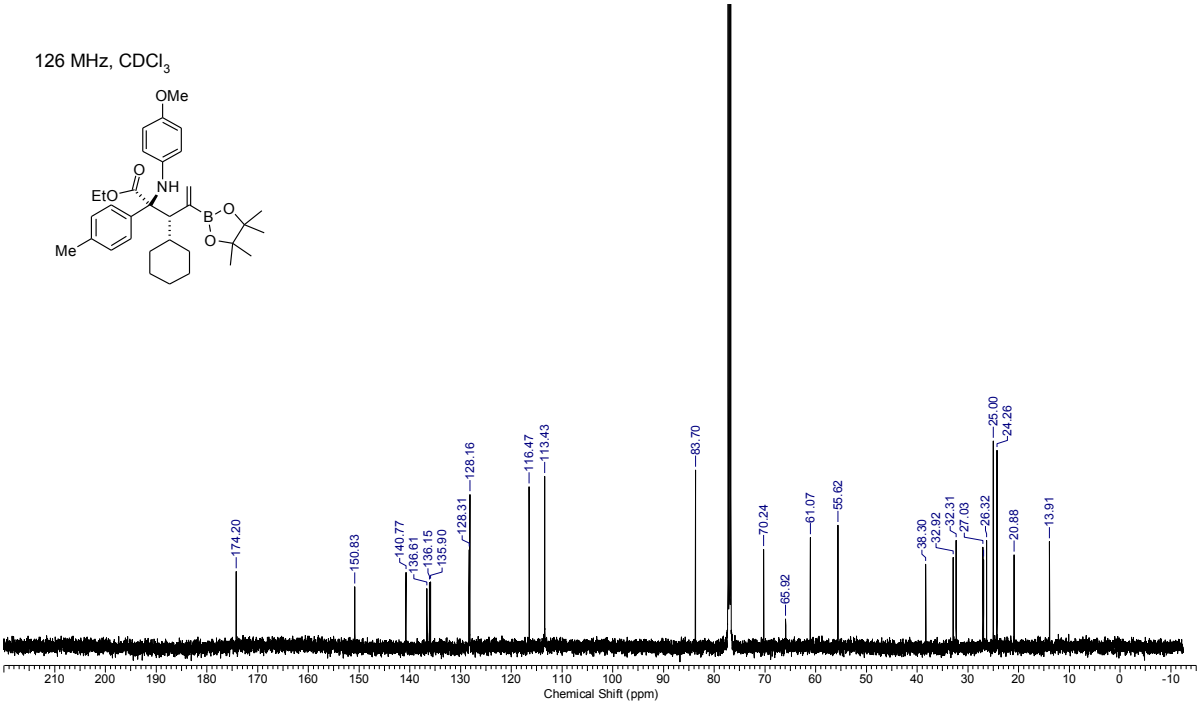
rac-Ethyl (2_S_,3_S_)-3-cyclohexyl-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3e)



***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)pent-4-enoate (3f)**

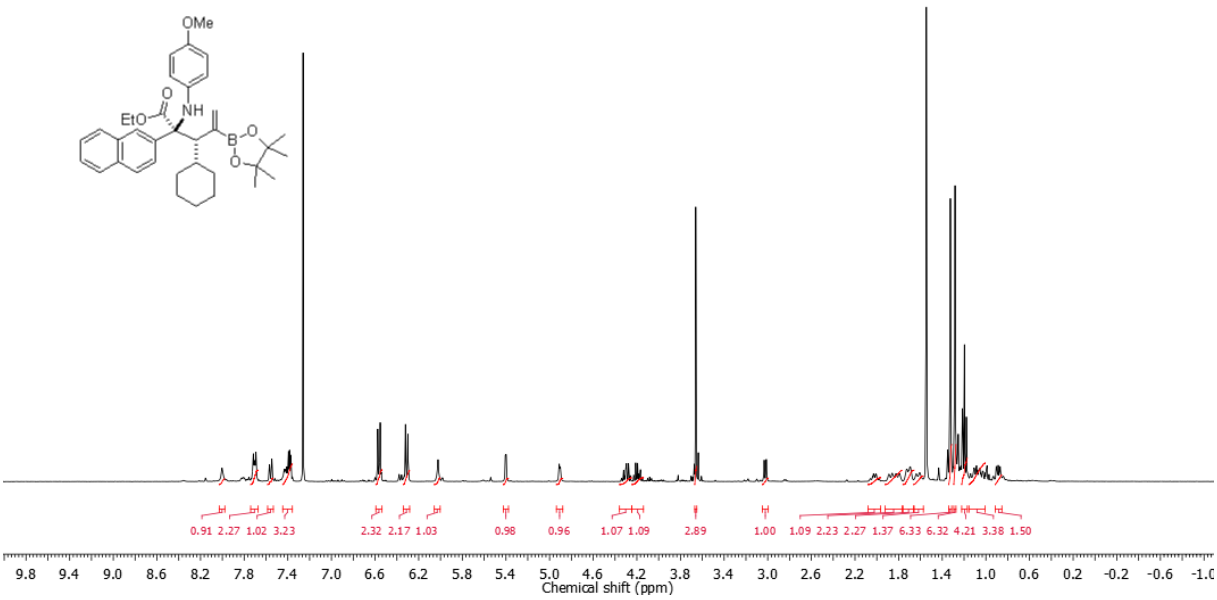


***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)pent-4-enoate (3f)**



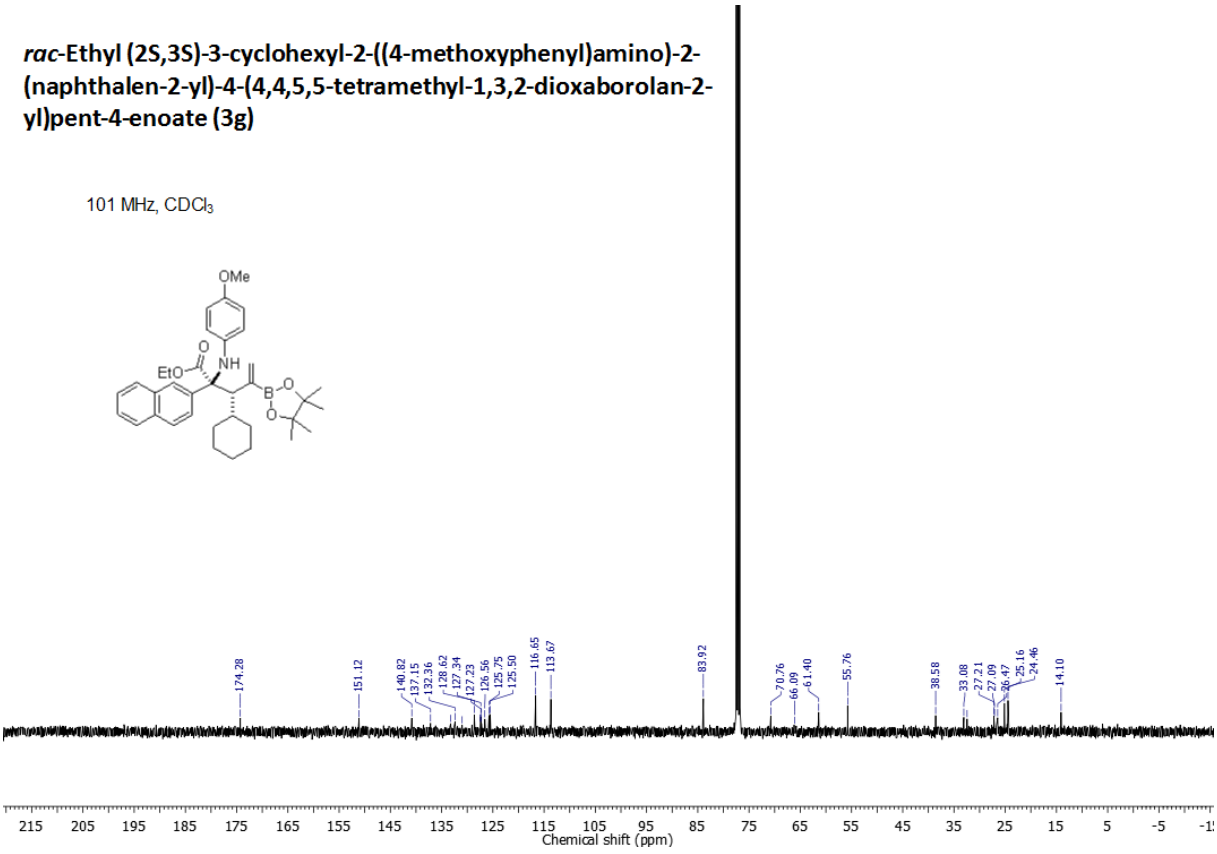
rac-Ethyl (2S,3S)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3g)

400 MHz, $CDCl_3$

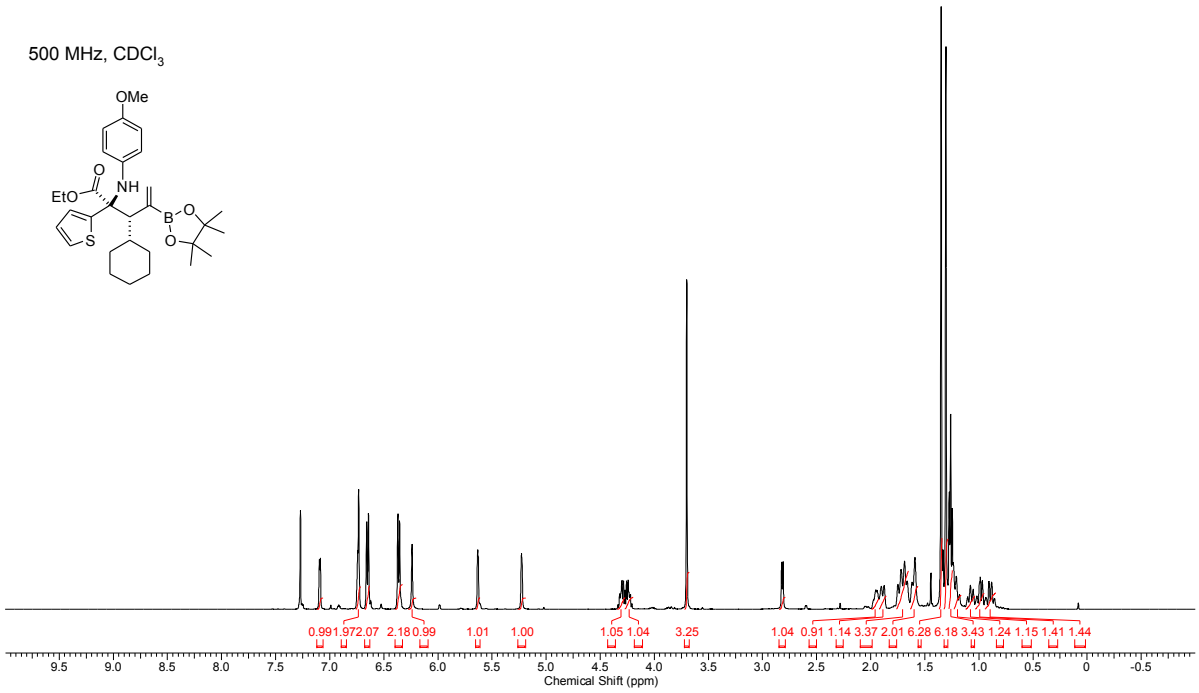


rac-Ethyl (2S,3S)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3g)

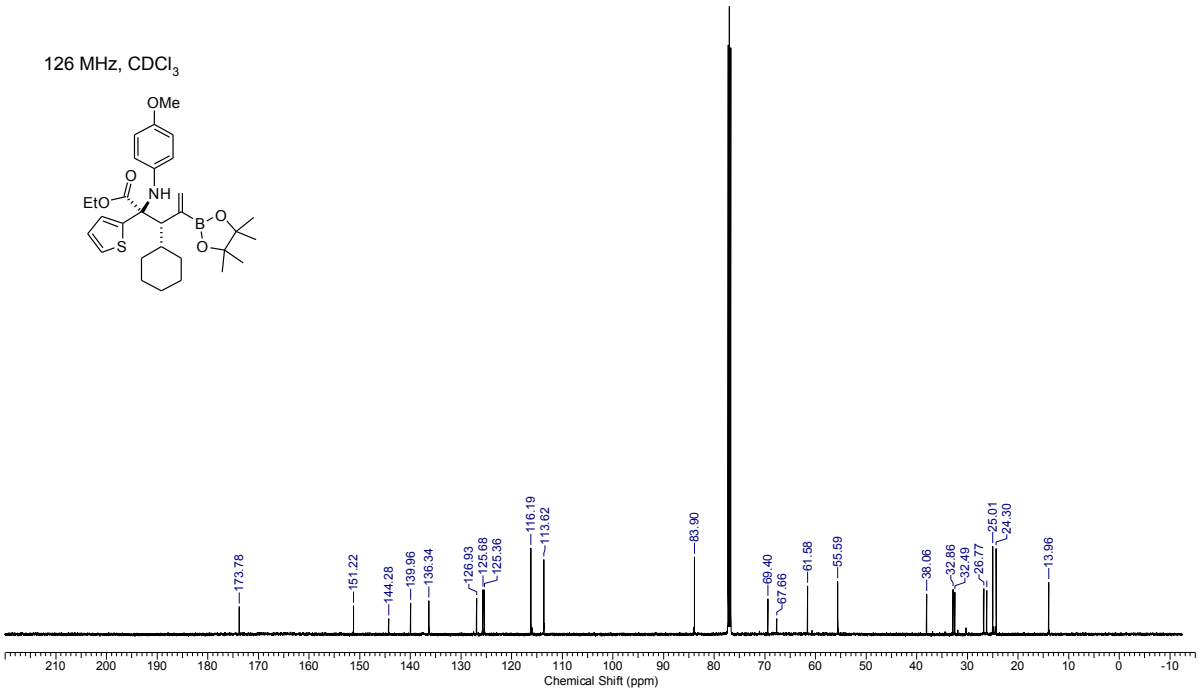
101 MHz, $CDCl_3$



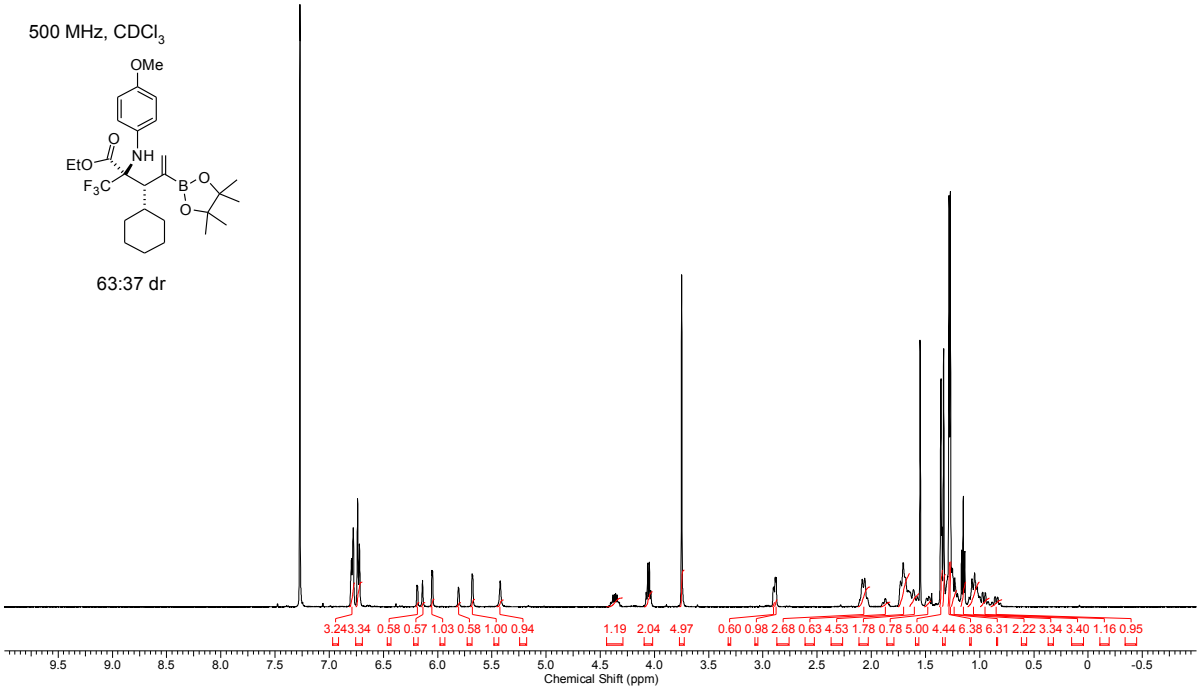
***rac*-Ethyl (2*R*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)pent-4-enoate (3h)**



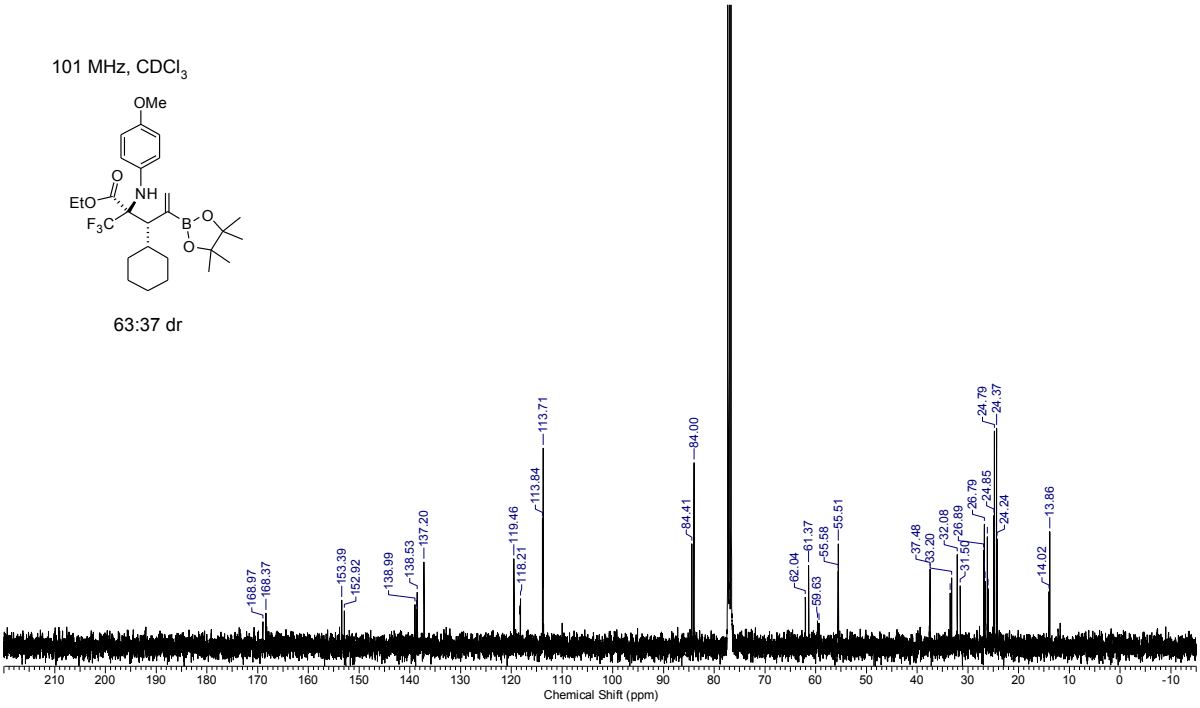
***rac*-Ethyl (2*R*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)pent-4-enoate (3h)**



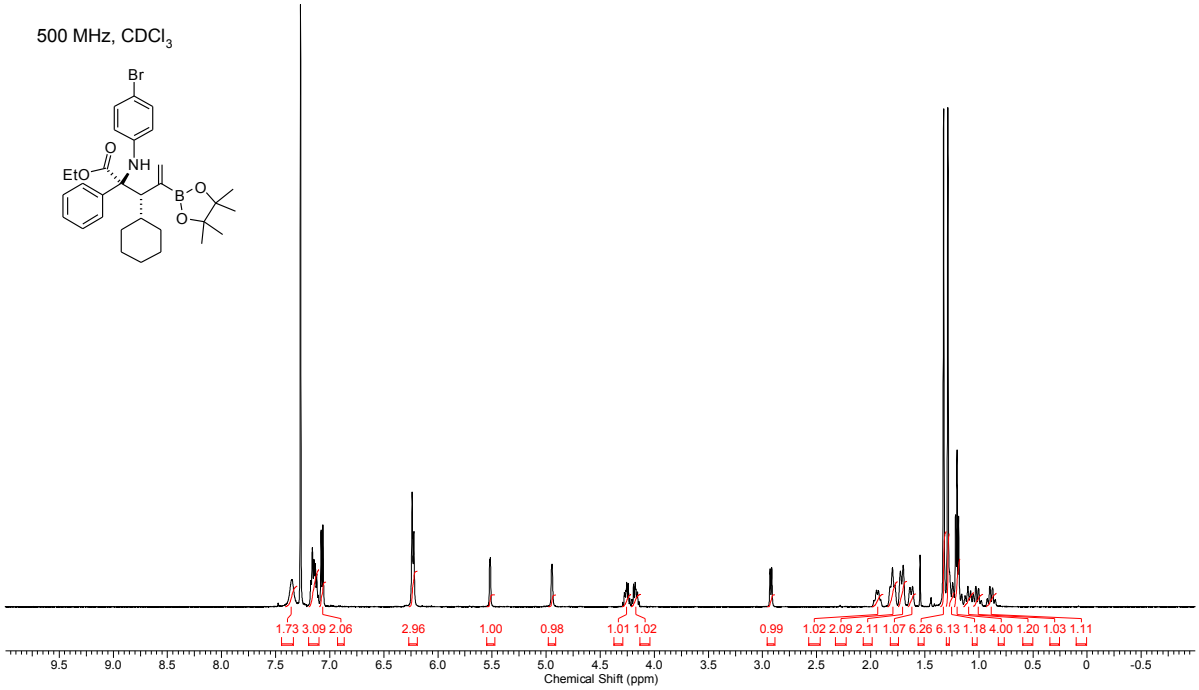
***rac*-Ethyl 3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trifluoromethyl)pent-4-enoate (3i)**



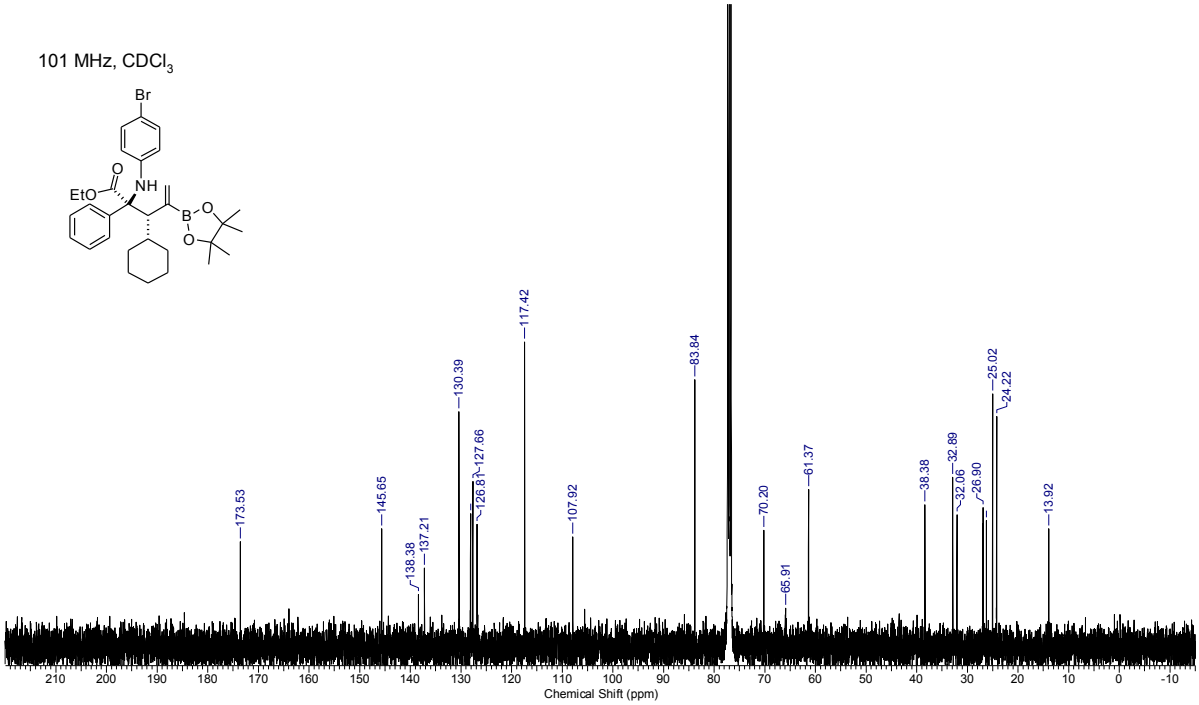
***rac*-Ethyl (2*R*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trifluoromethyl)pent-4-enoate (3i)**



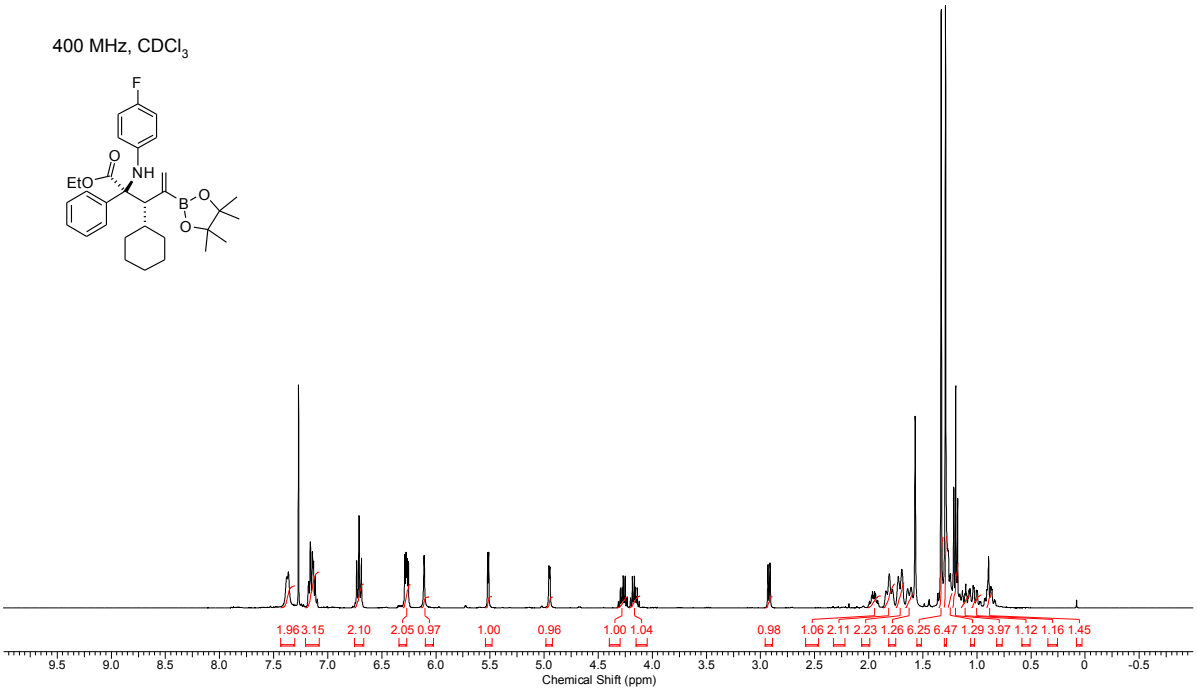
***rac*-Ethyl (2*S*,3*S*)-2-((4-bromophenyl)amino)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3j)**



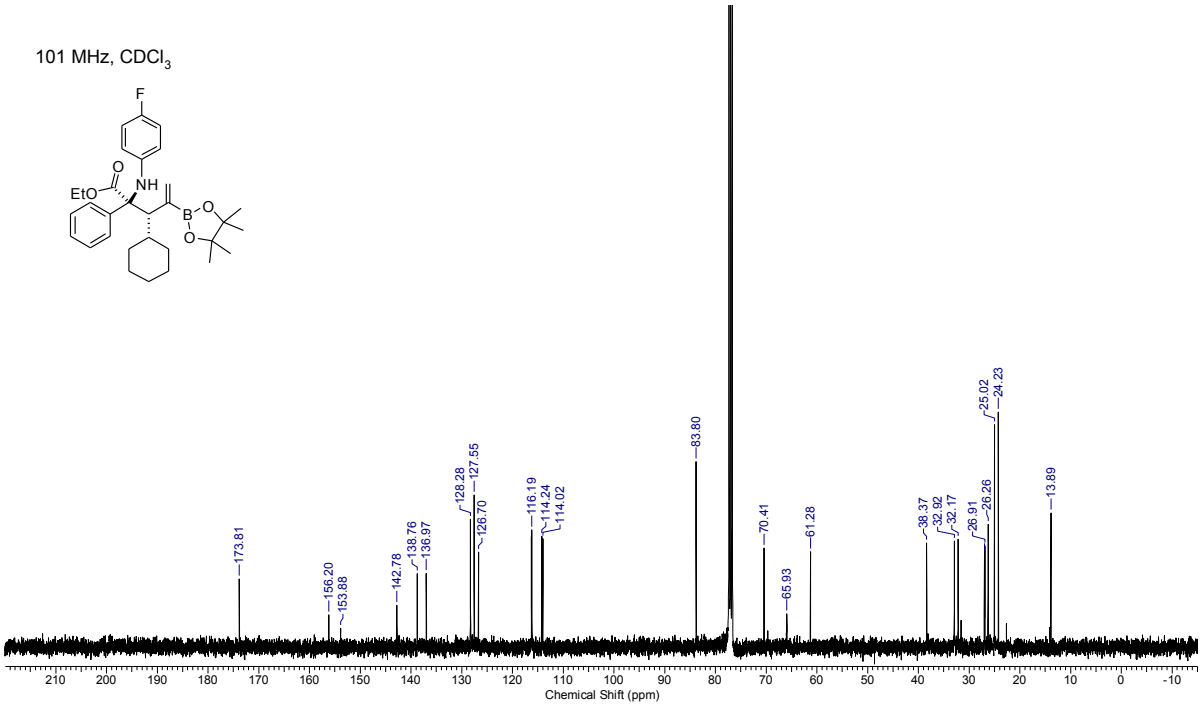
***rac*-Ethyl (2*S*,3*S*)-2-((4-bromophenyl)amino)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3j)**



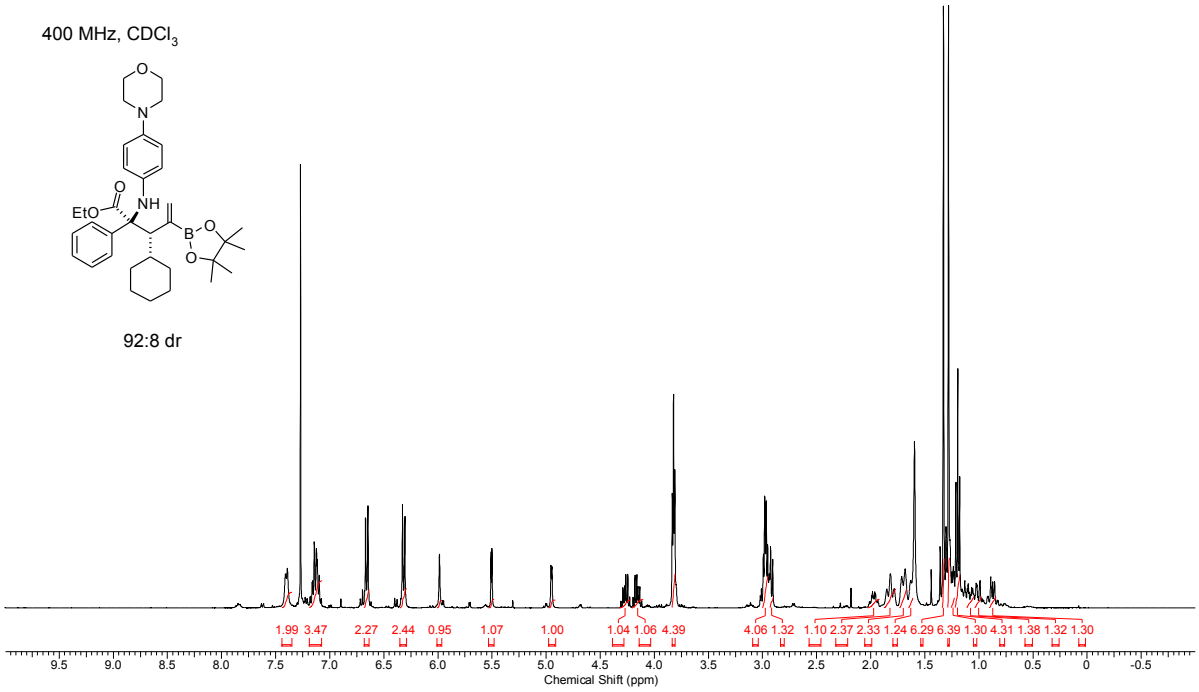
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-fluorophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3k)**



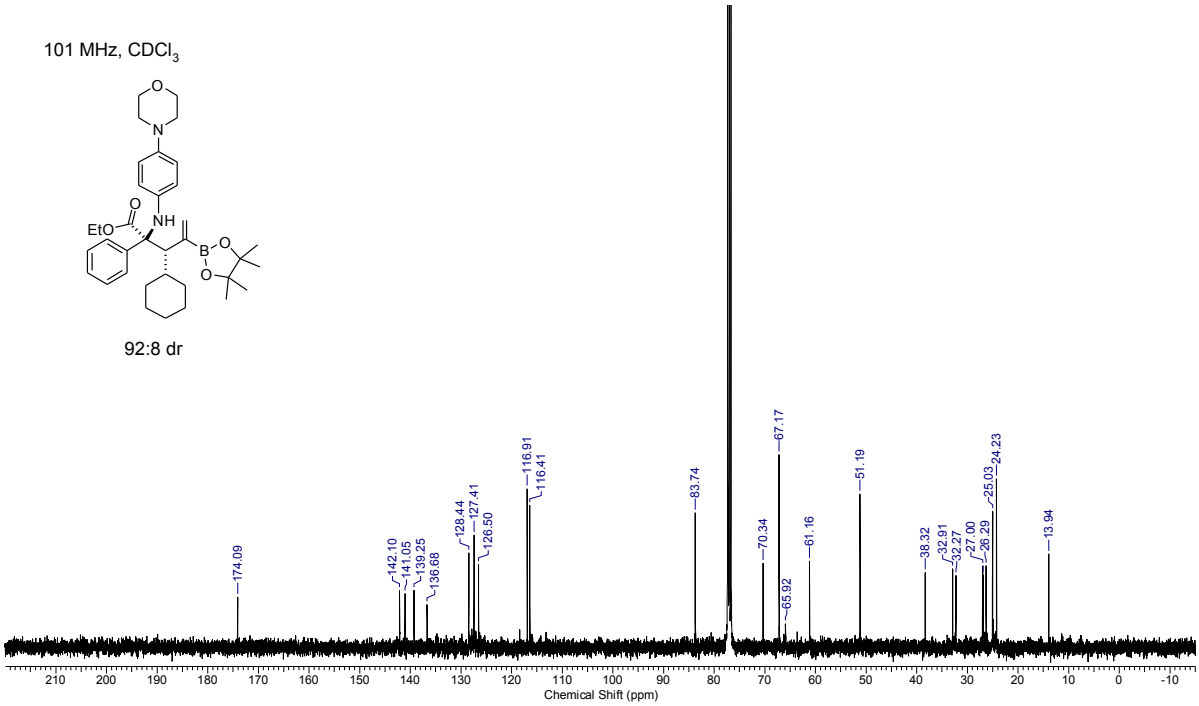
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-fluorophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3k)**



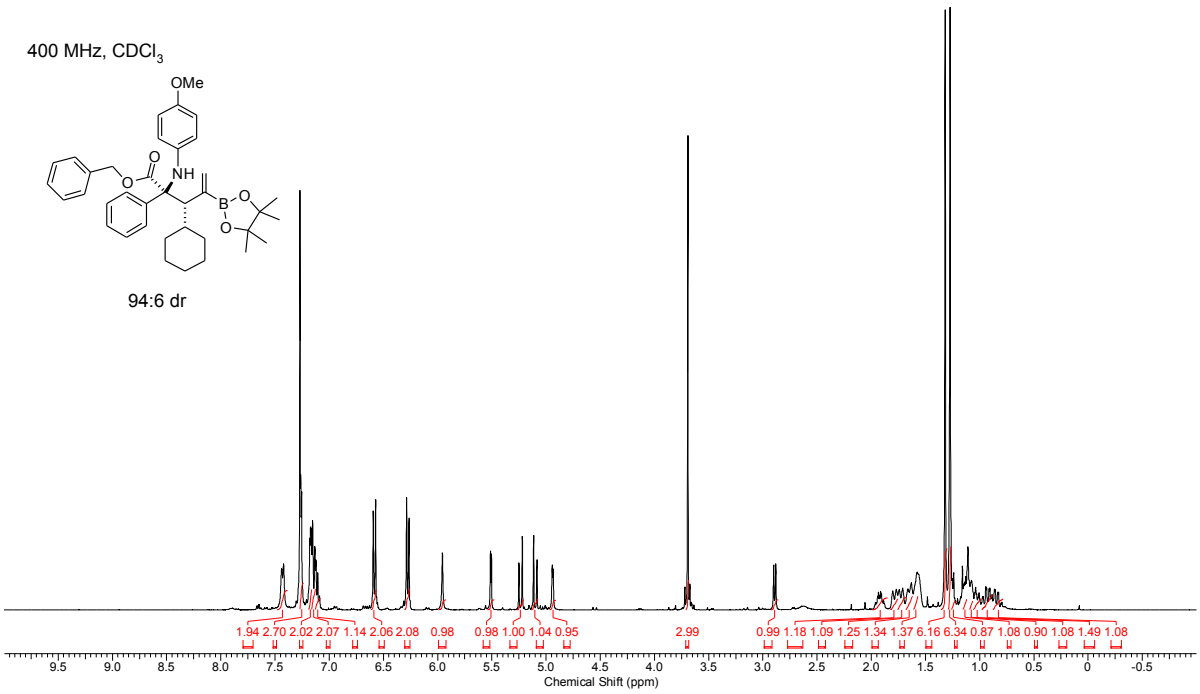
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-morpholinophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3l)**



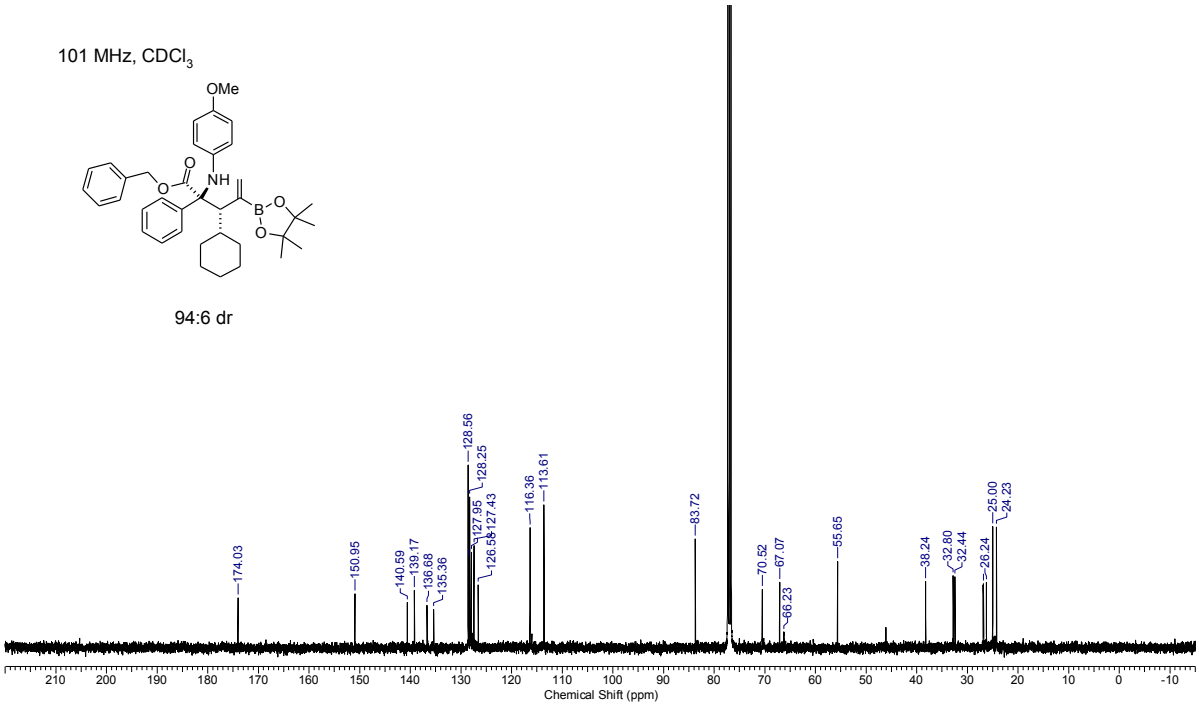
***rac*-Ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-morpholinophenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3l)**



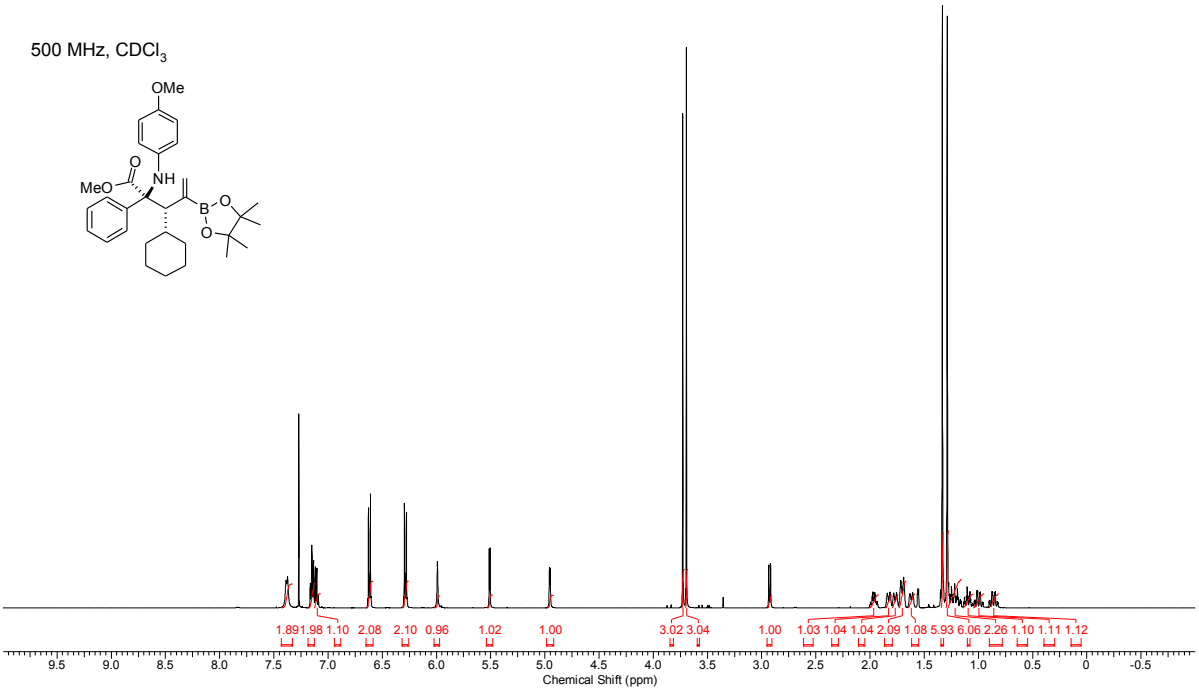
***rac*-Benzyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3n)**



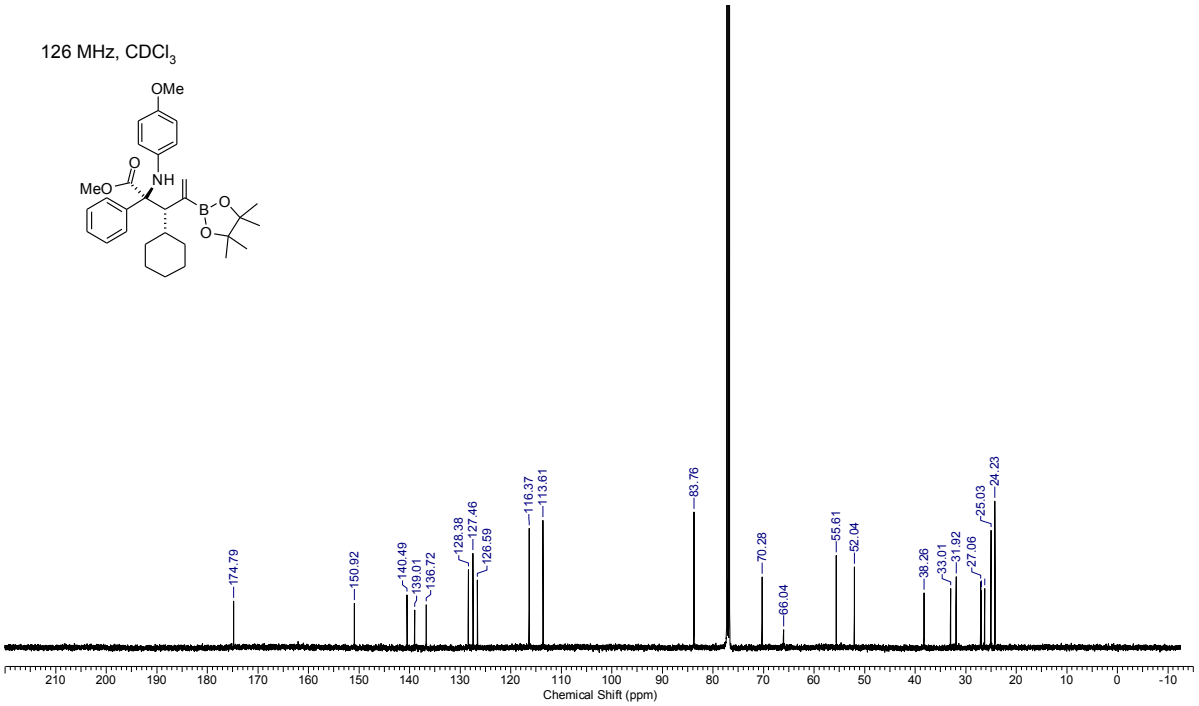
***rac*-Benzyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3n)**



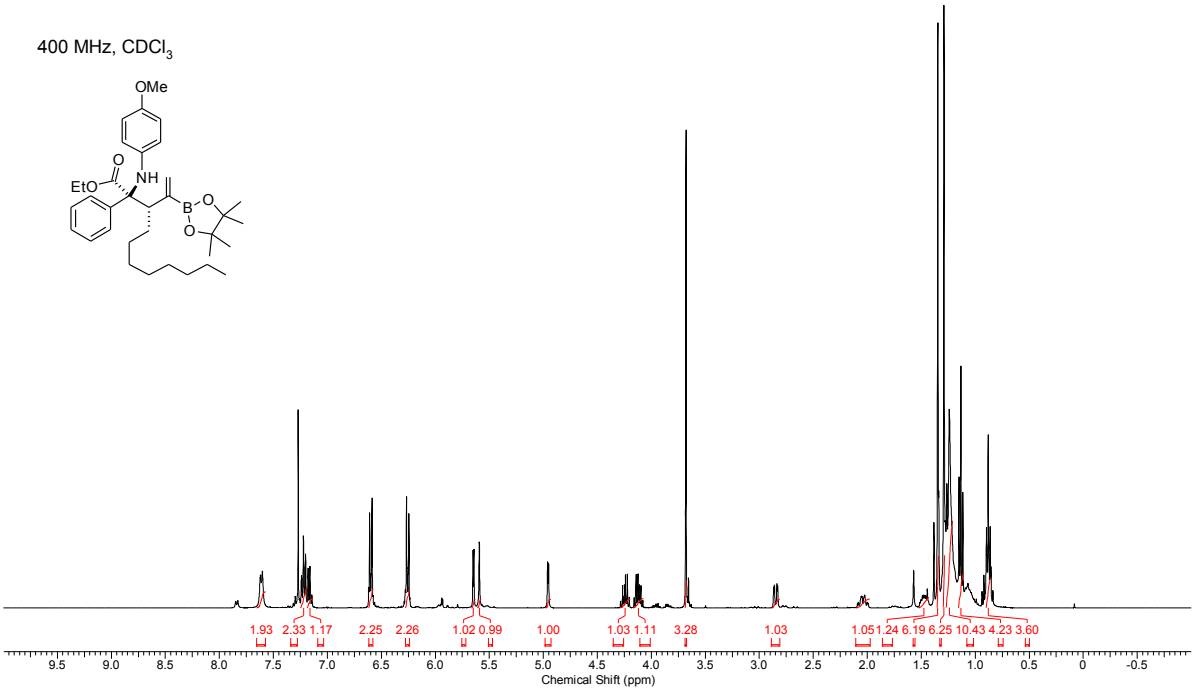
***rac*-Methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3o)**



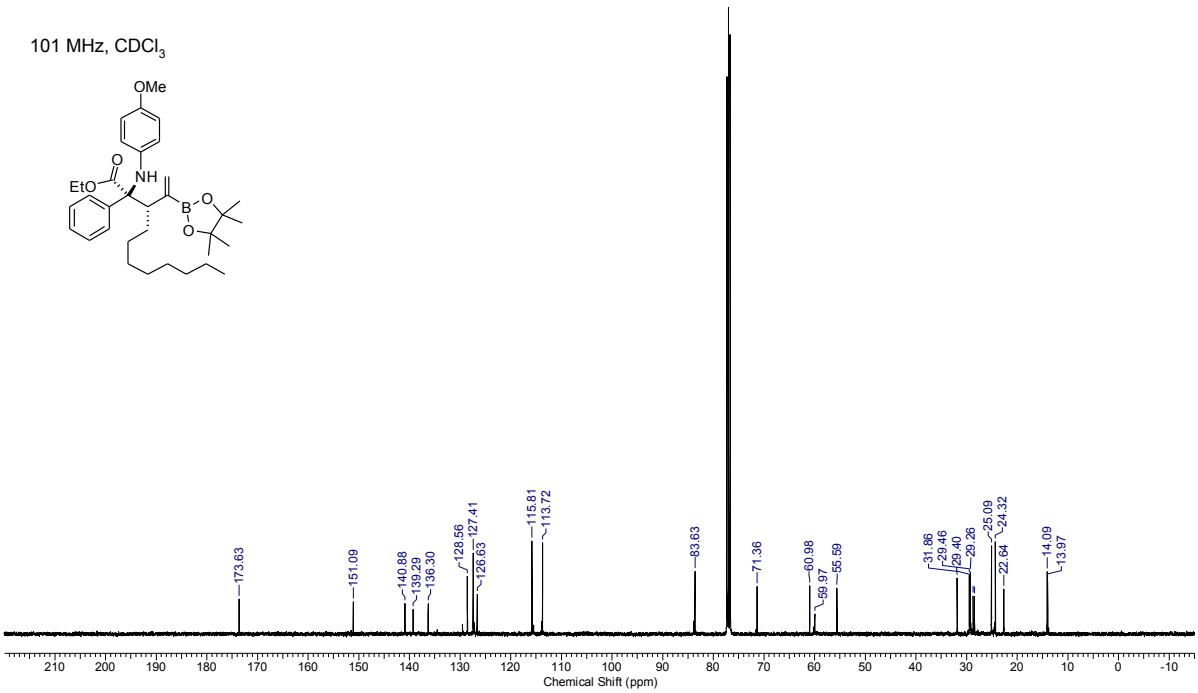
***rac*-Methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3o)**



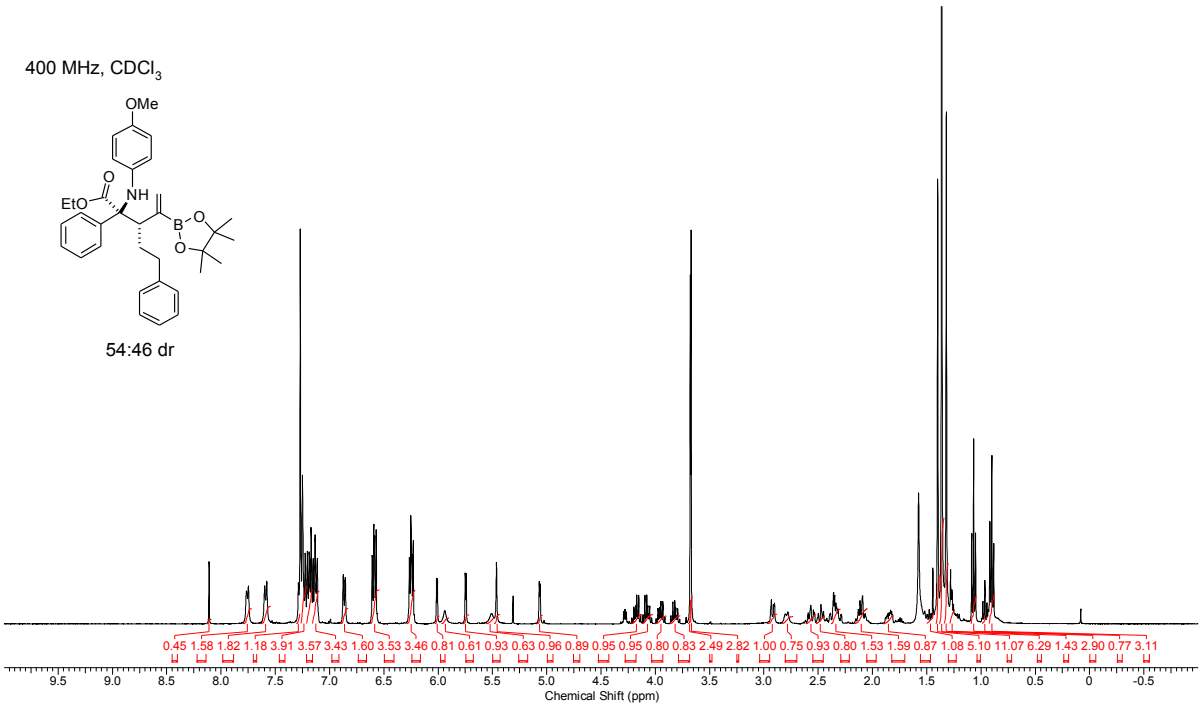
***rac*-Ethyl (2*S*,3*S*)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,2-oxaborolan-2-yl)vinyl)undecanoate (3p)**



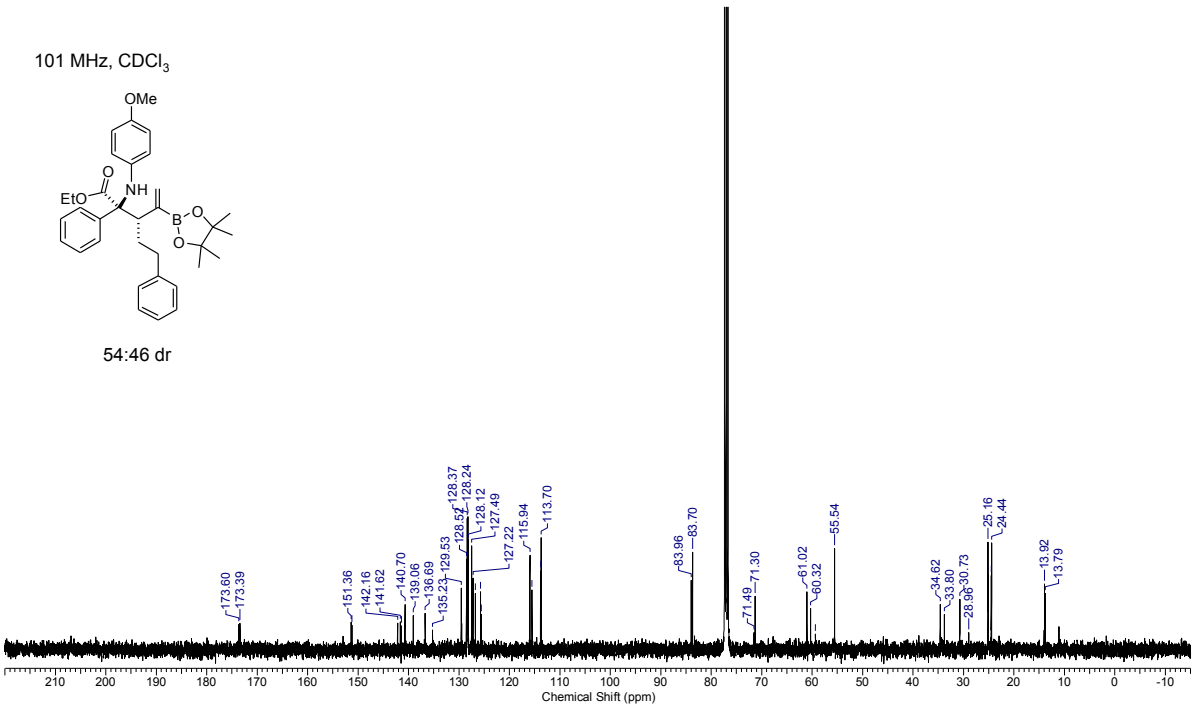
rac-Ethyl (2S,3S)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,2-oxaborolan-2-yl)vinyl)undecanoate (3p)



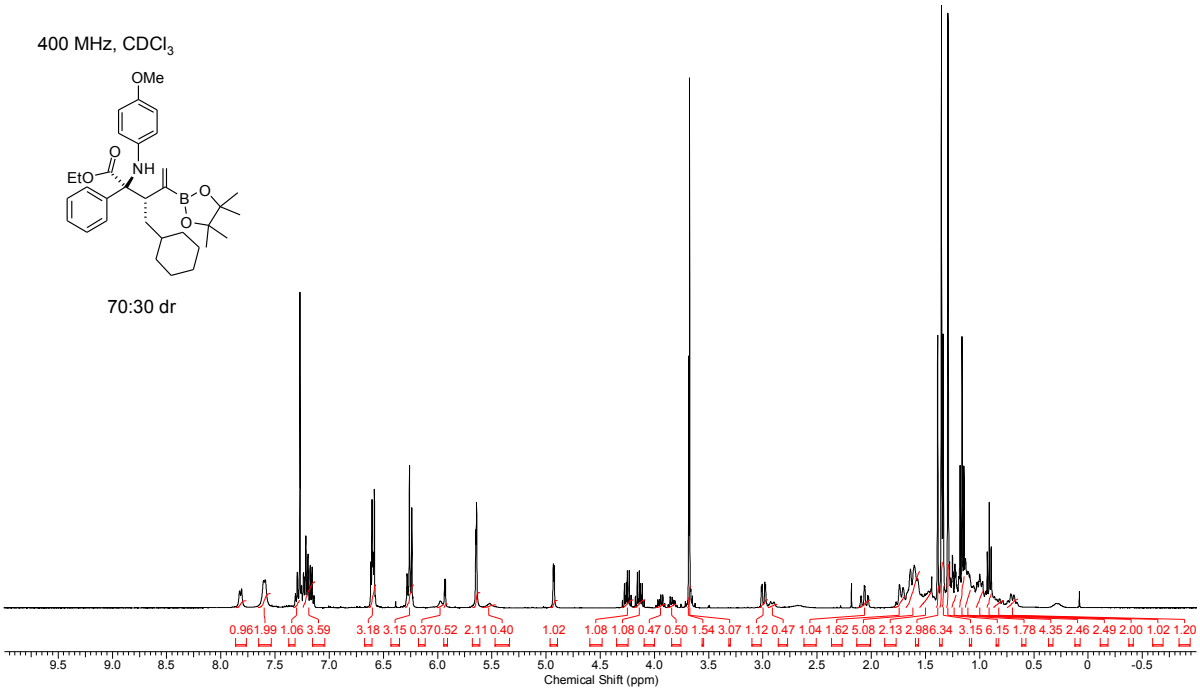
rac-Ethyl (2_S_,3_S_)-2-((4-methoxyphenyl)amino)-3-phenethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3q)



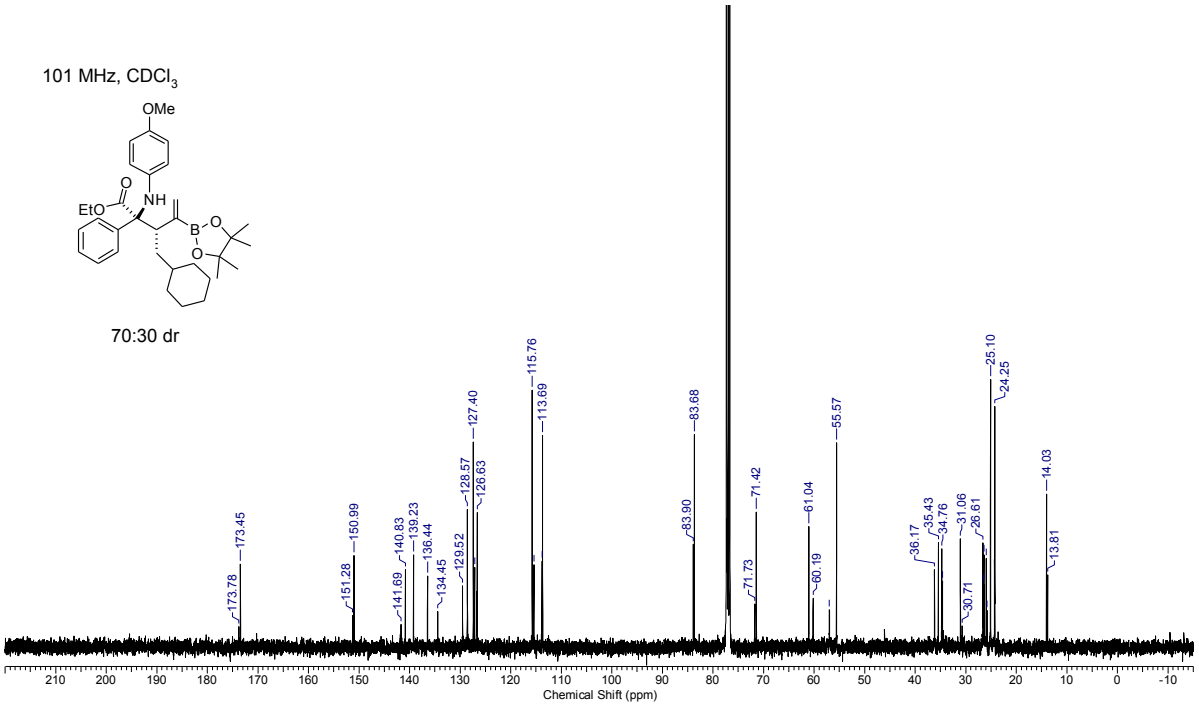
rac-Ethyl (2_S_,3_S_)-2-((4-methoxyphenyl)amino)-3-phenethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3q)



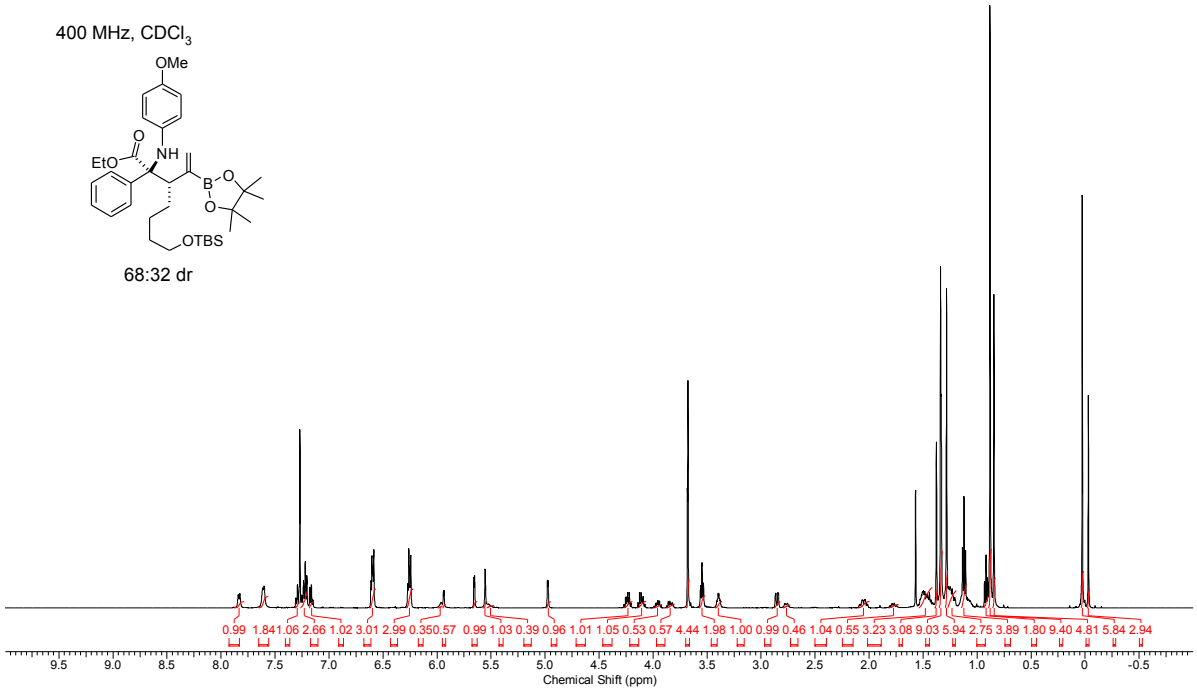
***rac*-Ethyl (2*S*,3*S*)-3-(cyclohexylmethyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3r)**



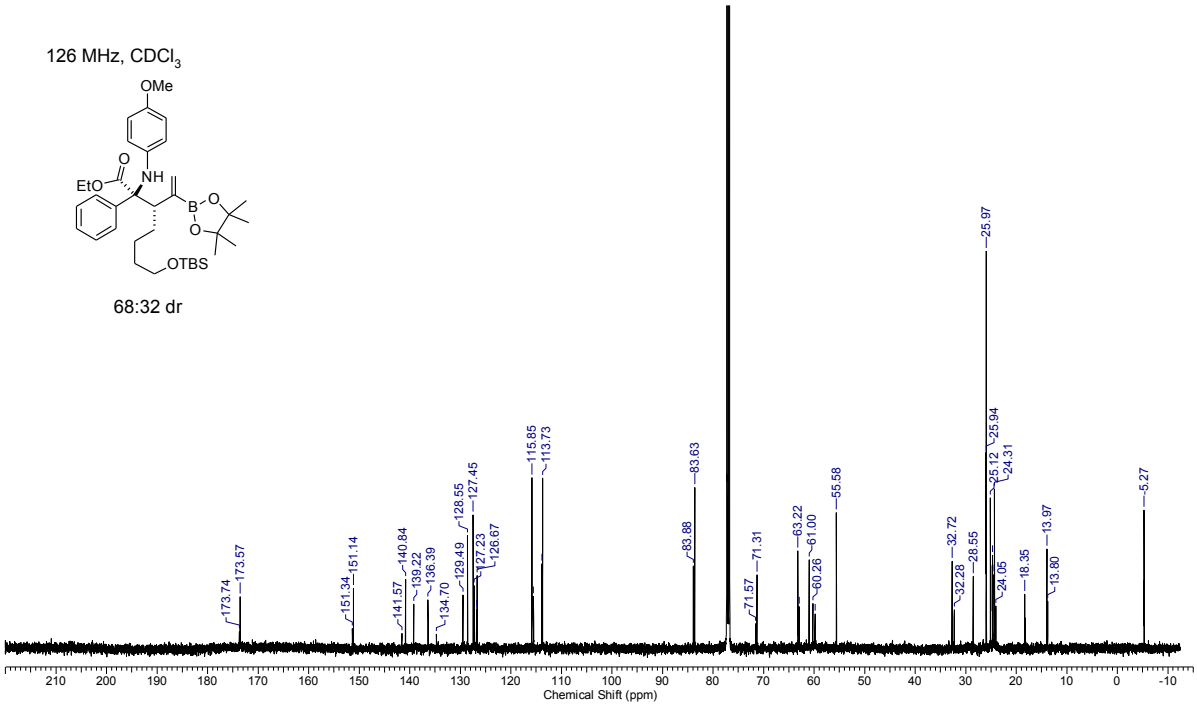
***rac*-Ethyl (2*S*,3*S*)-3-(cyclohexylmethyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3r)**



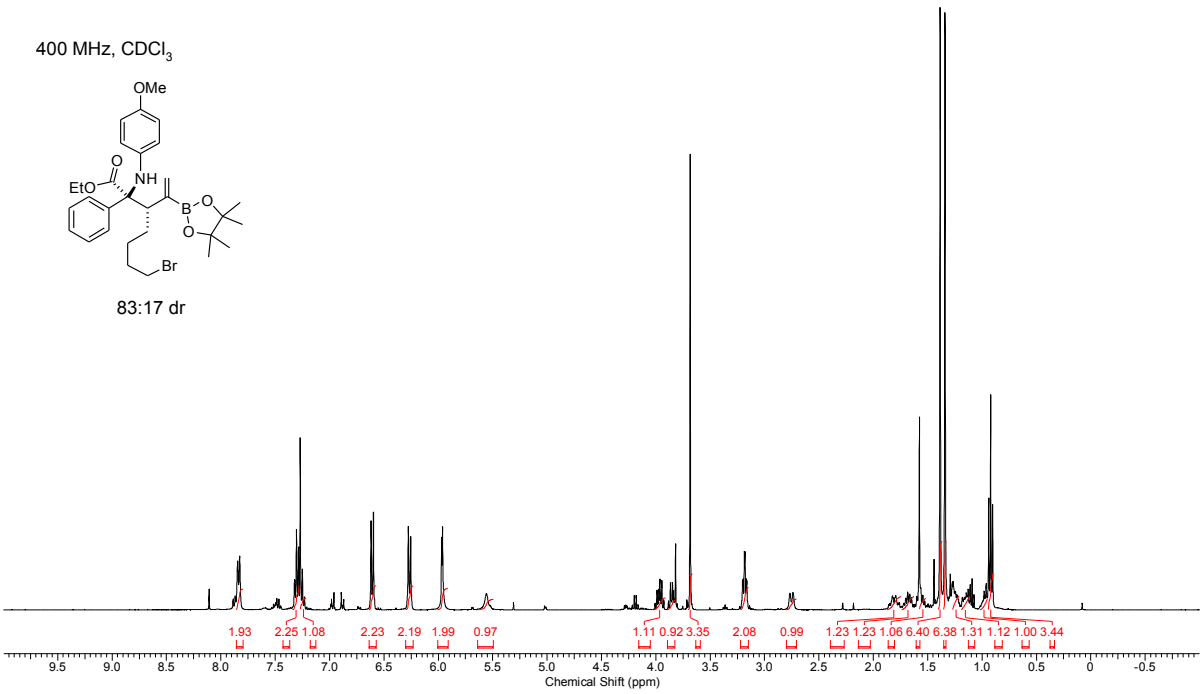
***rac*-Ethyl (2*S*,3*S*)-7-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3s)**



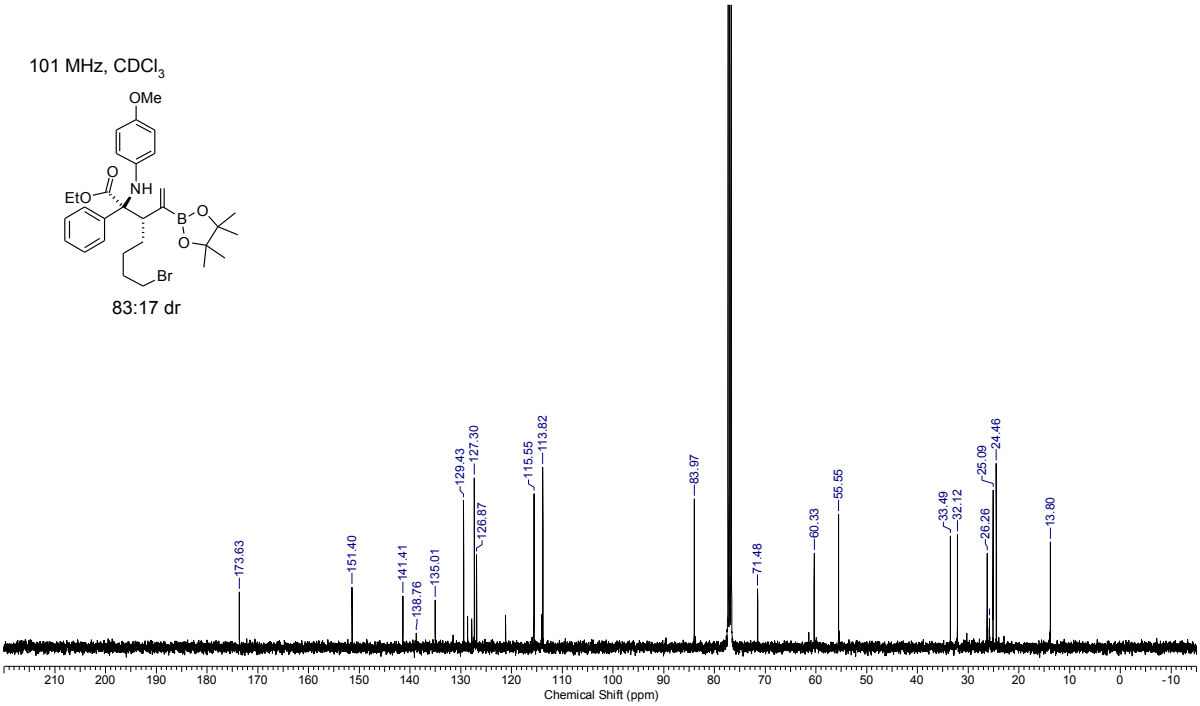
***rac*-Ethyl (2*S*,3*S*)-7-((*tert*-butyldimethylsilyl)oxy)-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3s)**



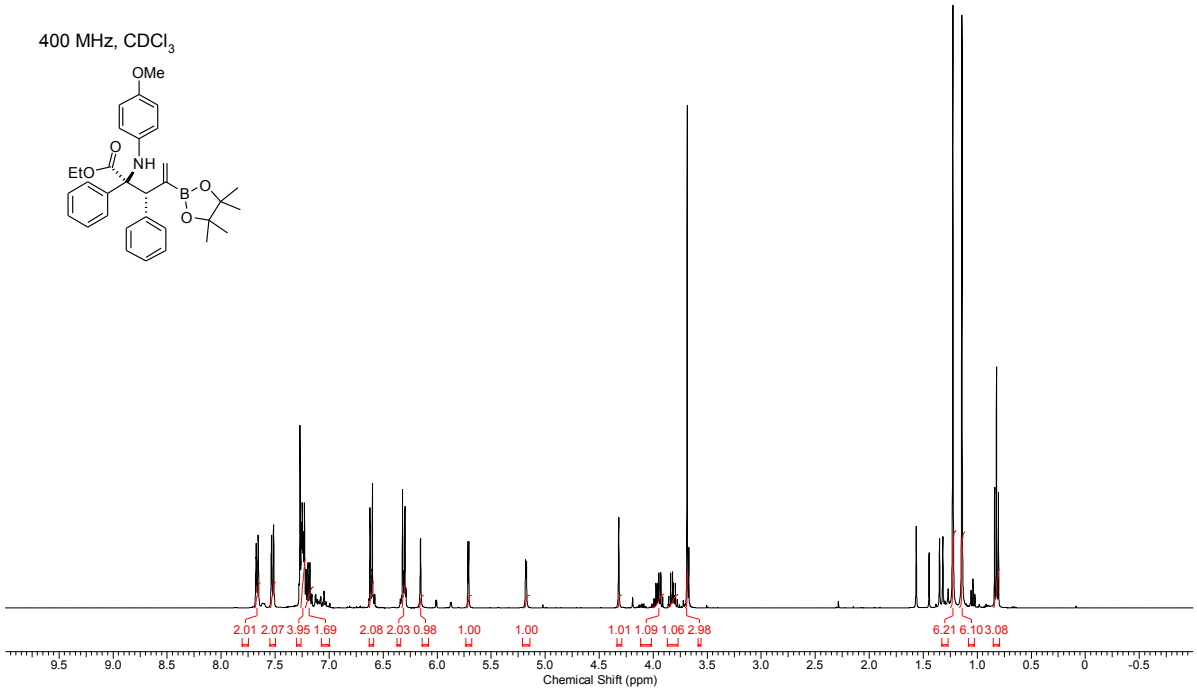
***rac*-Ethyl (2*S*,3*S*)-7-bromo-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3t)**



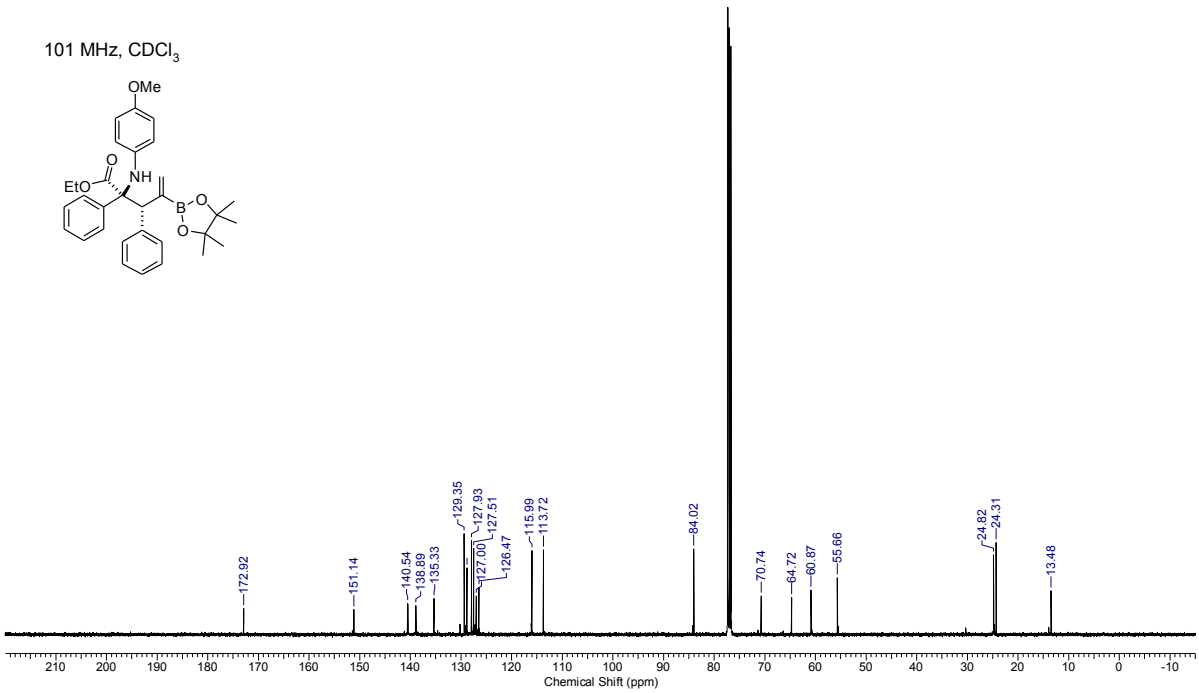
***rac*-Ethyl (2*S*,3*S*)-7-bromo-2-((4-methoxyphenyl)amino)-2-phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)heptanoate (3t)**



***rac*-Ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3u)**

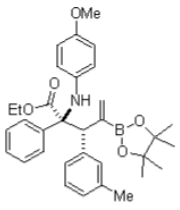


***rac*-Ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3u)**



rac-Ethyl (2S,3R)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate (3v)

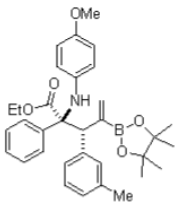
500 MHz, $CDCl_3$



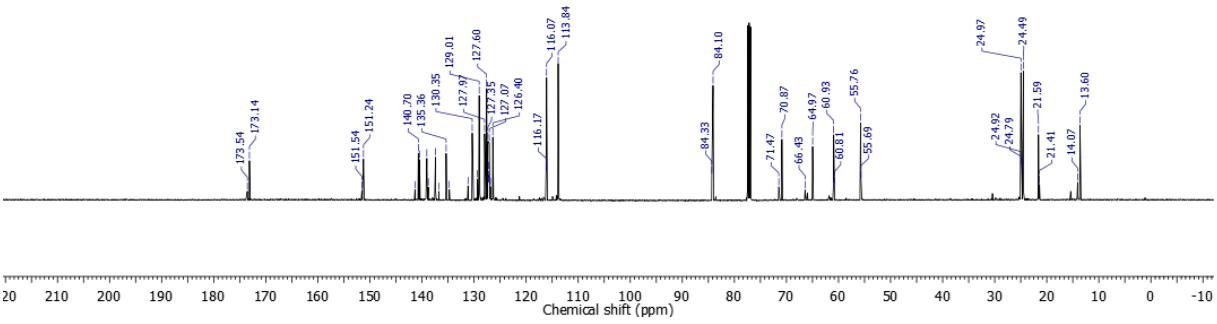
81:19 dr

rac-Ethyl (2S,3R)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate (3v)

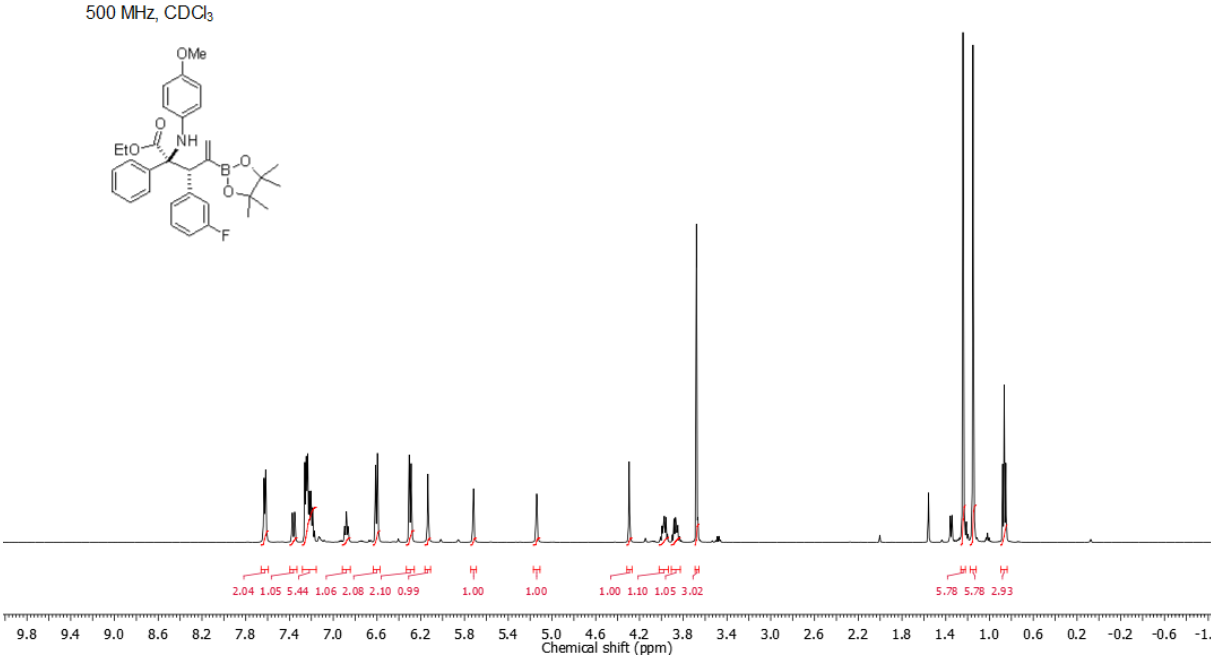
126 MHz, $CDCl_3$



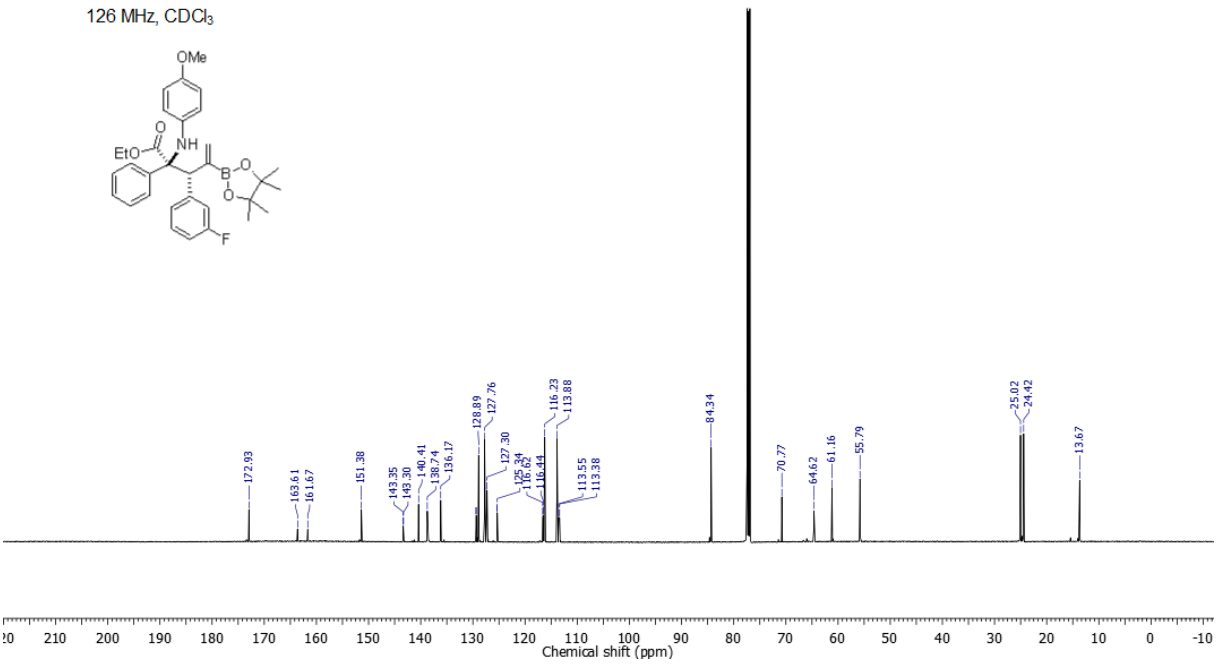
81:19 dr



rac-Ethyl (2S,3R)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3w)

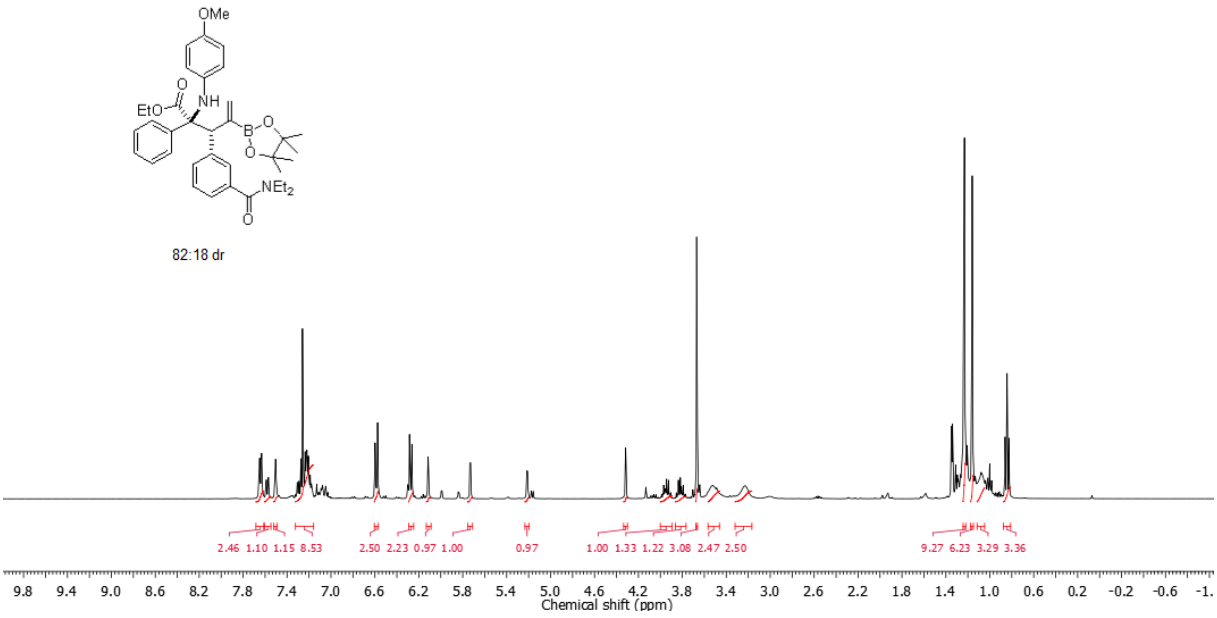


rac-Ethyl (2S,3R)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3w)



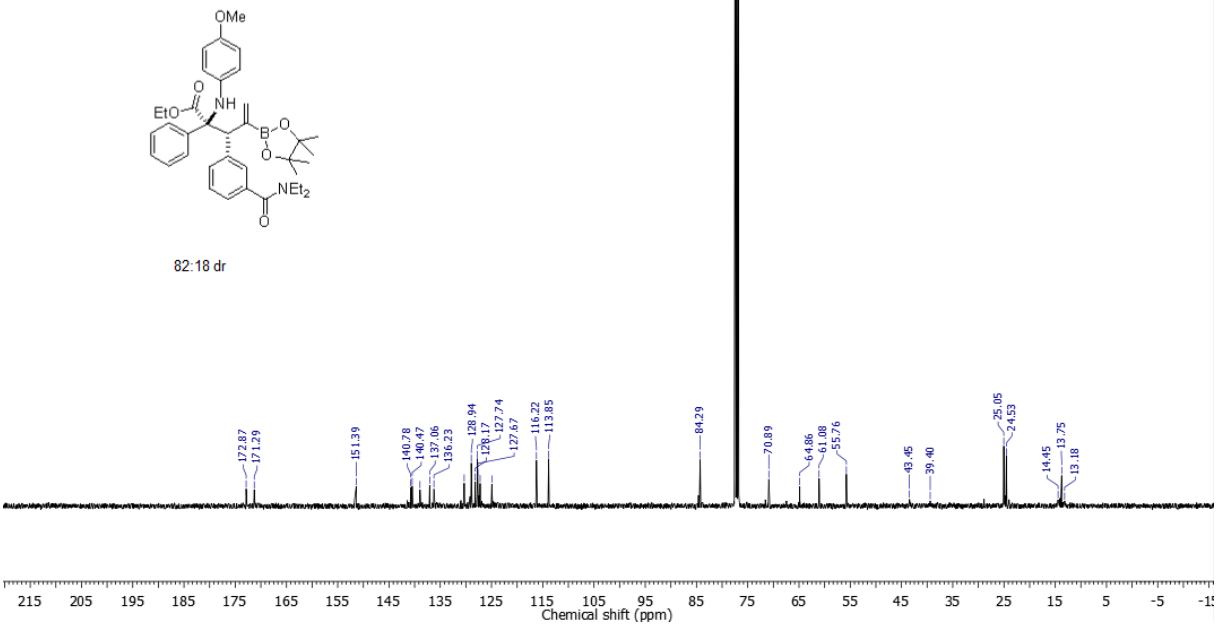
rac-Ethyl (2S,3R)-3-(3-(diethylcarbamoyl)phenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3x)

400 MHz, $CDCl_3$

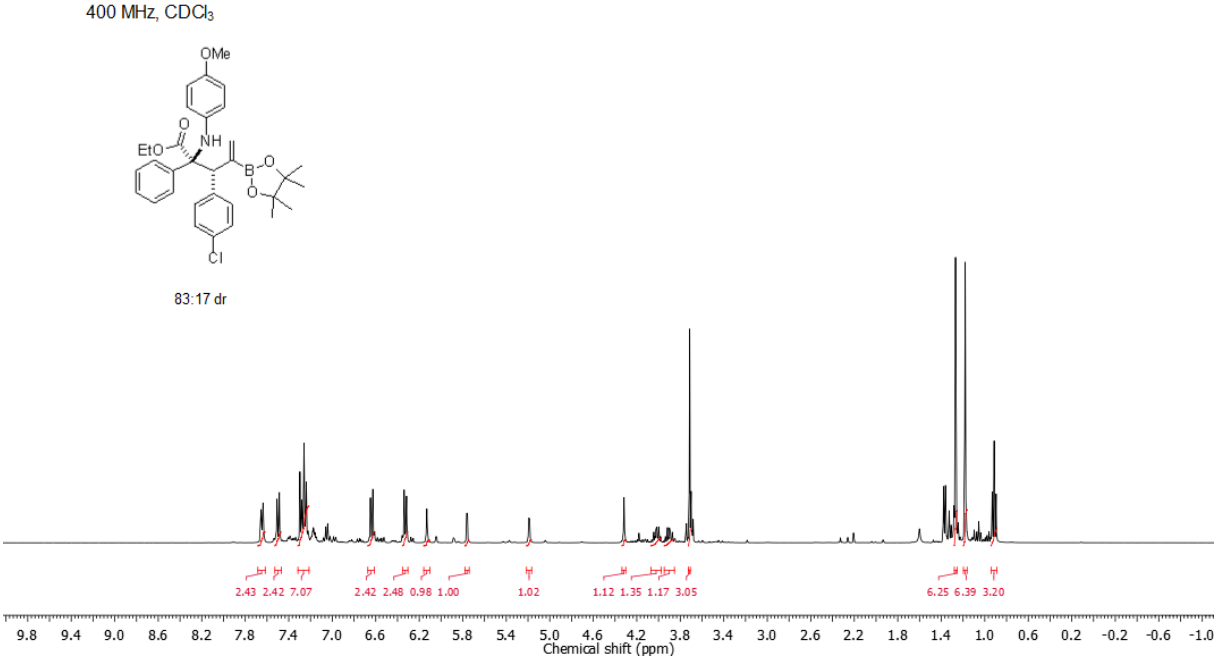


rac-Ethyl (2S,3R)-3-(3-(diethylcarbamoyl)phenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3x)

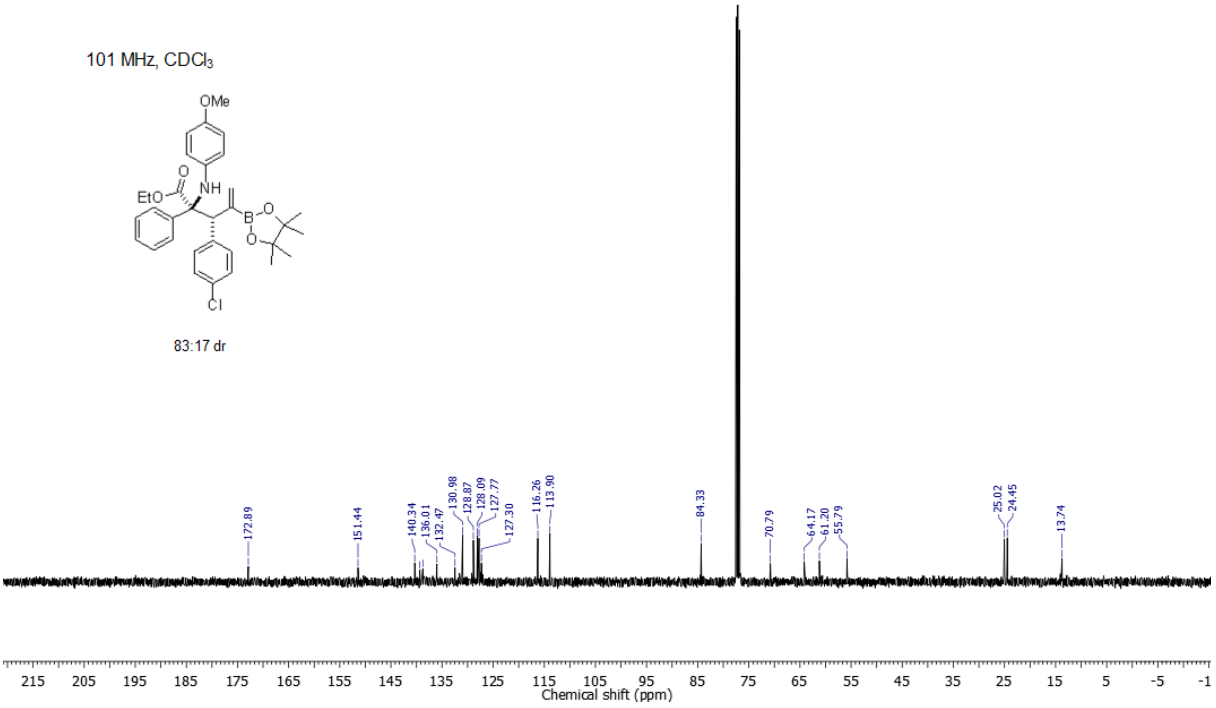
101 MHz, $CDCl_3$



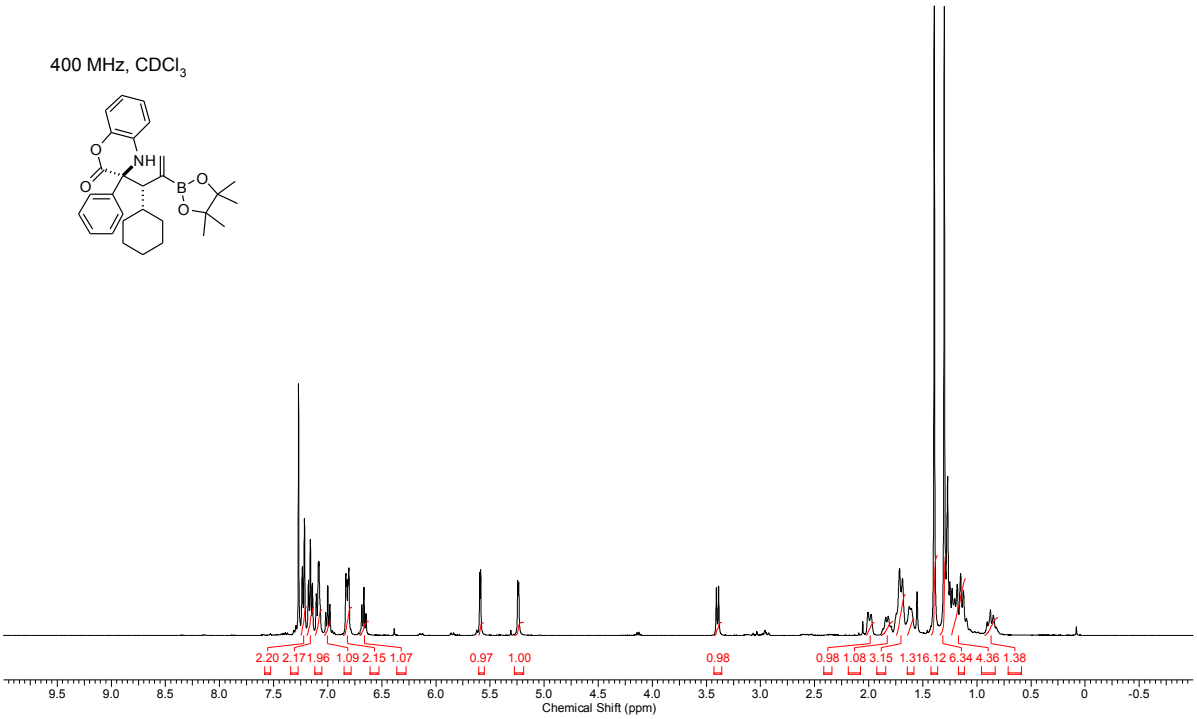
***rac*-Ethyl (2S,3R)-3-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3y)**



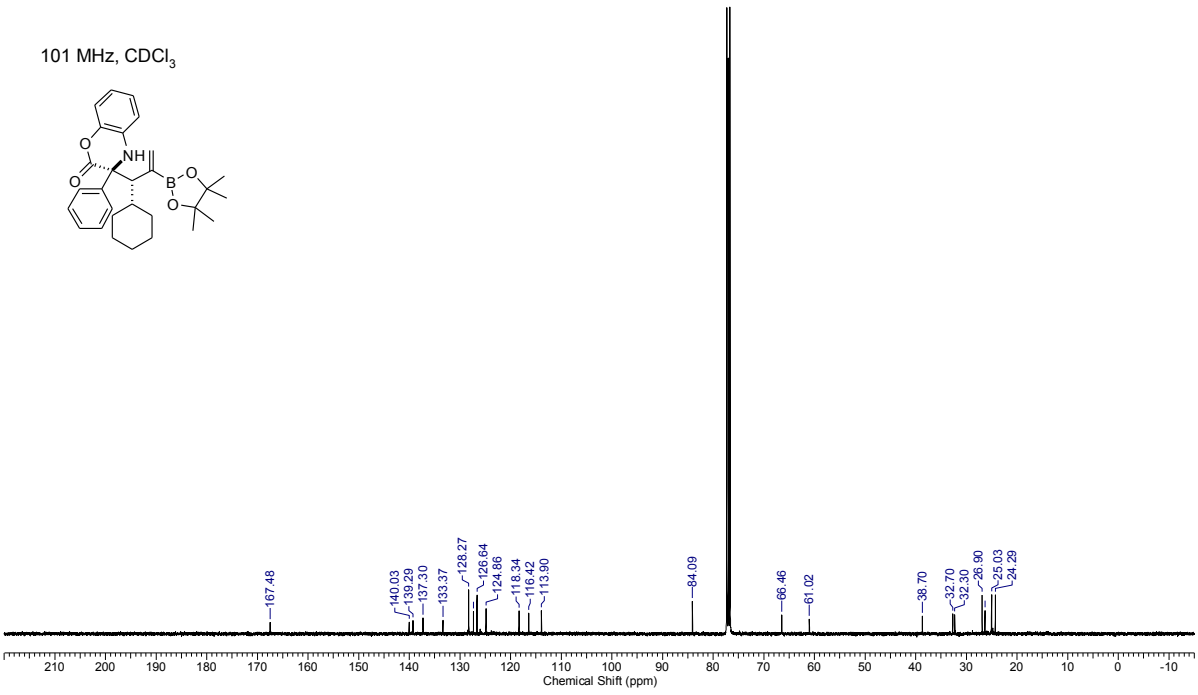
***rac*-Ethyl (2S,3R)-3-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3y)**



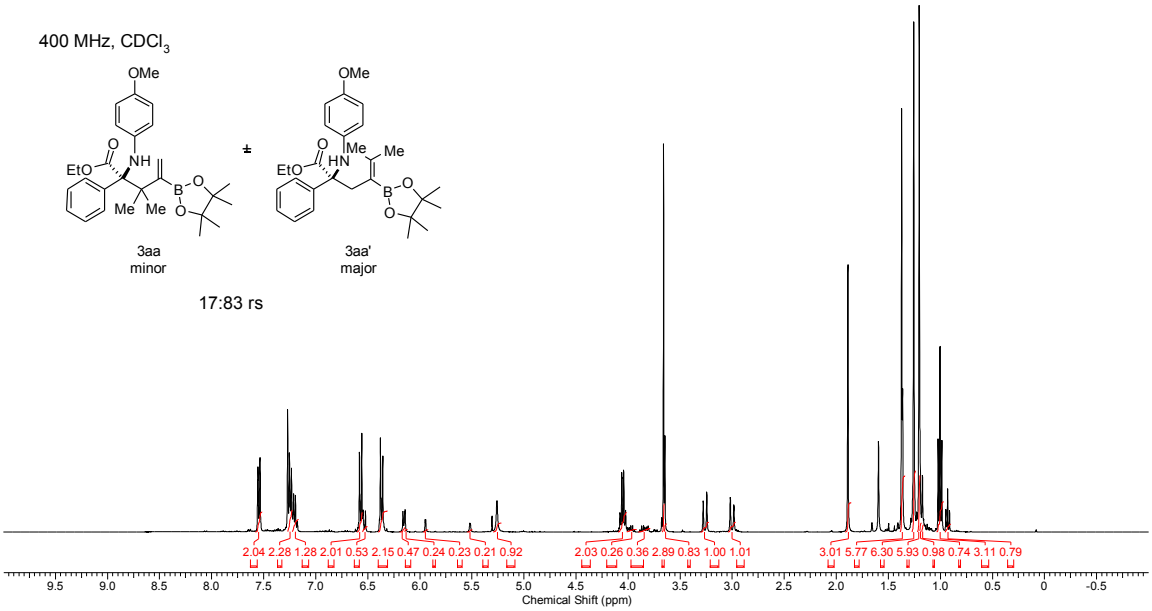
***rac*-(*S*)-3-((*S*)-1-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-3-phenyl-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (3z)**



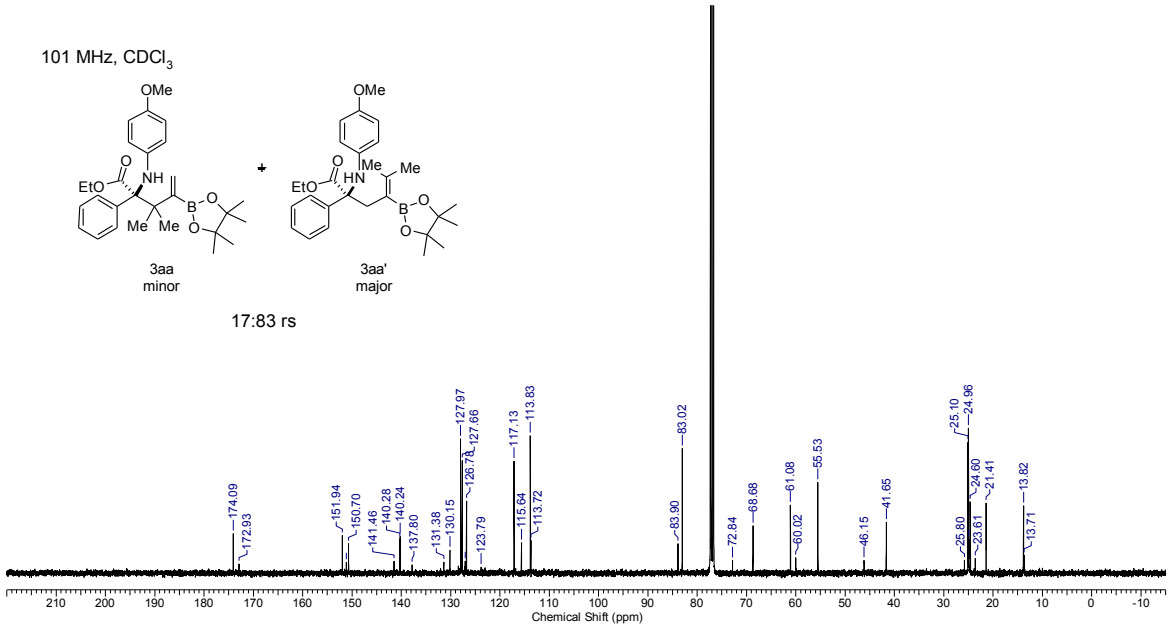
***rac*-(*S*)-3-((*S*)-1-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-3-phenyl-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (3z)**



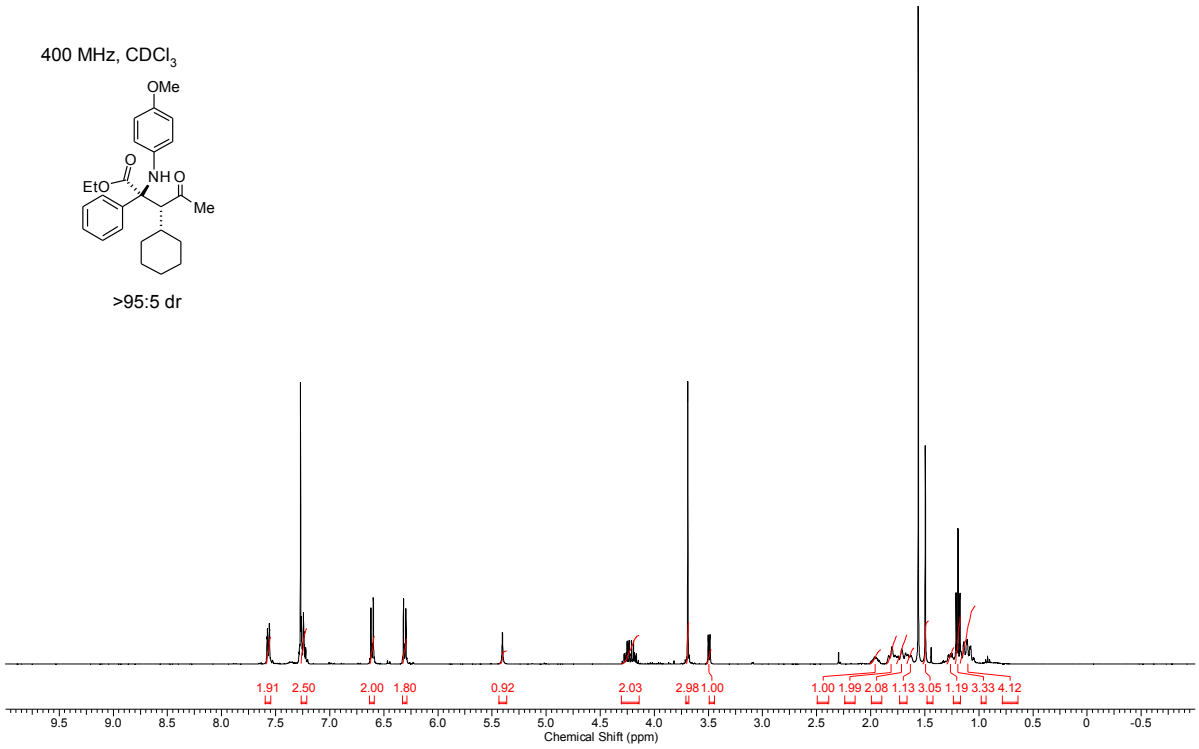
***rac*-Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3aa) and *rac*-Ethyl 2-((4-methoxyphenyl)amino)-5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (3aa')**



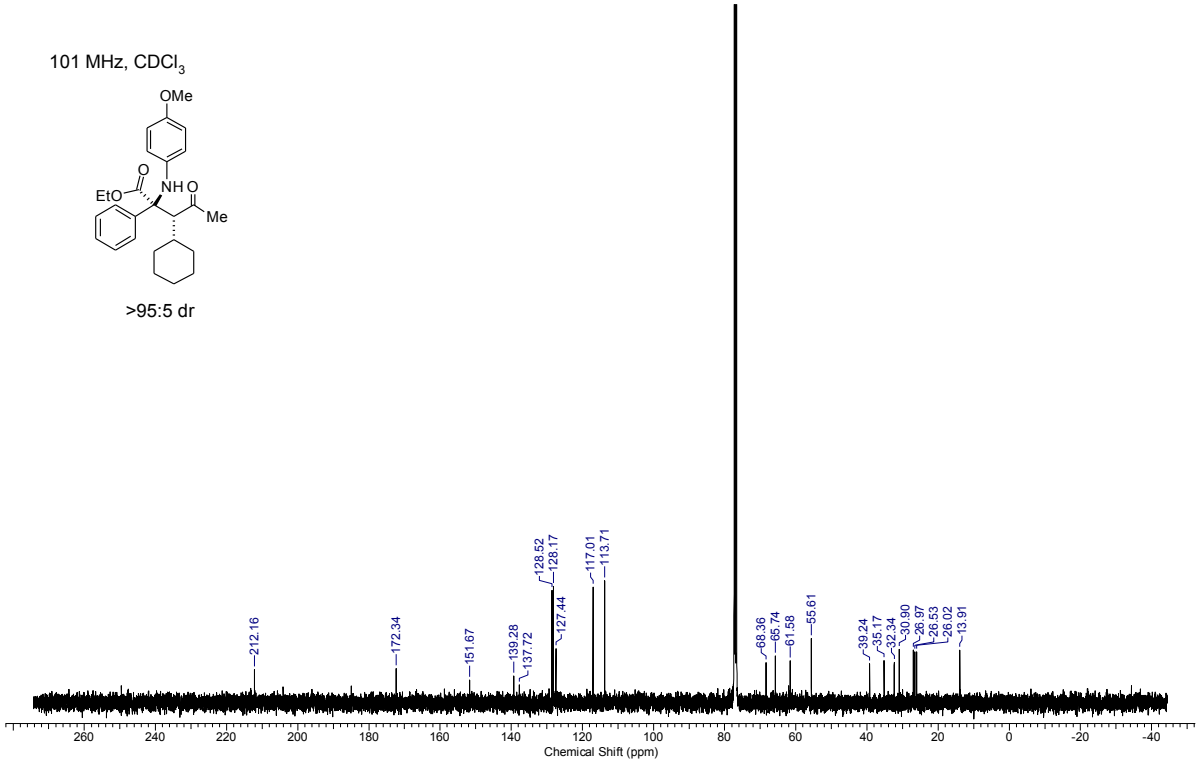
***rac*-Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (3aa) and *rac*-Ethyl 2-((4-methoxyphenyl)amino)-5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (3aa')**



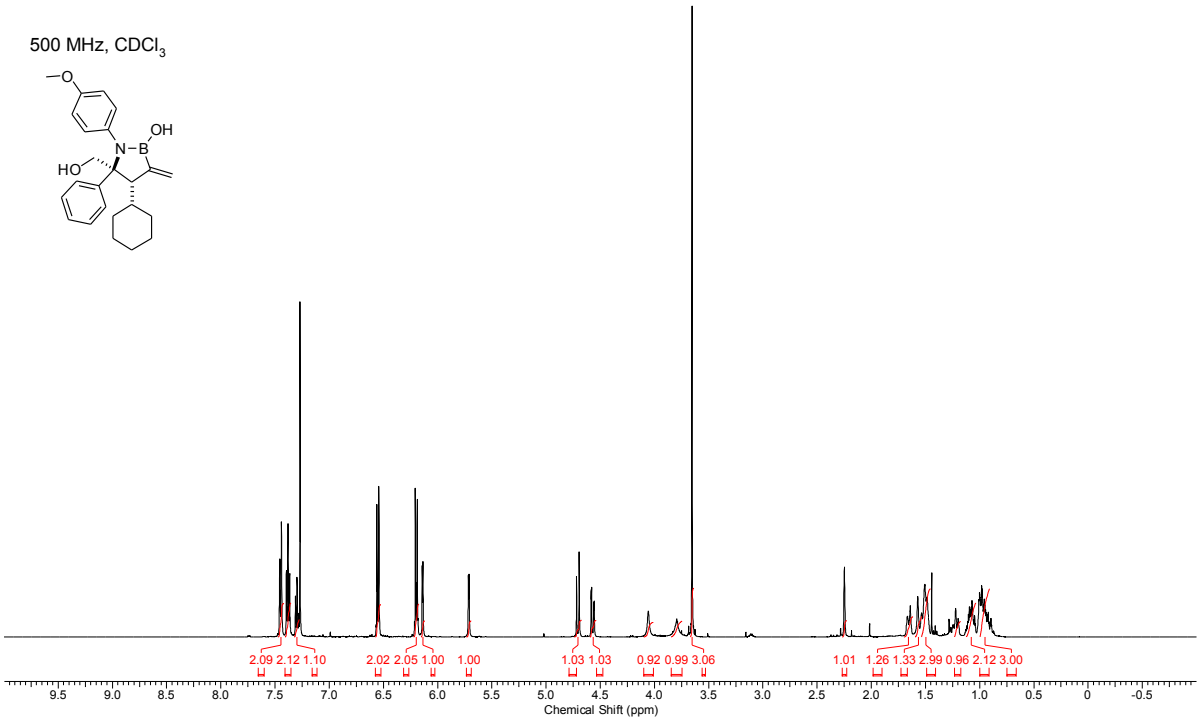
***rac*-Ethyl (2*S*,3*R*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-oxo-2-phenylpentanoate (4)**



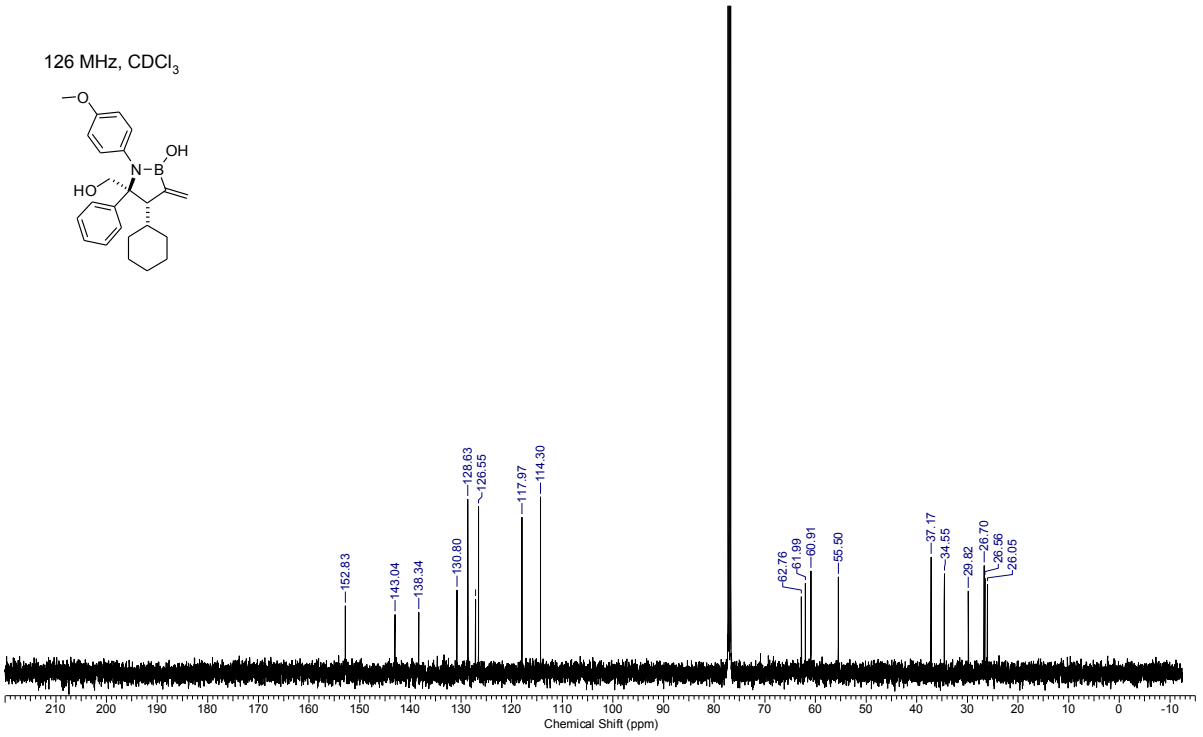
***rac*-Ethyl (2*S*,3*R*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-oxo-2-phenylpentanoate (4)**



***rac*-(4*S*,5*S*)-4-Cyclohexyl-5-(hydroxymethyl)-1-(4-methoxyphenyl)-3-methylene-5-phenyl-1,2-azaborolidin-2-ol (5)**

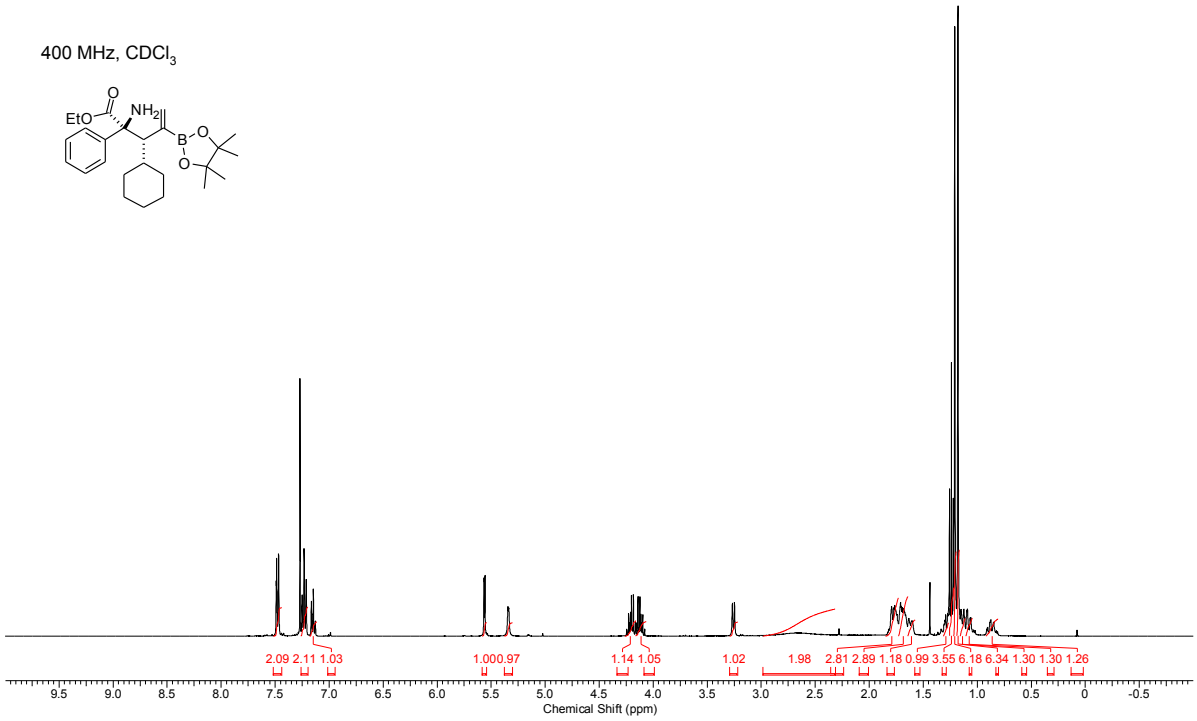


***rac*-(4*S*,5*S*)-4-Cyclohexyl-5-(hydroxymethyl)-1-(4-methoxyphenyl)-3-methylene-5-phenyl-1,2-azaborolidin-2-ol (5)**



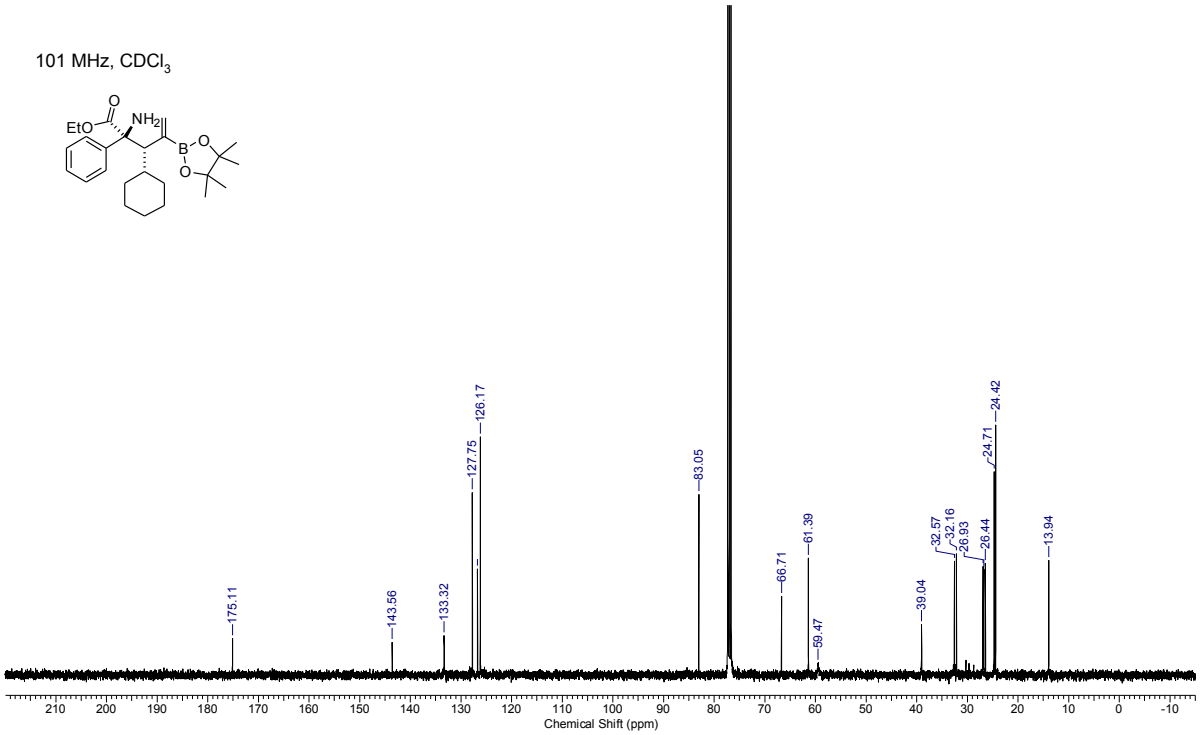
***rac*-Ethyl (2*S*,3*S*)-2-amino-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (6)**

400 MHz, $CDCl_3$

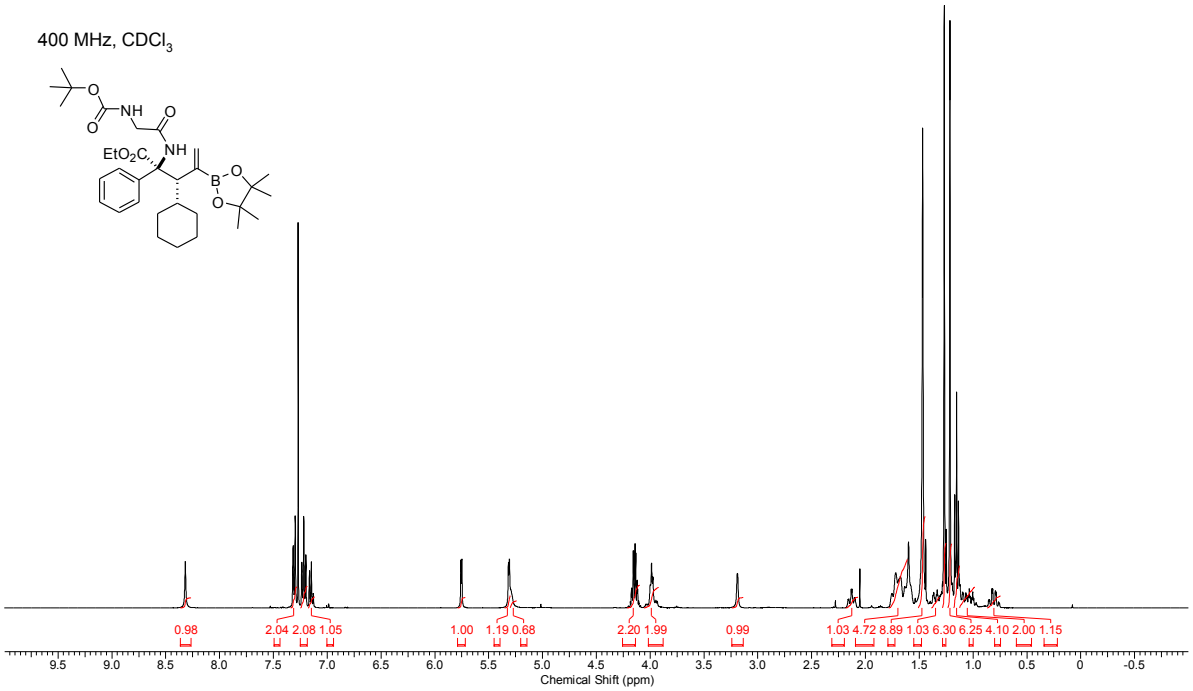


***rac*-Ethyl (2*S*,3*S*)-2-amino-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (6)**

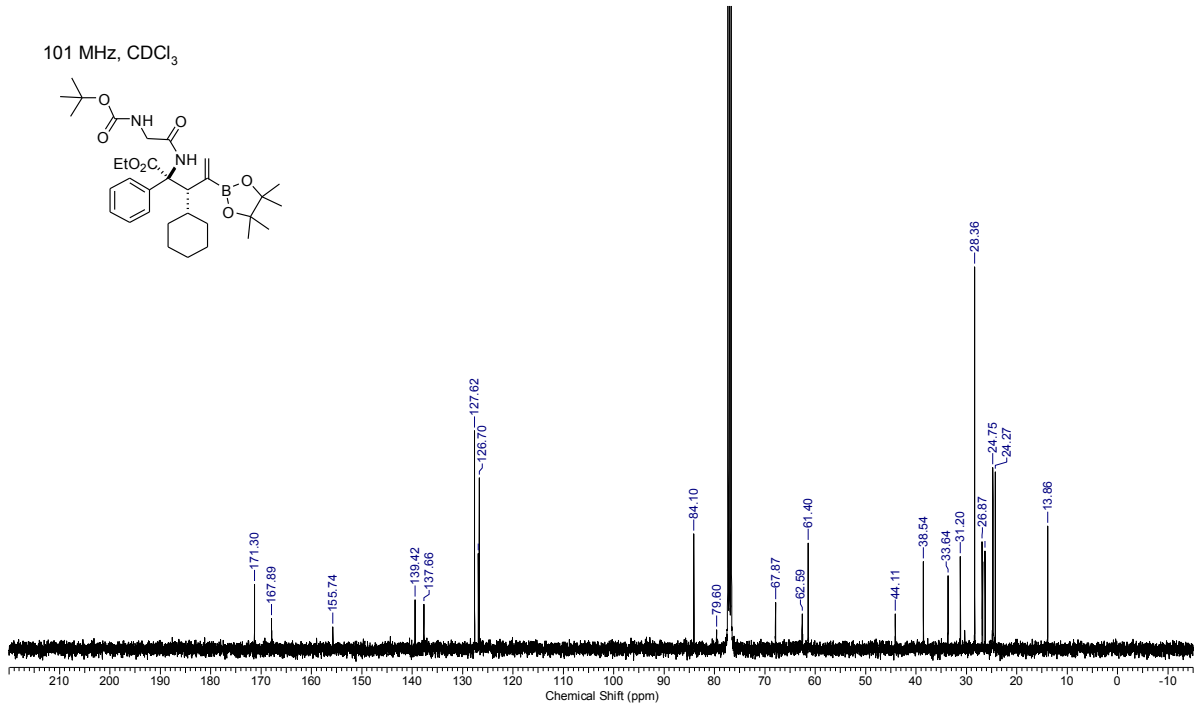
101 MHz, $CDCl_3$



***rac*-Ethyl (2*S*,3*S*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (7)**



***rac*-Ethyl (2*S*,3*S*)-2-(2-((*tert*-butoxycarbonyl)amino)acetamido)-3-cyclohexyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (7)**



X-ray Crystal Structures

Data Collection

X-ray data was collected at a temperature of 100 K or 150 K on a Rigaku FR-X diffractometer with an Atlas HP6000 detector with MoKα radiation, (λ = 0.71073 Å) for compounds **3c**, **3d**, **3v**, **3w**.

X-ray data was collected at a temperature of 150 K on an Agilent Technologies Supernova diffractometer equipped with an Eos CCD detector with MoKα radiation, (λ = 0.71073 Å) for compounds **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **3a**, **3o**, **3u**.

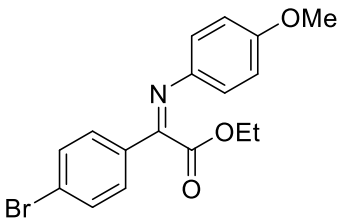
All diffractometers were equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data was measured using CrysAlisPro suite of programs.

Crystal structure determinations and refinements

X-ray data were processed and reduced using CrysAlisPro suite of programs. The crystal structures were solved and refined against all F2 values using the SHELX and Olex 2 suite of programs.[20,21] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealised geometries (riding model) and assigned fixed isotropic displacement parameters. Some carbon atoms were found disordered and modelled over two positions were possible. In such cases, C-C bond distances were restrained using DFIX and SADI commands. The atomic displacement parameters (adp) of the disordered atoms have been restrained using the RIGU command.

These data sets can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223 336033; or deposit@ccdc.cam.ac.uk).

X-ray structure of ethyl (*Z*)-2-(4-bromophenyl)-2-((4-methoxyphenyl)imino)acetate **1c** – CCDC: 1871104



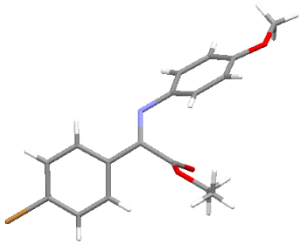


Table S5: Crystal data and structure refinement for ethyl (*Z*)-2-(4-bromophenyl)-2-((4-methoxyphenyl)imino)acetate **1c**.

Identification code	ethyl (*Z*)-2-(4-bromophenyl)-2-((4-methoxyphenyl)imino)acetate
Empirical formula	$C_{17}H_{16}BrNO_3$
Formula weight	362.22
Temperature/K	150.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9501(4)
b/Å	9.4952(5)
c/Å	11.4307(6)
α/°	73.104(5)
β/°	75.437(4)
γ/°	78.835(4)
Volume/Å^3	792.31(8)
Z	2
ρ_{calc}g/cm^3	1.518
μ/mm^{-1}	2.606
F(000)	368.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.878 to 58.01
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	10378
Independent reflections	3696 [R_{int} = 0.0407, R_{sigma} = 0.0489]
Data/restraints/parameters	3696/0/201
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0776
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.0853
Largest diff. peak/hole / e Å^{-3}	0.34/-0.45

X-ray structure of ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate **1d** – CCDC: 1871097

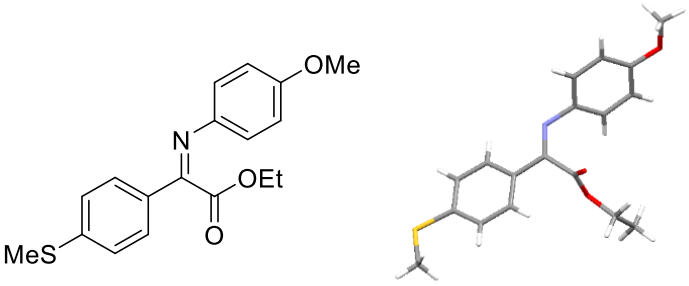
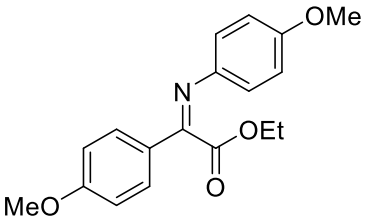


Table S6: Crystal data and structure refinement for ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate **1d**.

Identification code	ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(4-(methylthio)phenyl)acetate
Empirical formula	$C_{18}H_{19}NO_3S$
Formula weight	329.40
Temperature/K	150.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.2382(8)
b/Å	9.2717(9)
c/Å	10.5995(9)
α/°	68.295(9)
β/°	80.090(7)
γ/°	81.698(7)
Volume/Å^3	827.69(14)
Z	2
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.210
F(000)	348.0
Crystal size/mm^3	0.5 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.724 to 57.932
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 14
Reflections collected	10813
Independent reflections	3837 [R_{int} = 0.0526, R_{sigma} = 0.0727]
Data/restraints/parameters	3837/0/211
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1171
Final R indexes [all data]	R_1 = 0.0955, wR_2 = 0.1461
Largest diff. peak/hole / e Å^{-3}	0.30/-0.33

X-ray structure of ethyl (*Z*)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)acetate **1e** – CCDC: 1871093



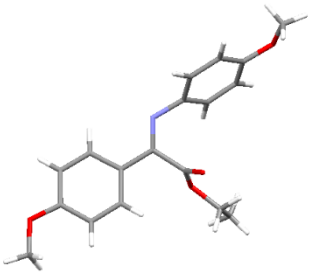
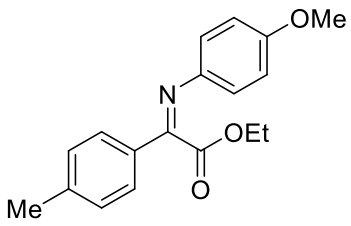


Table S7: Crystal data and structure refinement for ethyl (*Z*)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)acetate **1e**.

Identification code	ethyl (*Z*)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)acetate
Empirical formula	$C_{18}H_{19}NO_4$
Formula weight	313.34
Temperature/K	293(1)
Crystal system	triclinic
Space group	P-1
a/Å	9.1497(7)
b/Å	9.3649(7)
c/Å	10.9164(8)
α/°	65.756(7)
β/°	74.906(6)
γ/°	79.307(7)
Volume/Å^3	820.17(12)
Z	2
ρ_{calc}g/cm^3	1.269
μ/mm^{-1}	0.090
F(000)	332.0
Crystal size/mm^3	0.3 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.564 to 57.948
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	10655
Independent reflections	3839 [R_{int} = 0.0403, R_{sigma} = 0.0540]
Data/restraints/parameters	3839/0/211
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1403
Final R indexes [all data]	R_1 = 0.1263, wR_2 = 0.1895
Largest diff. peak/hole / e Å^{-3}	0.14/-0.18

X-ray structure of ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(*p*-tolyl)acetate **1f** – CCDC: 1871094



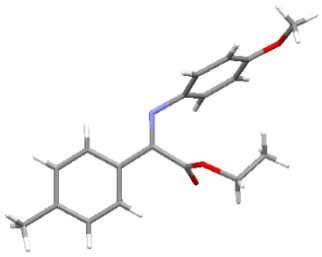


Table S8: Crystal data and structure refinement for ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(*p*-tolyl)acetate **1f**.

Identification code	ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(*p*-tolyl)acetate
Empirical formula	$C_{18}H_{19}NO_3$
Formula weight	297.34
Temperature/K	150.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7826(5)
b/Å	7.8823(4)
c/Å	15.4754(7)
α/°	90
β/°	93.667(4)
γ/°	90
Volume/Å^3	1556.05(12)
Z	4
ρ_{calc}g/cm^3	1.269
μ/mm^{-1}	0.086
F(000)	632.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.276 to 57.728
Index ranges	-17 ≤ h ≤ 17, -10 ≤ k ≤ 8, -20 ≤ l ≤ 20
Reflections collected	10336
Independent reflections	3613 [R_{int} = 0.0398, R_{sigma} = 0.0547]
Data/restraints/parameters	3613/0/202
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1282
Final R indexes [all data]	R_1 = 0.0825, wR_2 = 0.1535
Largest diff. peak/hole / e Å^{-3}	0.25/-0.28

X-ray structure of ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate **1g** – CCDC: 1871099

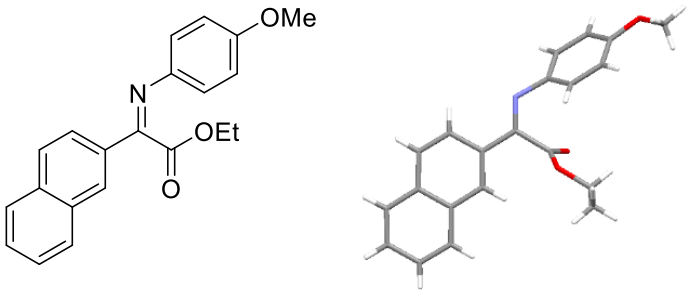


Table S9: Crystal data and structure refinement for ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate **1g**.

Identification code	ethyl (*Z*)-2-((4-methoxyphenyl)imino)-2-(naphthalen-2-yl)acetate
Empirical formula	$C_{21}H_{19}NO_3$
Formula weight	333.37
Temperature/K	149.9(3)
Crystal system	triclinic
Space group	P-1
a/Å	8.8271(6)
b/Å	10.7792(9)
c/Å	11.1856(8)
α/°	61.811(8)
β/°	69.041(7)
γ/°	78.745(6)
Volume/Å^3	875.56(13)
Z	2
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.085
F(000)	352.0
Crystal size/mm^3	0.25 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.488 to 57.512
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -14 ≤ l ≤ 15
Reflections collected	11384
Independent reflections	4058 [R_{int} = 0.0449, R_{sigma} = 0.0616]
Data/restraints/parameters	4058/0/228
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1208
Final R indexes [all data]	R_1 = 0.1055, wR_2 = 0.1551
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27

X-ray structure of ethyl (*E*)-2-((4-methoxyphenyl)imino)-2-(thiophen-2-yl)acetate **1h** – CCDC: 1871096

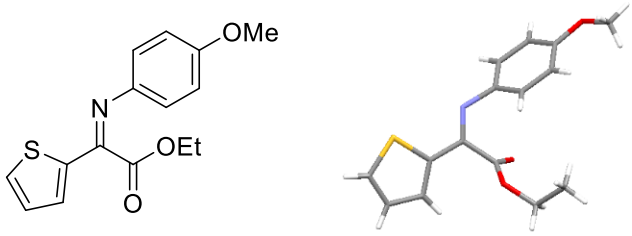
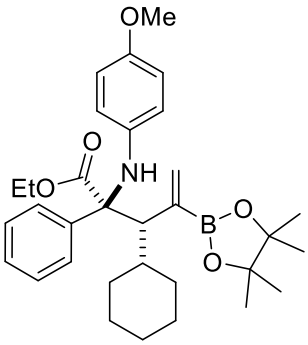


Table S10: Crystal data and structure refinement for ethyl (*E*)-2-((4-methoxyphenyl)imino)-2-(thiophen-2-yl)acetate **1h**.

Identification code	ethyl (*E*)-2-((4-methoxyphenyl)imino)-2-(thiophen-2-yl)acetate
Empirical formula	$C_{15}H_{15}NO_3S$
Formula weight	289.34
Temperature/K	150.01(18)
Crystal system	monoclinic
Space group	Pc
a/Å	9.0485(11)
b/Å	10.3116(6)
c/Å	8.6960(9)
α/°	90
β/°	117.652(14)
γ/°	90
Volume/Å^3	718.70(15)
Z	2
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.231
F(000)	304.0
Crystal size/mm^3	0.5 × 0.3 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.438 to 49.958
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -10 ≤ l ≤ 10
Reflections collected	2486
Independent reflections	1878 [R_{int} = 0.0214, R_{sigma} = 0.0500]
Data/restraints/parameters	1878/2/184
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0753
Final R indexes [all data]	R_1 = 0.0411, wR_2 = 0.0793
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17
Flack parameter	0.03(9)

X-ray structure of *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3a** – CCDC: 1871092



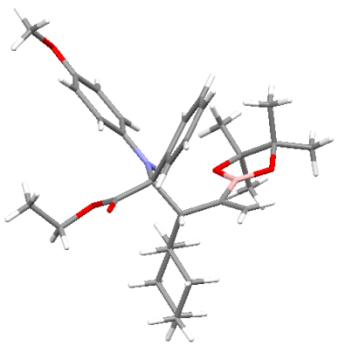
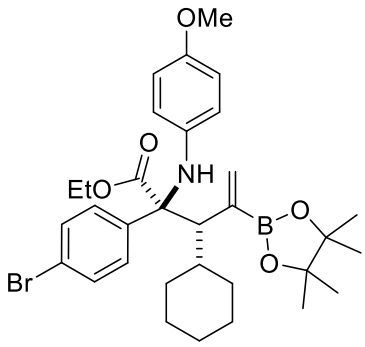


Table S11: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3a.**

Identification code	*rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate
Empirical formula	$C_{32}H_{44}BNO_5$
Formula weight	533.49
Temperature/K	149.9(4)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2170(6)
b/Å	11.6345(4)
c/Å	15.2004(5)
α/°	90
β/°	103.642(3)
γ/°	90
Volume/Å^3	2958.91(18)
Z	4
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.079
F(000)	1152.0
Crystal size/mm^3	0.6 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.534 to 57.976
Index ranges	-19 ≤ h ≤ 23, -11 ≤ k ≤ 14, -20 ≤ l ≤ 13
Reflections collected	17641
Independent reflections	6883 [R_{int} = 0.0326, R_{sigma} = 0.0436]
Data/restraints/parameters	6883/0/366
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1178
Final R indexes [all data]	R_1 = 0.0674, wR_2 = 0.1257
Largest diff. peak/hole / e Å^{-3}	0.32/-0.26

X-ray structure of ethyl *rac*-(2*S*,3*S*)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3c** – CCDC: 1871100



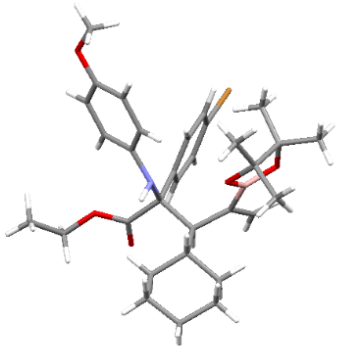
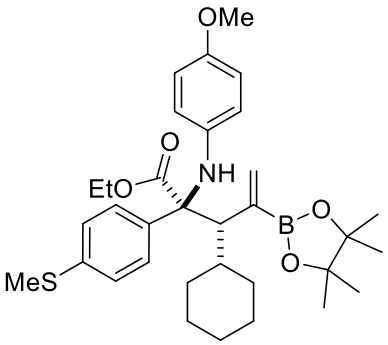


Table S12: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*S*)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3c**.

Identification code	*rac*-ethyl (2*S*,3*S*)-2-(4-bromophenyl)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate
Empirical formula	$C_{32}H_{43}BBrNO_5$
Formula weight	612.39
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	10.1641(7)
b/Å	10.5800(12)
c/Å	15.5576(17)
α/°	100.398(9)
β/°	100.500(7)
γ/°	104.669(7)
Volume/Å^3	1545.5(3)
Z	2
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	1.370
F(000)	644.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.736 to 50.7
Index ranges	-10 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 15
Reflections collected	11014
Independent reflections	5658 [R_{int} = 0.0763, R_{sigma} = 0.1085]
Data/restraints/parameters	5658/0/367
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1388
Final R indexes [all data]	R_1 = 0.0980, wR_2 = 0.1638
Largest diff. peak/hole / e Å^{-3}	0.94/-0.69

X-ray structure of *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4 (methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3d** – CCDC: 1871103



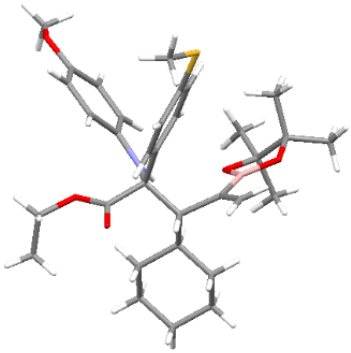
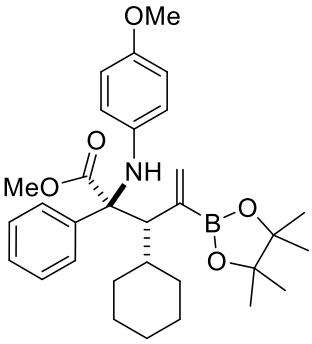


Table S13: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3d.**

Identification code	*rac*-ethyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-(4-(methylthio)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pent-4-enoate
Empirical formula	$C_{33}H_{46}BNO_5S$
Formula weight	579.58
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	9.9671(6)
b/Å	11.8555(8)
c/Å	13.5226(7)
α/°	91.143(5)
β/°	93.483(5)
γ/°	98.164(5)
Volume/Å^3	1578.12(17)
Z	2
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.143
F(000)	624.0
Crystal size/mm^3	0.5 × 0.5 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.88 to 56.56
Index ranges	-13 ≤ h ≤ 12, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	14379
Independent reflections	7197 [R_{int} = 0.0504, R_{sigma} = 0.1024]
Data/restraints/parameters	7197/0/377
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0631, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.1343, wR_2 = 0.1352
Largest diff. peak/hole / e Å^{-3}	0.45/-0.39

X-ray structure of *rac*-methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3o** – CCDC: 1871098



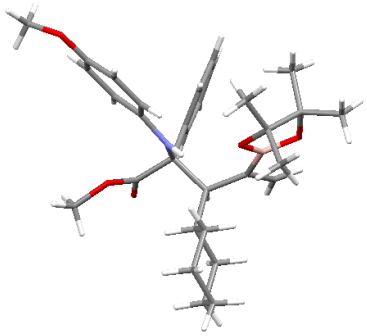
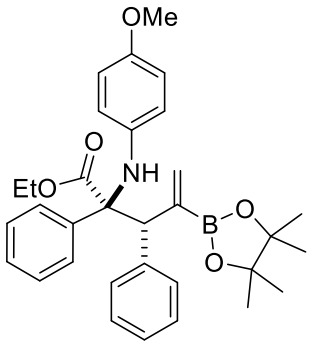


Table S14: Crystal data and structure refinement for *rac*-methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3o.**

Identification code	*rac*-methyl (2*S*,3*S*)-3-cyclohexyl-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pent-4-enoate
Empirical formula	$C_{31}H_{42}BNO_5$
Formula weight	519.46
Temperature/K	150.0(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.7642(7)
b/Å	11.6105(5)
c/Å	15.0601(7)
α/°	90
β/°	100.923(4)
γ/°	90
Volume/Å^3	2878.2(2)
Z	4
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	0.079
F(000)	1120.0
Crystal size/mm^3	0.5 × 0.4 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.348 to 58.312
Index ranges	-21 ≤ h ≤ 22, -15 ≤ k ≤ 14, -20 ≤ l ≤ 19
Reflections collected	15314
Independent reflections	6632 [R_{int} = 0.0406, R_{sigma} = 0.0545]
Data/restraints/parameters	6632/0/349
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1261
Final R indexes [all data]	R_1 = 0.0756, wR_2 = 0.1405
Largest diff. peak/hole / e Å^{-3}	0.33/-0.39

X-ray structure of *rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3u** – CCDC: 1871095



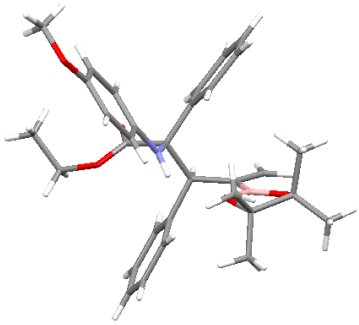
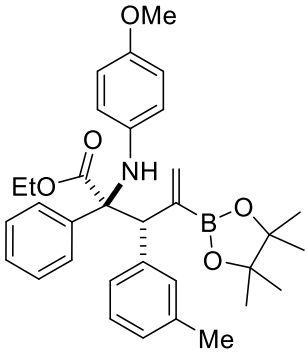


Table S15: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3u.**

Identification code	*rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pent-4-enoate
Empirical formula	$C_{32}H_{38}BNO_5$
Formula weight	527.44
Temperature/K	150.0(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.1408(7)
b/Å	10.9829(4)
c/Å	15.7412(8)
α/°	90
β/°	101.768(4)
γ/°	90
Volume/Å^3	2901.1(2)
Z	4
ρ_{calc}g/cm^3	1.208
μ/mm^{-1}	0.080
F(000)	1128.0
Crystal size/mm^3	0.8 × 0.8 × 0.8
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.11 to 57.92
Index ranges	-22 ≤ h ≤ 10, -7 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	10735
Independent reflections	6470 [R_{int} = 0.0283, R_{sigma} = 0.0512]
Data/restraints/parameters	6470/0/366
Goodness-of-fit on F^2	0.912
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1143
Final R indexes [all data]	R_1 = 0.0718, wR_2 = 0.1303
Largest diff. peak/hole / e Å^{-3}	0.37/-0.30

X-ray structure of *rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate **3v** – CCDC: 1871102



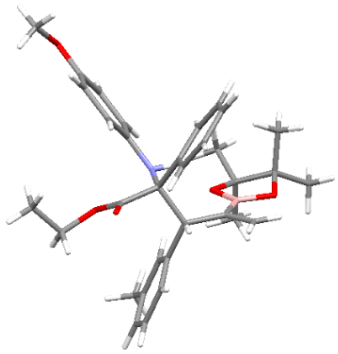
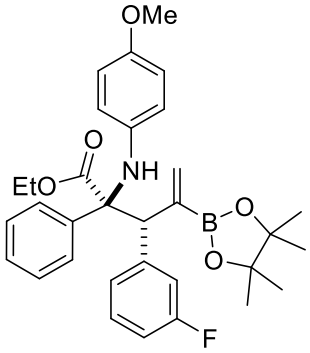


Table S16: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate **3v**.

Identification code	*rac*-ethyl (2*S*,3*R*)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)pent-4-enoate
Empirical formula	$C_{33}H_{40}BNO_5$
Formula weight	541.47
Temperature/K	160
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2140(14)
b/Å	11.3358(7)
c/Å	15.8990(15)
α/°	90
β/°	103.239(9)
γ/°	90
Volume/Å^3	3020.0(4)
Z	4
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.079
F(000)	1160.0
Crystal size/mm^3	0.3 × 0.3 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.026 to 52.74
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	27858
Independent reflections	6167 [R_{int} = 0.0988, R_{sigma} = 0.1019]
Data/restraints/parameters	6167/0/368
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1390
Final R indexes [all data]	R_1 = 0.1606, wR_2 = 0.1798
Largest diff. peak/hole / e Å^{-3}	0.28/-0.31

X-ray structure of *rac*-ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3w** – CCDC: 1871101



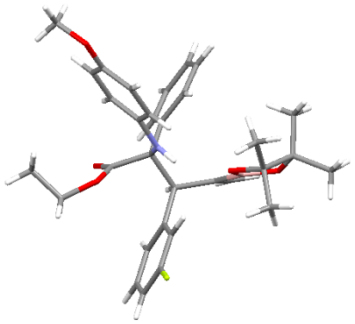


Table S17: Crystal data and structure refinement for *rac*-ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate **3w.**

Identification code	*rac*-ethyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate
Empirical formula	$C_{32}H_{37}BFNO_5$
Formula weight	545.43
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2850(9)
b/Å	11.0449(6)
c/Å	15.7475(10)
α/°	90
β/°	102.556(6)
γ/°	90
Volume/Å^3	2934.5(3)
Z	4
ρ_{calc}g/cm^3	1.235
μ/mm^{-1}	0.086
F(000)	1160.0
Crystal size/mm^3	0.4 × 0.3 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.038 to 51.358
Index ranges	-17 ≤ h ≤ 21, -12 ≤ k ≤ 13, -15 ≤ l ≤ 19
Reflections collected	14970
Independent reflections	5546 [R_{int} = 0.0356, R_{sigma} = 0.0498]
Data/restraints/parameters	5546/0/367
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1028
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1274
Largest diff. peak/hole / e Å^{-3}	0.39/-0.27

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