Enantioselective and regiodivergent copper-catalyzed electrophilic arylation of allylic amides with diaryliodonium salts

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Supporting Information

Experimental procedures and data

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

1. General Information

Solvents: All anhydrous solvents were dried by standard techniques and freshly distilled before use or purchased in anhydrous form and used directly. Diethyl ether and tetrahydrofuran were distilled from lithium aluminium hydride and calcium hydride; acetonitrile, toluene and dichloromethane were distilled from calcium hydride; 1,2-dichloroethane and 1,4-dioxane were purchased from Acros Organics. HPLC grade *iso*-propanol and *n*-hexane were purchased from Fisher Scientific. For purification purposes, petroleum ether 40-60, hexanes and ethyl acetate were distilled before use; diethyl ether was used as purchased from Sigma Aldrich.

Reagents: All reagents were purified by standard procedures or used as purchased at the highest commercial quality.[1] Copper(II) triflate was stored and transferred in a glove-box under an atmosphere of nitrogen. Bisoxazoline ligand (+)-2,2'-Isopropylidenebis[(4*R*)-4-phenyl-2-oxazoline] was stored at -18 ^{o}C under a head-space of nitrogen and transferred in a glove-box under an atmosphere of nitrogen.

Reactions: Unless otherwise stated, all reactions were carried out in oven-dried glassware under an atmosphere of nitrogen and were monitored by TLC or by ^{1}H NMR as appropriate.

Substrates: Full experimental procedures for the synthesis of substrates **1a-e** and **1g** and have been previously reported by our laboratory and are not given within this document.[2] Substrates **1f**, **1h** and **1i** were prepared according to modified procedures given in section 2.

Iodonium salts: Aryl(mesityl)iodonium triflates were, in general, able to be synthesised in a one-pot procedure from the appropriate iodoarene and mesitylene according to the procedure of Olofsson.[3] Full experimental procedures for the synthesis of the triflate precursors to iodonium salts **2h** and **2p** are given in section 2. Full experimental procedures for the synthesis of all other employed aryl(mesityl)iodonium triflates have been previously reported by our laboratory and are not given within this document.[4] All aryl(mesityl)iodonium hexafluorophosphate salts (**2b** and **2d-r**) were synthesised from the corresponding triflate species according to the procedure given in section 2, dried *in vacuo* for a minimum of 18 hours and stored in a vacuum desiccator over P_2O_{10}. Diphenyliodonium hexafluorophosphate **2c** was purchased from Sigma Aldrich and used directly.

Chromatography: All flash chromatography for the preparation of allylic amides and enamides was carried out using Merck 9385 Kieselgel 60 silica gel under a positive pressure of nitrogen. All flash chromatography for the preparation of oxazines was carried out using Merck aluminium oxide 90 standardized under a positive

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[1] Armarego, W. L. F.; Perrin, D. D., *Purification of Laboratory Chemicals*, 5th Ed. Butterworth-Heinemann, **1996**.
[2] Cahard, E.; Bremeyer, N.; Gaunt, M. J. *Angew. Chemie. Int. Ed.* **2013**, *52*, 9284.
[3] (a) Bielawski, M.; Olofsson, B. *Chem. Comm.* **2007**, *24*, 2521; (b) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**, *349*, 2610.
[4] (a) Phipps, R. J.; Gaunt, M. J. *Science* **2009**, *323*, 1593; (b) Bigot, A.; Williamson, A. E.; Gaunt, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 13778; (c) Suero, M. G.; Bayle, E. D.; Collins, B. S. L.; Gaunt, M. J. *J. Am. Chem. Soc.* **2013**, *135*, 5332.

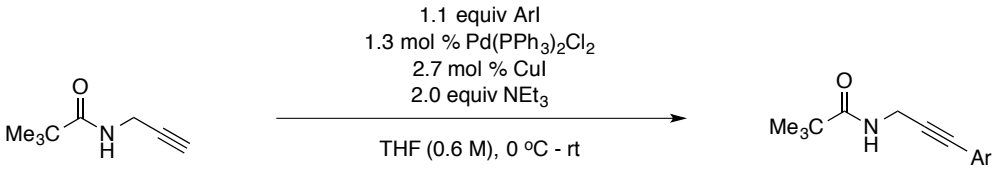
pressure of nitrogen. Thin layer chromatography was carried out on Merck Kieselgel 60 PF254 0.2 mm plates. Visualisation was accomplished using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or acidic potassium permanganate solutions as appropriate.

Data collection: ^{1}H NMR spectra were recorded on a Bruker DPX 400 or 500 spectrometer in deuterochloroform ($CDCl_3$), unless stated otherwise. ^{13}C NMR spectra were recorded at 100 or 125 MHz on the same machines. ^{19}F NMR spectra were recorded at 376 MHz on a Bruker DPX 400 spectrometer. Chemical shifts (δ) are quoted in parts per million (p.p.m.) relative to residual solvent ($CHCl_3$: δ = 7.27 p.p.m. for ^{1}H and δ = 77.16 p.p.m. for ^{13}C; d_6-DMSO: δ = 2.50 p.p.m. for ^{1}H and δ = 39.52 p.p.m. for ^{13}C). Coupling constants (J) are quoted to the nearest 0.1 Hz. The following abbreviations are used to indicate the multiplicity of the signals: s = singlet; d = doublet; t = triplet; q = quartet; qn = quintet; st = sextet, sp = septet; m = multiplet; br. = broad; and associated combinations, e.g. dd = doublet of doublets. The temperature of the acquisition of the NMR spectra was 298 ± 3K. DEPT135 and 2-dimensional experiments (COSY, HMBC and HMQC) were used to support assignments where appropriate but are not included in this document. NMR yields were determined with trimethyl benzene-1,3,5-tricarboxylate as an internal standard. High-resolution mass spectra (HRMS) were measured at the EPSRC Mass Spectrometry Service at the University of Swansea under electrospray ionisation (ESI). Infared (IR) spectra were recorded on a Perkin Elmer FT-IR spectrometer fitted with an ATR sampling accessory as either solids or neat films, either through direct application or deposited in $CHCl_3$ or CH_2Cl_2, with absorptions reported in wavenumbers (cm^{-1}). Optical rotations were measured in $CHCl_3$ on a Perkin Elmer 343 Polarimeter using a sodium lamp (λ 589 nm, D-line). $[\alpha]_D$ values are reported at a given temperature (^{o}C) in 10^{-1} degrees cm^2 g^{-1} with concentration in mg mL^{-1}. Melting points (m.p.) were recorded using a Reichert hot stage apparatus and are reported uncorrected. Chiral HPLC analysis was performed on a Shimadzu XR-LC apparatus with chiralpak (IB, IC and AD-H) or chiralcel OD columns in a mixed solvent system of *n*-hexane and *iso*-propanol. X-ray crystallography was performed on a Nonius Kappa CCD diffractometer or a Bruker D8-QUEST PHOTON-100 diffractometer using CuKa radiation (lambda = 1.5418 Å) at the Cambridge University Chemistry X-Ray Laboratory.

2. Experimental procedures

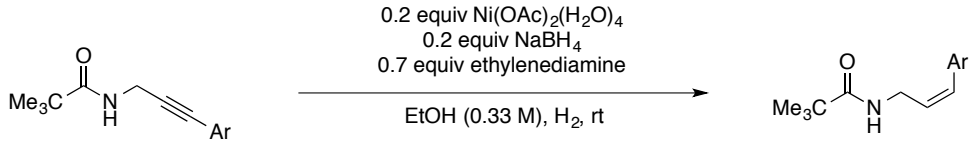
2.1. Preparation of allylic amide substrates

General procedure A: Preparation of Sonogoshira coupled alkynes



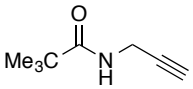
Dry triethylamine (2.0 equiv) was added slowly at 0 °C to a stirred solution/suspension of N-(prop-2-yn-1-yl)pivalamide (1.0 equiv, 0.60 M), aryl iodide (1.1 equiv), $Pd(PPh_3)_2Cl_2$ (1.3 mol%) and CuI (2.7 mol%) in dry tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and was stirred for the stated time. The resulting mixture was concentrated *in vacuo* and the residue dissolved in ethyl acetate, washed with water and brine, and dried over $MgSO_4$. The crude product solution was concentrated *in vacuo* and purified by silica flash column chromatography to furnish the aryl-coupled product.

General procedure B: Preparation of allylic amide substrates[5]



$NaBH_4$ (0.2 equiv, 1 M in abs. ethanol) was introduced to a stirred suspension of $Ni(OAc)_2(H_2O)_4$ (0.2 equiv, 0.1 M in abs. ethanol) under an atmosphere of hydrogen gas, with the resulting reductive mixture stirred for a further two hours. A solution of ethylenediamine (0.7 equiv) and the alkyne (1.0 equiv, 1 M in abs. ethanol) was then added and the resulting solution stirred for the given time under an H_2 atmosphere. The reaction mixture was then concentrated *in vacuo* and the residue suspended in ethyl acetate and filtered through a plug of silica eluting with further quantities of ethyl acetate. The resulting crude solution was concentrated *in vacuo* and purified by silica flash column chromatography to furnish the desired allylic amide substrate.

N-(prop-2-yn-1-yl)pivalamide **S1**[2]

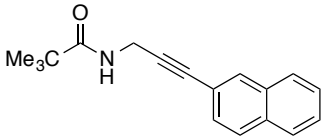


Dry triethylamine (34.0 mL, 241 mmol) was added dropwise to a solution of pivaloyl chloride (30.0 mL, 241 mmol) and propargylamine (14.0 mL, 219 mmol) in CH_2Cl_2 (340 mL) held at 0 °C. The resulting yellow

[5] Petrignet, J.; Boudhar, A.; Blond, G.; Suffert, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3285.

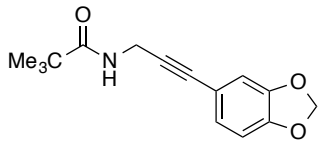
suspension was allowed to warm to room temperature and stirred for 15 hours before being quenched by the addition of 250 mL sat. aqueous NH_4Cl solution. The phases were separated and the aqueous layer washed with CH_2Cl_2 (2 x 50 mL). The organic layers were pooled, washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude product was purified by silica flash column chromatography, eluting with 50% ethyl acetate in petroleum ether 40-60, to give the title compound as an off-white solid (30.0 g, 216 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.81 (br. s, 1H), 4.04 (dd, J = 5.0 Hz, J = 2.5 Hz, 2H), 2.24 (t, J = 2.5 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.5, 80.2, 72.0, 39.0, 29.8, 27.9. Experimental data in agreement with previous literature report.[2]

N-(3-(naphthalen-2-yl)prop-2-yn-1-yl)pivalamide **S2**



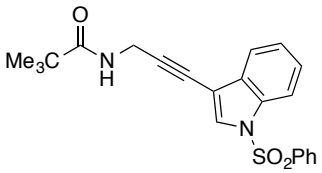
General procedure **A** was performed on a 6.0 mmol scale with *N-(prop-2-yn-1-yl)pivalamide* **S1** and 2-iodonapthalene in 10 mL of acetonitrile with stirring for 18 hours. Crude residue purified by silica column chromatography, eluting with 20 to 35% ethyl acetate in petroleum ether 40-60 to furnish the title compound as a yellow solid (1.2 g, 4.9 mmol, 82%). m.p. 104-107 ^{o}C; IR ν_{max}/cm^{-1} (film): 3329, 3056, 2968, 1637, 1597, 1514, 1483, 1352, 1201, 817, 743; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.83-7.77 (m, 2H), 7.78 (d, J = 8.3 Hz, 1H), 7.51-7.48 (m, 2H), 7.47 (dd, J = 8.5 Hz, J = 1.6 Hz, 1H), 5.88 (br. s, 1H), 4.33 (d, J = 5.0 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.0, 132.9, 132.9, 131.7, 128.4, 128.0, 127.7 (2C), 126.7 (2C), 119.8, 85.3, 83.8, 38.7, 30.4, 27.5; HRMS-ESI (*m/z*) found $[M+H]^+$ 266.1542, $C_{18}H_{20}NO$ requires 266.1539.

N-(3-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)pivalamide **S3**



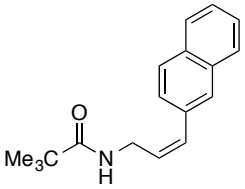
General procedure **A** was performed on a 14.4 mmol scale with *N-(prop-2-yn-1-yl)pivalamide* **S1** and 5-iodobenzo[*d*][1,3]dioxole in 12 mL of tetrahydrofuran with stirring for 6 hours. Crude residue purified by silica column chromatography, eluting with 20 to 40% ethyl acetate in petroleum ether 40-60 to furnish the title compound as an orange solid (2.84 g, 11.0 mmol, 76%). m.p. 83-85 ^{o}C; IR ν_{max}/cm^{-1} (film): 3337, 2964, 2905, 1641, 1502, 1489, 1441, 1330, 1245, 1209, 1102, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.93 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 6.85 (d, J = 1.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 5.92 (br. s, 1H), 4.22 (d, J = 5.0 Hz, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.1, 148.1, 147.5, 126.5, 115.9, 111.8, 108.5, 101.4, 83.5, 83.3, 38.8, 30.3, 27.6; HRMS-ESI (*m/z*) found $[M+H]^+$ 260.1280, $C_{15}H_{18}NO_3$ requires 260.1281.

N-(3-(1-(phenylsulfonyl)-1H-indol-3-yl)prop-2-yn-1-yl)pivalamide **S4**



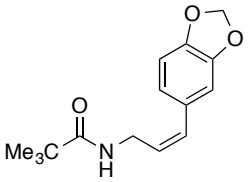
General procedure **A** was performed on a 3.7 mmol scale with *N-(prop-2-yn-1-yl)pivalamide* **S1** and 3-iodo-1-(phenylsulfonyl)-1H-indole in 6 mL of tetrahydrafuran with stirring for 18 hours. Crude residue purified by silica column chromatography, eluting with 20 to 50% ethyl acetate in petroleum ether 40-60 to furnish the title compound as a yellow solid (1.25 g, 3.2 mmol, 85%). m.p. 144-147 ^{o}C; IR ν_{max}/cm^{-1} (film): 3345, 2964, 1647, 1516, 1447, 1372, 1276, 1229, 1177, 1128, 733; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (dt, 1H, *J* = 8.3 Hz, *J* = 0.9 Hz), 7.91-7.87 (m, 2H), 7.73 (s, 1H), 7.61 (ddd, *J* = 7.8 Hz, *J* = 1.1 Hz, *J* = 0.8 Hz, 1H), 7.55 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.47-7.42 (m, 2H), 7.36 (ddd, *J* = 8.6 Hz, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 7.29 (ddd, *J* = 7.8 Hz, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 5.89 (br. s, 1H), 4.33 (d, *J* = 5.0 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.0, 137.8, 134.2, 134.1, 130.7, 129.4, 129.1, 126.9, 125.6, 123.9, 120.5, 113.6, 104.8, 89.5, 74.4, 38.7, 30.4, 27.5; HRMS-ESI (*m/z*) found $[M+H]^+$ 395.1417, $C_{22}H_{23}N_2O_3S$ requires 395.1424.

(Z)-N-(3-(naphthalen-2-yl)allyl)pivalamide **1f**



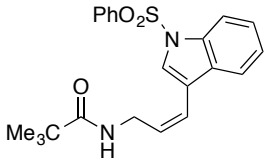
General procedure **B** was performed on a 4.2 mmol scale with *N-(3-(naphthalen-2-yl)prop-2-yn-1-yl)pivalamide* **S2** in a total volume of 10 mL ethanol with stirring for 18 hours. Crude residue purified by silica column chromatography, eluting with 20% ethyl acetate in petroleum ether 40-60 to furnish the title compound as a white solid (0.88 g, 3.3 mmol, 78%). m.p. 93-97 ^{o}C; IR ν_{max}/cm^{-1} (film): 3341, 3059, 2952, 1633, 1528, 1481, 1362, 1288, 1203, 822; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84-7.79 (m, 3H), 7.68 (s, 1H), 7.51-7.45 (m, 2H), 7.38 (dd, *J* = 8.3 Hz, *J* = 1.7 Hz, 1H), 6.23 (dt, *J* = 11.5 Hz, *J* = 1.9 Hz, 1H), 5.74 (dt, *J* = 11.5 Hz, *J* = 6.6 Hz, 2H), 4.27 (ddd, *J* = 7.1 Hz, *J* = 5.6 Hz, *J* = 1.9 Hz, 2H), 1.18 (s, 9H);^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.3, 133.8, 133.2, 132.4, 131.6, 128.8, 128.0, 127.9, 127.8, 127.6, 126.8, 126.3, 126.1, 38.6, 38.0, 27.6; HRMS-ESI (*m/z*) found $[M+H]^+$ 268.1697, $C_{18}H_{22}NO$ requires 268.1696.

(Z)-N-(3-(benzo[d][1,3]dioxol-5-yl)allyl)pivalamide **1h**



General procedure **B** was performed on a 9.8 mmol scale with *N-(3-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)pivalamide* **S3** in a total volume of 30 mL ethanol with stirring for 22 hours. Crude residue purified by silica column chromatography, eluting with 10 to 30% ethyl acetate in petroleum ether 40-60 to furnish the title compound as a white solid (2.09 g, 8.0 mmol, 81%). m.p. 53-55 ^{o}C; IR ν_{max}/cm^{-1} (film): 3333, 2964, 2901, 1633, 1524, 1504, 1488, 1441, 1237, 1207, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.77 (d, J = 7.9 Hz, 1H), 6.72-6.69 (m, 2H), 6.45 (dt, J = 11.6 Hz, J = 1.9 Hz, 1H), 5.94 (s, 2H), 5.78 (br. s, 1H), 5.54 (dt, J = 11.7 Hz, J = 6.6 Hz, 1H), 4.12 (ddd, J = 6.7 Hz, J = 5.3 Hz, J = 1.6 Hz, 2H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.4, 147.7, 146.8, 131.2, 130.5, 127.3, 122.7, 109.0, 108.3, 101.1, 38.7, 38.1, 27.6; HRMS-ESI (*m/z*) found $[M+H]^+$ 262.1437, $C_{15}H_{20}NO_3$ requires 262.1438.

(Z)-N-(3-(1-(phenylsulfonyl)-1H-indol-3-yl)allyl)pivalamide **1i**



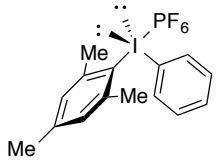
General procedure **B** was performed on a 3.3 mmol scale with *N-(3-(1-(phenylsulfonyl)-1H-indol-3-yl)prop-2-yn-1-yl)pivalamide* **S4** and 0.6 equiv of both $NaBH_4$ and $Ni(OAc)_2(H_2O)_4$ in total volume of 6 mL ethanol with stirring for 24 hours. Crude residue purified by silica column chromatography, eluting with 20 to 50% ethyl acetate in petroleum ether 40-60 to furnish the title compound as a white solid (1.69 g, 4.3 mmol, 70%). m.p. 115-118 ^{o}C; IR ν_{max}/cm^{-1} (film): 3349, 2968, 2909, 1641, 1518, 1447, 1368, 1175, 1136, 1092, 749; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, 1H, J = 8.3 Hz), 7.94-7.90 (m, 2H), 7.57-7.48 (m, 3H,), 7.47-7.43 (m, 2H), 7.35 (ddd, J = 8.3 Hz, J = 7.2 Hz, J = 0.9 Hz, 1H), 7.27 (ddd, J = 7.9 Hz, J = 7.2 Hz, J = 1.1 Hz, 1H), 6.56 (dq, J = 11.2 Hz, J = 0.9 Hz, 1H), 5.81 (br. dt, J = 11.4, J = 6.4 Hz, 2H), 4.33 (td, J = 6.4 Hz, J = 1.8 Hz, 2H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.3, 138.0, 134.6, 133.9, 130.3, 130.2, 129.4, 126.9, 125.2, 124.0, 123.5, 120.2, 119.5, 118.2, 113.6, 38.7, 27.6; HRMS-ESI (*m/z*) found $[M+H]^+$ 397.1577, $C_{22}H_{25}N_2O_3S$ requires 397.1580.

2.2. Preparation of Diaryiodonium hexafluorophosphates

General procedure C: Production by diaryliodonium hexafluorophosphate salts by ion exchange

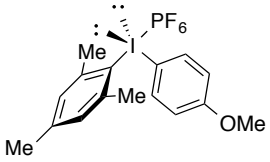
An equal volume of a saturated aqueous solution of sodium hexafluorophosphate was added to a solution of aryl(mesityl)iodonium triflate in CH_2Cl_2 (0.5 M). The resulting biphasic mixture was stirred at room temperature for the stated time before the phases were separated and the aqueous layer extracted with a further three portions of dichloromethane. The combined organic fractions were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the corresponding aryl(mesityl)iodonium hexafluorophosphate.

(mesityl)(phenyl)iodonium hexafluorophosphate(V) **2b**



General procedure **C** was performed on a 1.50 mmol scale with *(mesityl)(phenyl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (554 mg, 1.18 mmol, 79%). IR ν_{max}/cm^{-1} (powder): 1582, 1471, 1447, 1302, 1243, 1029, 991, 979, 824, 745; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.99 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.22 (s, 2H), 2.61 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.2, 141.6, 134.5, 131.9, 131.8, 129.8, 122.6, 114.5, 26.3, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -71.0 (d, J = 711.4 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 323.0291, $C_{15}H_{16}I$ requires 323.0291.

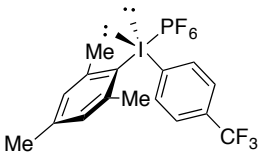
(4-methoxyphenyl)(mesityl)iodonium hexafluorophosphate(V) ***2d***[6]



General procedure **C** was performed on a 1.50 mmol scale with *(4-methoxyphenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (663 mg, 1.33 mmol, 87%). ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.93 (d, J = 9.1 Hz, 2H), 7.19 (s, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 2.62 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 161.8, 142.9, 141.4, 136.6, 129.7, 123.1, 117.5, 103.4, 55.7, 26.2, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -71.1 (d, J = 711.5 Hz). Experimental data in agreement with previous literature report.[6]

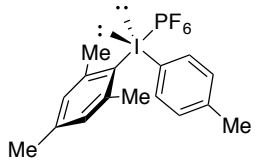
[6] Harvey, J. S.; Simonovich, S. P.; Jamison, C. R.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2011**, *133*, 13782.

(4-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate(V) **2e**



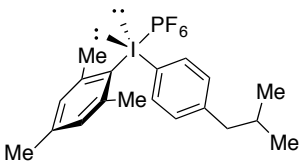
General procedure **C** was performed on a 2.00 mmol scale with *(4-trifluoromethylphenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (829 mg, 1.48 mmol, 74%). IR ν_{max}/cm^{-1} (powder): 1596, 1399, 1322, 1179, 1132, 1064, 999, 840, 773, 739; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 8.14 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.25 (s, 2H), 2.60 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 143.5, 141.8, 135.1, 131.7 (q, J = 32.4 Hz), 130.0, 128.4 (q, J = 4.0 Hz), 123.4 (q, J = 274.3 Hz), 122.6, 118.7 (q, J = 1.5 Hz), 26.3, 20.5; ^{19}F NMR (376 MHz, d$_6$-DMSO) δ: -62.6, -71.1 (d, J = 711.2 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 391.0161, $C_{16}H_{15}F_3I$ requires 391.0165.

(mesityl)(p-tolyl)iodonium hexafluorophosphate(V) ***2f***



General procedure **C** was performed on a 3.2 mmol scale with *(mesityl)(p-tolyl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (1.22 g, 2.4 mmol, 75%). IR ν_{max}/cm^{-1} (powder): 2971, 1739, 1441, 1366, 1229, 1217, 837; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 7.86 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (s, 2H), 2.59 (s, 6H), 2.32 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 143.1, 142.3, 141.5, 134.6, 132.5, 129.8, 122.7, 110.9, 26.3, 20.8, 20.5; ^{19}F NMR (376 MHz, d$_6$-DMSO) δ: -70.1 (d, J = 714.4 Hz), HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 337.0448, $C_{16}H_{18}I$ requires 337.0449.

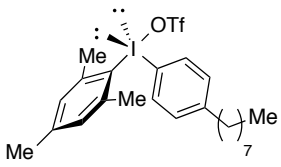
(4-isobutylphenyl)(mesityl)iodonium hexafluorophosphate(V) ***2g***



General procedure **C** was performed on a 1.80 mmol scale with *(4-isobutylphenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (836 mg, 1.52 mmol, 84%). IR ν_{max}/cm^{-1} (powder): 2970, 1739, 1456, 1366, 1229, 822, 750; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 7.88 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.21 (s, 2H), 2.60 (s, 6H), 2.50-2.46 (m, 2H) 2.29 (s, 3H), 1.81 (st, J = 6.8 Hz, 1H), 0.82 (d, 6H, J = 6.4 Hz); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 146.1, 143.5, 142.0, 134.9, 132.9, 130.2, 123.0, 111.6, 44.3, 29.9,

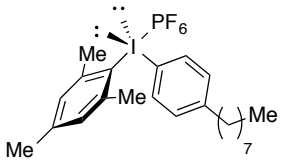
26.7, 22.4, 21.0; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 714.4 Hz); HRMS-ESI (m/z) found $[M\text{-}PF_6]^+$ 379.0915, $C_{19}H_{24}I$ requires 379.0917.

(mesityl)(4-octylphenyl)iodonium trifluoromethanesulfonate ***2h'***



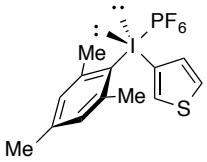
Iodomesitylene diacetate (3.0 g, 8.2 mmol) and 1-phenyloctane (2.05 mL, 9.2 mmol) were suspended in CH_2Cl_2 (61 mL) and cooled to 0°C. TfOH (0.8 mL, 7.7 mmol) was added dropwise at 0 °C and the reaction mixture warmed to room temperature and stirred for 1 hour. The reaction mixture was then concentrated *in vacuo*, and the residue precipitated on addition of cold diethyl ether (25 mL). The precipitate was collected by filtration and washed on the filter with further portions of cold diethyl ether (3 x 10 mL). The solid was dried *in vacuo* to give the corresponding triflate salt as a white powder (2.45 g, 4.0 mmol, 49%). m.p. 140-142 ^{o}C; IR ν_{max} /cm^{-1} (neat film): 2929, 2858, 1272, 1248, 1163, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.10 (s, 2H), 2.59 (s, 6H), 2.56 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.4 Hz, 1H), 2.30 (s, 3H), 1.54-1.51 (m, 2H), 1.22 (d, J = 9.2 Hz, 9H), 0.83 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 144.2, 142.3, 133.1, 132.3, 130.3, 120.8, 108.3, 35.5, 31.8, 31.0, 29.3, 29.1 (2C), 27.0, 22.6, 21.1, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -78.3; HRMS-ESI (m/z): found $[M+H\text{-}OTf]^+$ 436.1632, $C_{23}H_{33}I$ requires 436.1627.

(mesityl)(4-octylphenyl)iodonium hexafluorophosphate(V) ***2h***



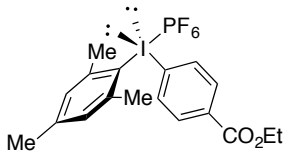
General procedure **C** was then performed on a 3.2 mmol scale with the generated *(mesityl)(4-octylphenyl)iodonium trifluoromethanesulfonate* **2h'** with stirring for 3 hours to yield the title compound as a white powder (1.8 g, 3.0 mmol, 94%). IR ν_{max}/cm^{-1} (powder): 2926, 1739, 1449, 1366, 1217, 836; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.88 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.20 (s, 2H), 2.60-2.56 (m, 8H), 2.28 (s, 3H), 1.52-1.50 (m, 2H), 1.22-1.20 (m, 10H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 143.5, 141.9, 135.0, 132.3, 130.2, 123.0, 111.5, 35.1, 31.7, 31.0, 29.2, 29.0 (2C), 26.7, 22.5, 20.9, 14.4; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 714.4 Hz), HRMS-ESI (m/z) found $[M\text{-}PF_6]^+$ 435.1534, $C_{23}H_{32}I$ requires 435.1543.

(thiophen-3-yl)(mesityl)iodonium hexafluorophosphate(V) **2i**



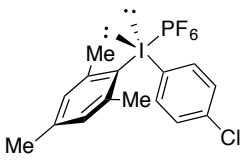
General procedure **C** was performed on a 1.50 mmol scale with *(thiophen-3-yl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (636 mg, 1.16 mmol, 77%). IR ν_{max}/cm^{-1} (powder): 1576, 1451, 1381, 1302, 1201, 1080, 1035, 981, 824, 773; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 8.50 (dd, *J* = 2.9 Hz, *J* = 1.2 Hz, 1H), 7.79 (dd, *J* = 5.2 Hz, *J* = 2.9 Hz, 1H), 7.53 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 7.20 (s, 2H), 2.63 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 143.0, 141.2, 135.2, 131.3, 130.7, 129.7, 123.6, 98.8, 26.3, 20.5; ^{19}F NMR (376 MHz, d$_6$-DMSO) δ: -70.2 (d, *J* = 711.5 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 328.9854, $C_{13}H_{14}IS$ requires 328.9855.

(4-(ethoxycarbonyl)phenl)(mesityl)iodonium hexafluorophosphate(V) **2j**



General procedure **C** was performed on a 2.00 mmol scale with *(4-(ethoxycarbonyl)phenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (851 mg, 1.50 mmol, 75%). IR ν_{max}/cm^{-1} (powder): 1701, 1582, 1473, 1449, 1393, 1294, 1276, 1134, 1114, 997, 979, 838; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 8.09 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.24 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 6H), 2.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 164.6, 143.4, 141.7, 134.7, 132.7, 132.0, 129.9, 122.7, 119.3, 61.5, 26.3, 20.5, 14.0; ^{19}F NMR (376 MHz, d$_6$-DMSO) δ: -70.1 (d, *J* = 711.1 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 395.0499, $C_{18}H_{20}O_2I$ requires 395.0502.

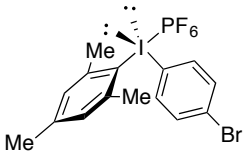
(4-chlorophenyl)(mesityl)iodonium hexafluorophosphate(V) **2k**



General procedure **C** was performed on a 2.00 mmol scale with *(4-chlorophenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (999 mg, 1.85 mmol, 93%). IR ν_{max}/cm^{-1} (powder): 1469, 1391, 1086, 997, 977, 937, 848, 830, 813, 802; ^{1}H NMR (400 MHz, d$_6$-DMSO) δ: 7.97 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.23 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ: 143.3,

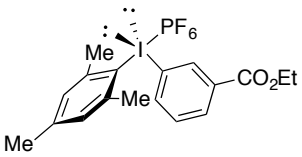
141.6, 137.0, 136.2, 131.8, 129.9, 122.8, 112.3, 26.3, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 711.5 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 356.9904, $C_{18}H_{20}ClI$ requires 356.9901.

(4-bromophenyl)(mesityl)iodonium hexafluorophosphate(V) **2l**



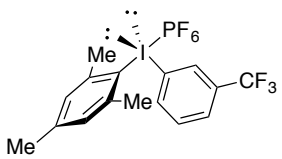
General procedure **C** was performed on a 2.00 mmol scale with *(4-bromophenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (633 mg, 1.10 mmol, 55%). IR ν_{max}/cm^{-1} (powder): 1469, 1383; 1300, 1062, 993, 848, 830, 805, 668; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.88 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.22 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.3, 141.6, 136.3, 134.7, 129.9, 125.8, 122.7, 113.0, 26.3, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 711.5 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 400.9399, $C_{15}H_{15}BrI$ requires 400.9396.

(3-(ethoxycarbonyl)phenyl)(mesityl)iodonium hexafluorophosphate(V) **2m**



General procedure **C** was performed on a 2.00 mmol scale with *(3-(ethoxycarbonyl)phenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (1.03 g, 1.90 mmol, 95%). IR ν_{max}/cm^{-1} (powder): 1726, 1451, 1366, 1298, 1255, 1130, 1094, 832, 739, 704; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.47 (t, J = 1.6 Hz, 1H), 8.14 (dt, J = 7.6 Hz, J = 1.1 Hz, 1H), 8.6 (ddd, J = 8.1 Hz, J = 1.7 Hz, J = 0.9 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.25 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 2.59 (s, 6H), 2.31 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 163.9, 143.4, 141.7, 138.1, 134.3, 132.7, 132.3, 131.9, 129.9, 122.5, 114.4, 61.6, 26.3, 20.5, 14.0; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 711.1 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 395.0498, $C_{19}H_{20}O_2I$ requires 395.0502.

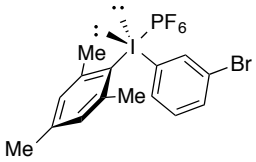
(3-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate(V) **2n**



General procedure **C** was performed on a 2.00 mmol scale with *(3-trifluoromethylphenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (1.04 g, 1.94 mmol, 97%). IR ν_{max}/cm^{-1} (powder): 2349, 1421, 1320, 1304, 1280, 1177, 1136, 1080, 842, 797, 678; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.48 (s, 1H), 8.11 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.23 (s, 2H), 2.61

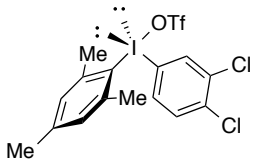
(s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.5, 141.8, 138.1, 132.9, 131.4 (q, J = 32.8 Hz), 131.1 (q, J = 3.8 Hz), 129.9, 128.5 (q, J = 3.5 Hz), 122.9 (q, J = 273.2 Hz), 122.6, 114.7, 26.3, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -61.3, -70.1 (d, J = 711.1 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 391.0162, $C_{16}H_{15}F_3I$ requires 391.0165.

(3-bromophenyl)(mesityl)iodonium hexafluorophosphate(V) **2o**[6]



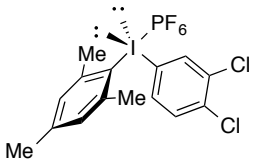
General procedure **C** was performed on a 1.50 mmol scale with *(3-bromophenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (699 mg, 1.28 mmol, 85%). ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.28 (t, J = 1.7 Hz, 1H), 7.89 (ddd, J = 7.9 Hz, J = 1.6 Hz, J = 0.8 Hz, 1H), 7.83 (ddd, J = 8.1 Hz, J = 1.8 Hz, J = 0.8 Hz, 1H), 7.44 (t, J = 8.1 Hz, 1H), 7.23 (s, 2H), 2.61 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.4, 141.7, 136.2, 134.8, 133.5, 133.1, 129.9, 123.4, 122.6, 115.0, 26.3, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -71.0 (d, J = 711.5 Hz). Experimental data in agreement with previous report.[6]

(3,4-dichlorophenyl)(mesityl)iodonium trifluoromethanesulfonate **2p'**



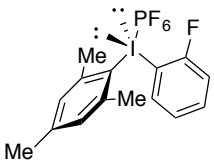
Prepared according to a modified procedure of Olofsson.[3] TfOH (0.66 mL, 7.5 mmol) was added dropwise to a stirred solution of 1,2-dichloro-4-iodobenzene (1.36 g, 5.0 mmol) and *m*CPBA (70%, 1.27 g, 5.5 mmol - previously dried *in vacuo* for 2 hours) in dichloromethane (10 mL) held at 0 ^{o}C. The resulting yellow suspension was allowed to warm to room temperature and stirred for a further two hours before being cooled back to 0 ^{o}C and undergoing a dropwise addition of mesitylene (0.77 mL, 5.5 mmol). The resulting orange suspension was allowed to warm to room temperature and stirred for 15 hours. The reaction mixture was then concentrated *in vacuo* and the residue precipitated with cold diethyl ether (10 mL). The solid was collected by filtration, washed on the filter with further portions of cold diethyl ether (3 x 5 mL) and dried *in vacuo* to yield the corresponding triflate as a white powder (2.46 g, 4.55 mmol, 91%). m.p. 161-164 ^{o}C; IR ν_{max}/cm^{-1} (powder): 1586, 1567, 1457, 1372, 1259, 1249, 1221, 1175, 1138, 1027; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.36 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 8.6 Hz, J = 2.3 Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.24 (s, 2H), 2.60 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.5, 141.8, 135.7, 135.4, 134.3, 133.5, 133.4, 129.9, 122.8, 120.7 (q, J = 322.3 Hz), 112.4, 26.3, 20.6; HRMS-ESI (*m/z*) found $[M\text{-}OTf]^+$ 390.9514, $C_{15}H_{14}Cl_2I$ requires 390.9512.

(3,4-dichlorophenyl)(mesityl)iodonium hexafluorophosphate(V) **2p**



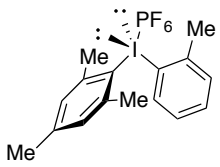
General procedure **C** was then performed on a 2.00 mmol scale with the generated *(3,4-dichlorophenyl)(mesityl)iodonium trifluoromethanesulfonate* **2p'** with stirring for 24 hours to yield the title compound as a white powder (978 mg, 1.82 mmol, 91%). IR ν_{max}/cm^{-1} (powder): 1588, 1560, 1453, 1380, 1368, 1302, 1251, 1136, 1027, 824; ^{1}H NMR (500 MHz, d_6-DMSO) δ: 8.35 (d, J = 2.0 Hz, 1H), 7.84 (dd, J = 8.7 Hz, J = 2.3 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.24 (s, 2H), 2.60 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, d_6-DMSO) δ: 143.5, 141.9, 135.7, 135.4, 134.3, 133.6, 133.5, 130.0, 122.9, 112.5, 26.4, 20.6; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -71.1 (d, J = 711.3 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 390.9500, $C_{15}H_{14}Cl_2I$ requires 390.9512.

(2-fluorophenyl)(mesityl)iodonium hexafluorophosphate(V) ***2q***



General procedure **C** was performed on a 2.00 mmol scale with *(2-fluorophenyl)(mesityl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (923 mg, 1.90 mmol, 95%). IR ν_{max}/cm^{-1} (film): 3011, 1739, 1474, 1366, 1231, 829, 759; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.26 (ddd, J = 8.0 Hz, J = 6.2 Hz, J = 1.3 Hz, 1H), 7.75-7.68 (m, 1H), 7.56 (td, J = 8.9 Hz, J = 1.3 Hz, 1H), 7.35 (td, J = 8.0 Hz, J = 1.3 Hz, 1H), 7.20 (s, 2H), 2.62 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 159.5 (d, J = 248.8 Hz), 143.2, 141.6, 137.5, 135.4 (d, J = 8.3 Hz), 129.8, 127.6 (d, 3.0 Hz), 122.8, 117.1 (d, J = 22.1 Hz), 101.5 (d, J = 23.5 Hz), 26.1, 20.5; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -97.6, -70.1 (d, J = 714.4 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 341.0197, $C_{15}H_{15}FI$ requires 341.0197;

(mesityl)(o-tolyl)iodonium hexafluorophosphate(V) ***2r***

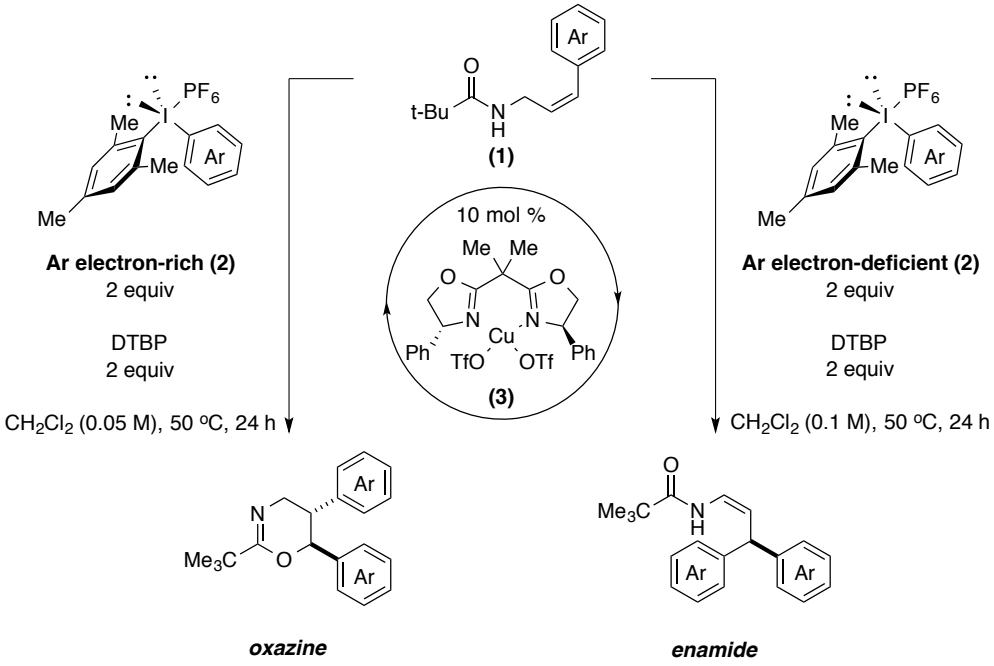


General procedure **C** was performed on a 2.00 mmol scale with *(mesityl)(o-tolyl)iodonium triflate* with stirring for 24 hours to yield the title compound as a white powder (792 mg, 1.64 mmol, 82%). IR ν_{max}/cm^{-1} (powder): 3016, 1739, 1456, 1366, 1229, 822; ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.95 (d, 1H, J = 8.0 Hz), 7.57-7.55 (m, 2H), 7.27-7.21 (m, 3H), 2.57-2.56 (m, 9H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 143.4, 142.1, 141.1, 137.1,

32.9, 132.3, 130.4, 122.3, 119.0, 26.6, 24.9, 20.9; ^{19}F NMR (376 MHz, d_6-DMSO) δ: -70.1 (d, J = 714.4 Hz); HRMS-ESI (*m/z*) found $[M\text{-}PF_6]^+$ 337.0450, $C_{16}H_{18}I$ requires 337.0448

2.3. Enantioselective arylation of allylic amide with diaryliodonium salts

General Procedure D: Regiodivergent copper-catalysed enantioselective allylic amide arylation

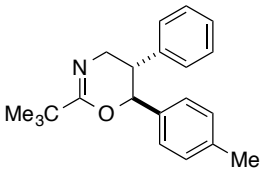


An oven-dried microwave tube was charged with the appropriate allylic amide (1.0 equiv) and diaryliodonium hexafluorophosphate (2.0 equiv), sealed, and back-filled with nitrogen. CH_2Cl_2 was added *via* syringe followed by the addition of di-*tert* butylpyridine (DTBP, 2.0 equiv) and a pre-formed stock solution of **3**[7] (10 mol%, unless otherwise stated). The resulting green solution (0.05-0.1 M *wrt* allylic amide loading) was heated at 50 ^{o}C for 24 hours (unless otherwise stated), cooled to room temperature and poured into an equal volume of sat. aqueous $NaHCO_3$ solution. The phases were separated and the aqueous layer extracted with a further two portions of CH_2Cl_2. The combined organic fractions were dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and the crude residue purified by column chromatography to furnish the desired enantioenriched arylated product.

[7] The stock solution of **3** is prepared as follows: in a glove-box under an inert atmosphere, an oven-dried microwave tube containing ~200 mg freshly activated 4 Å molecular sieves and a stirrer bar was charged with anhydrous $Cu(OTf)_2$ (72 mg, 0.2 mmol) and sealed. Subsequently, a solution of (+)-2,2-isopropylidenebis[(4R)-4-phenyl-2-oxazoline] ((+)PhBOX) (74 mg, 0.22 mmol) in dry dichloromethane (2 mL) was introduced to the anhydrous $Cu(OTf)_2$ and the resulting green solution stirred at room temperature for 15 hours. The resulting green solution was stored in the sealed tube under N_2 at -18 ^{o}C and used as required.

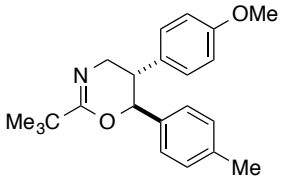
Oxazine products

(5R,6R)-2-(tert-butyl)-5-phenyl-6-(4-tolyl)-5,6-dihydro-4H-1,3-oxazine **4a**[2]



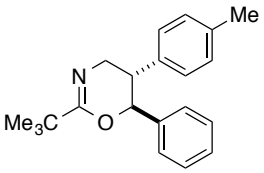
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(p-tolyl)allyl)pivalamide* **1a** (116 mg, 0.50 mmol) and *(mesityl)(phenyl)iodonium hexafluorophosphate* **2b** (468 mg, 1.00 mmol). Alumina column chromatography, eluting with a gradient of 5 to 10% diethyl ether in petroleum ether 40-60, provided the title compound as a white solid (45 mg, 0.15 mmol, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.15 (m, 3H), 7.04-7.00 (m, 4H), 6.97 (d, J = 8.1 Hz, 2H), 5.10 (d, J = 10.0 Hz, 1H), 3.74-3.65 (m, 2H), 2.91 (dt, J = 9.5 Hz, J = 6.7 Hz, 1H), 2.28 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 139.4, 137.7, 136.4, 128.9, 128.6, 128.3, 127.1, 126.7, 81.2, 49.8, 45.6, 37.6, 28.0, 21.2; $[\alpha]^{26}_{D}$ = +92.9 ^{o} (1.0, $CHCl_3$); HPLC analysis (OD, 1% *i*-PrOH in *n*-hexane, 1 mL/min, 202 nm) indicated 98% ee: t_R (major) = 6.94 minutes, t_R (minor) = 8.34 minutes. Experimental data in agreement with previous literature report.[2]

(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(p-tolyl)-5,6-dihydro-4H-1,3-oxazine **4b**



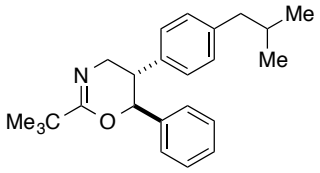
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(p-tolyl)allyl)pivalamide* **1a** (116 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol). Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (140 mg, 0.41 mmol, 83%). IR ν_{max}/cm^{-1} (film): 2960, 2927, 1671, 1612, 1514, 1264, 1246, 1100, 1034, 826.2, 814.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 5.03 (d, J = 10.5 Hz, 1H), 3.75 (s, 3H), 3.64-3.61 (m, 2H), 2.84 (dt, J = 10.5 Hz, J = 5.5 Hz, 1H), 2.29 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 158.6, 137.6, 136.6, 131.4, 129.2, 128.9, 126.7, 114.1, 81.4, 55.3, 50.0, 44.8, 37.6, 28.1, 21.3; HRMS-ESI (*m/z*) found $[M+H]^+$ 338.2117, $C_{22}H_{28}NO_2$ requires 338.2120; $[\alpha]^{22}_{D}$ = +119.7 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated >98% ee: t_R (major) = 9.22 minutes; t_R (minor) = 11.77 minutes.

(5S,6S)-2-(tert-butyl)-6-phenyl-5-(p-tolyl)-5,6-dihydro-4H-1,3-oxazine **4c**[2]



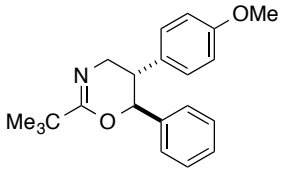
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol), *(mesityl)(p-tolyl)iodonium hexafluorophosphate* **2f** (482 mg, 1.00 mmol) and 15 mol% **3.** Alumina column chromatography, eluting with a gradient of 5 to 20% diethyl ether in petroleum ether 40-60, provided the title compound as a white solid (111 mg, 0.36 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.20 (m, 3H), 7.10-7.06 (m, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 5.09 (d, J = 10.0 Hz, 1H), 3.67-3.64 (m, 2H), 2.86 (td, J = 9.8 Hz, J = 8.4 Hz, 1H), 2.27 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 139.6, 136.7, 136.2, 129.4, 128.2 (2C), 128.0, 126.8, 81.3, 49.9, 45.3, 37.6, 28.1, 21.2; $[\alpha]^{25}_{D}$ = +93.8 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated 95% ee: t_R (major) = 6.17 minutes, t_R (minor) = 7.41 minutes. Experimental data in agreement with previous literature report.[2]

(5S,6S)-2-(tert-butyl)-5-(4-isobutylphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4d**[2]



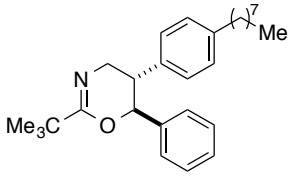
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (108 mg, 0.5 mmol) and *(4-isobutylphenyl)(mesityl)iodonium hexafluorophosphate* **2g** (524 mg, 1.0 mmol). Alumina column chromatography, eluting with a gradient of 5 to 20% diethyl ether in petroleum ether 40-60, provided the title compound as a white solid (110 mg, 0.31 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.18 (m, 3H), 7.03-7.01 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 5.07 (d, J = 10.0 Hz, 1H), 3.68 (d, J = 7.5 Hz, 2H), 2.83 (q, J = 10.0 Hz, 1H), 2.39 (d, J = 7.5 Hz, 2H), 1.83-1.77 (m, 1H), 1.27 (s, 9H), 0.86 (dd, J = 6.5 Hz, J = 2.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 140.5, 139.6, 136.4, 129.3, 128.0, 127.9, 126.6, 81.5, 49.4, 45.4, 45.1, 37.6, 30.2, 28.0, 22.41, 22.37; $[\alpha]^{22}_{D}$ = +94.2 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated 95% ee: t_R (major) = 5.54 minutes, t_R (minor) = 6.59 minutes. Experimental data in agreement with previous literature report.[2]

(5R,6R)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4e**[2]



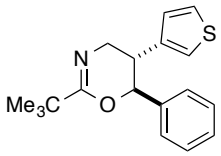
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol). Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (120 mg, 0.37 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.19 (m, 3H), 7.08-7.04 (m, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.7 Hz, 2H), 5.06 (d, J = 10.0 Hz, 1H), 3.74 (s, 3H), 3.69-3.60 (m, 2H), 2.85 (dt, J = 9.3 Hz, J = 6.9 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 158.6, 139.5, 131.2, 129.2, 128.1, 127.9, 126.7, 114.0, 81.5, 55.2, 49.8, 44.8, 37.6, 28.0; $[\alpha]^{27}_{D}$ = +100.9 ^{o} (1.1, $CHCl_3$); HPLC analysis (AD-H, 1% *i*-PrOH in *n*-hexane, 1 mL/min, 197 nm) indicated 93% ee: t_R (major) = 9.07 minutes, t_R (minor) = 10.44 minutes. Experimental data in agreement with previous literature report.[2]

(5S,6S)-2-(tert-butyl)-5-(4-octylphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4f**



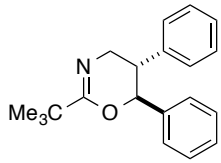
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(mesityl)(4-octylphenyl)iodonium hexafluorophosphate* **2h** (580 mg, 1.00 mmol). Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (145 mg, 0.36 mmol, 72%). IR ν_{max}/cm^{-1} (film): 2925, 2855, 1672, 1456, 1135, 1025, 757.15, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22-7.20 (m, 3H), 7.05-7.01 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H), 5.08 (d, J = 10.0 Hz, 1H), 3.67 (d, J = 7.6 Hz, 2H), 2.86 (dt, J = 8.0 Hz, J = 6.8 Hz, 1H), 2.52 (t, J = 7.6 Hz, 2H), 1.59-1.49 (m, 2H), 1.30-1.23 (m, 19H), 0.89 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 141.8, 139.7, 136.4, 128.6, 128.2, 128.1, 127.9, 126.7, 81.3, 49.7, 45.4, 37.6, 35.6, 32.0, 31.5, 29.6, 29.4, 28.1, 22.8, 14.3; HRMS-ESI (*m/z*) found $[M+H]^+$ 406.3101, $C_{28}H_{40}NO$ requires 406.3110; $[\alpha]^{22}_{D}$ = +68.5 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 205 nm) indicated 94% ee: t_R (major) = 5.17 minutes, t_R (minor) = 6.18 minutes.

(5S,6S)-2-(tert-butyl)-6-phenyl-5-(thiophen-3-yl)-5,6-dihydro-4H-1,3-oxazine **4g**[2]

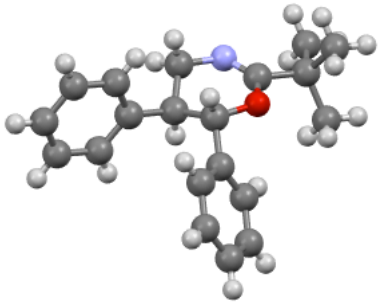


Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(mesityl)(3-thiophenyl)iodonium hexafluorophosphate* **2i** (474 mg, 1.00 mmol) with stirring for 24 hours. Alumina column chromatography, eluting with a gradient of 5 to 20% diethyl ether in petroleum ether 40-60, provided the title compound as a white solid (47 mg, 0.16 mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.25 (m, 3H), 7.20 (dd, J = 5.0 Hz, J = 3.0 Hz, 1H), 7.09-7.06 (m, 2H), 6.84 (dd, J = 2.8 Hz, J = 1.0 Hz, 1H), 6.72 (dd, J = 5.0 Hz, J = 1.2 Hz, 1H), 5.05 (d, J = 9.4 Hz, 1H), 3.69-3.67 (m, 2H), 3.08 (td, J = 8.7 Hz, J = 7.1 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 139.74, 139.73, 128.2, 128.1, 127.1, 126.5, 125.7, 121.8, 81.1, 49.0, 41.1, 37.6, 28.0; $[\alpha]^{26}_{D}$ = +57.1 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 248 nm) indicated 92% ee: t_R (major) = 6.10 minutes, t_R (minor) = 7.51 minutes. Experimental data in agreement with previous literature report.[2]

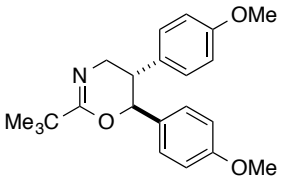
(5R,6R)-2-(tert-butyl)-5,6-diphenyl-5,6-dihydro-4H-1,3-oxazine **4h**[2]



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(mesityl)(phenyl)iodonium hexafluorophosphate* **2d** (468 mg, 1.00 mmol)**.** Alumina column chromatography, eluting with a gradient of 5 to 20% diethyl ether in petroleum ether 40-60, provided the title compound as a white solid (76 mg, 0.26 mmol, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.16 (m, 6H), 7.07-7.03 (m, 2H), 6.99 (dt, J = 6.6 Hz, J = 1.7 Hz, 2H), 5.13 (d, J = 9.9 Hz, 1H), 3.73-3.67 (m, 2H), 2.91 (dt, J = 9.9 Hz, J = 7.9 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.0, 139.2, 139.0, 128.7, 128.3, 128.2, 128.1, 127.2, 126.7, 81.6, 49.4, 45.6, 37.7, 28.0; $[\alpha]^{27}_{D}$ = +71.6 ^{o} (0.9, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 202 nm) indicated 91% ee: t_R (major) = 5.98 minutes, t_R (minor) = 7.95 minutes. Experimental data in agreement with previous literature report.[2] The X-Ray crystal structure is deposited in the Cambridge Crystallographic Data Centre, reference number CCDC 1021199. We thank the UK EPSRC (grant EP/K039520/1) for funding the purchase of the X-Ray diffractometer.

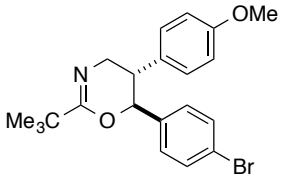


(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4i**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(4-methoxyphenyl)allyl)pivalamide* **1c** (124 mg, 0.50 mmol) and (*mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol) with stirring at 40 ^{o}C for 30 hours. Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (139 mg, 0.39 mmol, 79%). IR ν_{max}/cm^{-1} (film): 2960, 2917, 2837, 1667, 1613, 1512, 1245, 1177, 1136, 1033; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.97 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 4H), 5.00 (d, *J* = 10.1 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.67-3.57 (m, 2H), 2.81 (td, *J* = 15.3 Hz, *J* = 5.8 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.3, 159.2, 158.5, 131.8, 131.4, 129.2, 128.0, 114.1, 113.6, 81.1, 55.3 (2C), 50.1, 44.9, 37.6, 28.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 354.2065, $C_{22}H_{28}NO_3$ requires 354.2064; $[\alpha]^{29}_D$ = +92.4 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 238 nm) indicated 82% ee: t_R (major) = 12.23 minutes, t_R (minor) = 14.45 minutes.

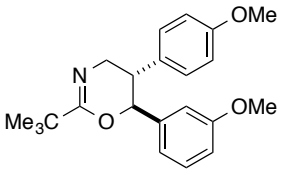
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-bromophenyl)-5,6-dihydro-4H-1,3-oxazine **4j**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(4-bromophenyl)allyl)pivalamide* **1d** (148 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol) with stirring for 43 hours. Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (129 mg, 0.32 mmol, 64%). IR ν_{max}/cm^{-1} (film): 2960, 2929, 1669, 1611, 1512, 1489, 1423, 1245, 1136, 1033; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.67-3.60 (m, 2H), 2.77 (td, *J* = 14.8 Hz, *J* = 6.5 Hz, 1H), 1.24 (s, 9H); ^{13}C

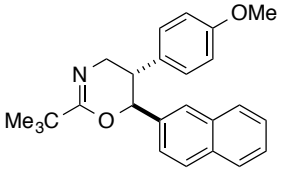
NMR (125 MHz, $CDCl_3$) δ: 165.8, 158.8, 138.7, 131.3, 130.8, 129.3, 128.5, 121.9, 114.2, 80.8, 55.3, 49.9, 45.0, 37.6, 28.0; HRMS-ESI (*m/z*) found $[M+H]^+$ 402.1063, $C_{21}H_{25}BrNO_2$ requires 402.1063; $[\alpha]^{29}_D$ = +97.3 ^{o} (1.0, $CHCl_3$), calculated with sample ee of 79%; HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 227 nm) indicated 91% ee: t_R (major) = 8.56 minutes, t_R (minor) = 9.65 minutes.

(5S,6S)-2-(tert-butyl)-6-(3-methoxyphenyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4k**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(3-methoxyphenyl)allyl)pivalamide* **1e** (124 mg, 0.50 mmol), *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol) with 15 mol% **3**. Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (148 mg, 0.42 mmol, 84%). IR ν_{max}/cm^{-1} (film): 3676, 2972, 2902, 1668, 1611, 1514, 1250, 1136, 1066, 1050, 751; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (t, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.77-6.73 (m, 3H), 6.62-6.60 (m, 2H), 5.04 (d, *J* = 9.6 Hz, 1H), 3.75 (s, 3H) 3.69 (s, 3H), 3.65-3.63 (m, 2H), 2.83 (dt, *J* = 9.3 Hz, *J* = 6.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 159.4, 158.6, 141.2, 131.2, 129.3, 129.1, 119.1, 114.1, 113.4, 112.2, 81.3, 55.3, 55.2, 49.7, 44.8, 37.6, 28.0; HRMS-ESI (*m/z*) found $[M+H]^+$ 354.2063, $C_{22}H_{28}NO_3$ requires 354.2069; $[\alpha]^{22}_D$ = +64.6 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated 93% ee: t_R (major) = 9.98 minutes, t_R (minor) = 13.98 minutes.

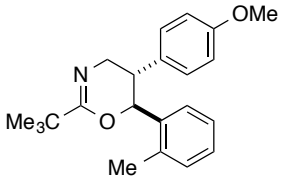
*(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(naphthalen-2-yl)-5,6-dihydro-4H-1,3-oxazin*e **4l**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(naphthalen-2-yl)allyl)pivalamide* **1f** (134 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol). Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (128 mg, 0.34 mmol, 69%). IR ν_{max}/cm^{-1} (film): 2971, 2902, 1670, 1612, 1513, 1394, 1263, 1248, 1135, 1066, 1037, 826, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.77 (m, 1H), 7.74-7.72 (m, 2H), 7.53 (s, 1H), 7.46-7.43 (m, 2H) 7.21 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 2H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 3H), 3.70-3.69 (m, 2H), 3.03-2.97 (dt, *J* = 10.0 Hz, *J* = 6.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 158.6, 136.9, 133.1, 133.0, 131.1, 129.2, 128.2, 128.0, 127.7, 126.3, 126.1 (2C), 124.3, 114.1, 81.7, 55.2, 49.9, 44.6, 37.7, 28.1; HRMS-ESI (*m/z*)

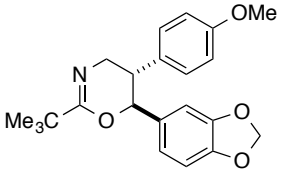
found $[M+H]^+$ 374.2114, $C_{25}H_{28}NO_2$ requires 374.2120; $[\alpha]^{22}_D$ = +91.8 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated 95% ee: t_R (major) = 10.06 minutes, t_R (minor) = 12.67 minutes.

(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(o-tolyl)-5,6-dihydro-4H-1,3-oxazine **4m**



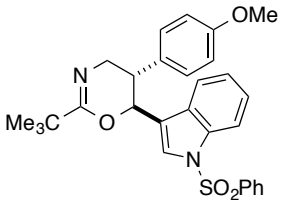
Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(o-tolyl)allyl)pivalamide* **1g** (116 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol). Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (78 mg, 0.23 mmol, 46%). IR ν_{max}/cm^{-1} (film): 2973, 2901, 1670, 1514, 1394, 1249, 1136, 1066, 880, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 6.8 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.14 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.31 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 3H), 3.73-3.68 (m, 2H), 3.00 (dt, *J* = 9.6 Hz, *J* = 5.6 Hz, 1H), 1.98 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 158.6, 137.8, 136.0, 131.0, 130.3, 129.3, 127.8, 126.8, 126.1, 113.9, 55.3, 49.1, 43.5, 37.6, 28.0, 19.3; HRMS-ESI (*m/z*) found $[M+H]^+$ 338.2117, $C_{22}H_{28}NO_2$ requires 338.2120; $[\alpha]^{22}_D$ = +63.9 ^{o} (1.0, $CHCl_3$); HPLC analysis (AD-H, 1% *i*-PrOH in *n*-hexane, 1 mL/min, 190 nm) indicated 90% ee: t_R (major) = 9.12 minutes, t_R (minor) = 10.43 minutes.

(5S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-2-(tert-butyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4n**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(benzo[d][1,3]dioxol-5-yl)allyl)pivalamide* **1h** (131 mg, 0.50 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.00 mmol) with stirring for 15 hours. Alumina column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (148 mg, 0.40 mmol, 80%). IR ν_{max}/cm^{-1} (film): 2964, 1669, 1613, 1514, 1491, 1443, 1247, 1179, 1140, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.91 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.45 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 5.92 (q, *J* = 1.4 Hz, 2H), 4.96 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H), 3.64-3.56 (m, 2H), 2.80 (td, *J* = 15.2 Hz, *J* = 5.9 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2, 158.6, 147.6, 147.2, 133.4, 131.2, 129.2, 120.8, 114.1, 107.9, 107.0, 101.1, 81.3, 55.3, 50.1, 44.9, 37.5, 28.0; HRMS-ESI (*m/z*) found $[M+H]^+$ 368.1858, $C_{22}H_{26}NO_4$ requires 368.1856; $[\alpha]^{24}_D$ = +140.4 ^{o} (1.0, $CHCl_3$); HPLC analysis (AD-H, 1% *i*-PrOH in *n*-hexane, 1 mL/min, 231 nm) indicated 89% ee: t_R (major) = 22.46 minutes, t_R (minor) = 29.61 minutes.

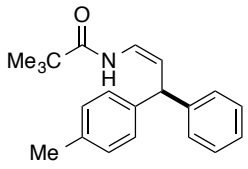
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(1-(phenylsulfonyl)-1H-indol-3-yl)-5,6-dihydro-4H-1,3-oxazine **4o**



Prepared according to general procedure **D** at a concentration of 0.05 M and performed with *(Z)-N-(3-(1-(phenylsulfonyl)-1H-indol-3-yl)allyl)pivalamide* **1i** (198 mg, 0.5 mmol) and *(mesityl)(4-methoxyphenyl)iodonium hexafluorophosphate* **2d** (498 mg, 1.0 mmol) with stirring for 2.5 hours. Alumina column chromatography, eluting with a gradient of 10 to 85% diethyl ether in petroleum ether 40-60, provided the title compound as an off-white solid (153 mg, 0.31 mmol, 61%). IR ν_{max}/cm^{-1} (film): 2960, 2925, 1669, 1611, 1510, 1449, 1368, 1245, 1177, 1123; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.3 Hz, 1H), 7.55-7.49 (m, 4H), 7.35-7.31 (m, 2H), 7.28 (t, J = 8.3 Hz, 1H), 7.24 (s, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 5.32 (d, J = 10.4 Hz, 1H), 3.80 (s, 3H), 3.74 (dd, J = 16.2 Hz, J = 5.2 Hz, 1H), 3.63 (dd, J = 16.4 Hz, J = 10.8 Hz, 1H), 3.26 (td, J = 10.8 Hz, J = 5.2 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 158.6, 137.9, 135.3, 133.8, 131.6, 129.3, 129.0, 128.8, 126.7, 125.1, 125.0, 123.5, 120.7, 120.5, 114.3, 113.8, 75.3, 55.4, 50.5, 42.2, 37.7, 28.0; HRMS-ESI (*m/z*) found $[M+H]^+$ 503.1988, $C_{29}H_{31}SN_2O_4$ requires 503.1999; $[\alpha]^{24}_D$ = +49.6 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 5% *i*-PrOH in *n*-hexane, 1 mL/min, 222 nm) indicated 91% ee: t_R (major) = 23.32 minutes, t_R (minor) = 35.79 minutes.

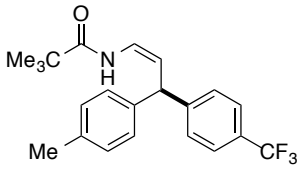
Enamide products

(S,Z)-N-(3-phenyl-3-(p-tolyl)prop-1-en-1-yl)pivalamide ***5a***



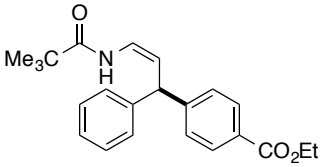
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-(p-tolyl)allyl)pivalamide* **1a** (116 mg, 0.50 mmol) and *(mesityl)(phenyl)iodonium hexafluorophosphate* **2b** (468 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 5 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound (16 mg, 0.05 mmol, 10%) as a white solid. IR ν_{max}/cm^{-1} (film): 3427, 2962, 1651, 1484, 1278, 1177, 801, 747, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.27 (m, 4H), 7.25-7.13 (m, 5H), 6.89-6.87 (m, 2H), 5.22 (dd, J = 8.4 Hz, J = 5.6 Hz, 1H), 4.79 (d, J = 6.0 Hz, 1H), 2.32 (s, 3H), 0.93 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.5, 143.9, 140.6, 136.7, 129.8, 129.1, 128.3, 128.2, 126.9, 122.7, 113.0, 49.1, 27.1, 21.1. HRMS-ESI (*m/z*) found $[M+H]^+$ 308.2009, $C_{21}H_{26}NO$ requires 308.2012. $[\alpha]^{26}_D$ = -10.8 ^{o} (1.0, $CHCl_3$), calculated with sample ee of 94%; HPLC analysis (OD, 1% *i*-PrOH in *n*-hexane, 1 mL/min, 236 nm) indicated 96% ee: t_R (major) = 13.13 minutes, t_R (minor) = 14.09 minutes.

(Z)-N-(3-(4-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5b**



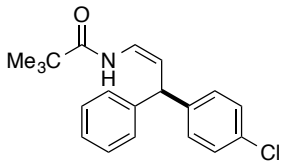
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-(4-tolyl)allyl)pivalamide* **1a** (116 mg, 0.50 mmol) and *(4-(trifluoromethyl)phenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound (138 mg, 0.37 mmol, 74%) as a white solid. IR ν_{max} /cm^{-1} (film): 3432, 2966, 1649, 1483, 1462, 1324, 1162, 1120, 1067, 1018, 812, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.17 (s, 4H), 6.95-6.83 (m, 2H), 5.18 (dd, *J* = 8.6 Hz, *J* = 5.8 Hz, 1H), 4.85 (d, *J* = 5.8 Hz, 1H), 2.34 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 148.1 (q, *J* = 1.2 Hz), 139.4, 137.2, 130.1, 129.2 (q, *J* = 32.4 Hz), 128.6, 128.3, 125.9 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.9 Hz), 123.3, 111.8, 48.9, 38.8, 27.1, 21.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 376.1883, $C_{22}H_{25}NOF_3$ requires 376.1883. $[\alpha]^{27}_D$ = -13.3 ^{o} (1.2, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 203 nm) indicated 96% ee: t_R (minor) = 7.11 minutes, t_R (major) = 8.75 minutes.

ethyl (R,Z)-4-(1-phenyl-3-pivalamidoallyl)benzoate **5c**



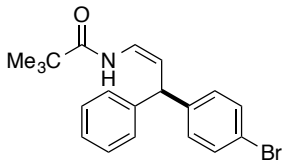
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(ethyl 4-benzoate)(mesityl)iodonium hexafluorophosphate* **2j** (540 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 20% ethyl acetate in petroleum ether 40-60, provided the title compound (101 mg, 0.27 mmol, 55%) as a colourless oil. IR ν_{max}/cm^{-1} (film): 3438, 2966, 1716, 1650, 1486, 1367, 1276, 1178, 1104, 1021, 752, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 4H), 7.27-7.22 (m, 3H), 6.94-6.86 (m, 2H), 5.20 (dd, *J* = 8.4 Hz, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 166.4, 148.8, 142.7, 130.3, 129.3, 129.2, 128.3, 128.2, 127.3, 123.2, 111.9, 61.1, 49.3, 38.8, 27.1, 14.4; HRMS-ESI (*m/z*) found $[M+H]^+$ 366.2056, $C_{23}H_{28}NO_3$ requires 366.2064. $[\alpha]^{27}_D$ = -4.3 ^{o} (1.0, $CHCl_3$), calculated with sample ee of 94%; HPLC analysis (IB, 5% *i*-PrOH in *n*-hexane, 1 mL/min) indicated 93% ee: t_R (major) = 10.23 minutes, t_R (minor) = 11.81 minutes.

(Z)-N-(3-(4-chlorophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5d**



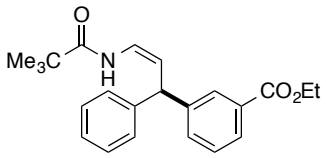
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(4-chlorophenyl)(mesityl)iodonium hexafluorophosphate* **2k** (503 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound (87 mg, 0.26 mmol, 53%) as a white solid. IR ν_{max}/cm^{-1} (film): 3436, 2964, 1647, 1485, 1461, 1398, 1367, 1276, 1174, 1091, 1014, 814, 801, 757, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.22 (m, 7H), 7.19 (d, J = 8.4 Hz, 2H), 6.91-6.86 (m, 2H), 5.16 (dd, J = 8.5 Hz, J = 6.0 Hz, 1H), 4.78 (d, J = 6.0 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 143.0, 142.2, 132.8, 129.6, 129.3, 129.1, 128.3, 127.3, 123.1, 112.1, 48.7, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 328.1459, $C_{20}H_{23}NOCl$ requires 328.1463. $[\alpha]^{27}_D$ = -12.8 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 218 nm) indicated 94% ee: t_R (minor) = 9.16 minutes, t_R (major) = 13.95 minutes.

(Z)-N-(3-(4-bromophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5e**



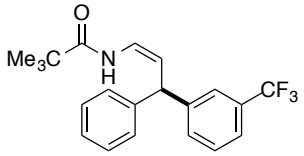
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(4-bromophenyl)(mesityl)iodonium hexafluorophosphate* **2l** (547 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound (104 mg, 0.28 mmol, 55%) as an off-white solid. IR ν_{max}/cm^{-1} (film): 3437, 2964, 1647, 1482, 1461, 1398, 1275, 1245, 1173, 1072, 1010, 940, 798, 736, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J = 8.4 Hz, 2H), 7.35 (m, 2H), 7.28-7.24 (m, 3H), 7.15 (d, J = 8.4 Hz, 2H), 6.93-6.84 (m, 2H), 5.17 (dd, J = 8.5 Hz, J = 6.0 Hz, 1H), 4.78 (d, J = 5.6 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 143.0, 142.8, 132.1, 130.0, 129.3, 128.3, 127.3, 123.2, 120.8, 112.0, 48.8, 38.8, 27.2; HRMS-ESI (*m/z*) found $[M+H]^+$ 372.0961, $C_{20}H_{23}NOBr$ requires 372.0958. $[\alpha]^{27}_D$ = -7.8 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 256 nm) indicated 92% ee: t_R (minor) = 9.71 minutes, t_R (major) = 15.85 minutes.

ethyl (R,Z)-3-(1-phenyl-3-pivalamidoallyl)benzoate **5f**



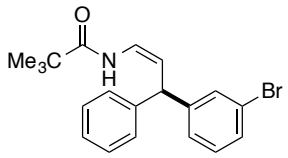
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(ethyl 3-benzoate)(mesityl)iodonium hexafluorophosphate* **2m** (540 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 20% ethyl acetate in petroleum ether 40-60, provided the title compound (95 mg, 0.26 mmol, 52%) as a colourless oil. IR ν_{max}/cm^{-1} (film): 3433, 2964, 1717, 1649, 1483, 1367, 1273, 1176, 1105, 1082, 1023, 749, 732, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.36-7.33 (m, 2H), 7.30-7.23 (m, 3H), 6.94-6.90 (m, 2H), 5.23 (dd, *J* = 8.4 Hz, *J* = 6.0 Hz, 1H), 4.88 (d, *J* = 6.0 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.5, 166.5, 144.2, 143.0, 132.6, 131.2, 129.3, 129.1, 128.3, 128.2, 127.2, 123.1, 112.2, 61.2, 49.2, 38.8, 27.1, 14.4; HRMS-ESI (*m/z*) found $[M+H]^+$ 366.2071, $C_{23}H_{28}NO_3$ requires 366.2064. $[\alpha]^{27}_D$ = -7.2˚ (1.0, $CHCl_3$); HPLC analysis (AD-H, 10% *i*-PrOH in *n*-hexane, 1 mL/min, 213 nm) indicated 92% ee: t_R (minor) = 7.51 minutes, t_R (major) = 8.56 minutes.

(Z)-N-(3-phenyl-3-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5g**



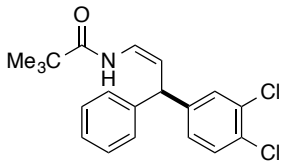
Prepared according to General procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(3-(trifluoromethyl)phenyl)(mesityl)iodonium hexafluorophosphate* **2n** (536 mg, 1.00 mmol). Silica column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound (108 mg, 0.30 mmol, 60%) as a white solid. IR ν_{max}/cm^{-1} (film): 3432, 2965, 1648, 1484, 1462, 1327, 1163, 1122, 1094, 1073, 907, 799, 733, 699, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (br. s, 1H), 7.49-7.39 (m, 3H), 7.36-7.32 (m, 2H), 7.27-7.22 (m, 3H), 6.94-6.84 (m, 2H), 5.18 (dd, *J* = 8.5 Hz, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 5.5 Hz, 1H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 144.8, 142.6, 131.7 (q, *J* = 1.0 Hz), 131.3 (q, *J* = 32.2 Hz), 129.5, 129.4, 128.3, 127.4, 124.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.4 Hz), 123.8 (q, *J* = 3.8 Hz), 123.3, 111.8, 49.1, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 362.1725, $C_{21}H_{23}NOF_3$ requires 362.1726. $[\alpha]^{27}_D$ = -15.1˚ (1.0, $CHCl_3$); HPLC analysis (IC, 10% *i*-PrOH in *n*-hexane, 1 mL/min, 213 nm) indicated 94% ee: t_R (minor) = 9.76 minutes, t_R (major) = 12.55 minutes.

(R)-N-[(1Z)-3-(3-bromophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5h**



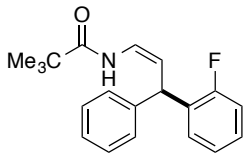
Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(3-bromophenyl)(mesityl)iodonium hexafluorophosphate* **2o** (547 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 20% ethyl acetate in petroleum ether 40-60, provided the title compound as a white crystalline solid (102 mg, 0.28 mmol, 55%); IR ν_{max}/cm^{-1} (film): 2963, 2849, 2321, 1649, 1487, 1277, 1181, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (t, J = 2.5 Hz, 1H), 7.39-7.32 (m, 3H), 7.29-7.23 (m, 3H), 7.21-7.18 (m, 2H), 6.91 (ddd, J = 10.9 Hz, J = 8.9 Hz, J = 2.0 Hz, 1H), 6.84 (br. d, J = 10.9 Hz, 1H), 5.18 (dd, J = 7.9 Hz, J = 5.9 Hz, 1H), 4.79 (dd, J = 5.7 Hz, J = 1.2 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 146.1, 142.7, 131.3, 130.6, 130.1, 129.3, 128.3, 127.4, 126.9, 123.2, 123.1, 111.9, 49.1, 38.8, 27.2; HRMS-ESI (*m/z*) found $[M]^+$ 372.0963, $C_{20}H_{22}NOBr$ requires 372.0958; $[\alpha]^{20}_D$ = -8.2 ^{o} (1.0, $CHCl_3$), calculated with sample ee of 92%; HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 219 nm) indicated 95% ee: t_R (minor) = 9.24 minutes, t_R (major) = 12.57 minutes.

(R)-N-[(1Z)-3-(3,4-dichlorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5i**



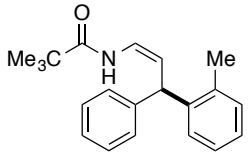
Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (108 mg, 0.50 mmol) and *(3,4-dichlorophenyl)(mesityl)iodonium hexafluorophosphate* **2p** (537 mg, 1.00 mmol). Silica column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as an amorphous white solid (105 mg, 0.29 mmol, 58%). IR ν_{max}/cm^{-1} (film): 3671, 3428, 2672, 2904, 2325, 1649, 1485, 1467, 1395, 1179, 1035; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-7.33 (m, 4H), 7.31-7.24 (m, 3H), 7.11 (ddd, J = 8.3 Hz, J = 2.1 Hz, J = 0.4 Hz, 1H), 6.92 (ddd, J = 11.0 Hz, J = 9.1 Hz, J = 2.2 Hz, 1H), 6.84 (br. d, J = 11.0 Hz, 1H), 5.14 (dd, J = 8.6 Hz, J = 6.0 Hz, 1H), 4.78 (dd, J = 5.8 Hz, J = 1.4 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.6, 144.1, 142.3, 133.0, 131.0, 130.9, 130.1, 129.5, 128.3, 127.6, 123.5, 111.3, 48.5, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 362.1076, $C_{20}H_{22}NOCl_2$ requires 362.1073; $[\alpha]^{22}_D$ = -15.9 ^{o} (0.8, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 246 nm) indicated 93% ee: t_R (minor) = 9.34 minutes, t_R (major) = 20.85 minutes.

(R)-N-[(1Z)-3-(2-fluorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5j**



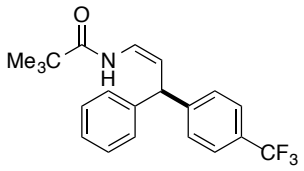
Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(2-fluorophenyl)(mesityl)iodonium hexafluorophosphate* **2q** (486 mg, 1.00 mmol). Silica column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as an amorphous white solid (65 mg, 0.21 mmol, 42%). IR ν_{max}/cm^{-1} (film): 3667, 3440, 2972, 2899, 1687, 1651, 1483, 1455, 1225, 1175, 755, 697; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.31 (m, 4H), 7.30-7.21 (m, 3H), 7.13 (td, *J* = 7.8 Hz, *J* = 1.1 Hz, 1H), 7.10-7.00 (m, 2H), 6.92 (ddd, *J* = 10.9 Hz, *J* = 8.2 Hz, *J* = 0.5 Hz, 1H), 5.25-5.17 (m, 2H), 1.02 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.6, 160.4 (d, *J* = 243.9 Hz), 142.2, 130.7 (d, *J* = 17.7 Hz), 129.7 (d, *J* = 3.1 Hz), 129.1, 128.6 (d, *J* = 8.7 Hz), 128.3, 127.1, 124.8 (d, *J* = 2.5 Hz), 123.0, 115.7 (d, *J* = 21.5 Hz), 111.4, 41.2, 38.8, 27.2; HRMS-ESI (*m/z*) found $[M+H]^+$ 312.1760, $C_{20}H_{23}NOF$ requires 312.1758; $[\alpha]^{22}_D$ = -54.3 ^{o} (1.0, $CHCl_3$); HPLC analysis (IC, 10% *i*-PrOH in *n*-hexane, 1 mL/min, 209 nm) indicated >98% ee: t_R (major) = 13.08 minutes, t_R (minor) = 13.79 minutes.

(R)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-phenylprop-1-en-1-yl]propanamide **5k**



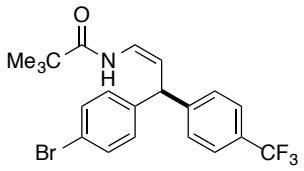
Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(2-methylphenyl)(mesityl)iodonium hexafluorophosphate* **2r** (482 mg, 1.00 mmol). Silica column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a colourless oil (61 mg, 0.20 mmol, 40%). IR ν_{max}/cm^{-1} (film): 3671, 3437, 2968, 2909, 1691, 1651, 1485, 1459, 1171, 1072, 1056; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.20 (m, 2H), 7.27-7.16 (m, 7H), 6.89 (ddd, *J* = 11.0 Hz, *J* = 9.3 Hz, *J* = 2.1 Hz, 1H), 6.82 (br. d, *J* = 9.8 Hz, 1H), 5.14 (dd, *J* = 8.8 Hz, *J* = 5.7 Hz, 1H), 5.01 (dd, *J* = 5.9 Hz, *J* = 1.4 Hz, 1H), 2.33 (s, 3H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.6, 142.8, 141.2, 136.5, 131.0, 129.0, 128.7, 128.6, 127.2, 126.9, 126.8, 122.8, 112.4, 46.2, 38.7, 27.1, 19.9; HRMS-ESI (*m/z*) found $[M+H]^+$ 308.2011, $C_{21}H_{26}NO$ requires 308.2009; $[\alpha]^{22}_D$ = +19.9 ^{o} (0.9, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 228 nm) indicated 97% ee: t_R (major) = 7.74 minutes, t_R (minor) = 8.57 minutes.

(R)-2,2-dimethyl-N-[(1Z)-3-phenyl-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5l**

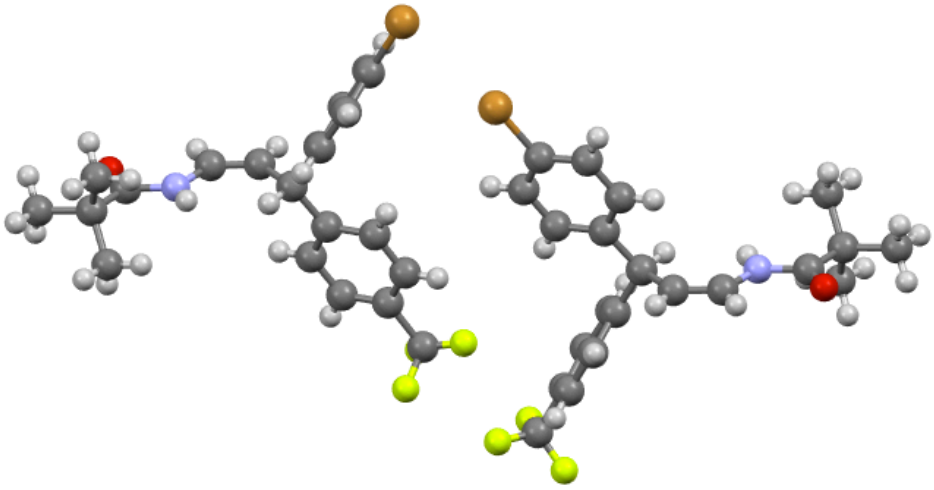


Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-phenylallyl)pivalamide* **1b** (109 mg, 0.50 mmol) and *(4-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.0 mmol). Silica column chromatography, eluting with 5% ethyl acetate in petroleum ether 40-60, provided the title compound as a colourless oil (126 mg, 0.35 mmol, 70%). IR ν_{max}/cm^{-1} (film): 3670, 3424, 2972, 2901, 1651, 1484, 1326, 1249, 1165, 1118, 1066; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, J = 8.5 Hz, 2H), 7.42-7.34 (m, 4H), 7.32-7.27 (m, 3H), 6.93 (ddd, J = 11.1 Hz, J = 9.3 Hz, J = 2.2 Hz), 6.84 (br. d, J = 10.8 Hz, 1H), 5.20 (dd, J = 9.1 Hz, J = 6.1 Hz, 1H), 4.89 (d, J = 5.3 Hz, 1H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.6, 147.9, 142.5, 129.4, 129.1 (q, J = 32.4 Hz), 128.6, 128.4, 127.5, 126.0 (q, J = 3.1 Hz), 124.2 (q, J = 272.5 Hz), 123.2, 111.6, 49.2, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 362.1726, $C_{21}H_{23}F_3NO$ requires 362.1726; $[\alpha]^{22}_D$ = -10.0 ^{o} (1.1, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 217 nm) indicated 91% ee: t_R (minor) = 7.20 minutes, t_R (major) = 9.14 minutes.

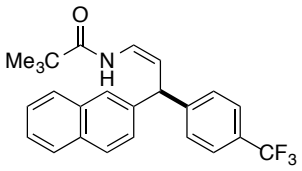
(S)-N-[(1Z)-3-(4-bromophenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]-2,2-dimethylpropanamide **5m**



Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-(4-bromophenyl)allyl)pivalamide* **1d** (148 mg, 0.50 mmol) and *(4-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound as a white solid (62 mg, 0.14 mmol, 28%). IR ν_{max}/cm^{-1} (film): 3678, 2972, 2909, 1649, 1615, 1487, 1461, 1324, 1120, 1066, 1015, 801; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, J = 8.0 Hz, 2H), 7.48 (dt, J = 8.5 Hz, J = 1.8 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.15 (dt, J = 8.4 Hz, J = 1.8 Hz, 2H), 6.94 (ddd, J = 11.1 Hz, J = 9.2 Hz, J = 2.0 Hz, 1H), 6.80 (br. d, J = 10.4 Hz, 1H), 5.15 (dd, J = 8.7 Hz, J = 6.3 Hz, 1H), 4.84 (d, J = 5.9 Hz, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 147.2, 141.6, 132.4, 130.0, 129.6 (q, J = 31.9 Hz), 128.6, 126.1 (q, J = 3.7 Hz), 124.1 (q, J = 271.4 Hz), 123.6, 121.3, 111.0, 48.4, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 440.0826, $C_{21}H_{21}NOF_3Br$ requires 440.0831; $[\alpha]^{22}_D$ = -4.4 ^{o} (1.4, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 237 nm) indicated 89% ee: t_R (major) = 8.28 minutes, t_R (minor) = 9.45 minutes; The X-Ray crystal structure is deposited in the Cambridge Crystallographic Data Centre, reference number CCDC 1050909.

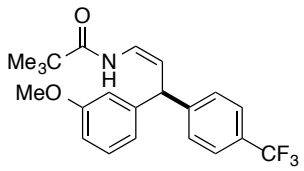


(S)-2,2-dimethyl-N-[(1Z)-3-(naphthalen-2-yl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5n**



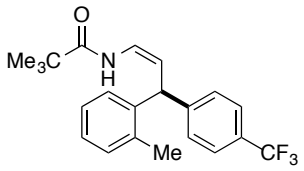
Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-(naphthalen-2-yl)allyl)pivalamide* **1f** (134 mg, 0.50 mmol) and *(4-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound as a yellow oil (107 mg, 0.26 mmol, 52%). IR ν_{max}/cm^{-1} (film): 3687, 2972, 2904, 1651, 1483, 1465, 1322, 1259, 1165, 1118, 1068, 1021, 815; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-7.78 (m, 3H), 7.73 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.54-7.47 (m, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.39 (dd, J = 8.6 Hz, J = 2.1 Hz, 1H), 7.00 (ddd, J = 11.2 Hz, J = 9.1 Hz, J = 2.2 Hz, 1H), 6.92 (br. d, J = 10.4 Hz, 1H), 5.29 (dd, J = 8.5 Hz, J = 6.4 Hz, 1H), 5.07 (d, J = 5.9 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 147.6, 139.8, 133.6, 132.6, 129.3, 129.3 (q, J = 33.1 Hz), 128.7, 127.8, 126.74, 126.68, 126.5, 126.3, 126.0 (q, J = 3.7 Hz), 124.2 (q, J = 270.7 Hz), 123.5, 111.3, 49.2, 38.7, 27.0; HRMS-ESI (*m/z*) found $[M+H]^+$ 412.1871, $C_{25}H_{25}NOF_3$ requires 412.1883; $[\alpha]^{22}_D$ = -17.7 ^{o} (1.5, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 227 nm) indicated 95% ee: t_R (major) = 9.69 minutes, t_R (minor) = 10.36 minutes.

(Z)-N-(3-(3-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5o**



Prepared according to general procedure **D** at a concentration of 0.1 M and using *(Z)-N-(3-(3-methoxyphenyl)allyl)pivalamide* **1e** (124 mg, 0.50 mmol) and *(4-(trifluoromethyl)phenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound (135 mg, 0.34 mmol, 69%) as a colourless oil. IR ν_{max}/cm^{-1} (film): 3433, 2965, 1649, 1599, 1484, 1464, 1322, 1262, 1162, 1120, 1067, 1018, 842, 767, 732, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 6.96-6.87 (m, 3H), 6.83-6.80 (m, 2H), 5.19 (dd, J = 8.3 Hz, J = 5.9 Hz, 1H), 4.86 (d, J = 5.9 Hz, 1H), 3.78 (s, 3H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 160.4, 147.69, 147.68, 144.1, 130.4, 129.2 (q, J = 32.4 Hz), 128.6, 125.9 (q, J = 3.7 Hz), 124.2 (q, J = 272.0 Hz), 123.4, 120.6, 114.4, 112.4, 111.5, 55.3, 49.1, 38.8, 27.1; HRMS-ESI (*m/z*) found $[M+H]^+$ 392.1829, $C_{22}H_{25}NO_2F_3$ requires 392.1832. $[\alpha]^{27}_D$ = -14.7 ^{o} (1.1, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 210 nm) indicated 90% ee: t_R (minor) = 8.58 minutes, t_R (major) = 9.79 minutes.

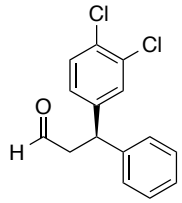
(S)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5p**



Prepared according to general procedure **D** at a concentration of 0.1 M and performed with *(Z)-N-(3-(2-tolyl)allyl)pivalamide* **1g** (116 mg, 0.50 mmol) and *(4-trifluoromethylphenyl)(mesityl)iodonium hexafluorophosphate* **2e** (536 mg, 1.00 mmol). Silica column chromatography, eluting with a gradient of 0 to 10% ethyl acetate in petroleum ether 40-60, provided the title compound as a colourless oil (49 mg, 0.13 mmol, 26%). IR ν_{max}/cm^{-1} (film): 3428, 2964, 1681, 1647, 1484, 1461, 1322, 1163, 1120, 1066, 1016, 749; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.25-7.17 (m, 4H), 6.90 (ddd, J = 10.7 Hz, J = 9.0 Hz, J = 1.7 Hz, 1H), 6.77 (br. d, J = 10.4 Hz, 1H), 5.12 (dd, J = 9.0 Hz, J = 5.9 Hz, 1H), 5.05 (d, 5.9 Hz, 1H), 2.32 (s, 3H), 0.92 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.6, 147.1, 140.1, 136.6, 131.3, 129.2 (q, J = 33.0 Hz), 128.9, 128.6, 127.6, 127.1, 125.8 (q, J = 3.4 Hz), 124.2 (q, J = 271.9 Hz), 123.3, 111.3, 45.9, 38.7, 27.1, 19.9; HRMS-ESI (*m/z*) found $[M+H]^+$ 376.1878, $C_{22}H_{25}NOF_3$ requires 376.1883; $[\alpha]^{20}_D$ = -31.2 ^{o} (1.9, $CHCl_3$); HPLC analysis (IC, 20% *i*-PrOH in *n*-hexane, 1 mL/min, 202 nm) indicated >98% ee: t_R (minor) = 6.50 minutes, t_R (major) = 8.51 minutes.

Enamide hydrolysis

(R)-3-(3,4-dichlorophenyl)-3-phenylpropanal **6**[8]



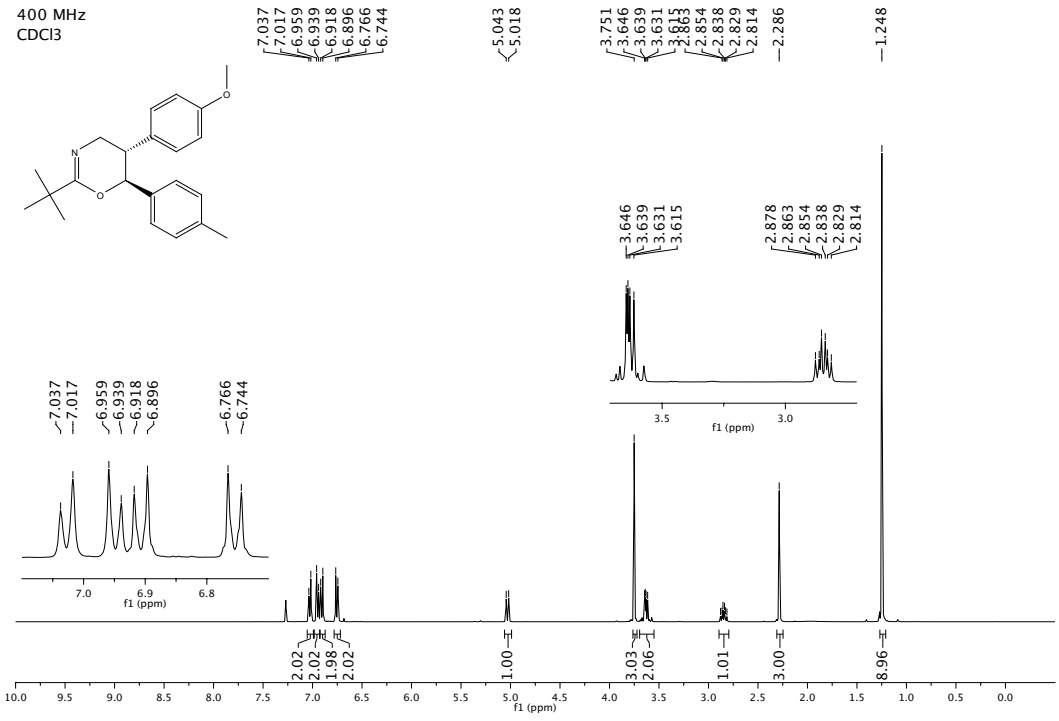
To a stirred solution of *(R)-N-[(1Z)-3-(3,4-dichlorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide* **5n** (91 mg, 0.25 mmol, 94% ee) in tetrahydrofuran was added concentrated hydrochloric acid (0.50 mL, 37% aqueous w/v solution) and the resulting yellow solution stirred for two hours at room temperature before undergoing a portion-wise addition of sodium carbonate (1.00 g). The suspension was stirred for a further fifteen minutes, filtered through anhydrous Na_2SO_3 and concentrated *in vacuo*. The crude residue was purified by silica column chromatography, eluting with 2 to 20% ethyl acetate in hexane, to give the title compound as a pale yellow oil (59 mg, 0.21 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (t, J = 1.5 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H) 7.35-7.29 (m, 3H), 7.26-7.18 (m, 3H), 7.08 (dd, J = 8.3 Hz, J = 2.2 Hz, 1H), 4.60 (t, J = 7.7 Hz, 1H), 3.23-3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.0, 143.8, 142.2, 132.8, 130.9, 130.8, 129.8, 129.1, 127.7, 127.28, 127.26, 49.3, 44.1; $[\alpha]^{24}_D$ = -11.1 ^{o} (1.05, $CHCl_3$), lit. $[\alpha]^{25}_D$ = -7.3 ^{o} (0.95, $CHCl_3$, 93% ee); HPLC analysis of the alcohol derivative ($NaBH_4$ treatment in MeOH/2_2) (AD-H, 2% *i*-PrOH in *n*-hexane, 1 mL/min, 209 nm) indicated 94% ee: t_R (major) = 33.54 minutes, t_R (minor) = 35.15 minutes. Experimental data in agreement with previous literature report.[8]

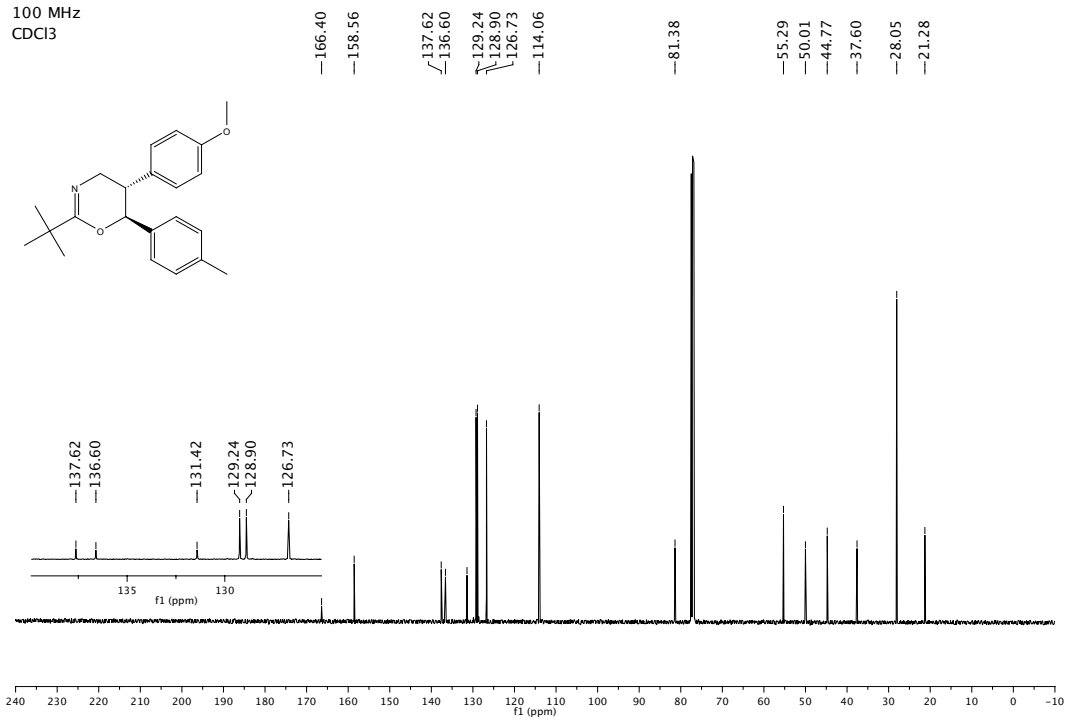
[8] Roesner, S.; Mansilla Casatejada, J.; Elford, T. G.; Sonawane, R. P.; Aggarwal, V. K. *Org. Lett.* **2011**, *13*, 5740.

3. NMR Spectra

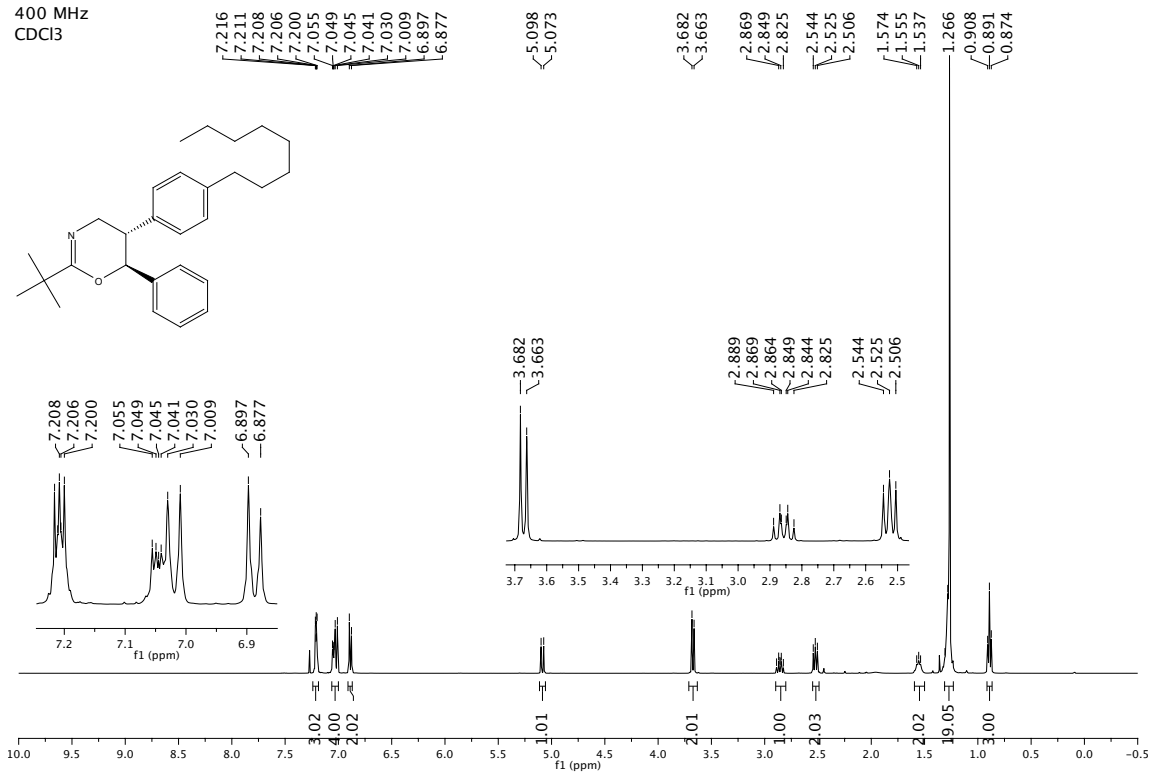
Oxazine products

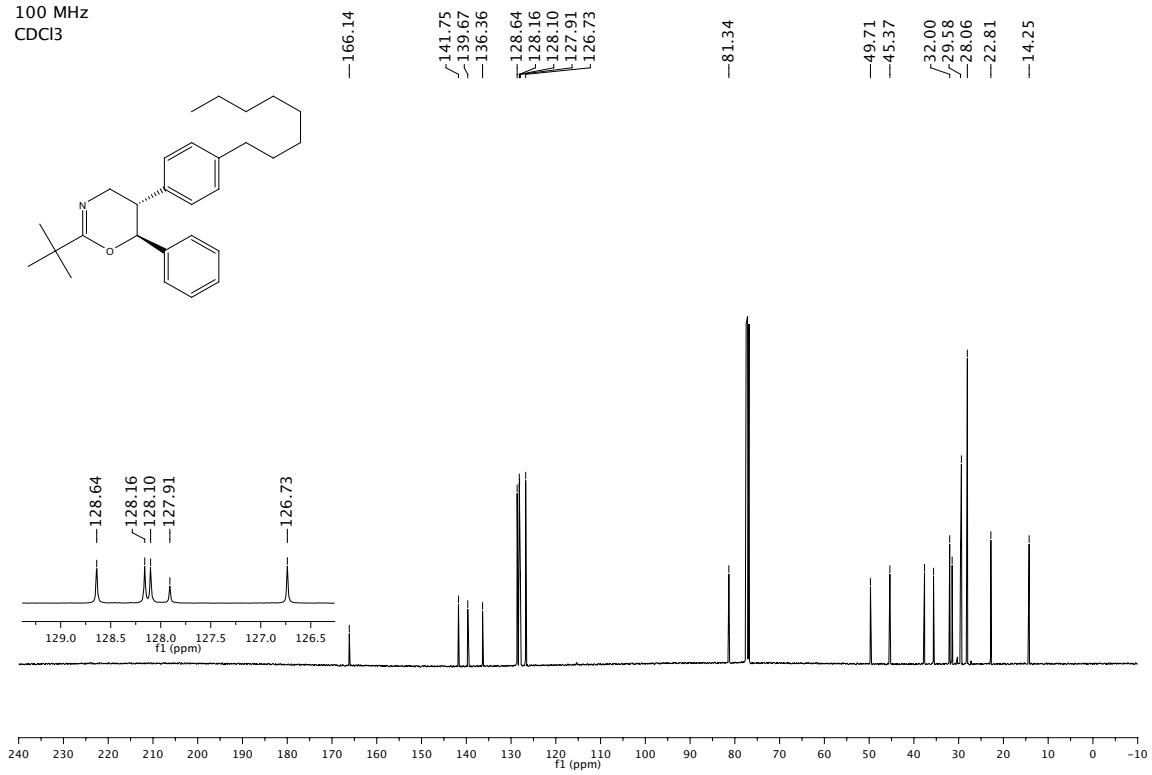
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(p-tolyl)-5,6-dihydro-4H-1,3-oxazine **4b**



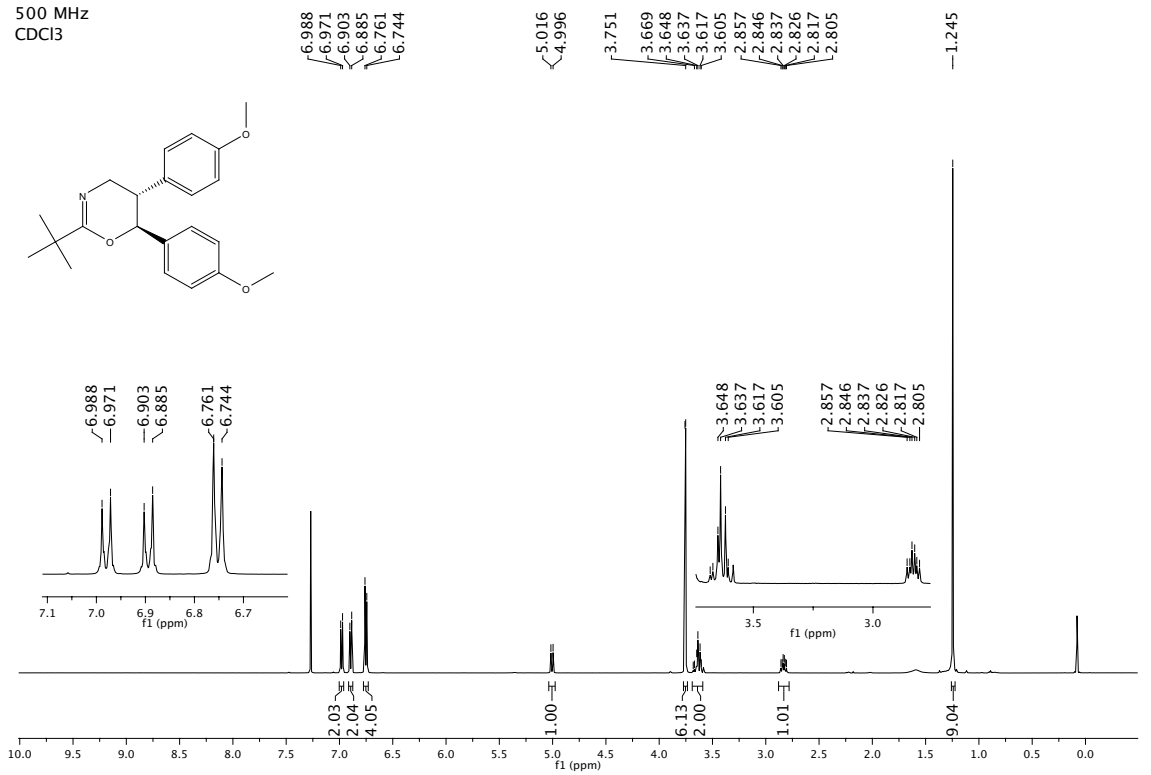


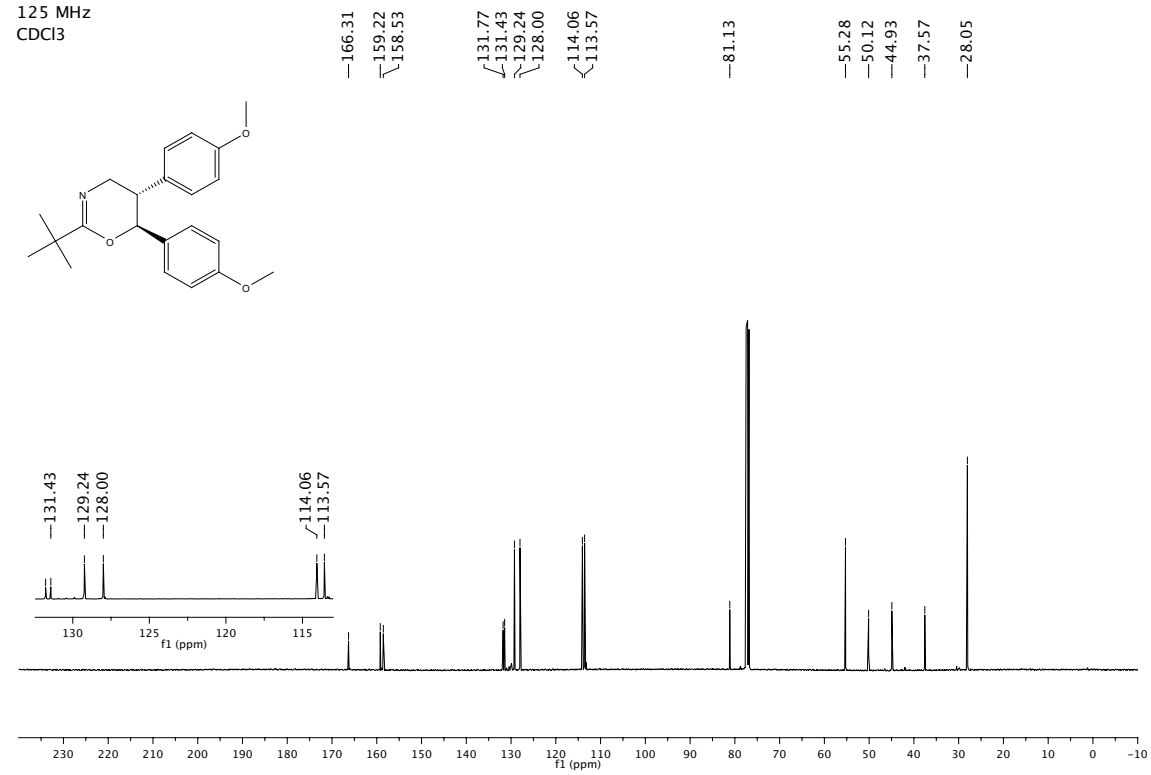
(5S,6S)-2-(tert-butyl)-5-(4-octylphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4f**



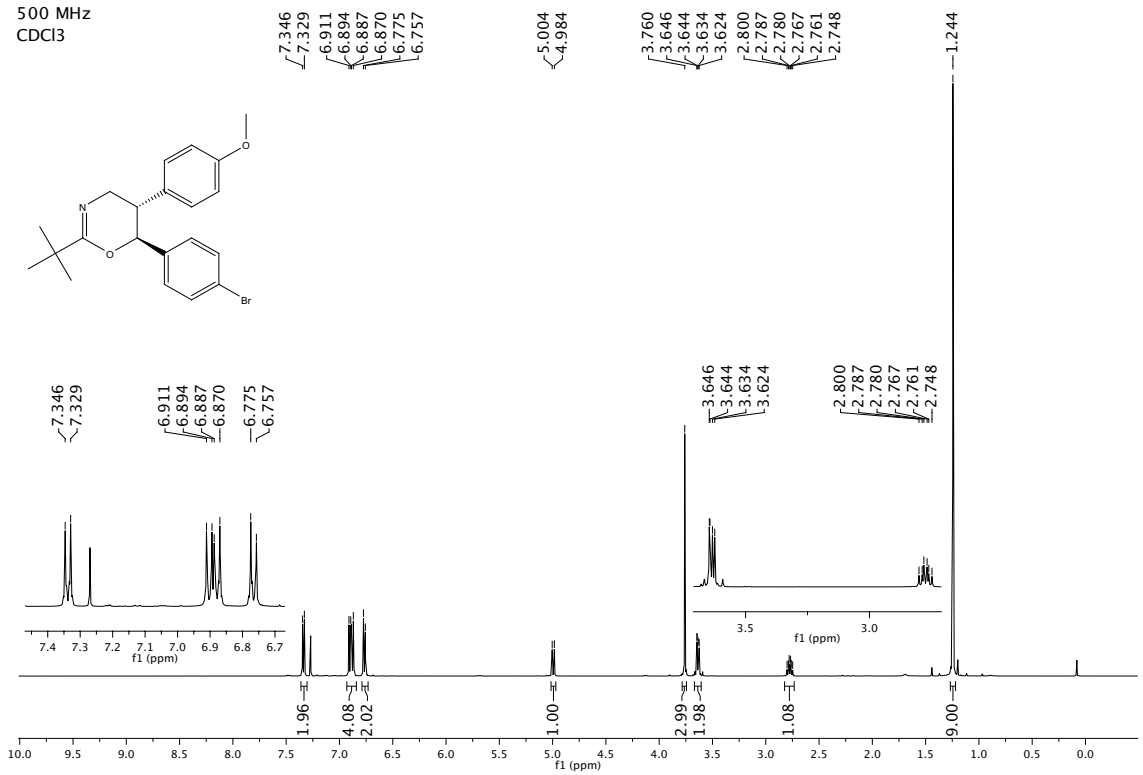


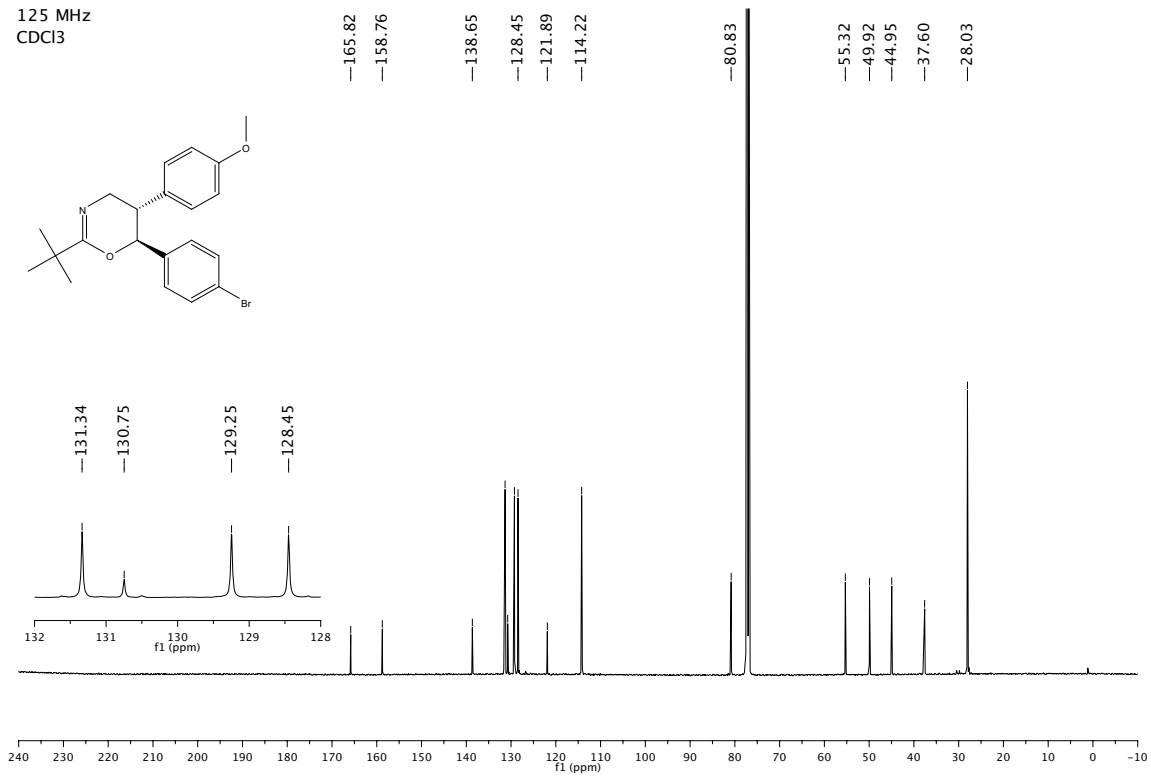
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4i**



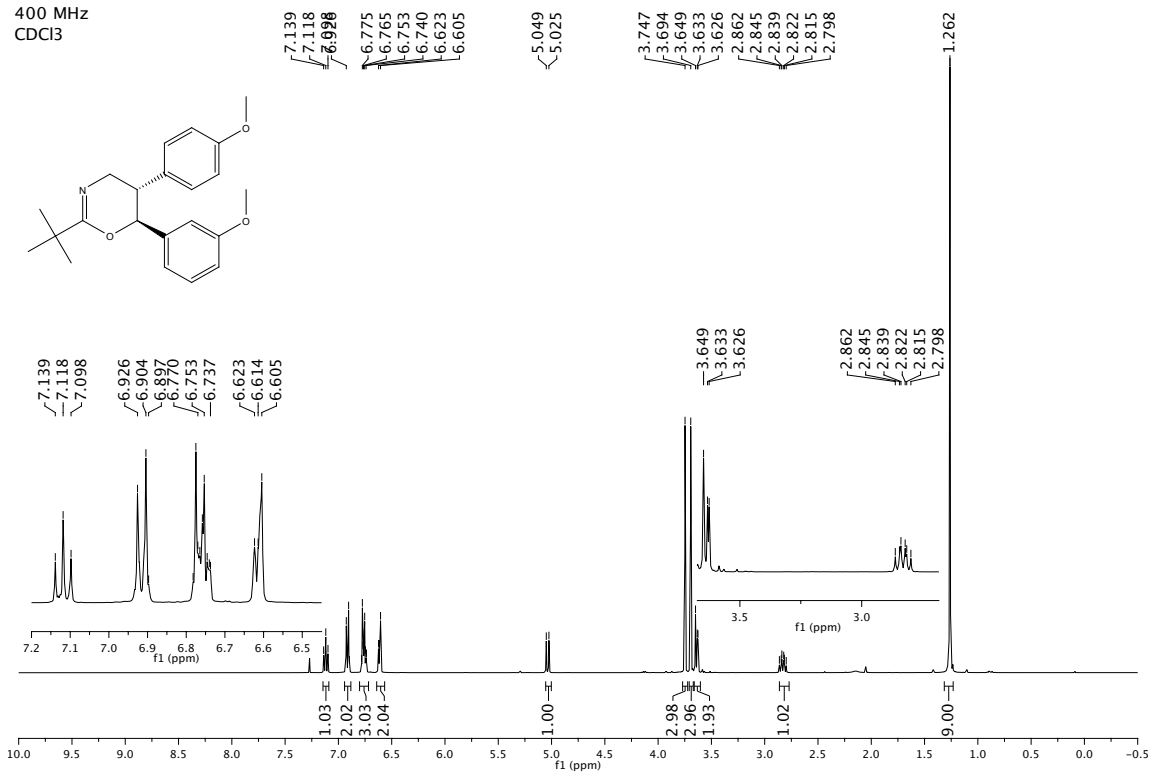


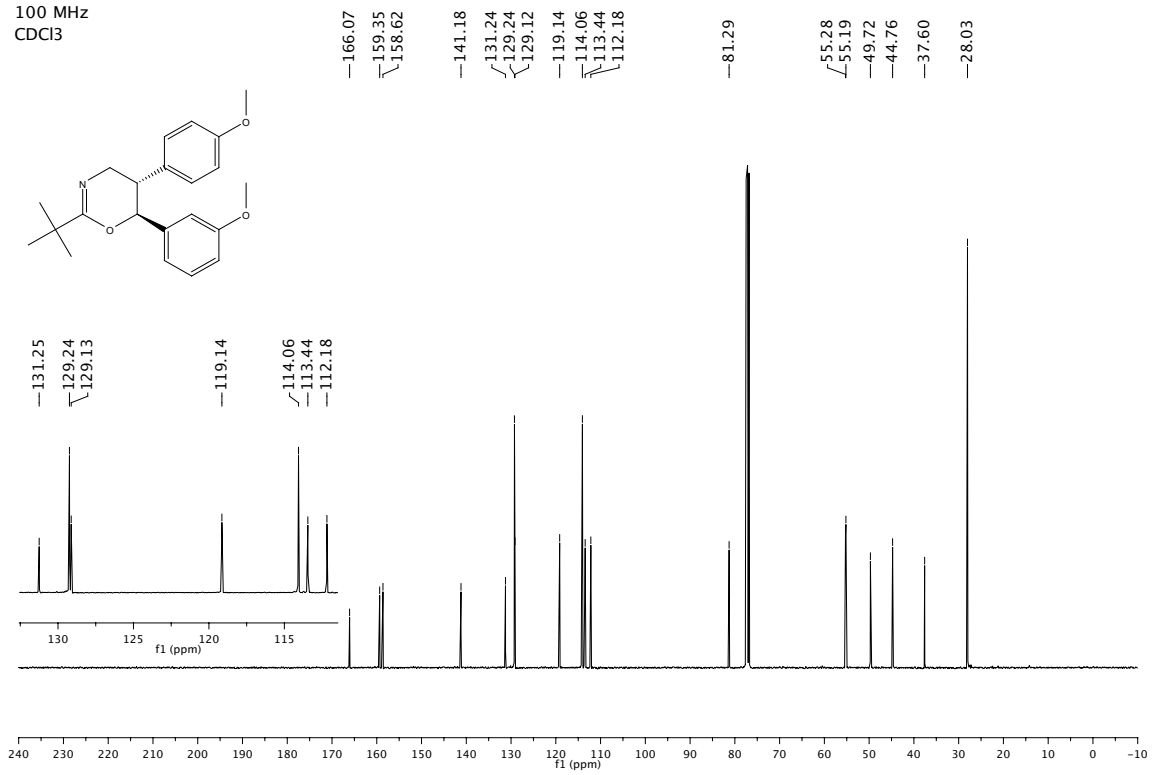
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-bromophenyl)-5,6-dihydro-4H-1,3-oxazine **4j**



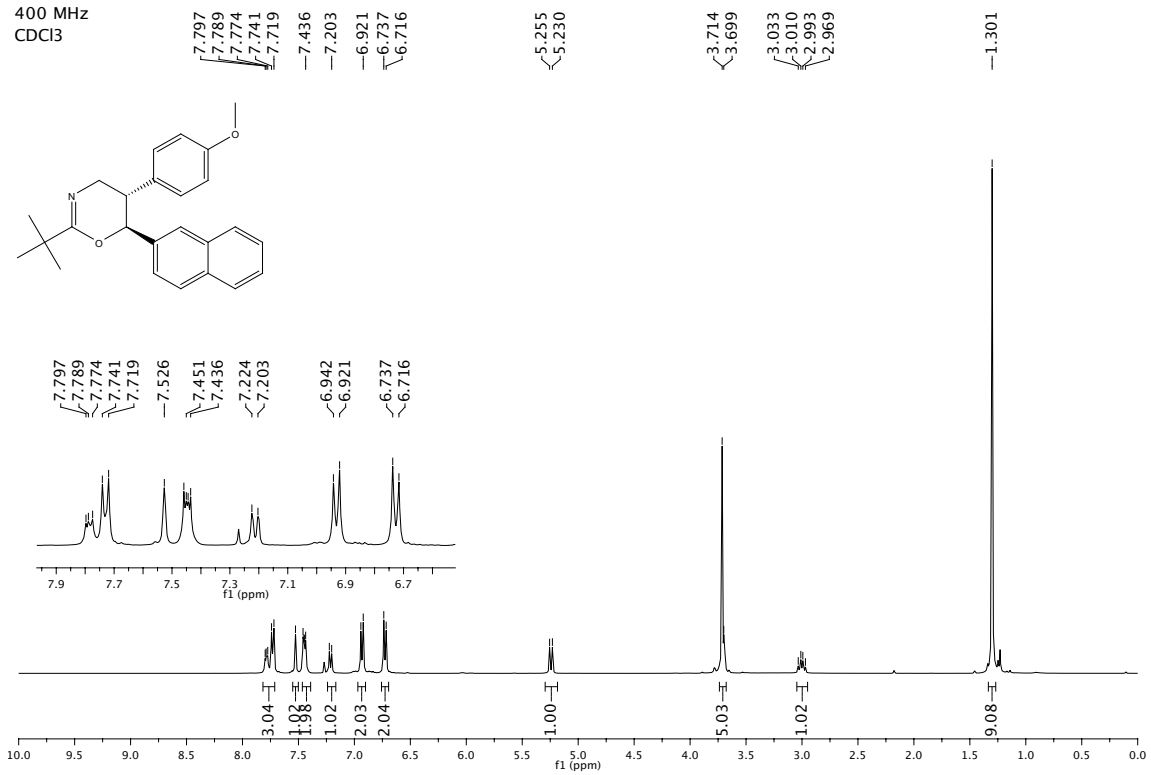


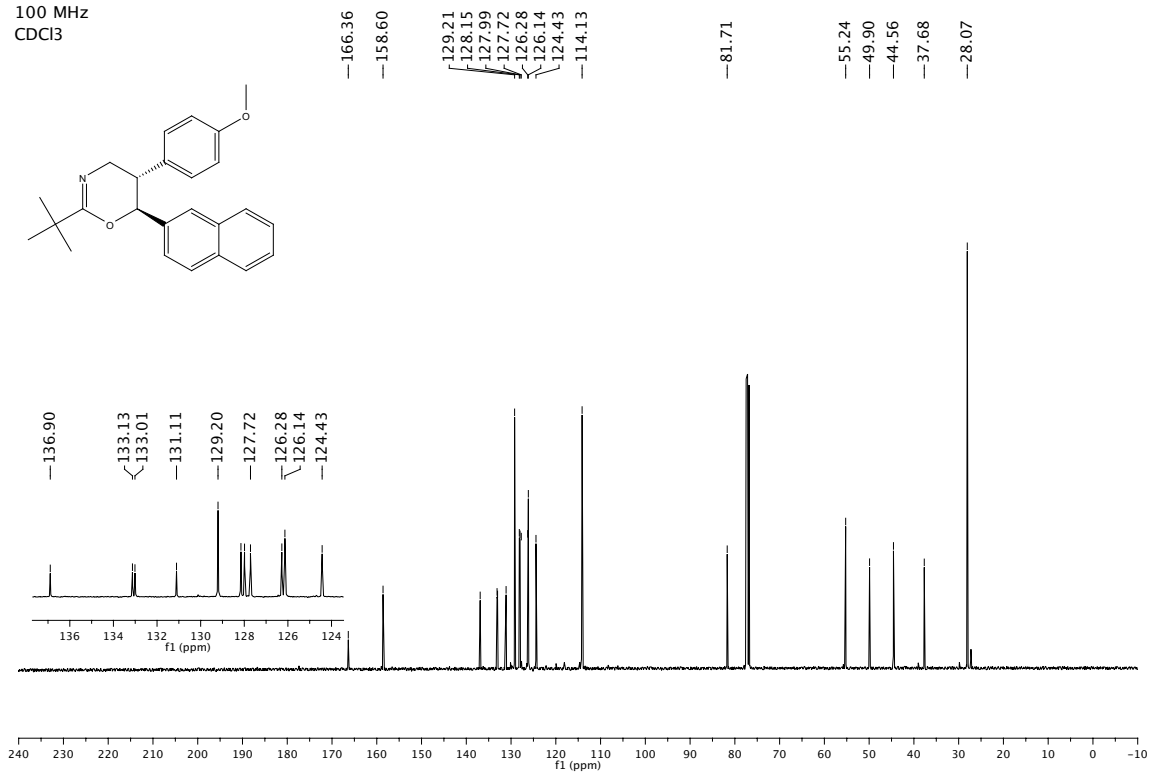
(5S,6S)-2-(tert-butyl)-6-(3-methoxyphenyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine ***4k***



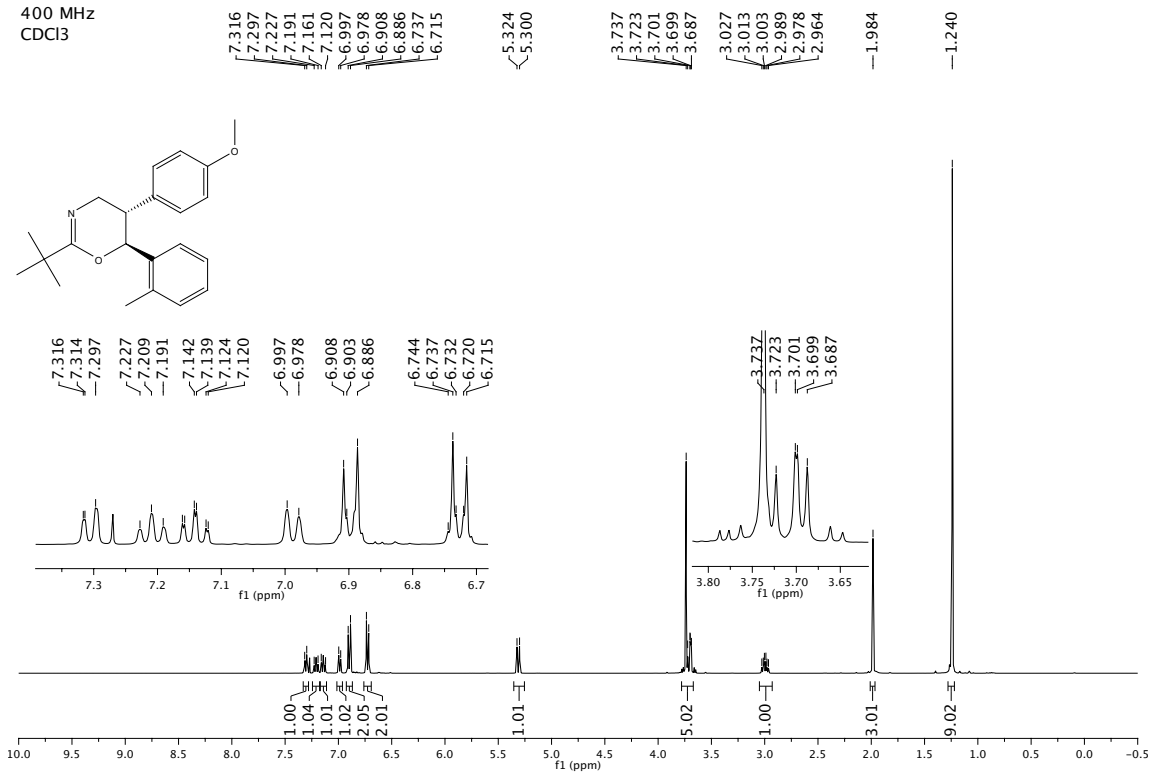


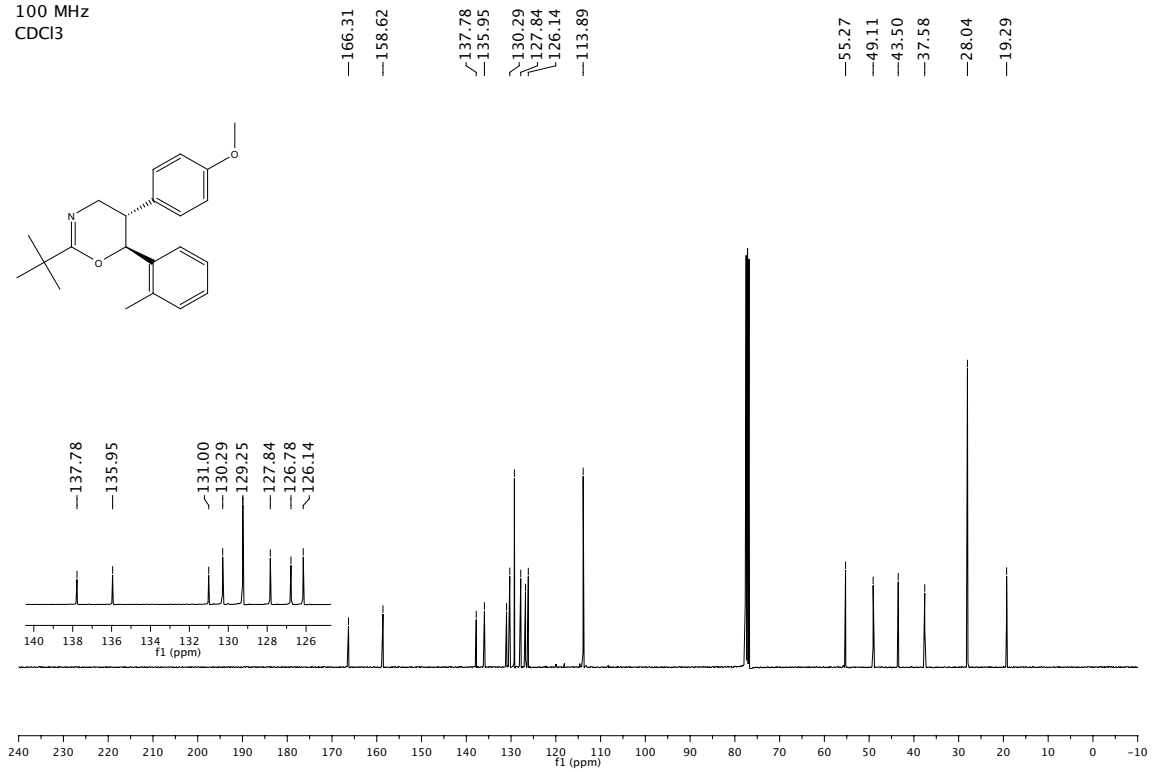
*(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(naphthalen-2-yl)-5,6-dihydro-4H-1,3-oxazin*e **4l**



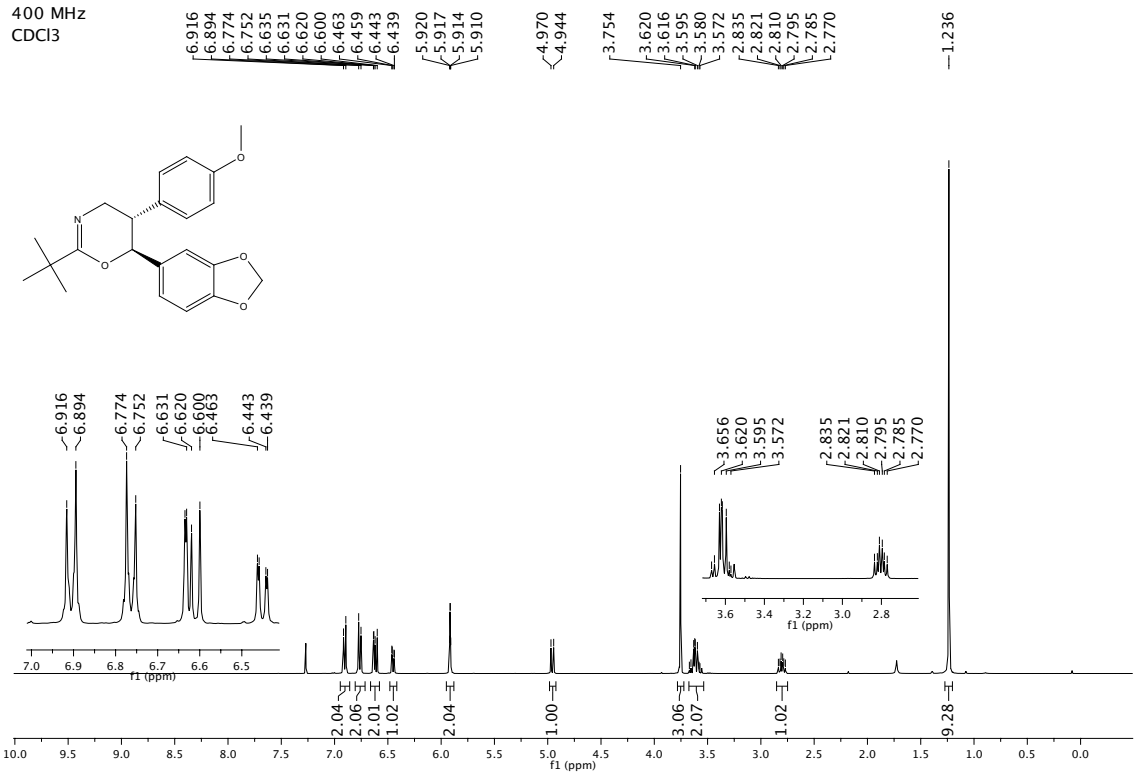


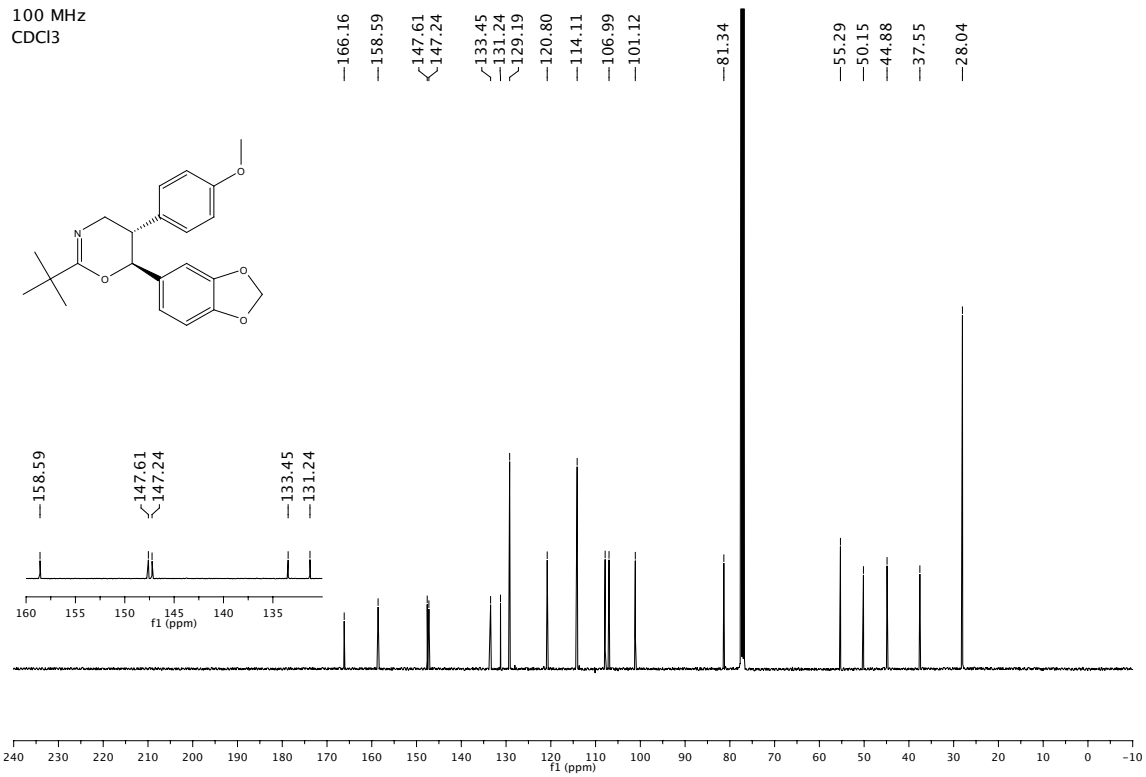
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(o-tolyl)-5,6-dihydro-4H-1,3-oxazine **4m**



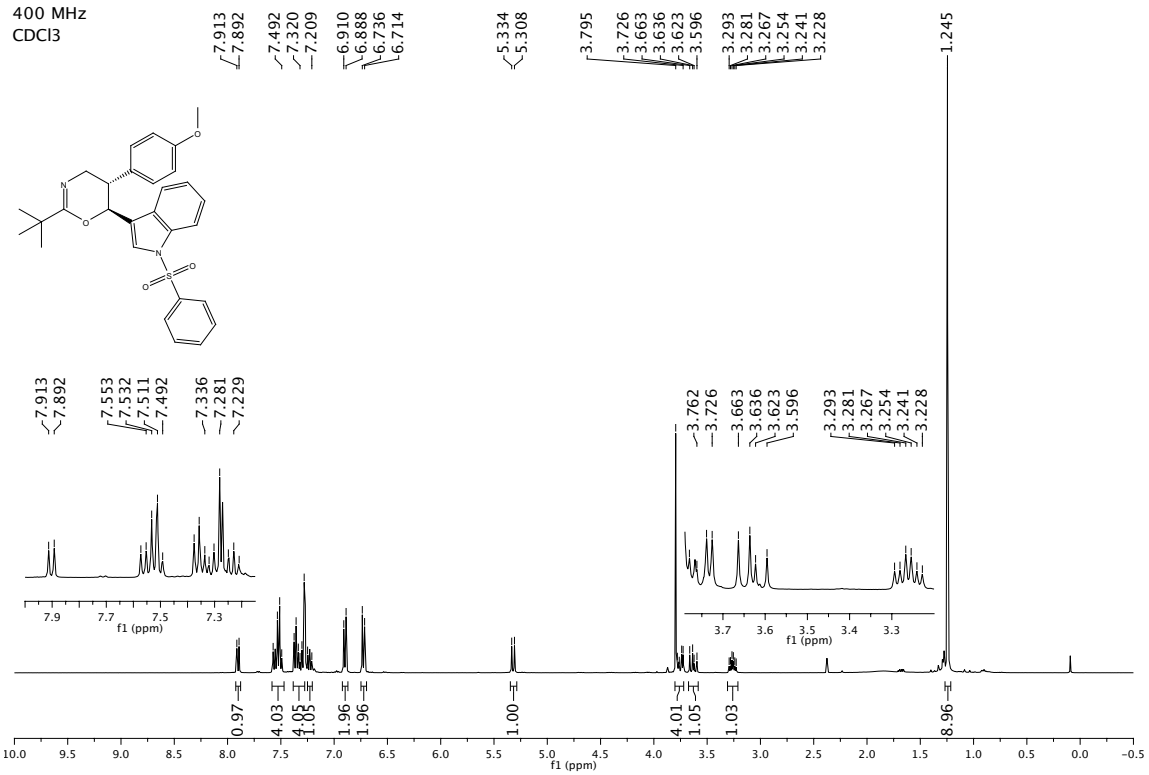


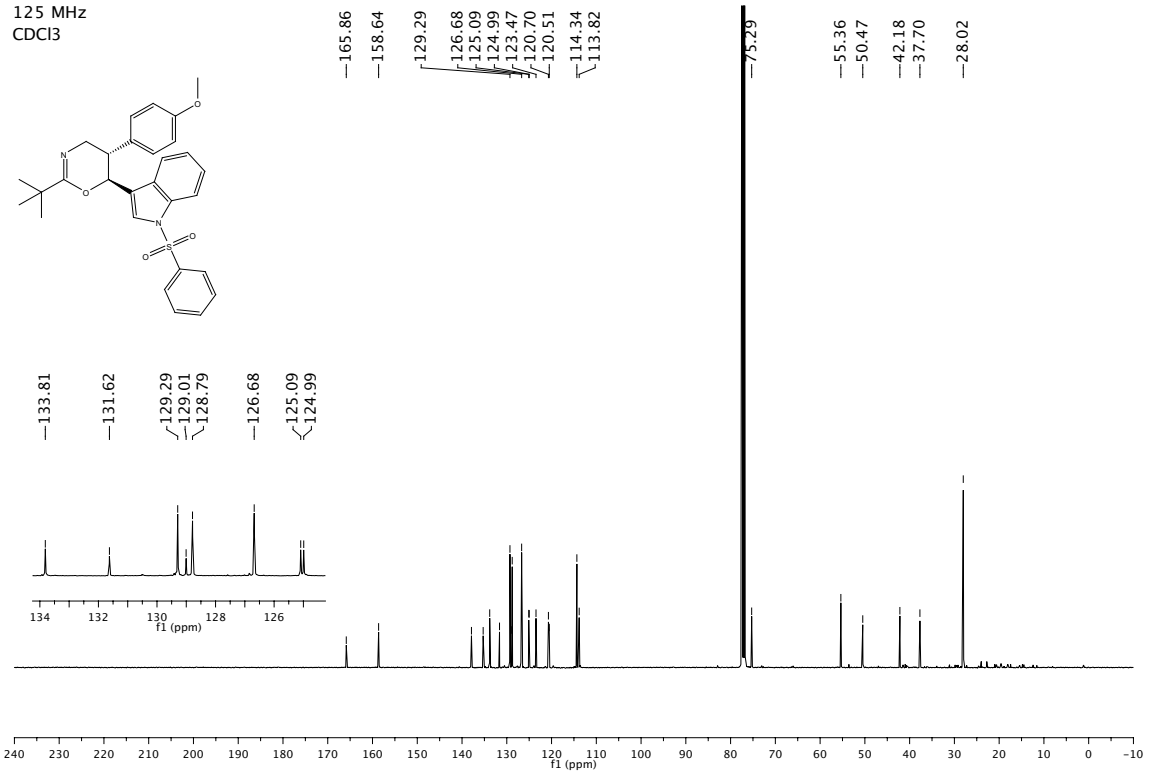
(5S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-2-(tert-butyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4n**





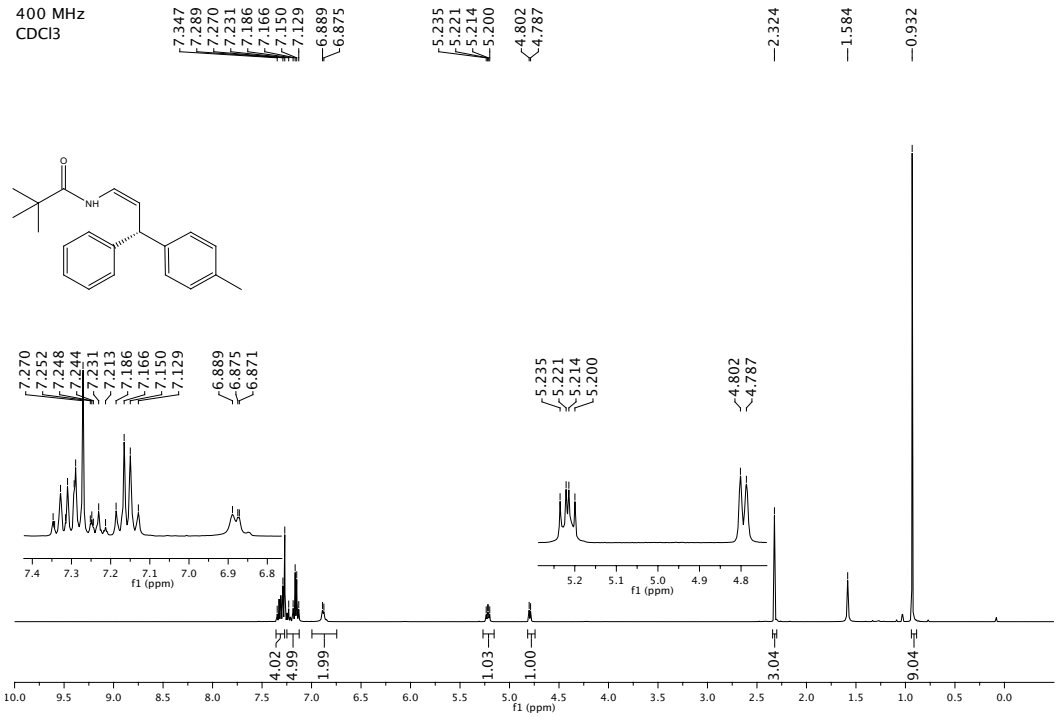
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(1-(phenylsulfonyl)-1H-indol-3-yl)-5,6-dihydro-4H-1,3-oxazine **4o**

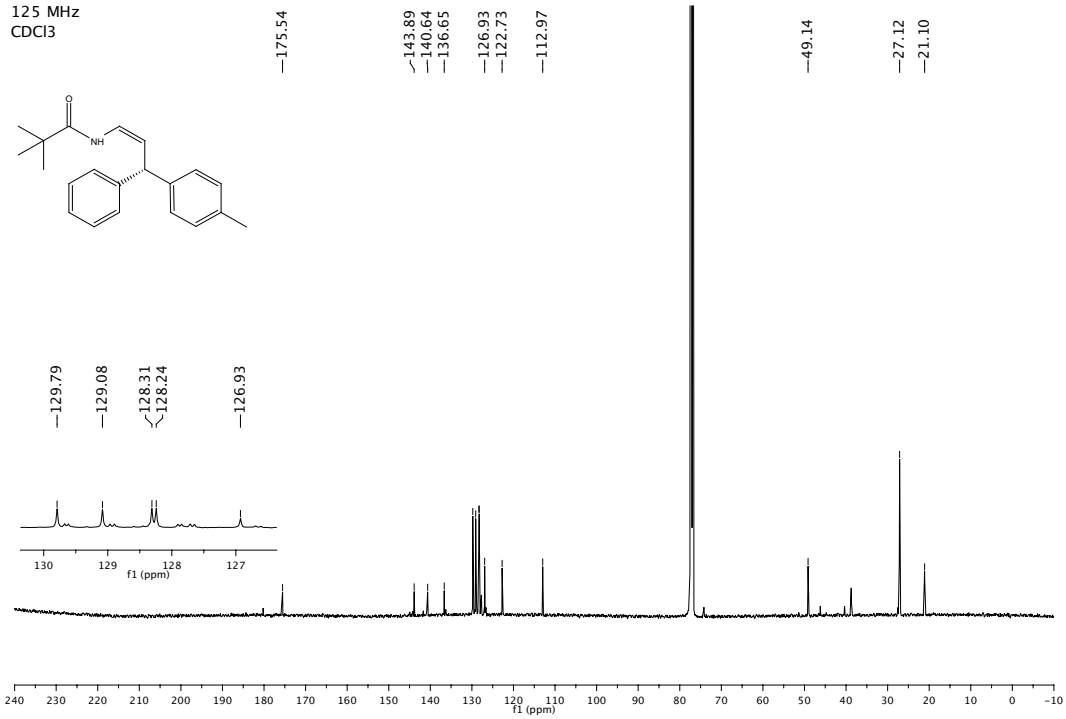




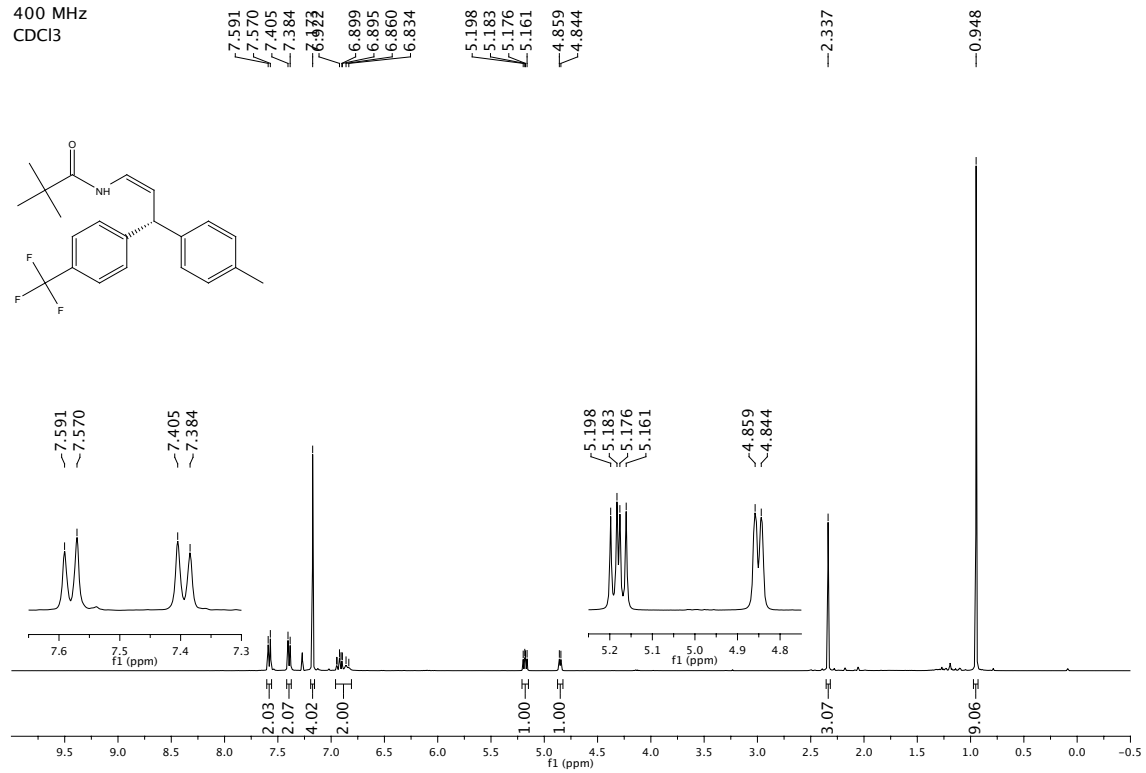
Enamide products

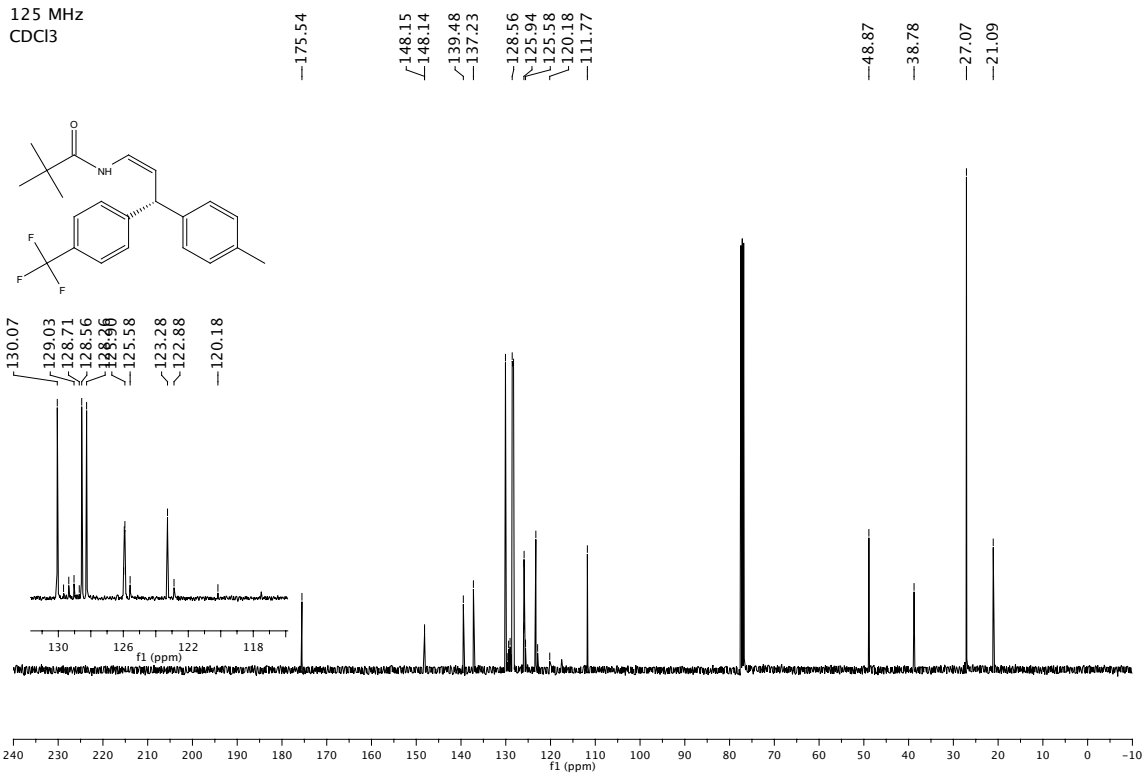
(S,Z)-N-(3-phenyl-3-(p-tolyl)prop-1-en-1-yl)pivalamide ***5a***



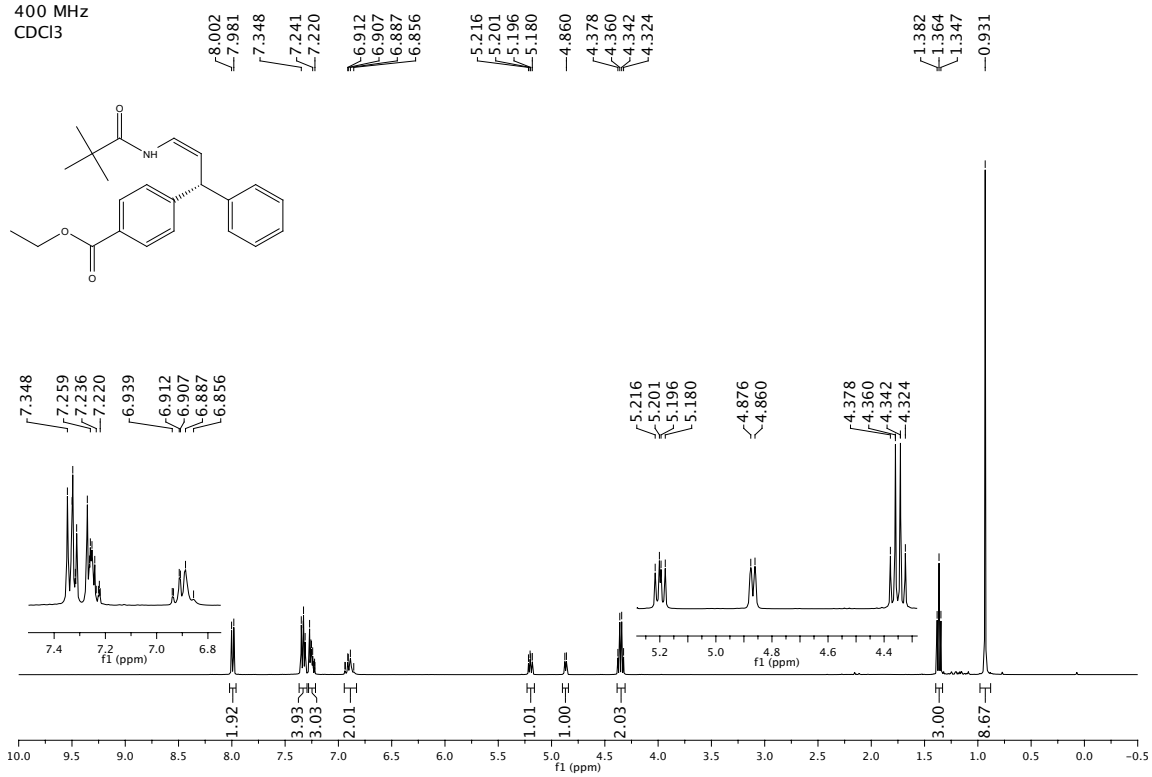


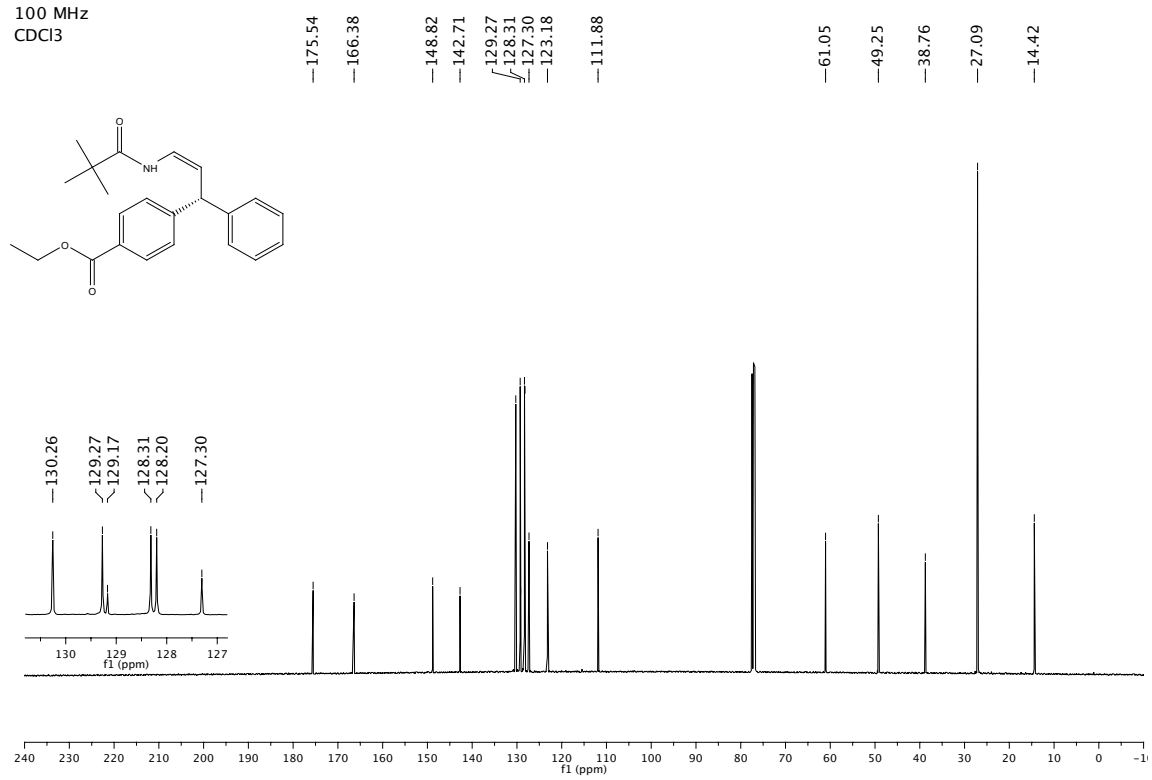
(Z)-N-(3-(4-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5b**



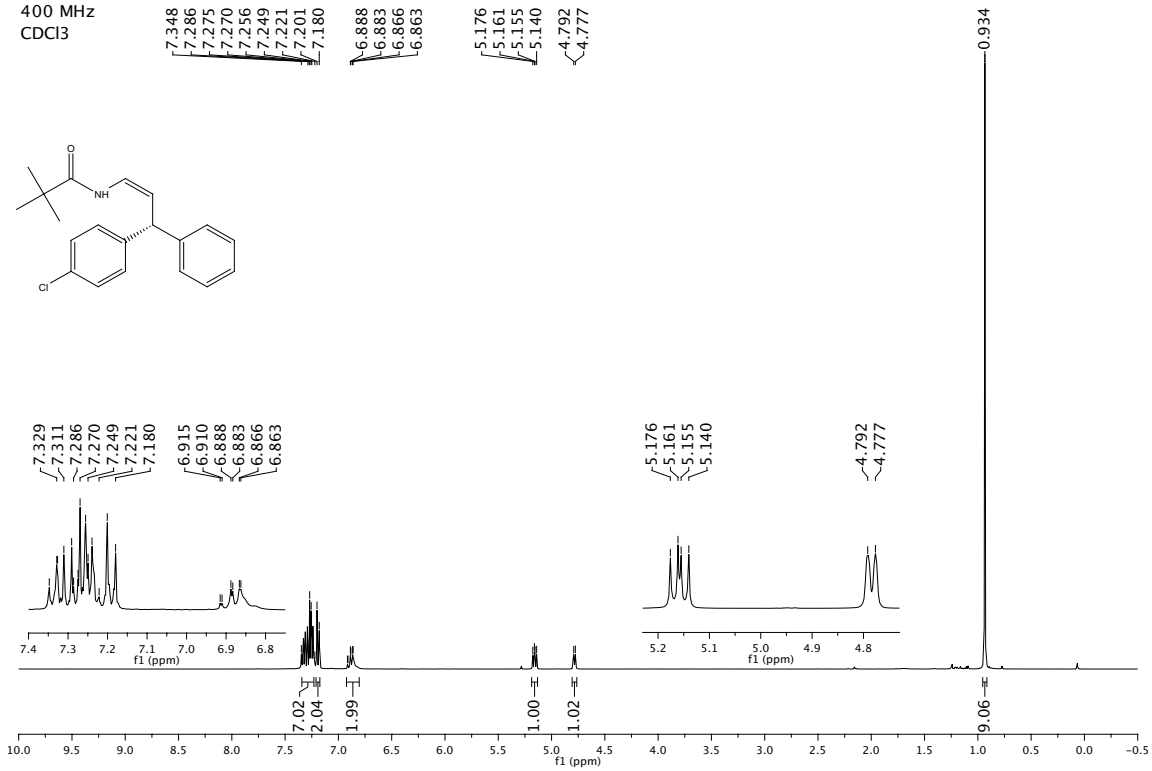


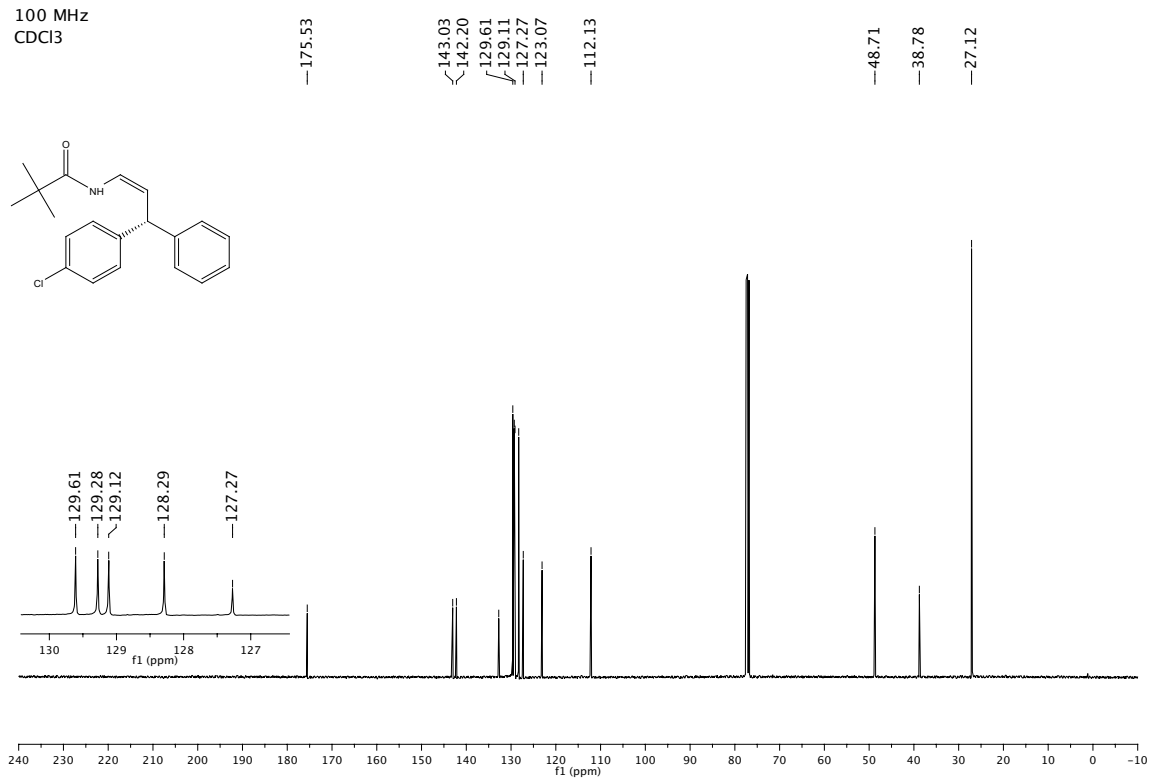
ethyl (R,Z)-4-(1-phenyl-3-pivalamidoallyl)benzoate **5c**



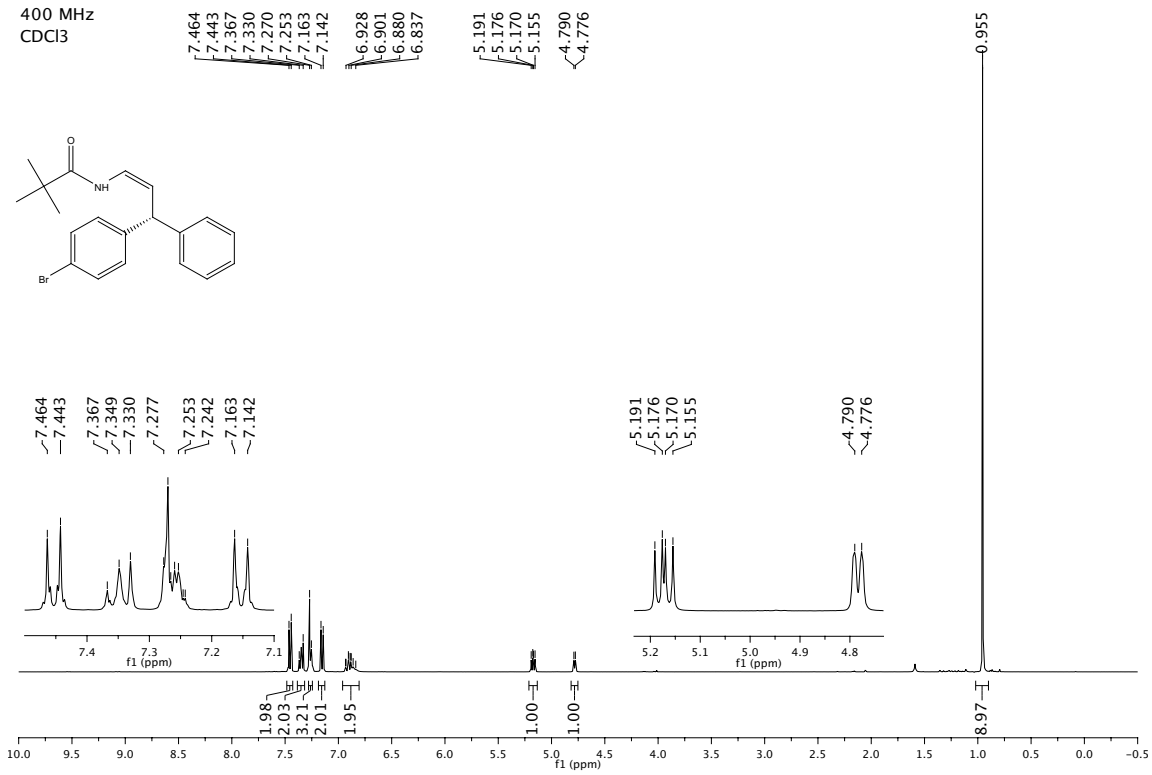


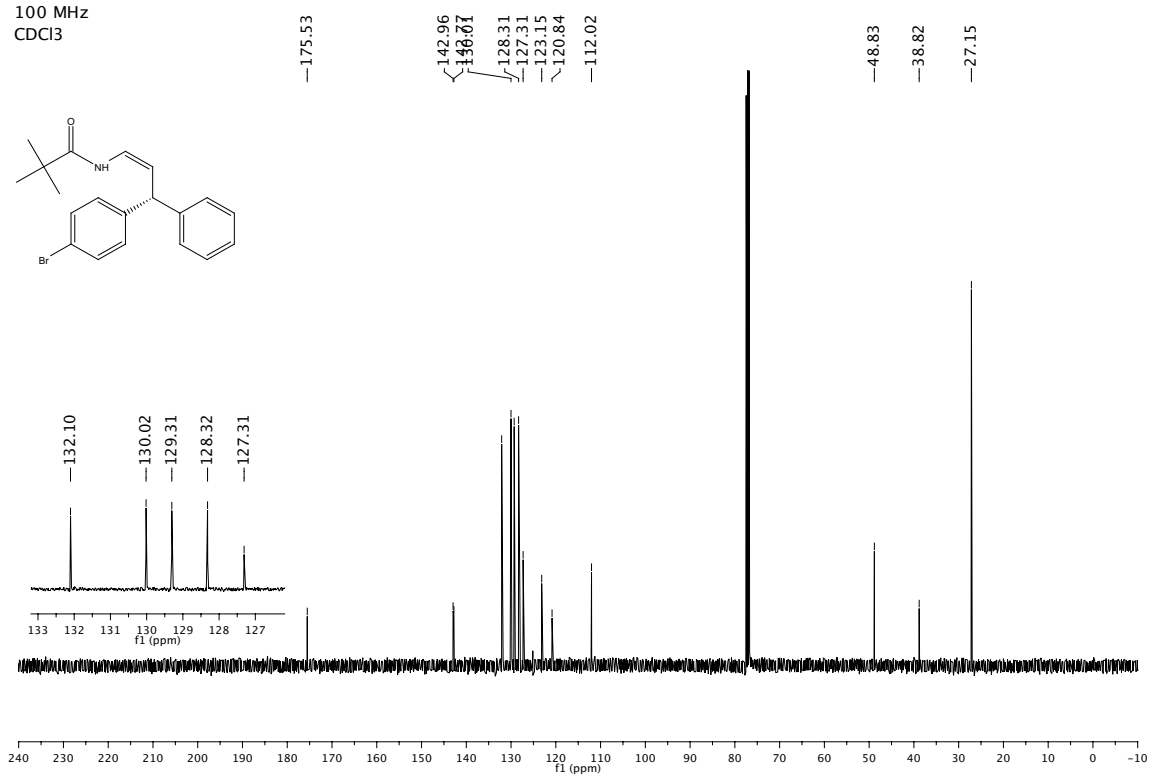
(Z)-N-(3-(4-chlorophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5d**



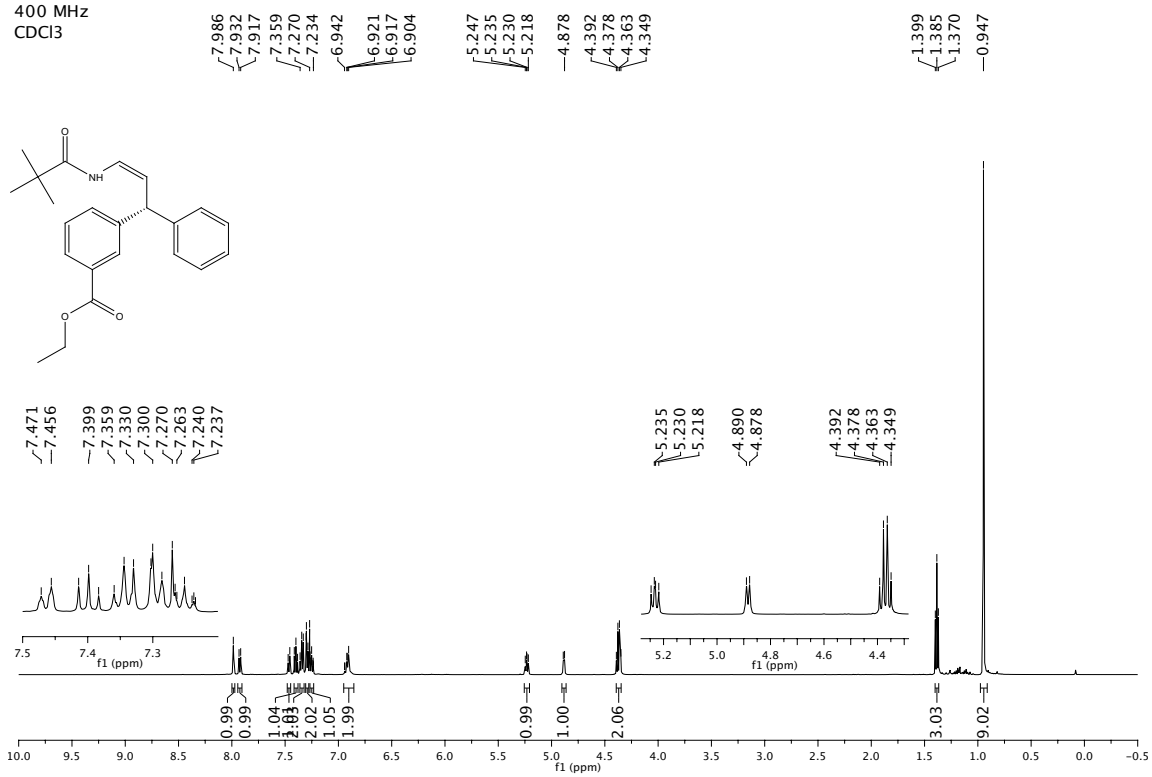


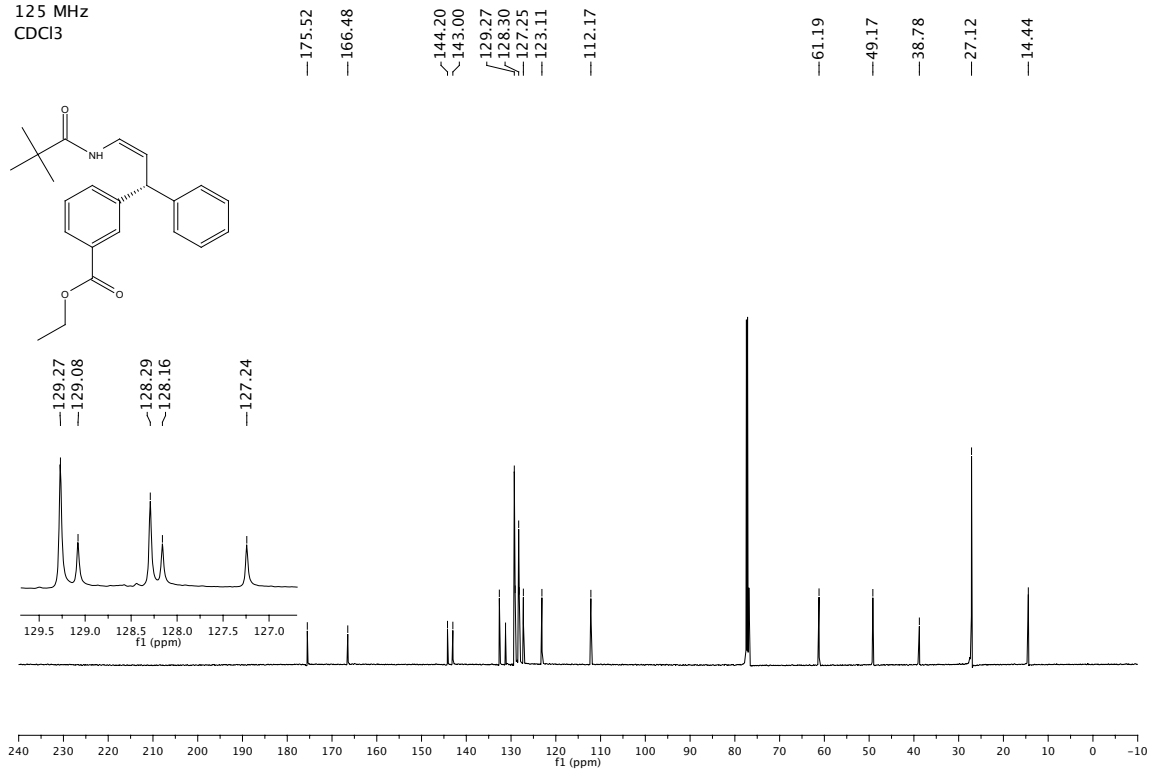
(Z)-N-(3-(4-bromophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5e**



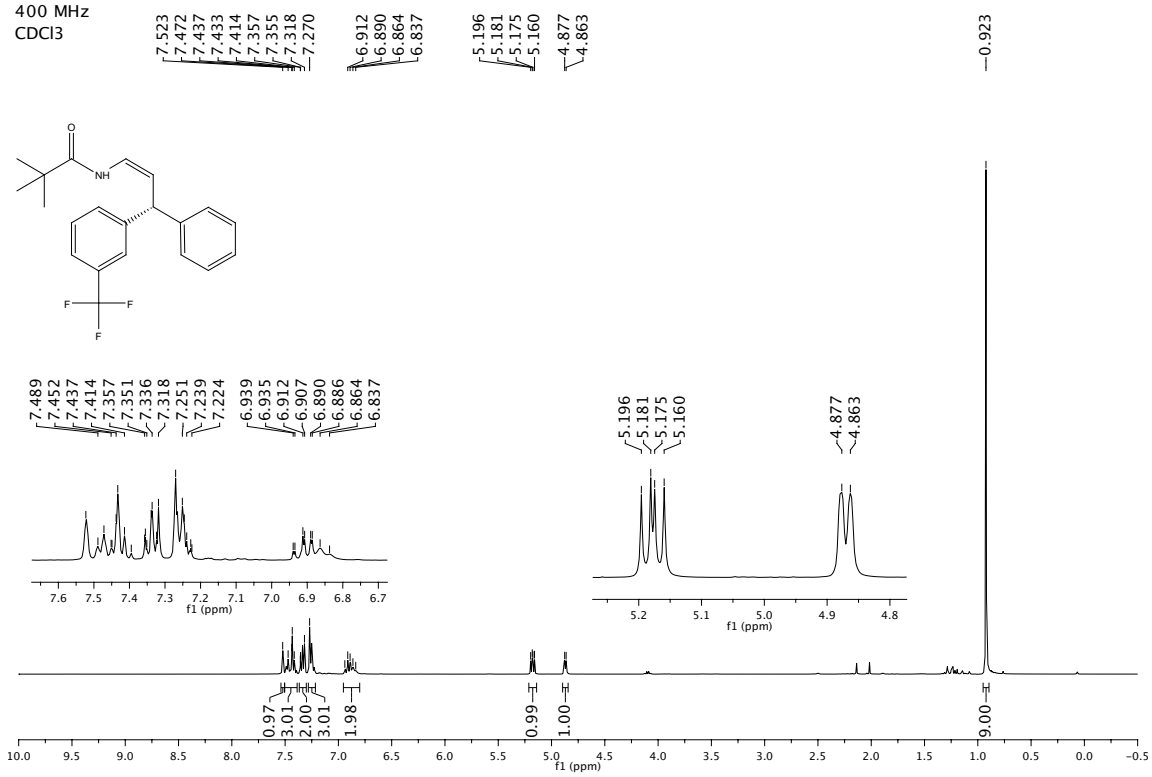


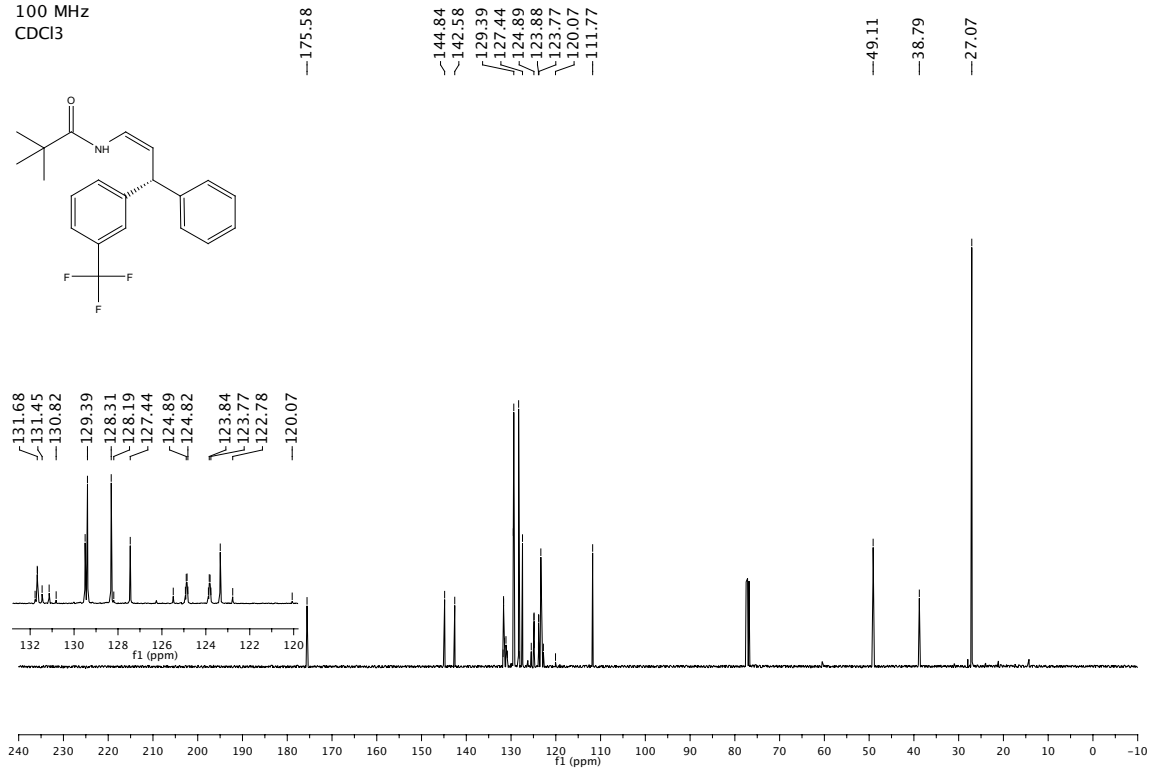
ethyl (R,Z)-3-(1-phenyl-3-pivalamidoallyl)benzoate **5f**



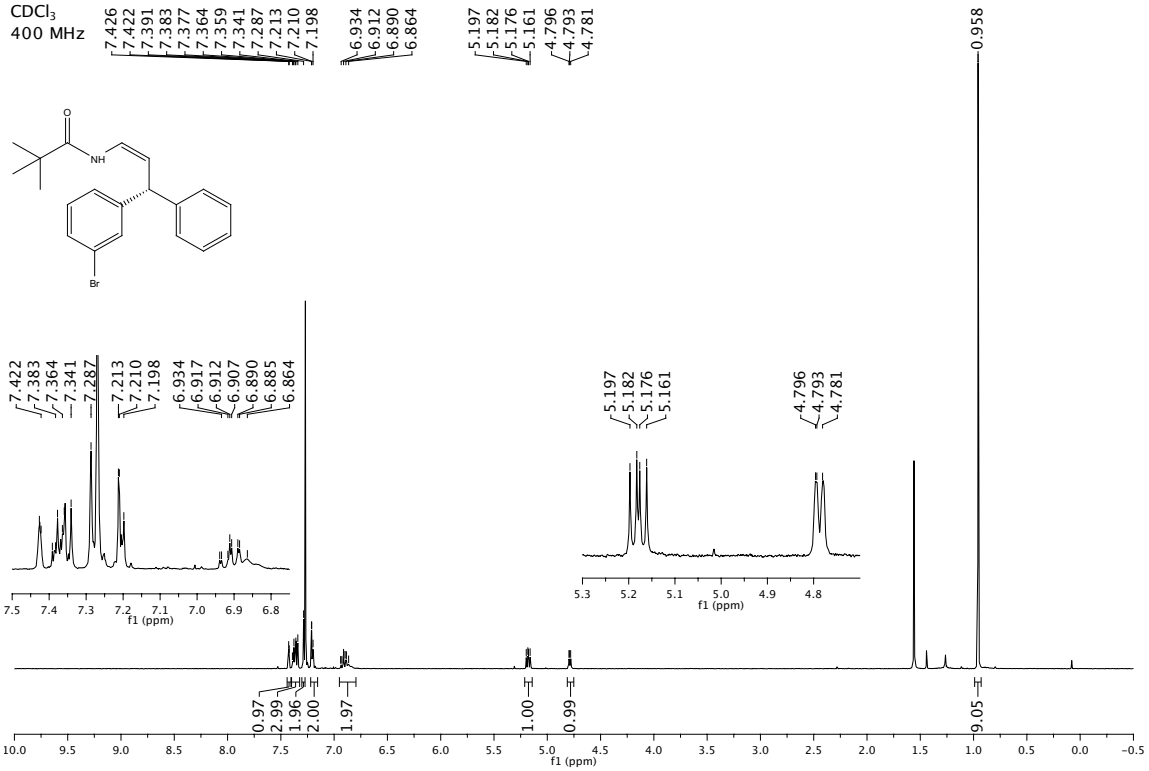


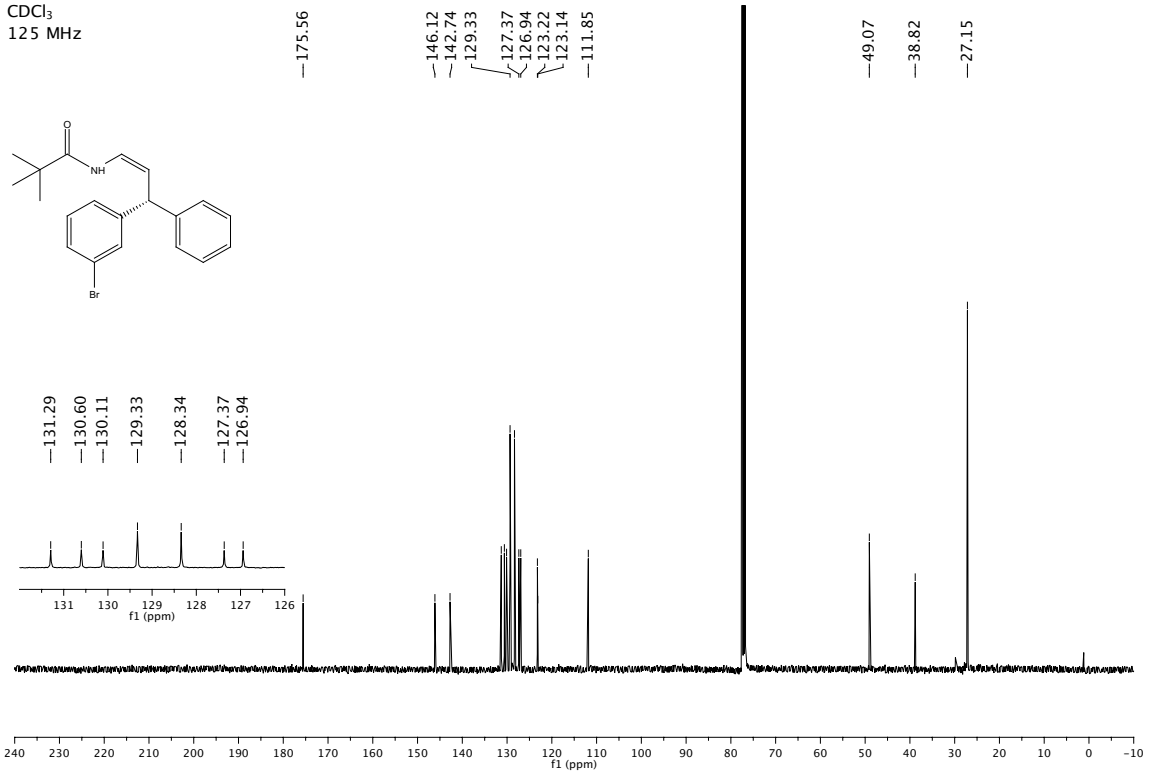
(Z)-N-(3-phenyl-3-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5g**



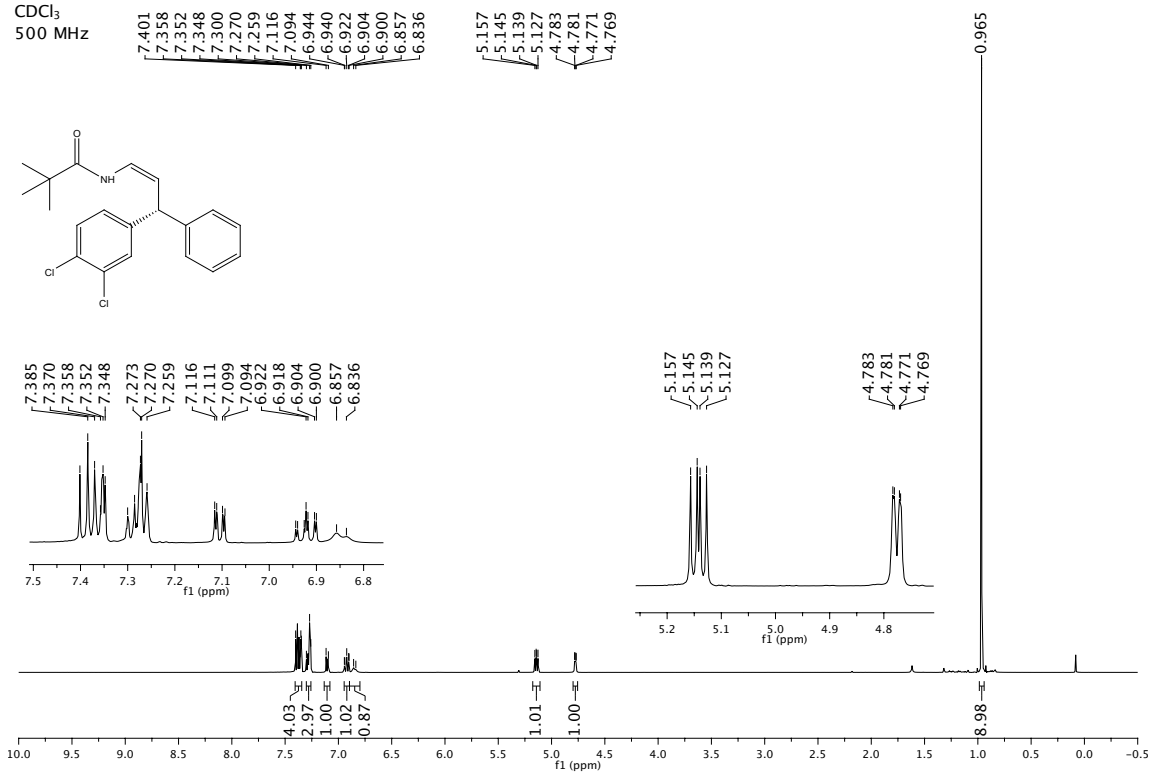


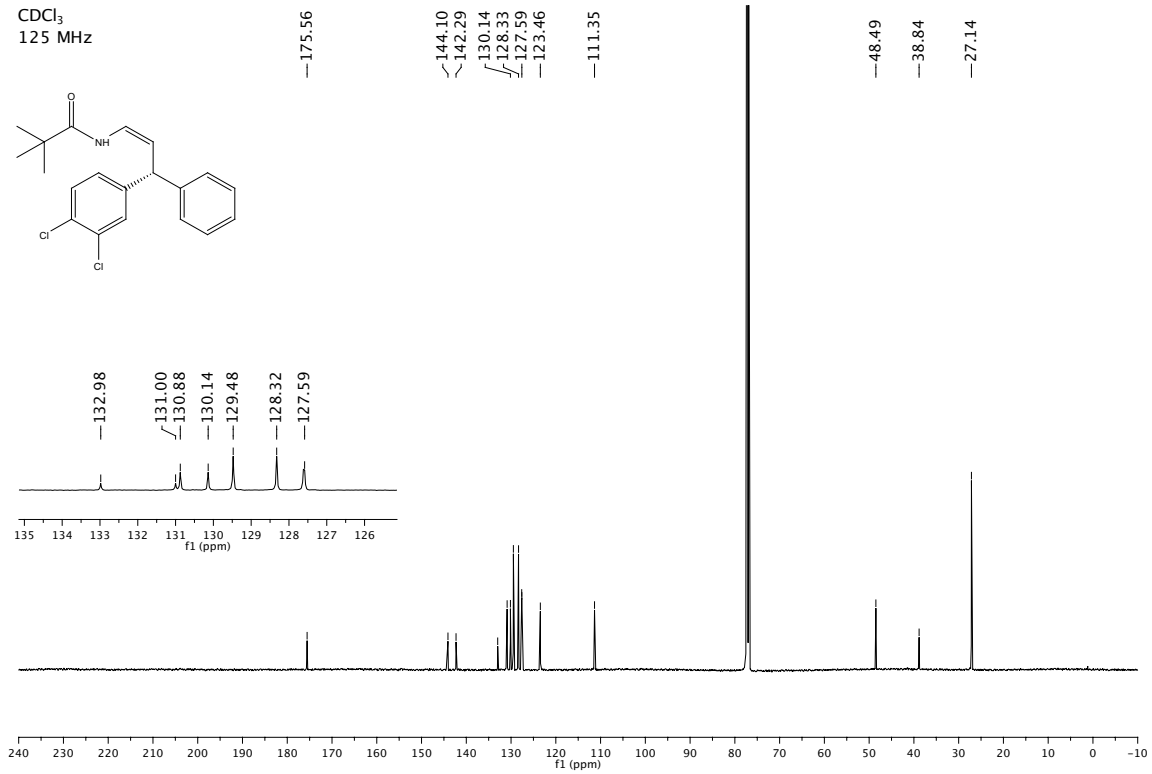
(R)-N-[(1Z)-3-(3-bromophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5h**



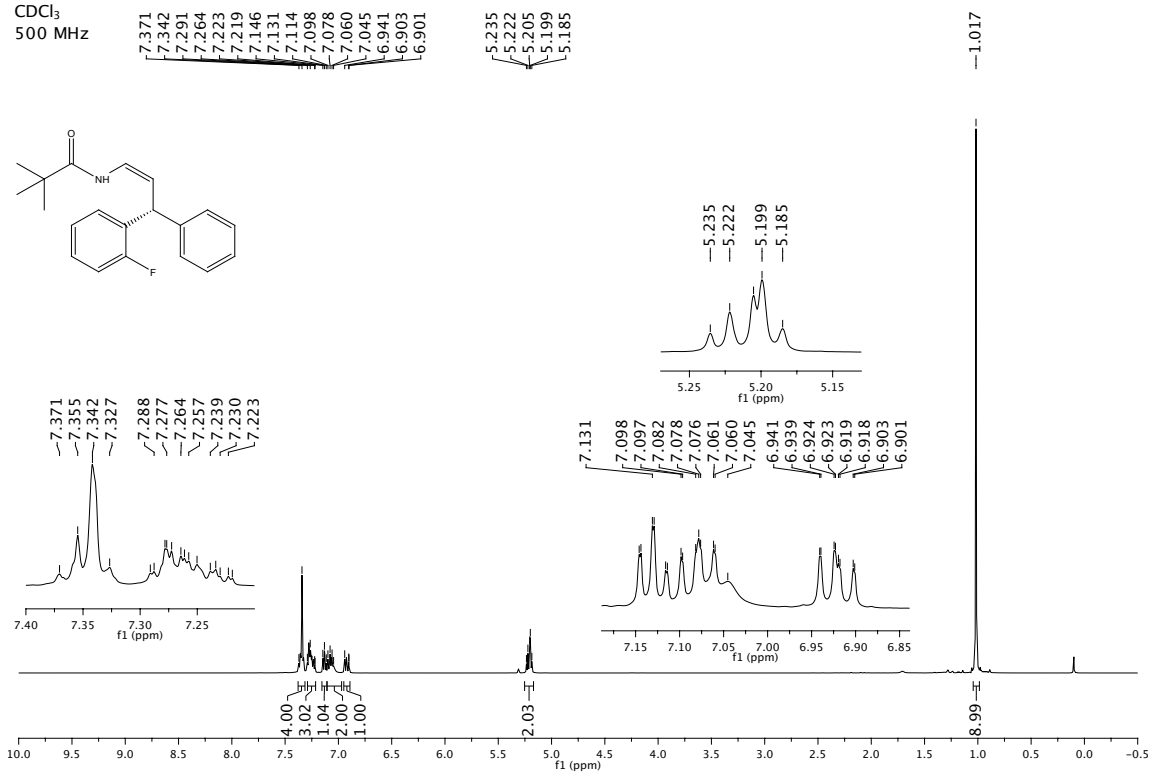


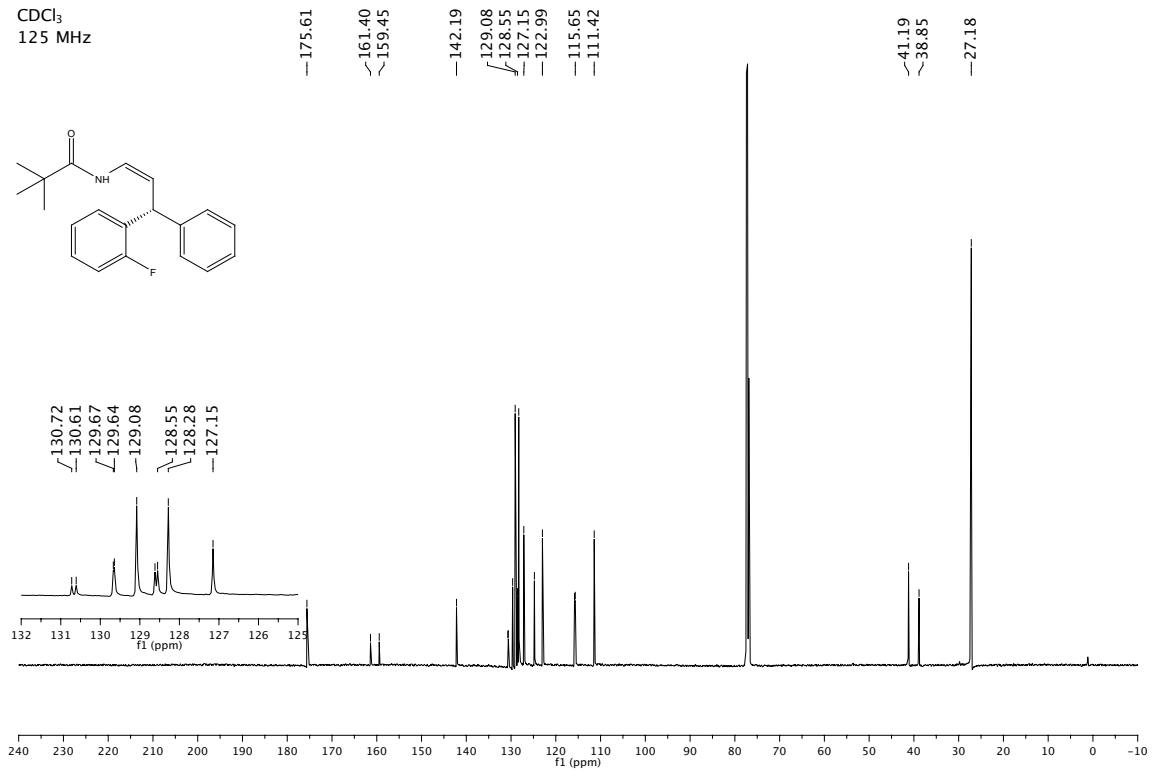
(R)-N-[(1Z)-3-(3,4-dichlorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5i**



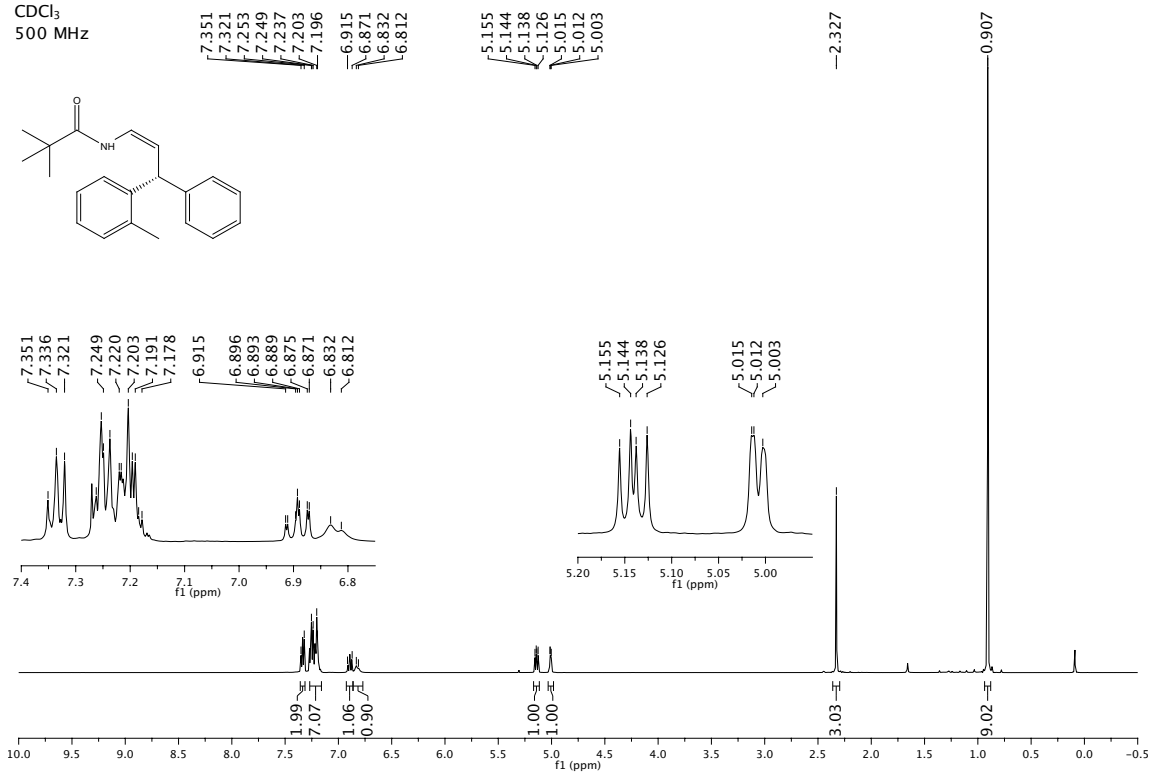


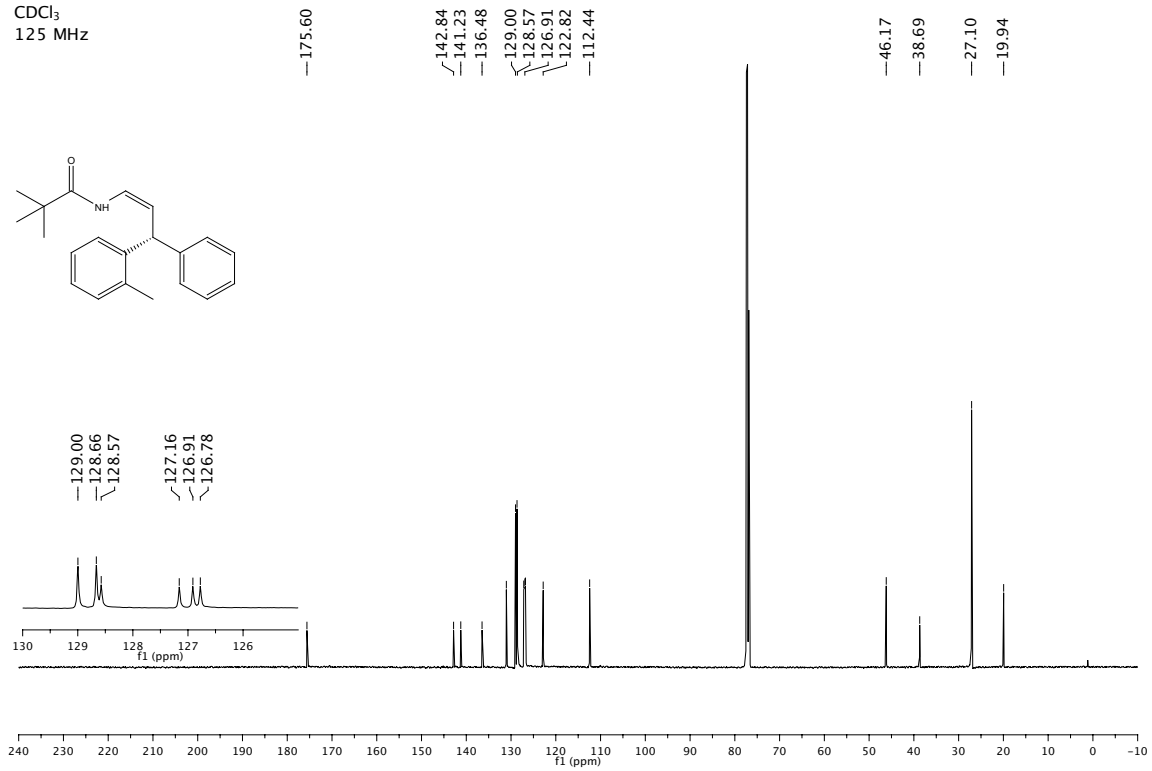
(R)-N-[(1Z)-3-(2-fluorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5j**



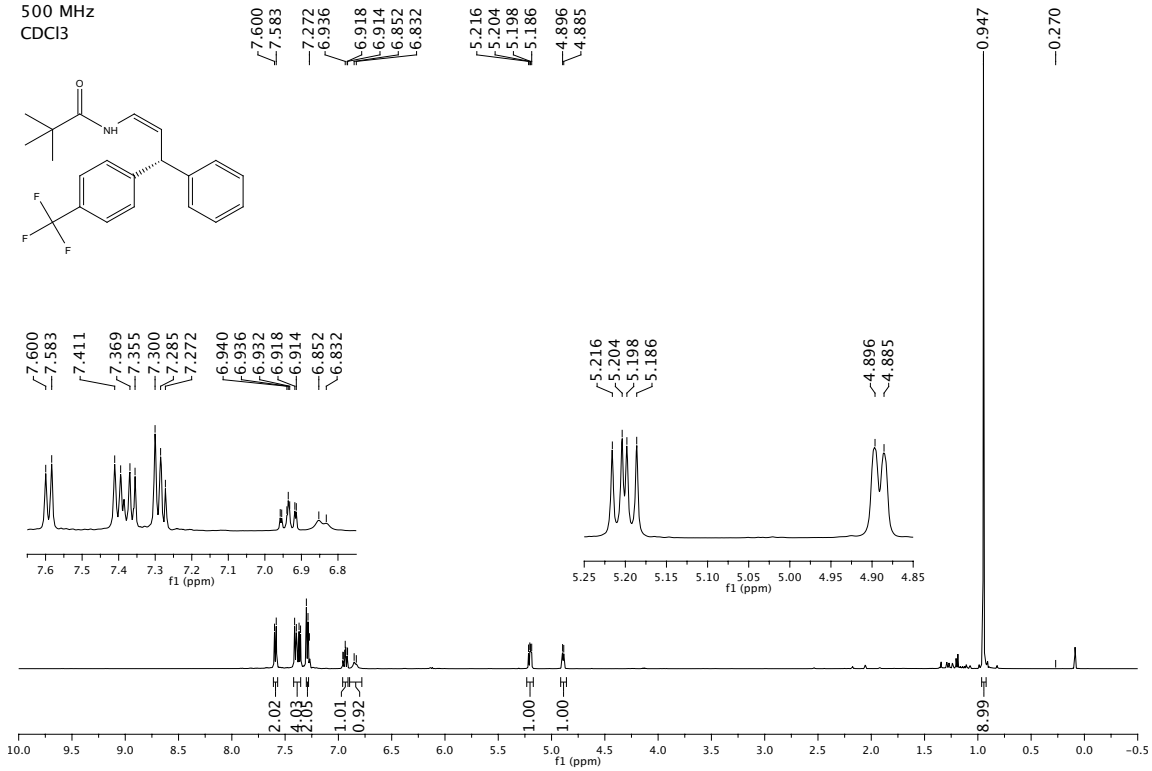


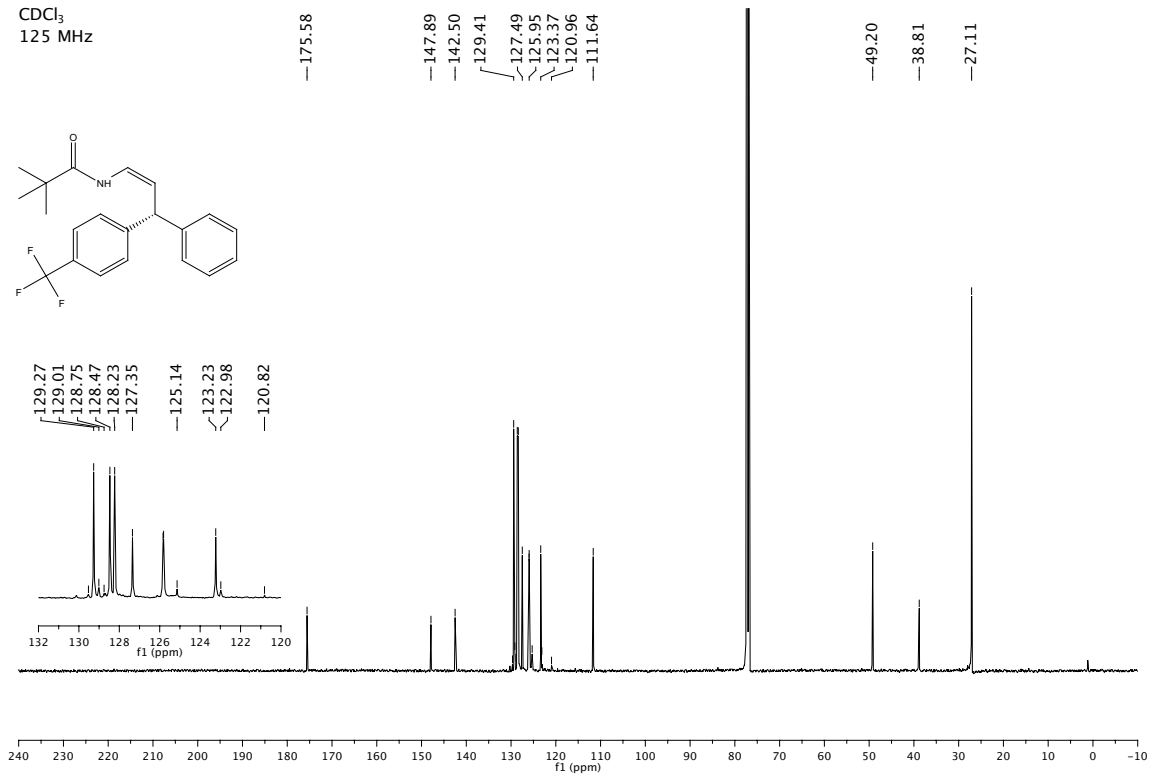
(R)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-phenylprop-1-en-1-yl]propanamide **5k**



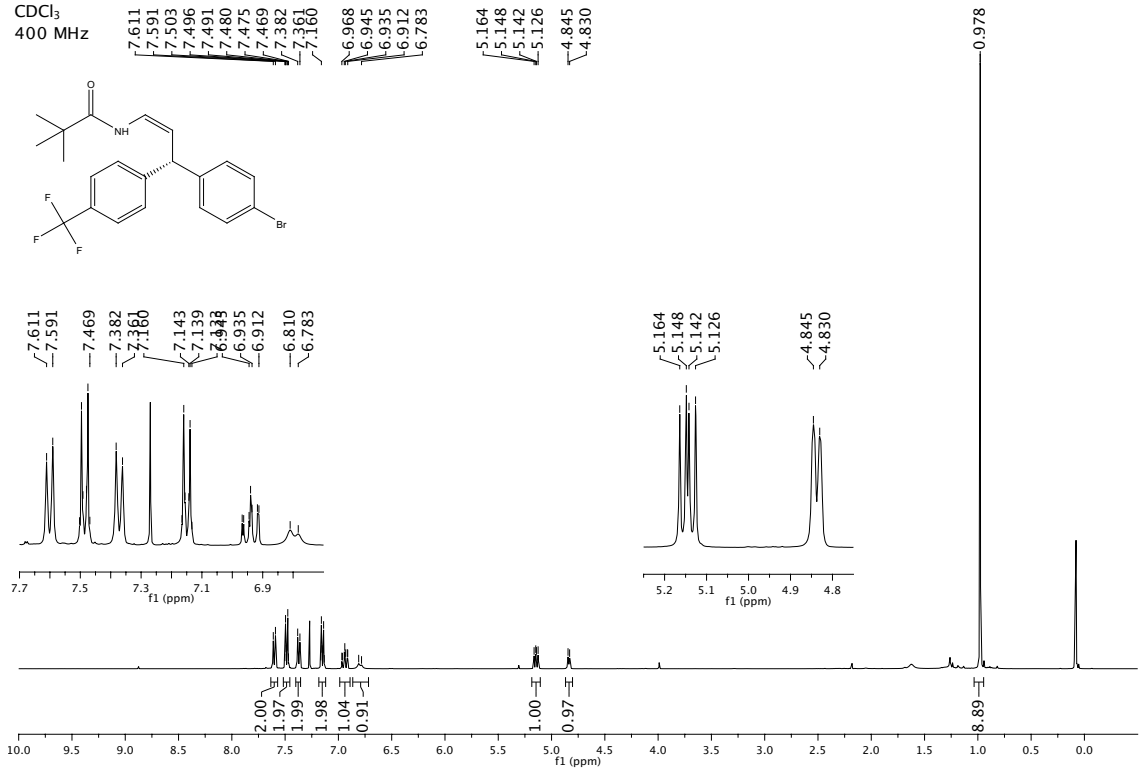


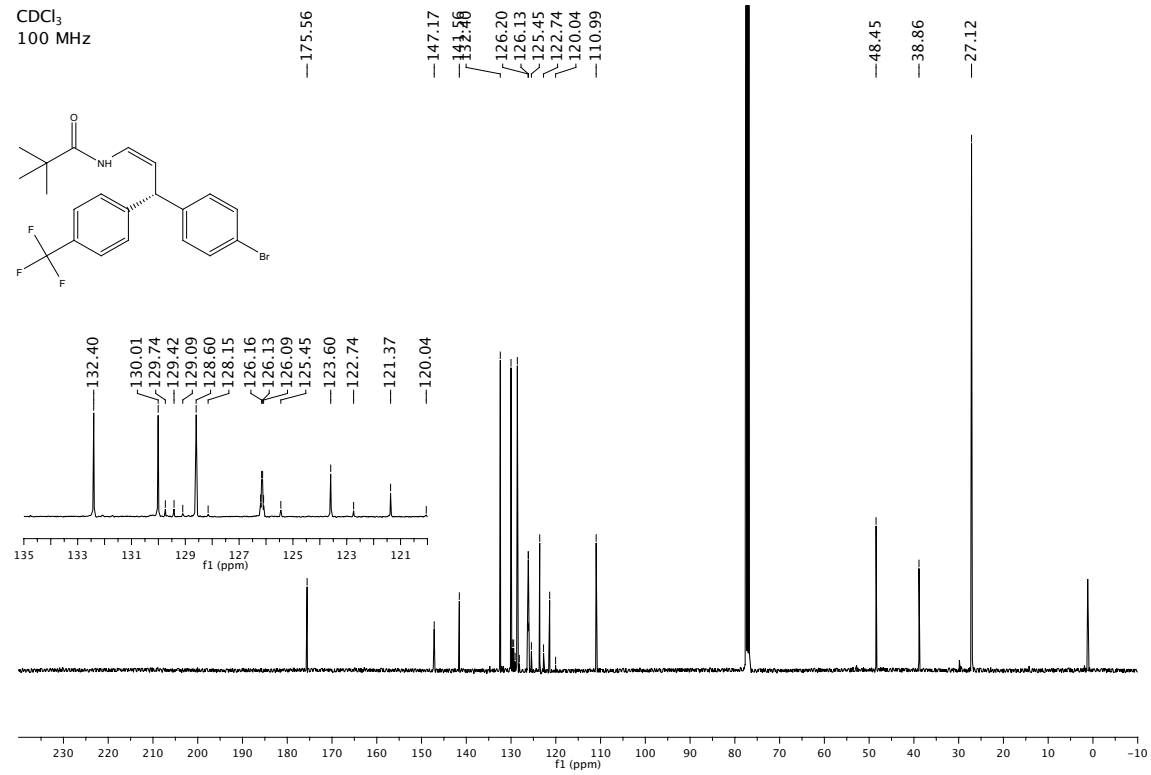
(R)-2,2-dimethyl-N-[(1Z)-3-phenyl-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5l**



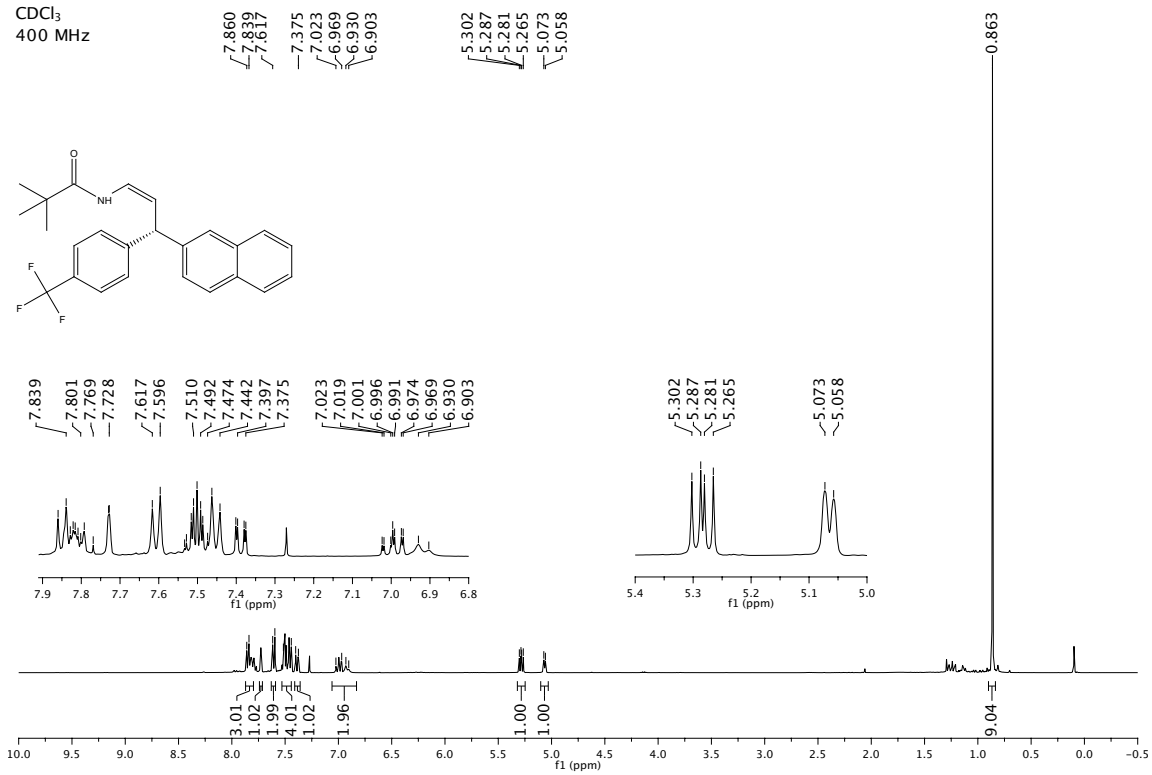


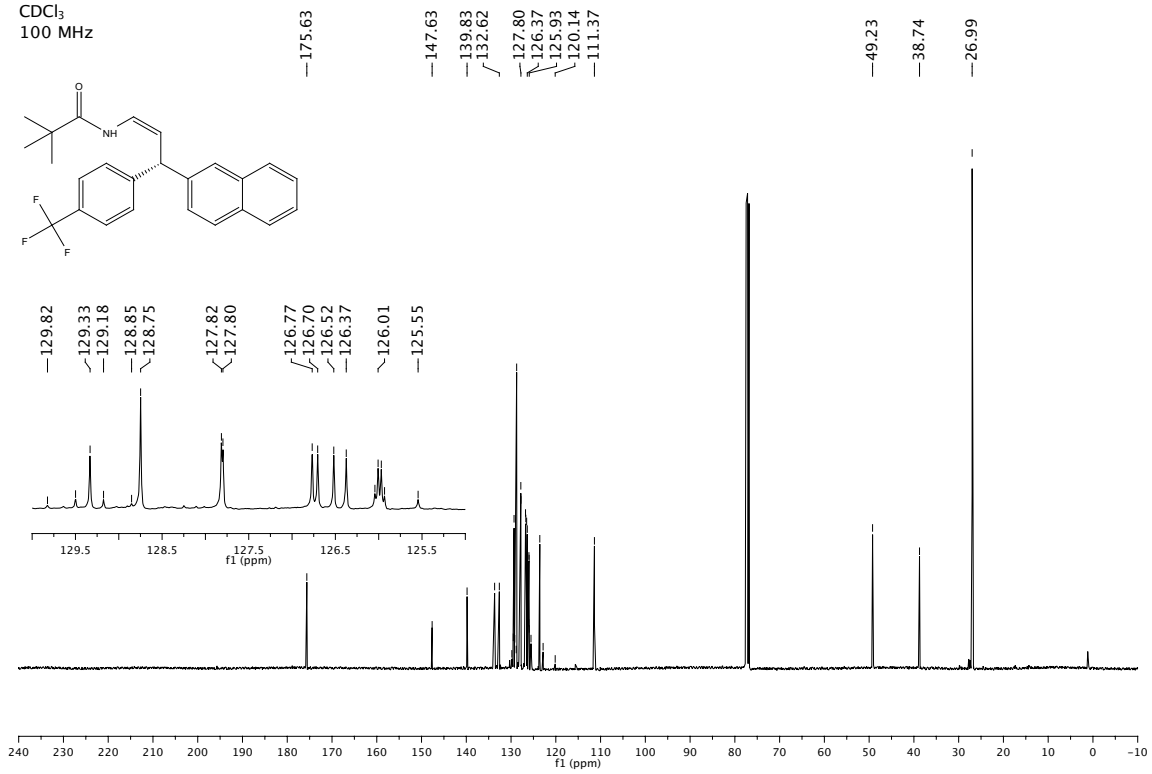
(S)-N-[(1Z)-3-(4-bromophenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]-2,2-dimethylpropanamide **5m**



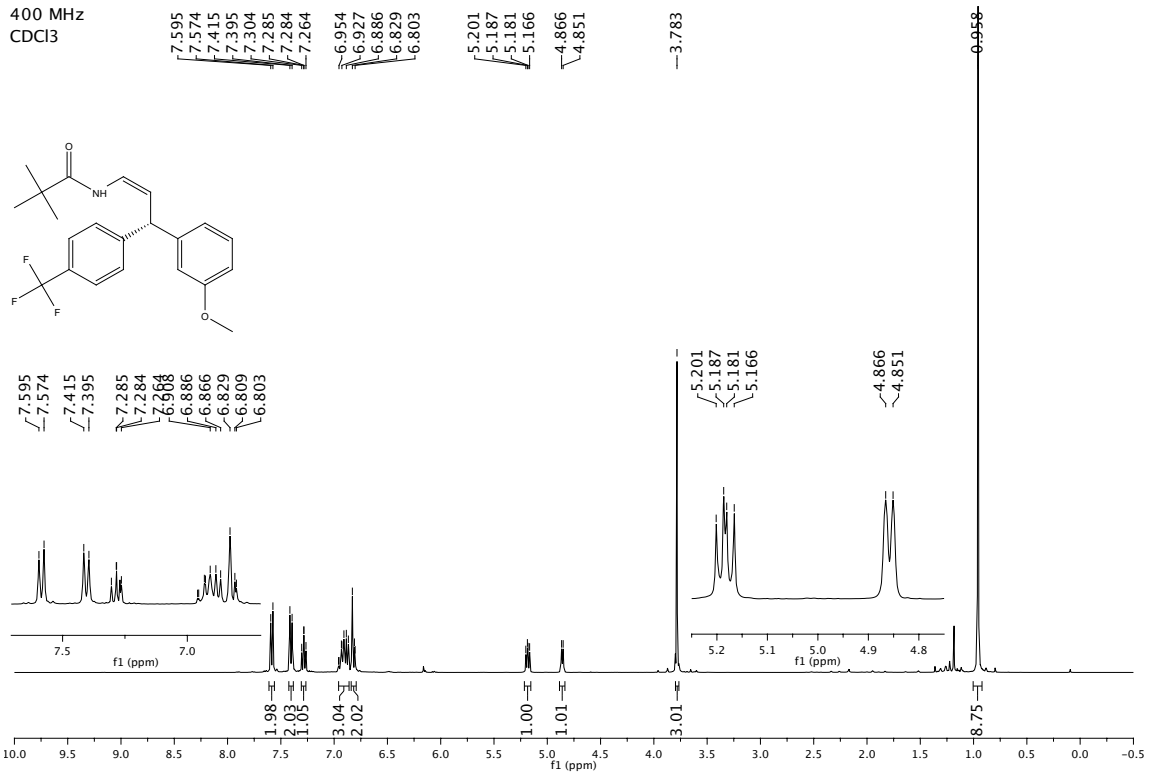


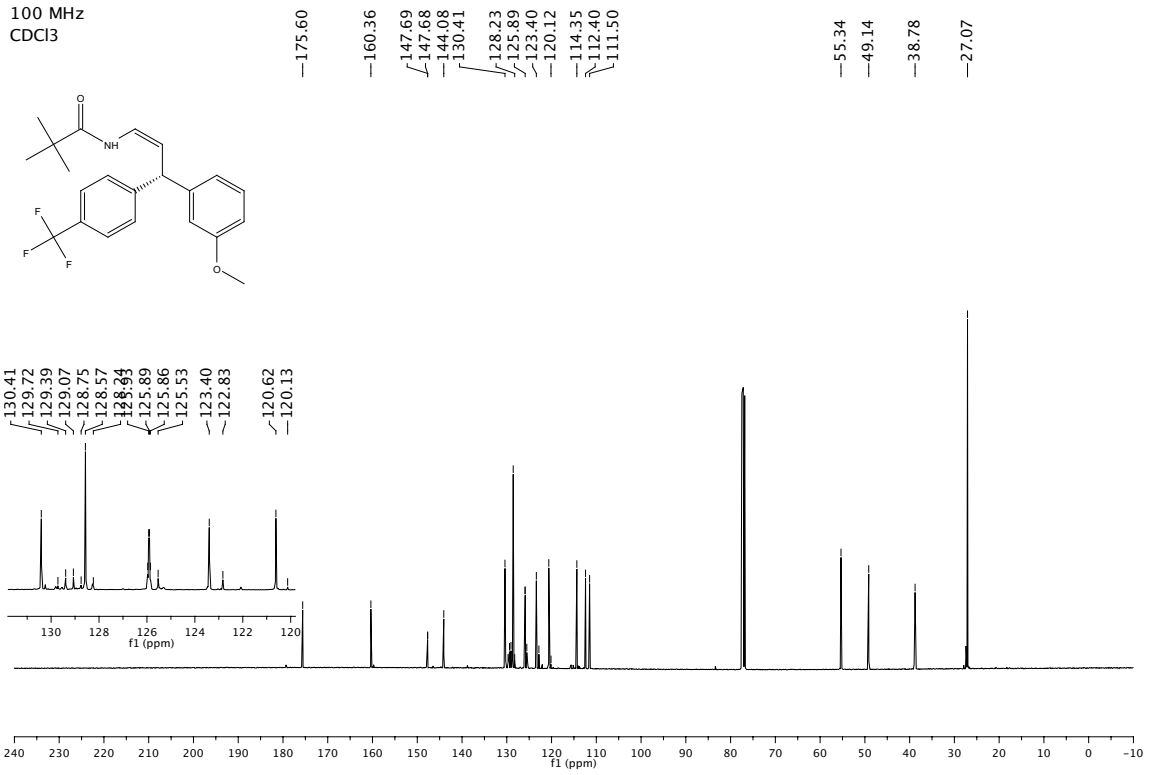
(S)-2,2-dimethyl-N-[(1Z)-3-(naphthalen-2-yl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5n**



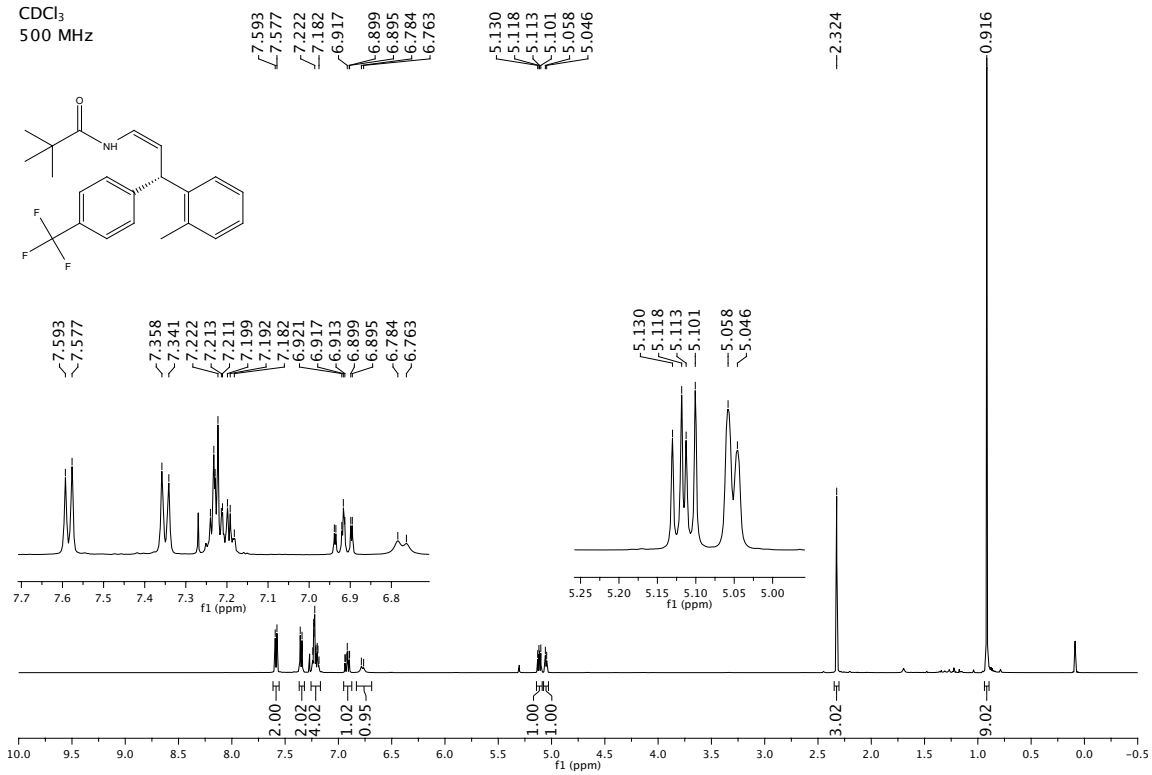


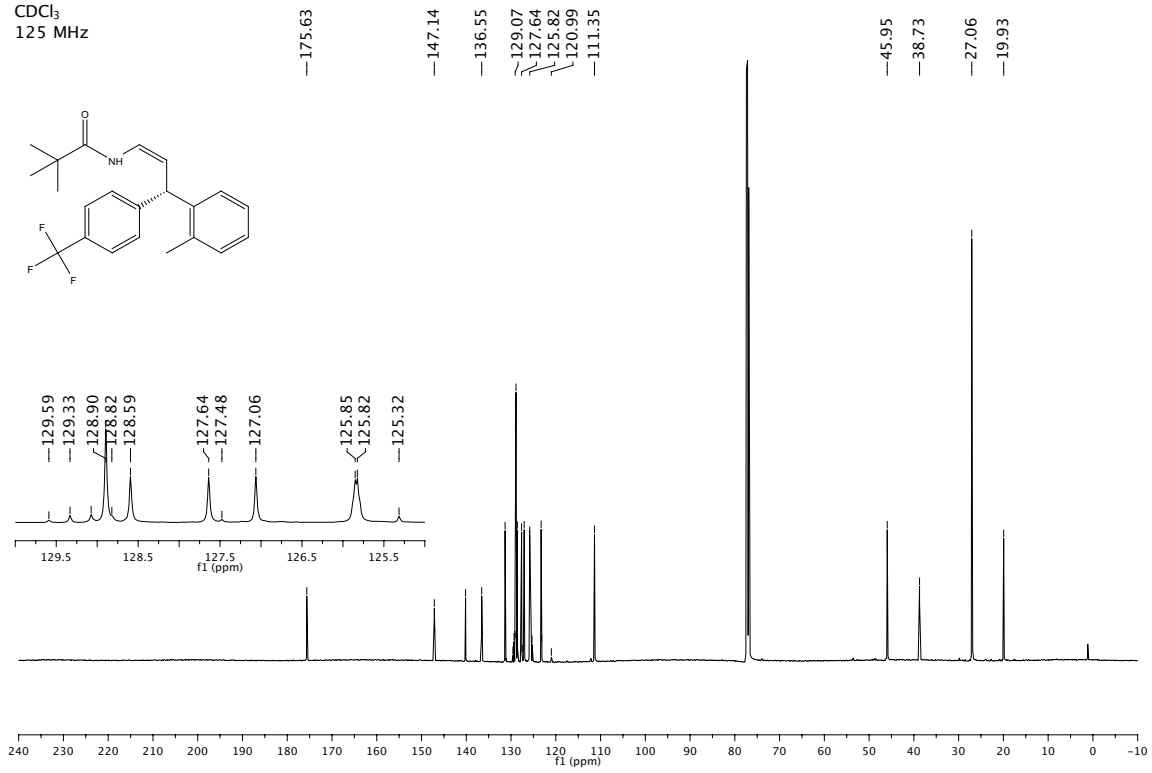
(Z)-N-(3-(3-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5o**





(S)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5p**

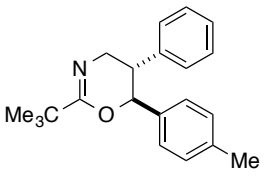


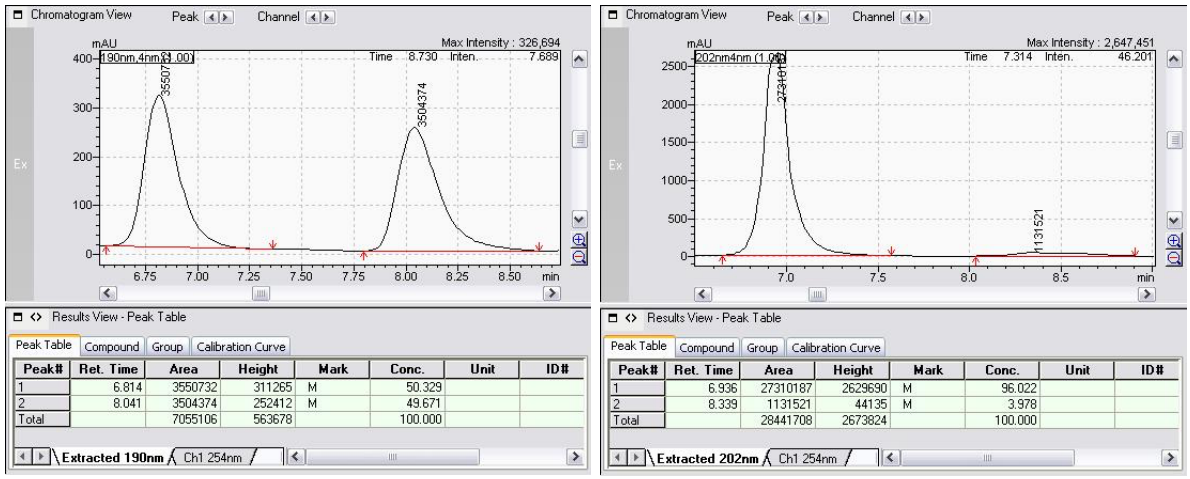


4. HPLC traces

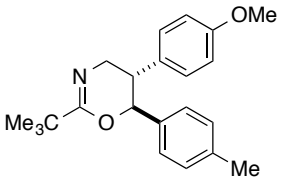
Oxazine products

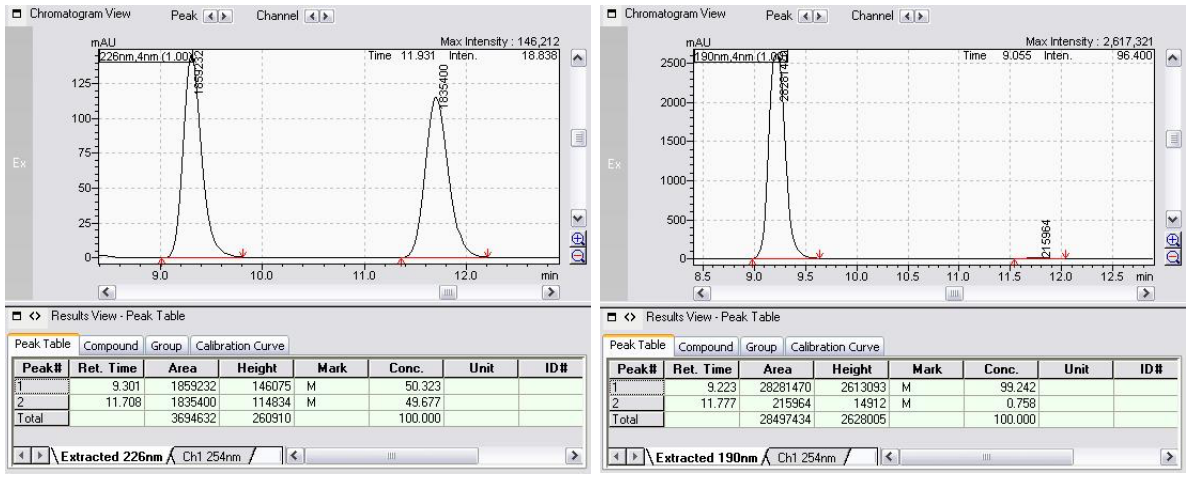
(5R,6R)-2-(tert-butyl)-5-phenyl-6-(4-tolyl)-5,6-dihydro-4H-1,3-oxazine **4a**



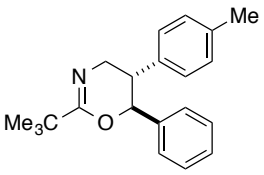


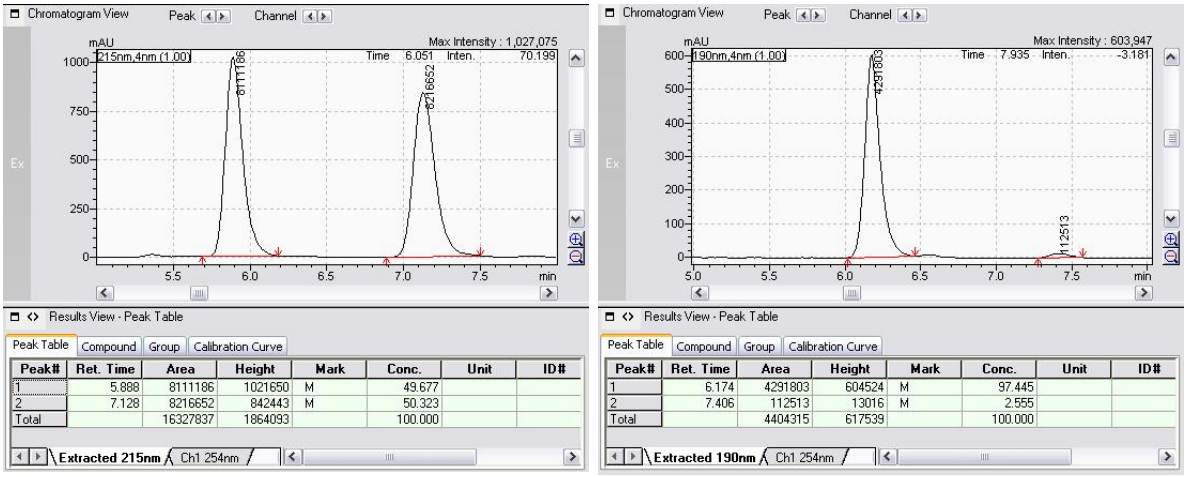
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(p-tolyl)-5,6-dihydro-4H-1,3-oxazine **4b**



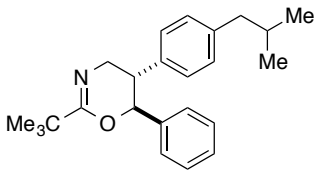


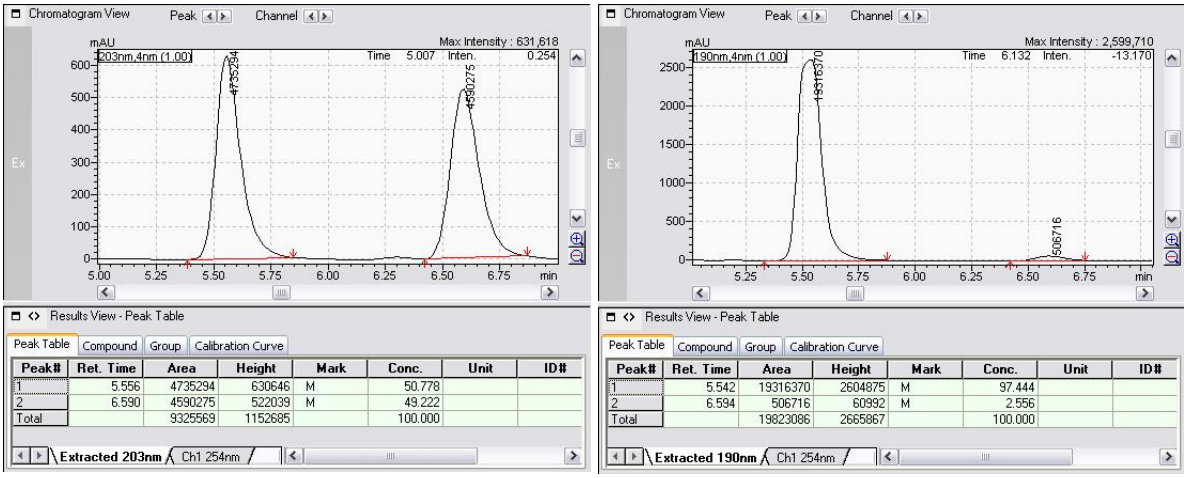
(5S,6S)-2-(tert-butyl)-6-phenyl-5-(p-tolyl)-5,6-dihydro-4H-1,3-oxazine **4c**



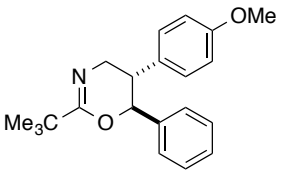


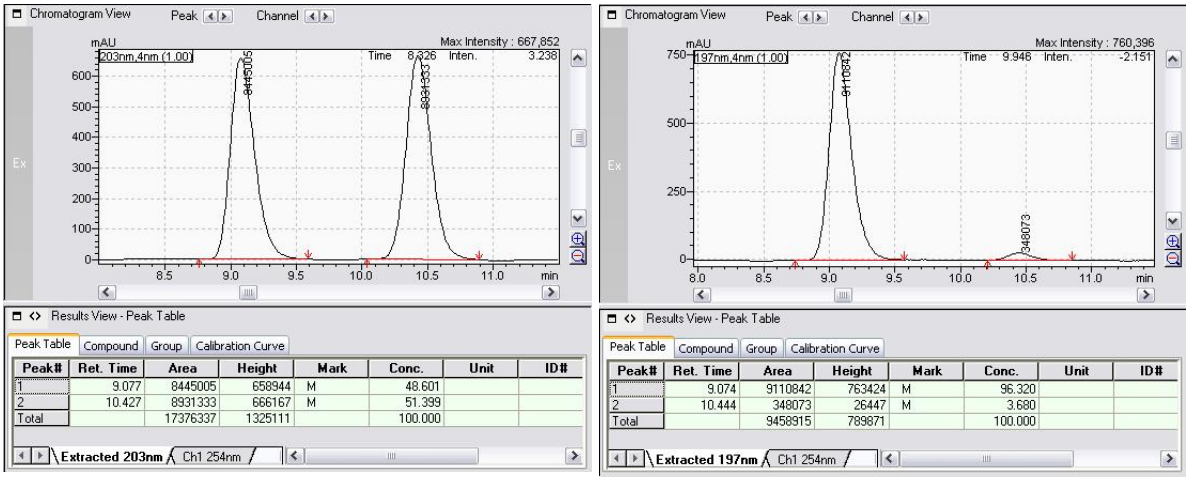
(5S,6S)-2-(tert-butyl)-5-(4-isobutylphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4d**[2]



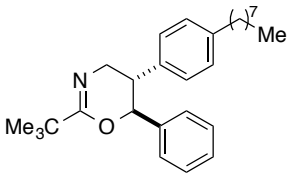


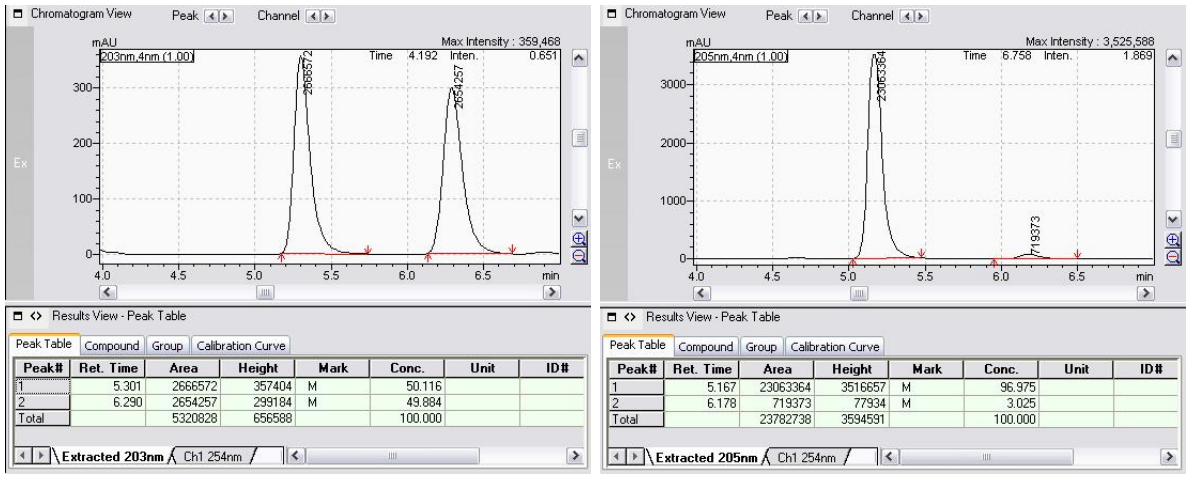
(5R,6R)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4e**[2]



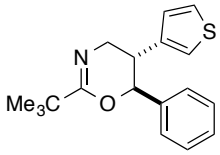


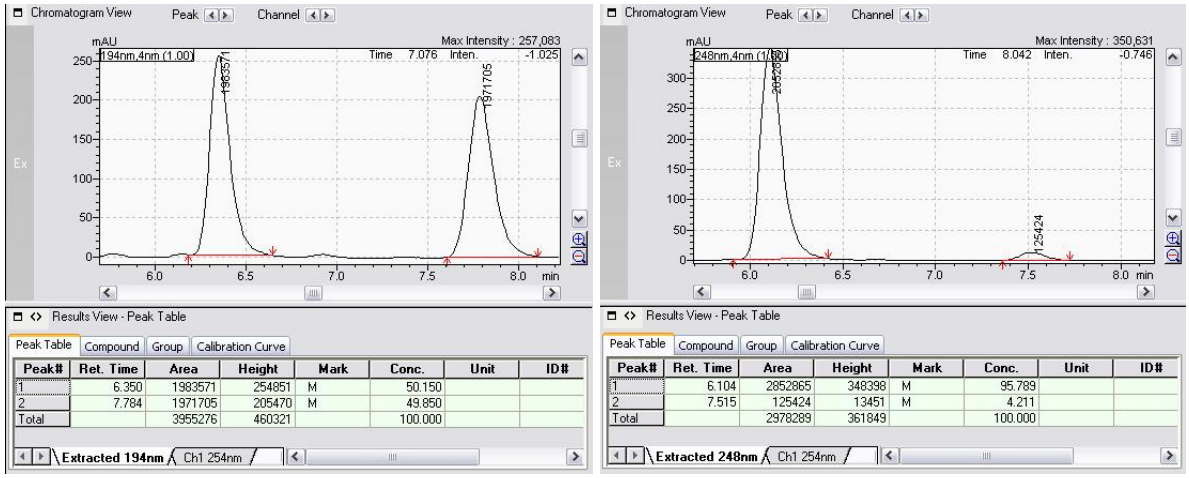
(5S,6S)-2-(tert-butyl)-5-(4-octylphenyl)-6-phenyl-5,6-dihydro-4H-1,3-oxazine **4f**



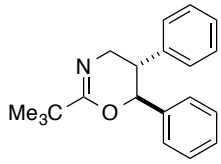


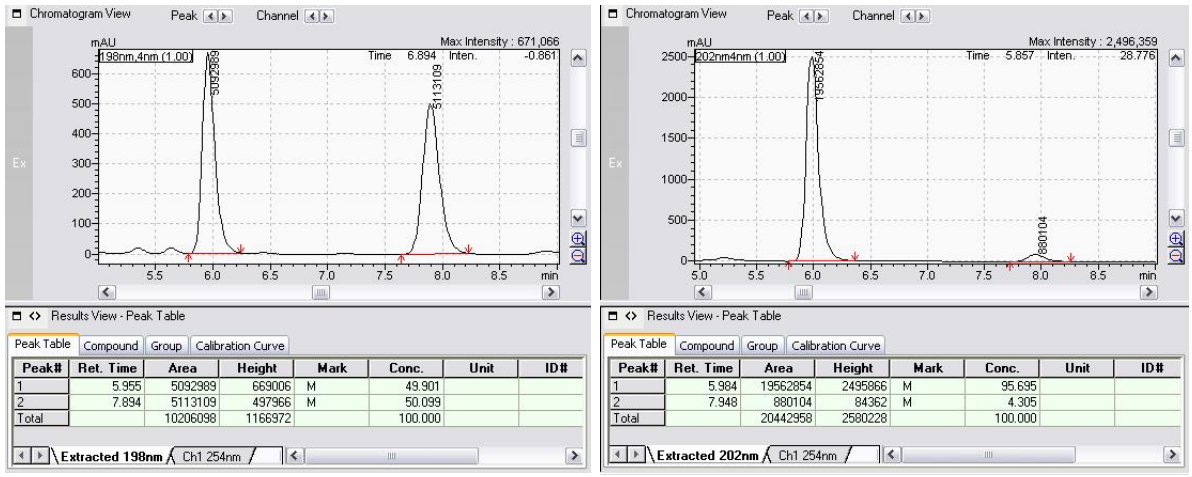
(5S,6S)-2-(tert-butyl)-6-phenyl-5-(thiophen-3-yl)-5,6-dihydro-4H-1,3-oxazine **4g**[2]



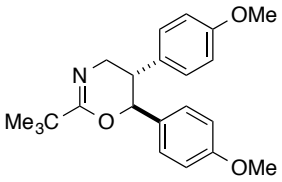


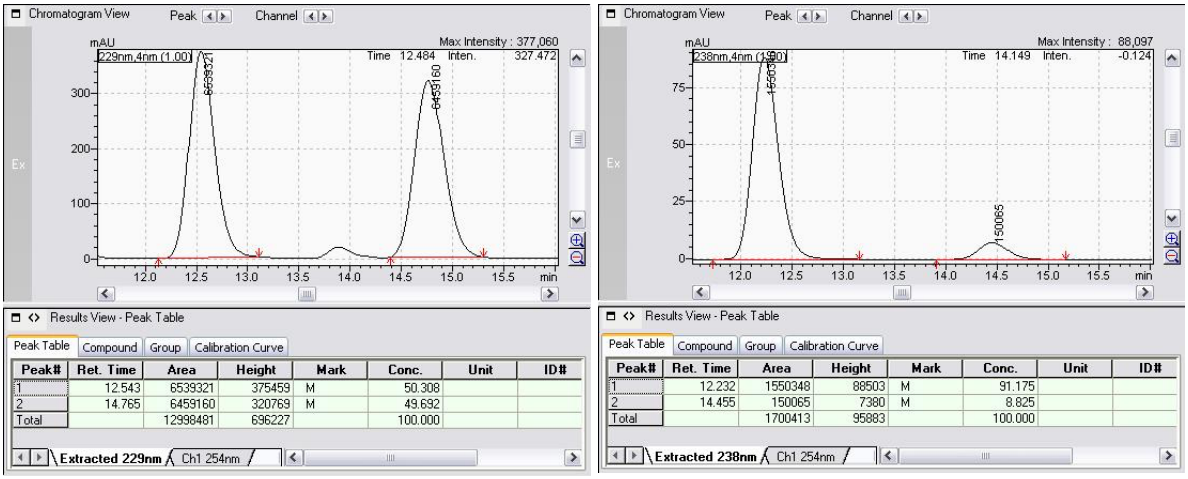
(5R,6R)-2-(tert-butyl)-5,6-diphenyl-5,6-dihydro-4H-1,3-oxazine **4h**



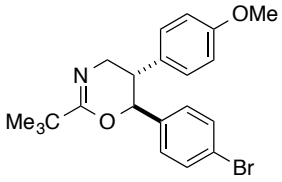


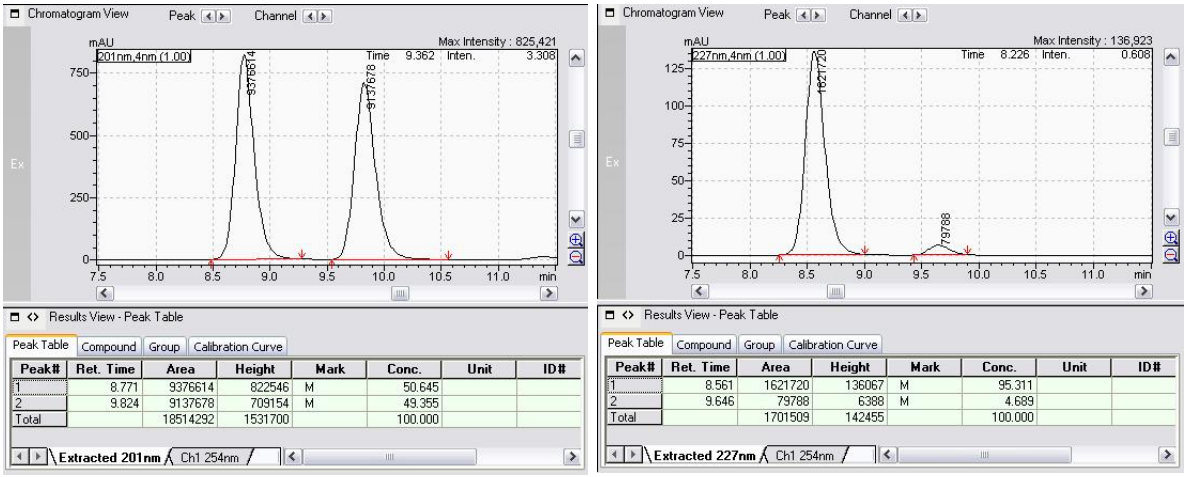
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4i**



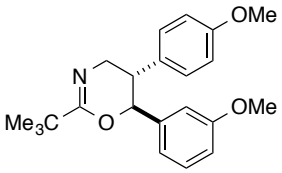


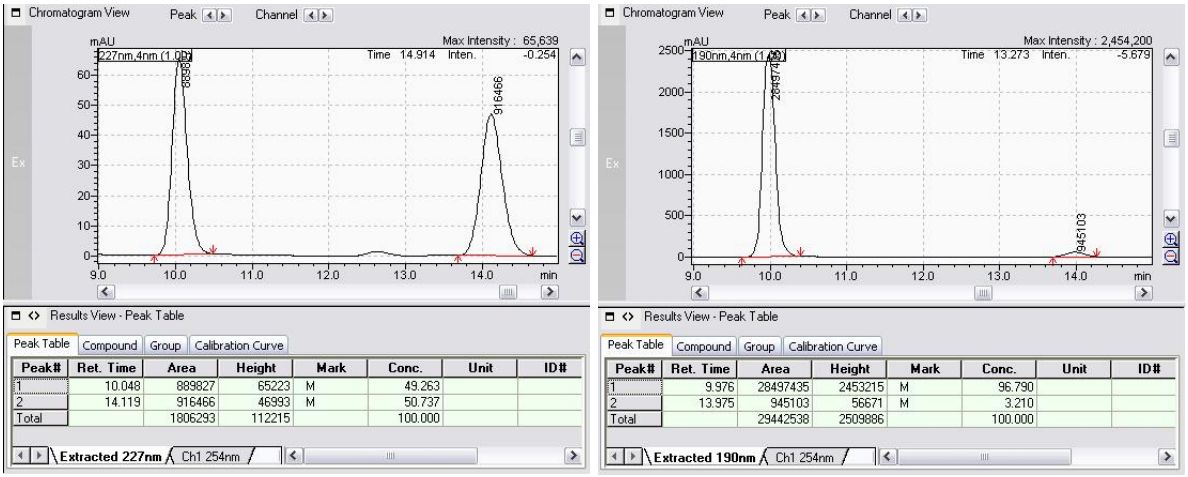
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(4-bromophenyl)-5,6-dihydro-4H-1,3-oxazine **4j**



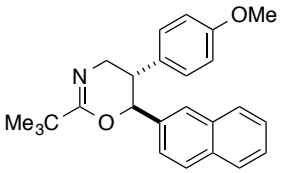


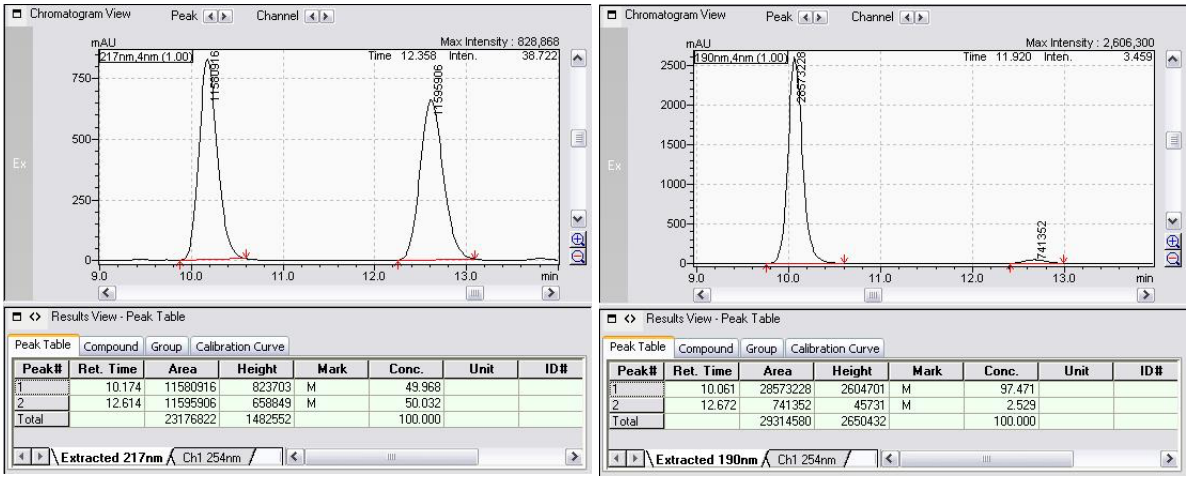
(5S,6S)-2-(tert-butyl)-6-(3-methoxyphenyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine ***4k***



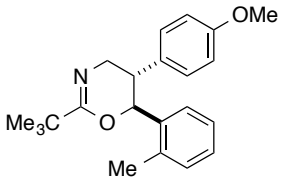


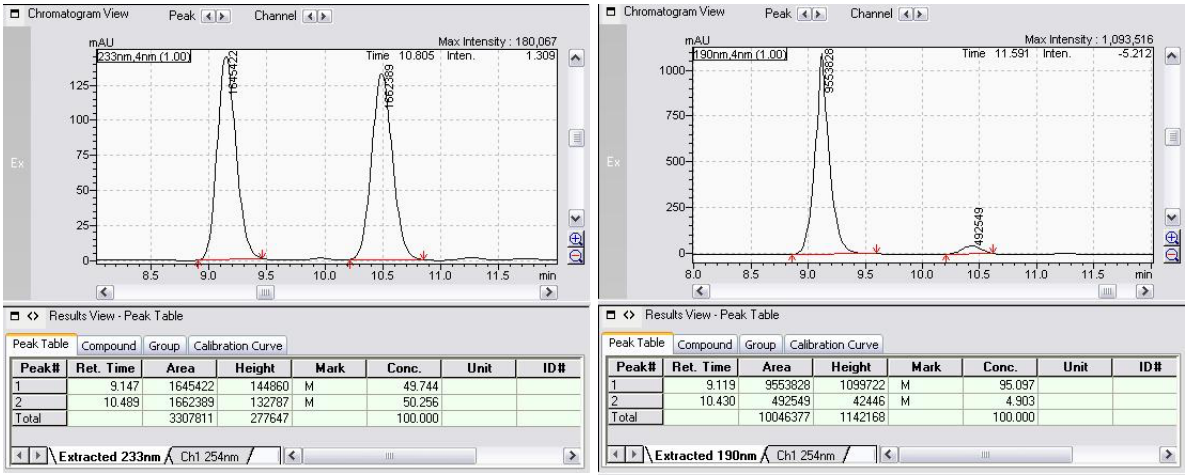
*(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(naphthalen-2-yl)-5,6-dihydro-4H-1,3-oxazin*e **4l**



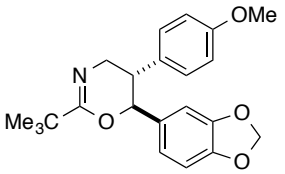


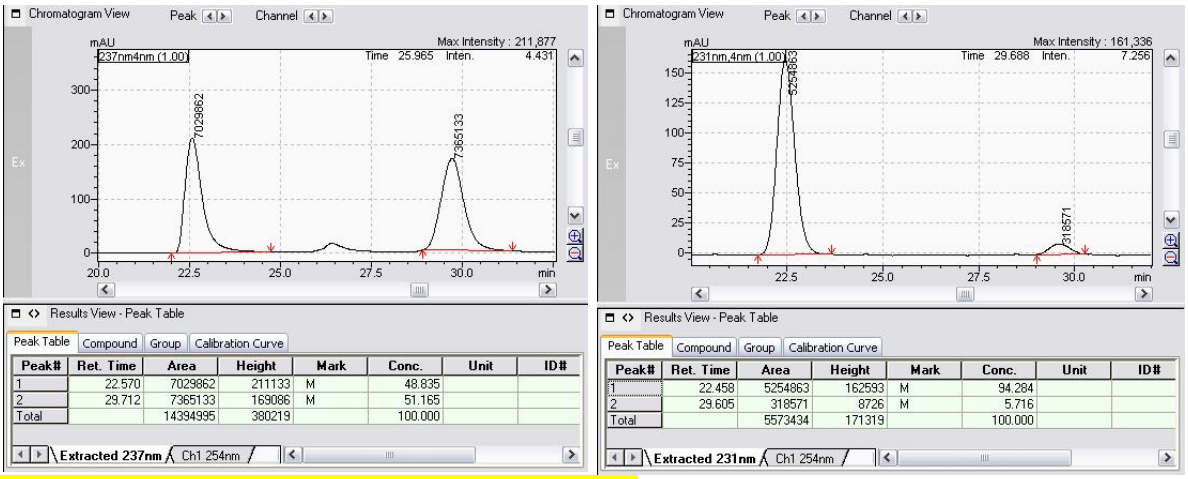
(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(o-tolyl)-5,6-dihydro-4H-1,3-oxazine **4m**





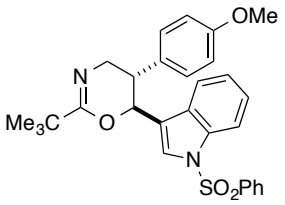
(5S,6S)-6-(benzo[d][1,3]dioxol-5-yl)-2-(tert-butyl)-5-(4-methoxyphenyl)-5,6-dihydro-4H-1,3-oxazine **4n**

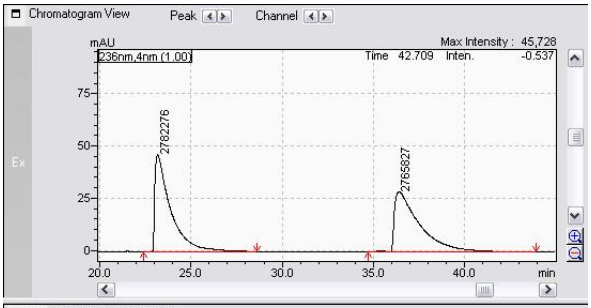


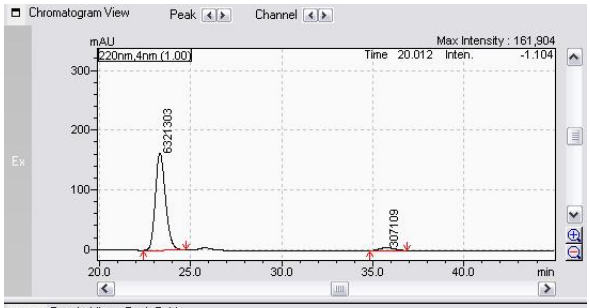


NOTE - THIS HAS CHANGED RELATIVE TO PREVIOUS VERSION

(5S,6S)-2-(tert-butyl)-5-(4-methoxyphenyl)-6-(1-(phenylsulfonyl)-1H-indol-3-yl)-5,6-dihydro-4H-1,3-oxazine **4o**



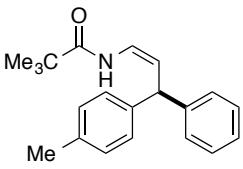


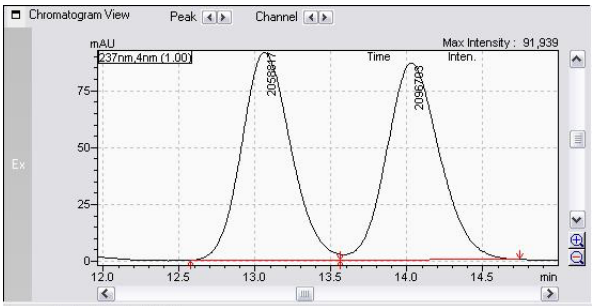


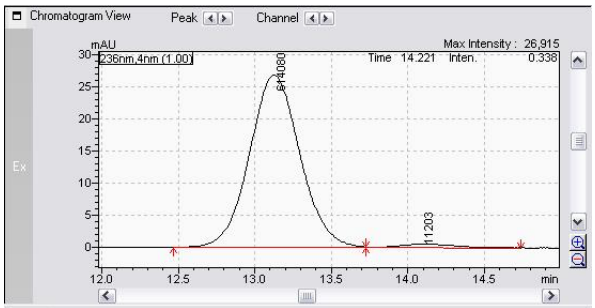
NOTE - THIS HAS CHANGED RELATIVE TO PREVIOUS VERSION

Enamide products

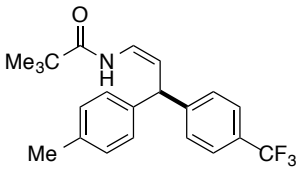
(S,Z)-N-(3-phenyl-3-(p-tolyl)prop-1-en-1-yl)pivalamide ***5a***

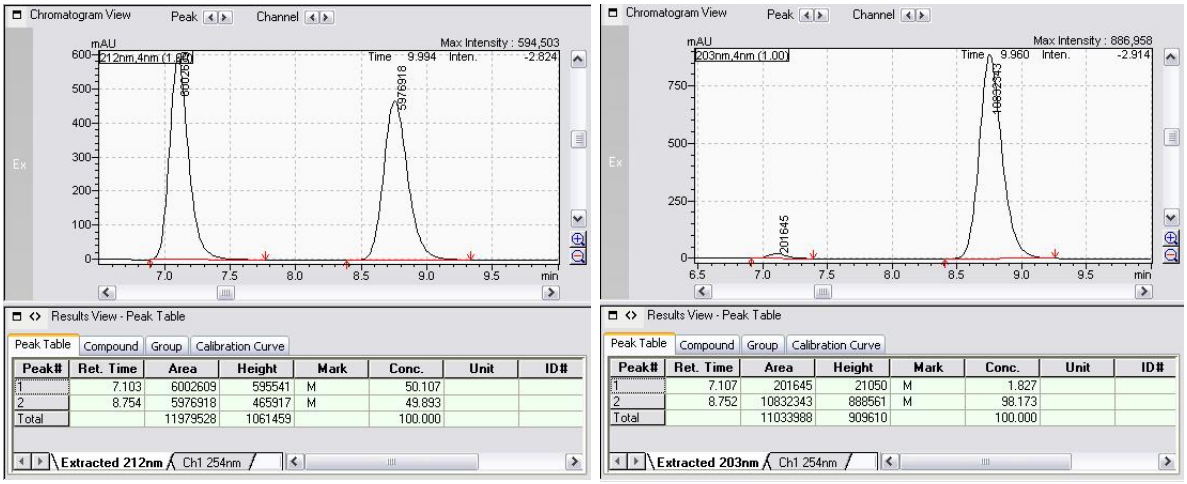




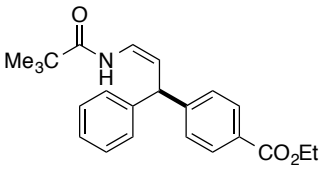


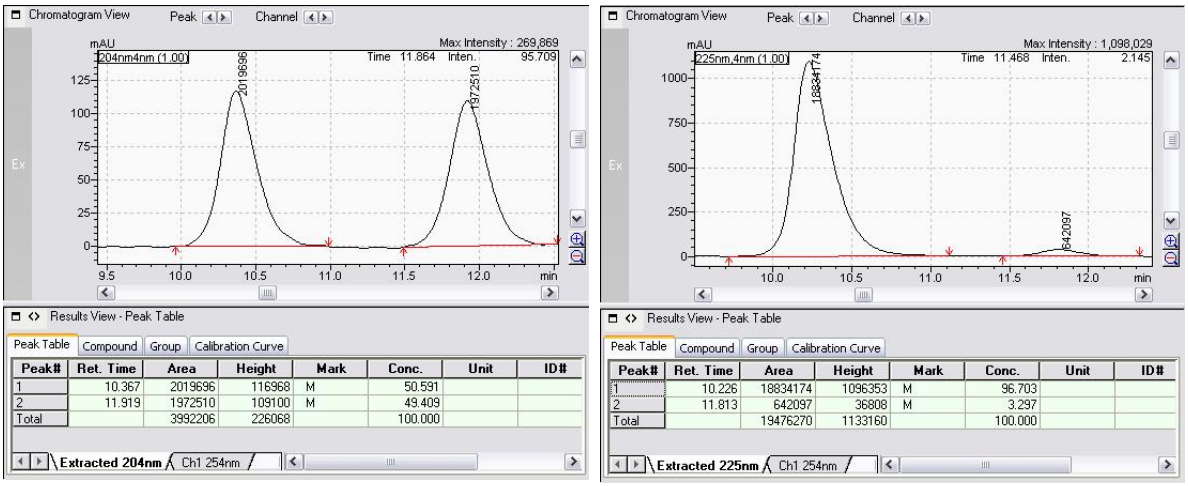
(Z)-N-(3-(4-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5b**



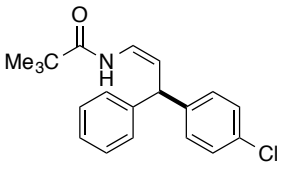


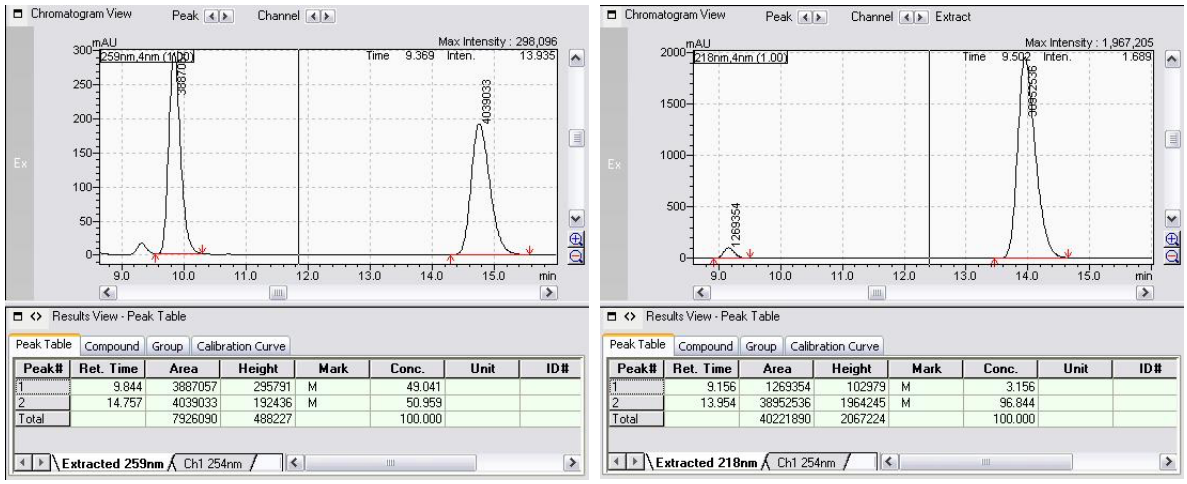
ethyl (R,Z)-4-(1-phenyl-3-pivalamidoallyl)benzoate **5c**



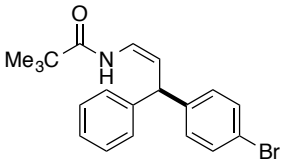


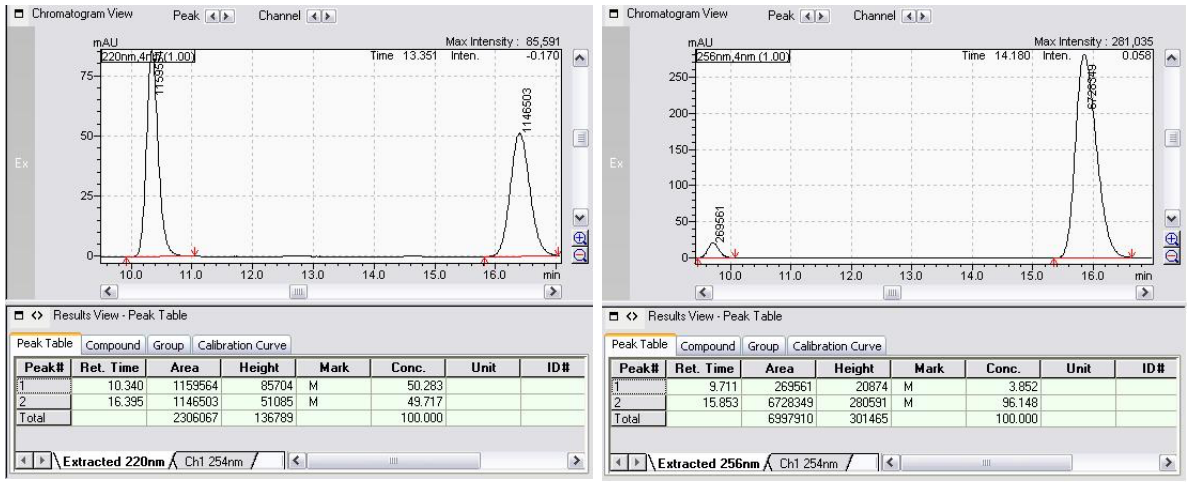
(Z)-N-(3-(4-chlorophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5d**



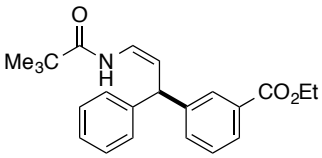


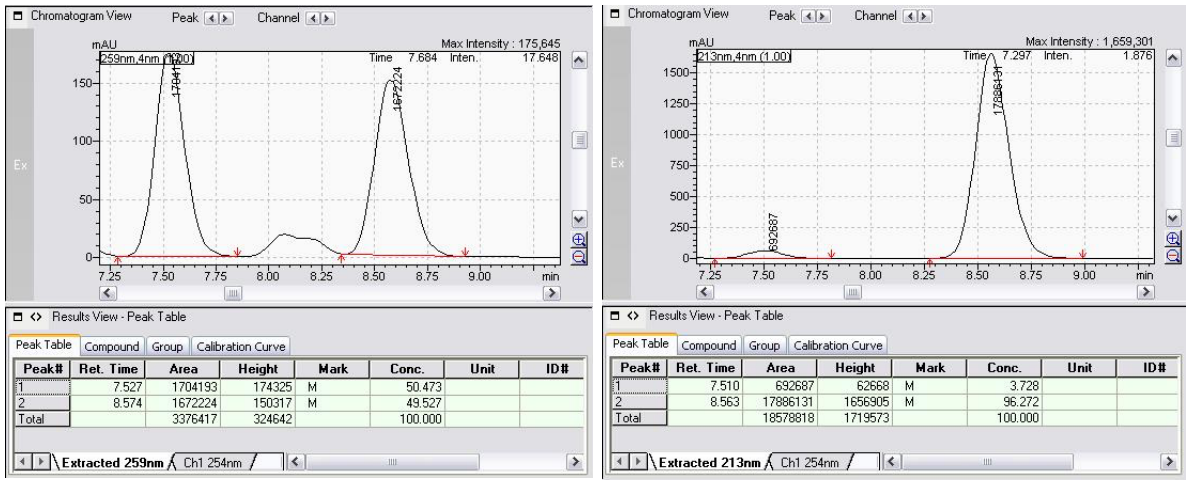
(Z)-N-(3-(4-bromophenyl)-3-phenylprop-1-en-1-yl)pivalamide **5e**



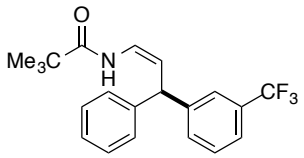


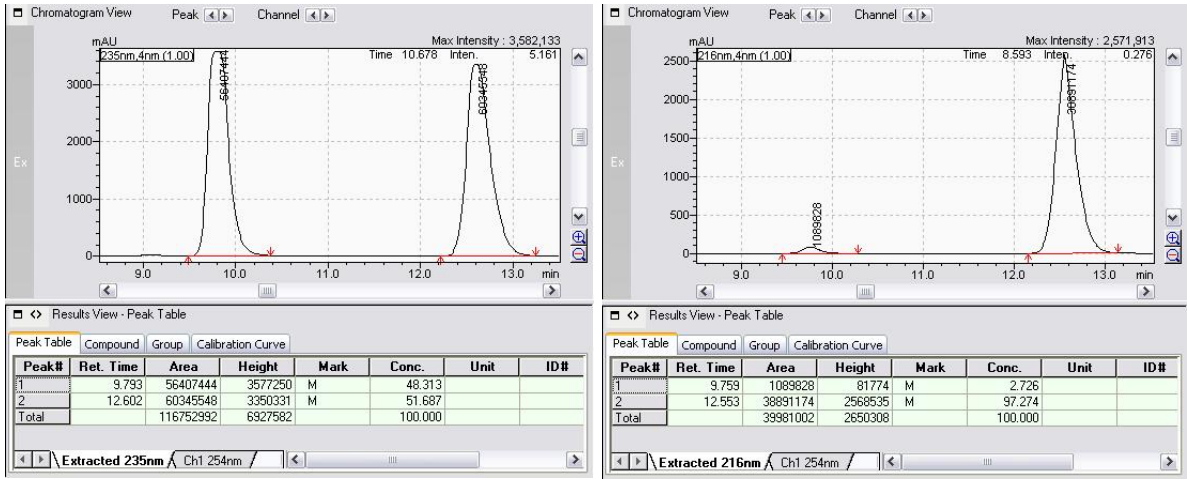
ethyl (R,Z)-3-(1-phenyl-3-pivalamidoallyl)benzoate **5f**



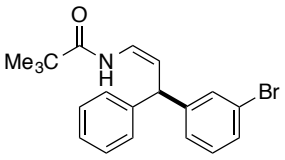


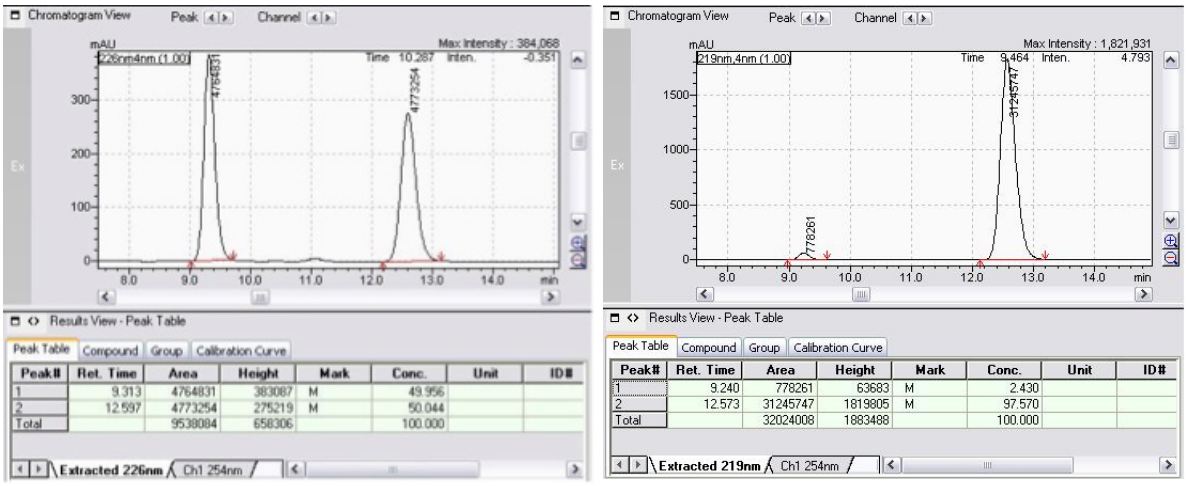
(Z)-N-(3-phenyl-3-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5g**



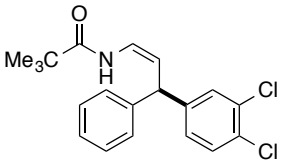


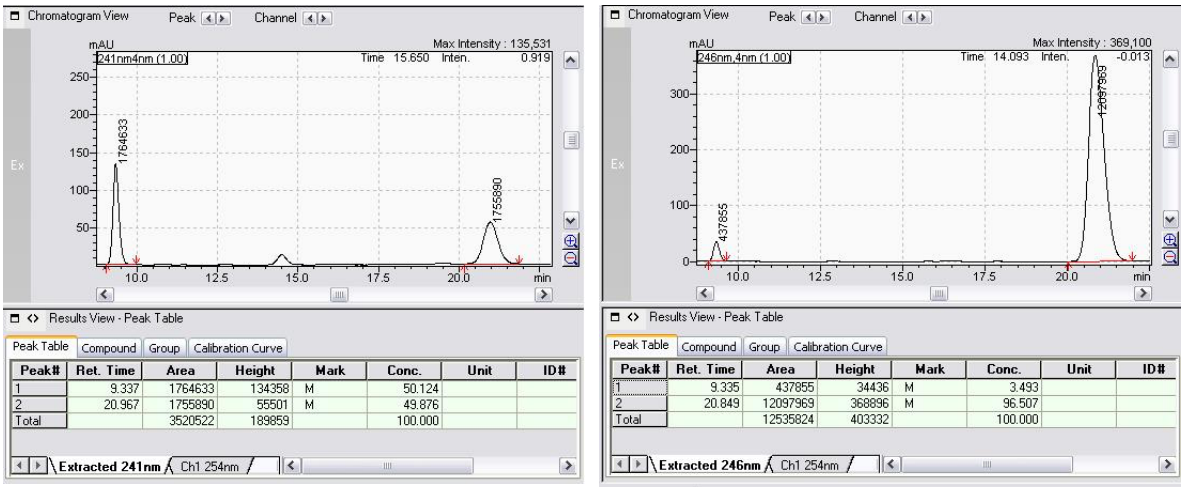
(R)-N-[(1Z)-3-(3-bromophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5h**



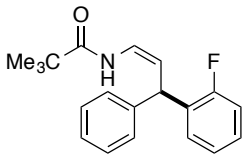


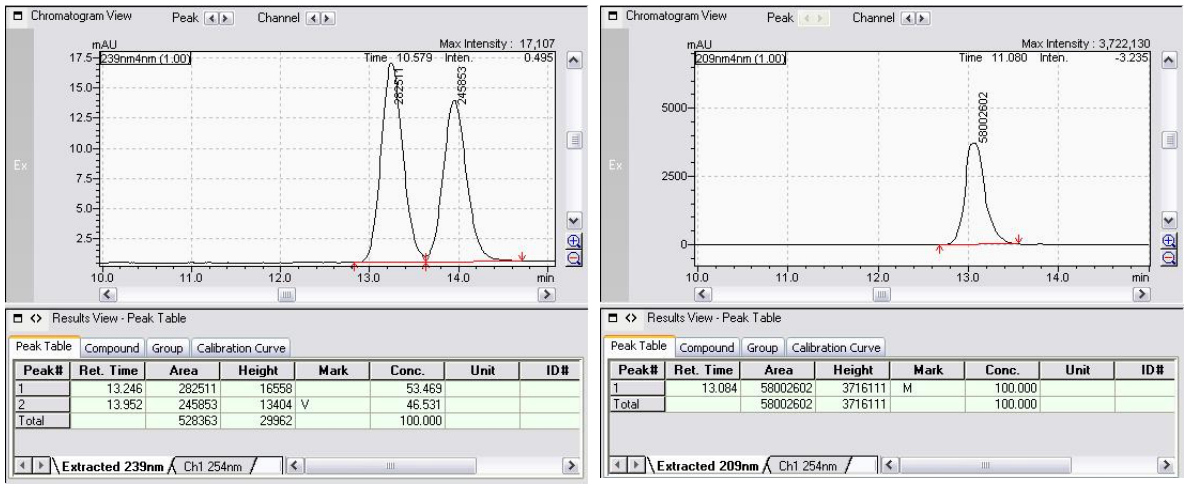
(R)-N-[(1Z)-3-(3,4-dichlorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5i**



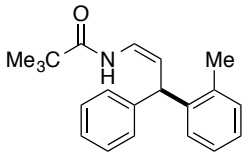


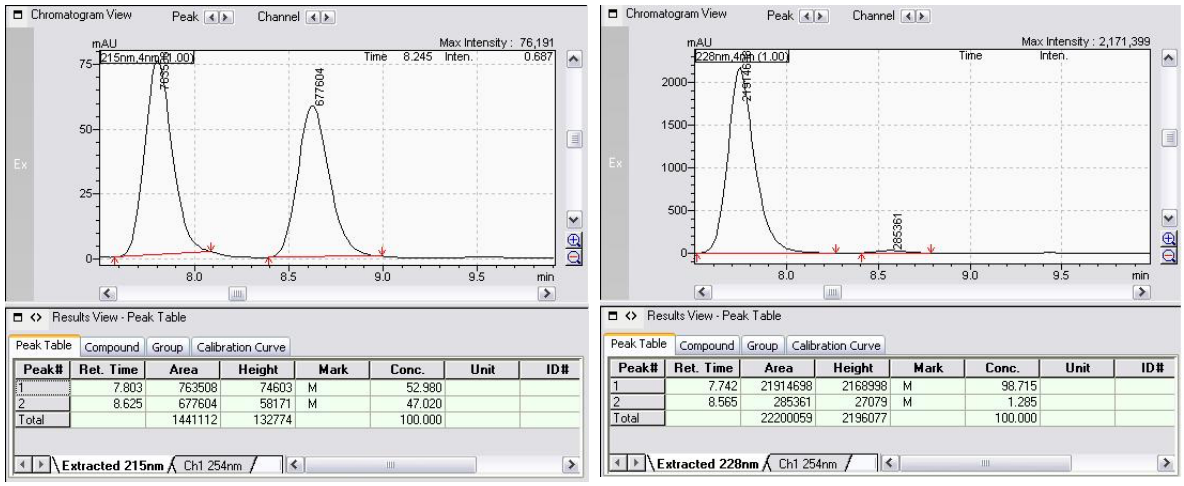
(R)-N-[(1Z)-3-(2-fluorophenyl)-3-phenylprop-1-en-1-yl]-2,2-dimethylpropanamide **5j**



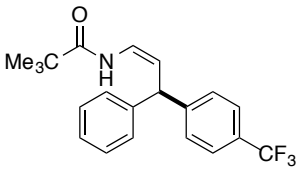


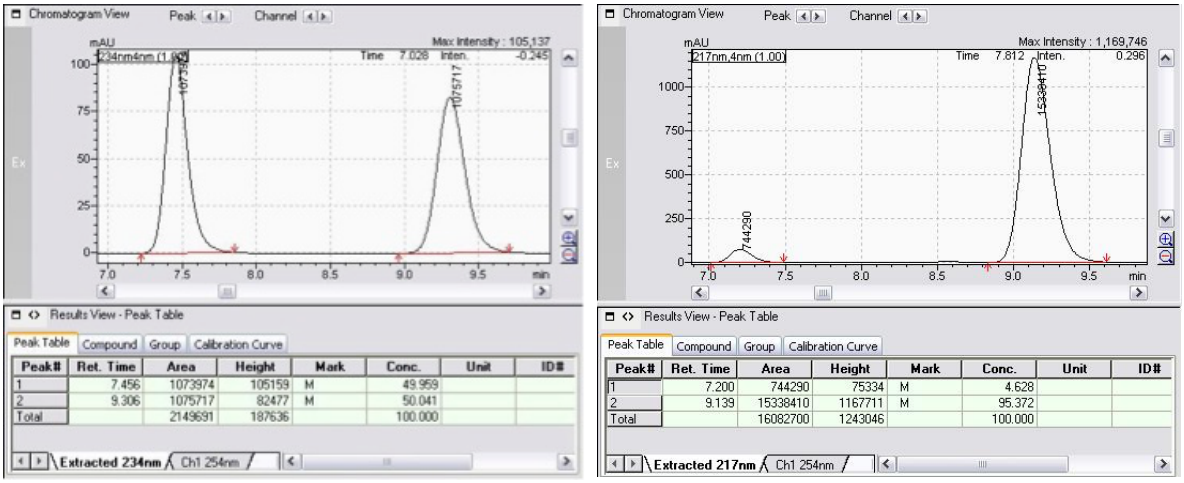
(R)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-phenylprop-1-en-1-yl]propanamide **5k**



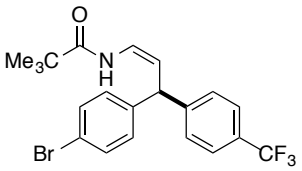


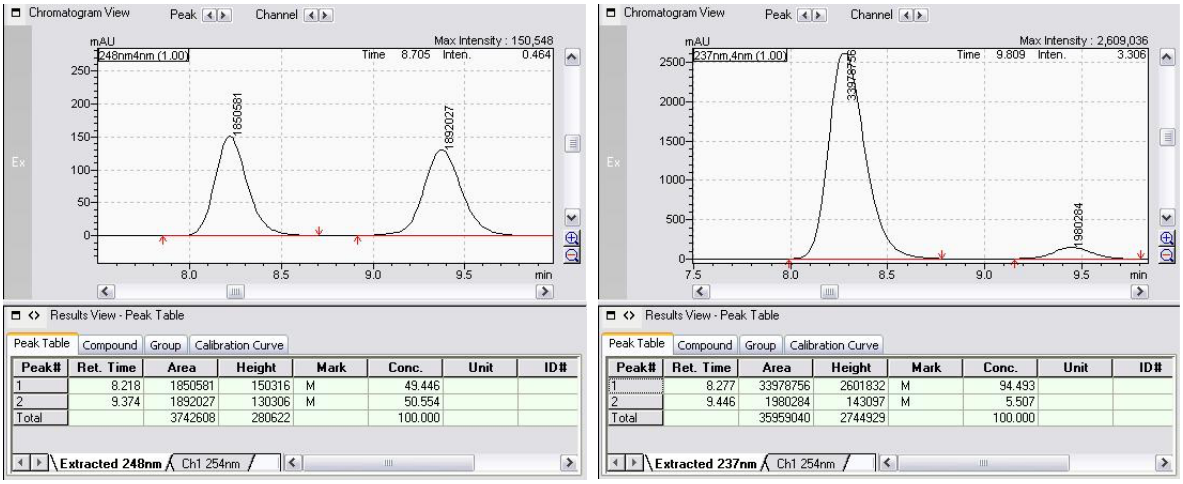
(R)-2,2-dimethyl-N-[(1Z)-3-phenyl-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5l**



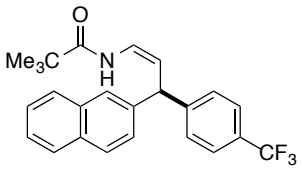


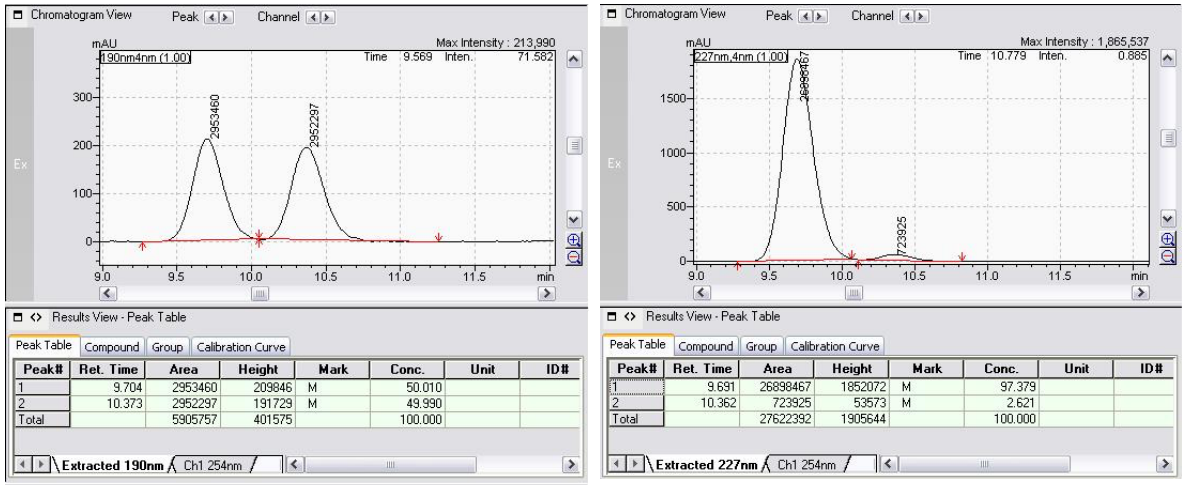
(S)-N-[(1Z)-3-(4-bromophenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]-2,2-dimethylpropanamide **5m**



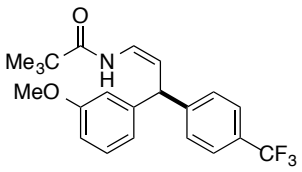


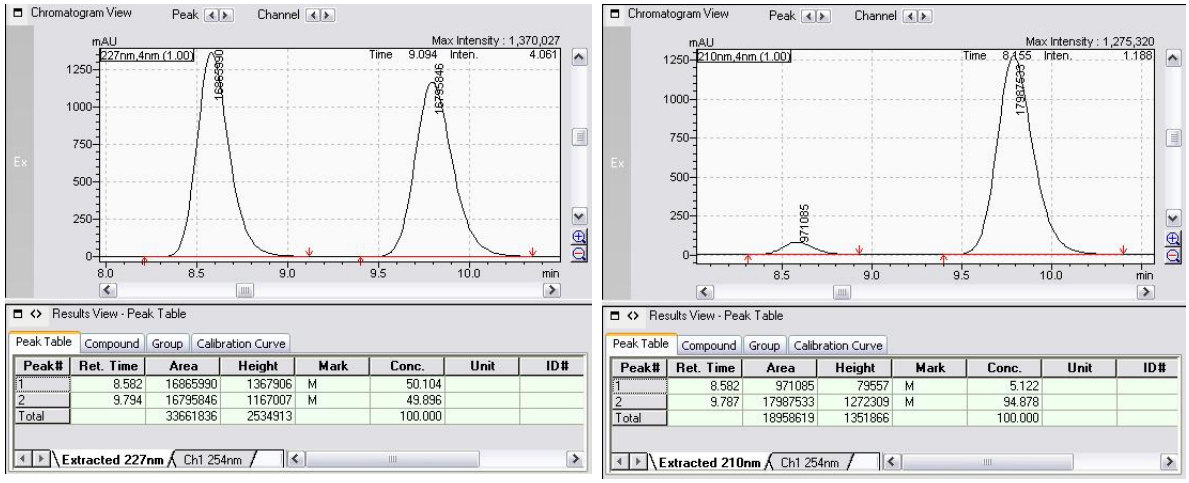
(S)-2,2-dimethyl-N-[(1Z)-3-(naphthalen-2-yl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5n**



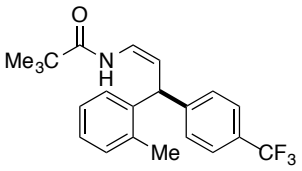


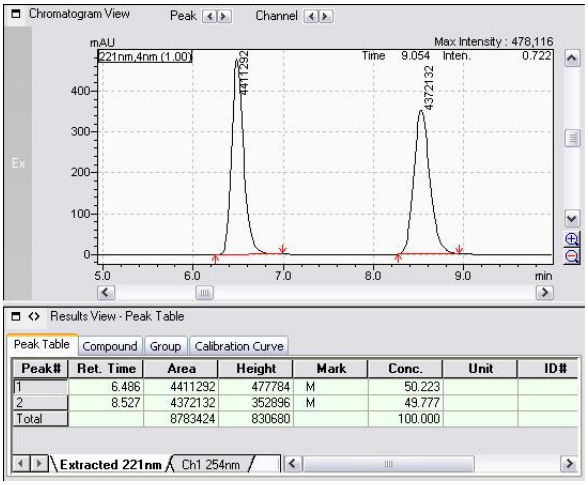
(Z)-N-(3-(3-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)pivalamide **5o**

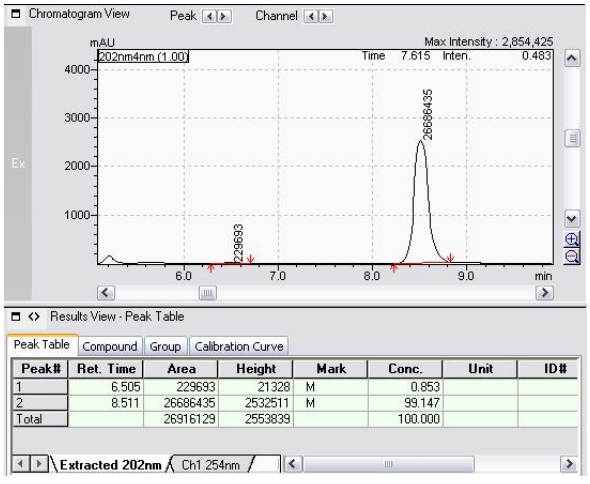




(S)-2,2-dimethyl-N-[(1Z)-3-(2-methylphenyl)-3-[4-(trifluoromethyl)phenyl]prop-1-en-1-yl]propanamide **5p**







Enamide hydrolysis

(R)-3-(3,4-dichlorophenyl)-3-phenylpropanal **6** *via* reduction to *(R)-3-(3,4-dichlorophenyl)-3-phenylpropan-1-ol*