

Supporting Information

Acyl Fluorides as Efficient Electrophiles for the Copper-Catalyzed Boroacylation of Allenes

Arnaud Boreux,^{†,‡} Kiran Indukuri,[†] Fabien Gagosz^{*,‡,||} and Olivier Riant^{*,†}

[†] *Institute of Condensed Matter and Nanosciences (IMCN), Molecules, Solids and Reactivity (MOST), Université catholique de Louvain (UCL), Place Louis Pasteur 1, 1348 Louvain-La-Neuve, Belgium.*

[‡] *Laboratoire de Synthèse Organique, UMR 7652 CNRS/Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France.*

^{||} *Department of Chemistry and Biomolecular Sciences, University of Ottawa, K1N 6N5, Ottawa, Canada.*

Corresponding email addresses: fgagosz@uottawa.ca; olivier.riant@uclouvain.be

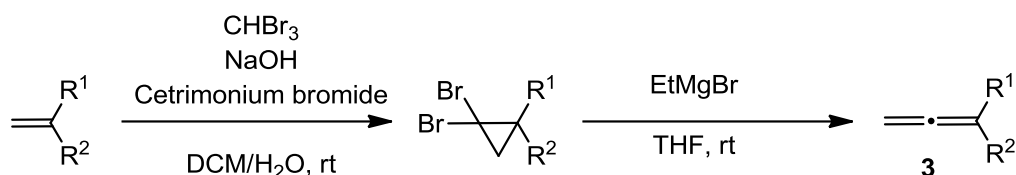
General information	2
Preparation of the allenes	3
Preparation of the acyl fluorides.....	11
Copper-catalyzed boroacylation of allenes	16
References	39
NMR spectra.....	41

General information

Copper-catalyzed reactions were performed in a flame-dried Schlenk under argon. THF used in these reactions was purchased from Acros (99.9% extra dry AcrosealedTM). Otherwise, THF was distilled over sodium and benzophenone. DCM was distilled over CaH₂. Solvents used for work-up were of technical grade. Dppf was purchased from Fluorochem. Benzoyl fluoride was purchased from VWR or Acros. Vinylidenecyclohexane was purchased from Sigma-Aldrich. 3-Methyl-1,2-butadiene was purchased from TCI. Copper(II) acetate was purchased from Acros. Other commercial reagents were purchased from Acros, Fluorochem, TCI, Sigma-Aldrich, VWR or Alfa-Aesar and used as received. Thin Layer Chromatography were performed on aluminium plates bearing a 0.25 mm of Merck Silica Gel 60F₂₅₄, visualized by fluorescence quenching at 254 nm and chemical revelation using acidic solution of para-anisaldehyde or basic solution of potassium permanganate. Flash chromatography was performed using silica gel 60 (40-63 μ m). NMR analysis was performed at room temperature on Bruker 300 MHz or 500 MHz Fourier Transform Spectrometer. Residual solvent peaks of CDCl₃ were used as internal references: 7.26 ppm for ¹H spectra and 77.16 ppm for ¹³C spectra. ¹⁹F NMR was recorded in CDCl₃ using C₆F₆ as an external standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constants (*J*) are given in Hz. The following abbreviations were used in order to describe the peaks multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, m = multiplet, br = broad. HRMS spectra were recorded using Thermo Scientific QExactive. Infrared absorptions were recorded as a liquid deposition on a ZnSe crystal on a Shimadzu FTIR 8400 Spectrophotometer.

Preparation of the allenes

Procedure A:



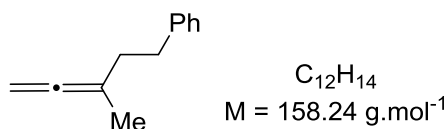
Step 1: The cyclopropanation of the 1,1-disubstituted alkene was carried out according to literature procedures.^{1,2}

To a solution of alkene (1.0 equiv) and cetrimonium bromide (0.12 equiv) in dichloromethane (0.16 mL/mmol alkene) was added dropwise aqueous solution of NaOH (4.6 equiv.; 0.5 mL water/mmol). After 5 min, CHBr_3 (2 equiv) in CH_2Cl_2 (0.08 mL/mmol alkene) was added and left stirring at room temperature for 2-3 days. Water and DCM were added. The aqueous phase was extracted with DCM. The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4 and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel afforded the pure cyclopropane products.

Step 2: The preparation of the 1,1-disubstituted allenes was carried out according to a literature procedure.²

EtMgBr (3.0 M in THF, 1.5 equiv) was added dropwise via syringe pump to a solution of cyclopropane (1.0 equiv) in dry THF (2 mL/mmol of cyclopropane) under nitrogen atmosphere at room temperature. The resulting mixture was allowed to stir at room temperature for an additional 30 minutes. Then the reaction was quenched by saturated NH_4Cl solution, and extracted with diethyl ether (15 mL \times 3). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4 . After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel afforded the desired allenes **3**.

(3-Methylpenta-3,4-dien-1-yl)benzene (**3a**)



Following procedure A starting with (3-methylbut-3-en-1-yl)benzene (36.3 mmol).³

Flash chromatography: PE

Overall yield: 55% of a colourless oil.

^1H NMR (δ , ppm) 7.32 – 7.17 (m, 5H), 4.62 (hex, $J = 3.2 \text{ Hz}$, 2H), 2.77 – 2.72 (m, 2H), (300 MHz, CDCl_3) 2.28 – 2.20 (m, 2H), 1.73 (t, $J = 3.1 \text{ Hz}$, 3H)

^{13}C NMR (δ , ppm) 206.3, 142.3, 128.5, 128.4, 125.9, 98.3, 74.7, 35.3, 34.0, 19.1

(75 MHz, CDCl₃)

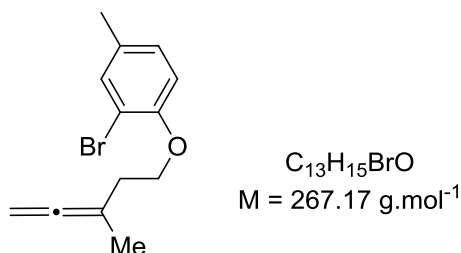
MS
(HRMS APCI)

Calcd for [M+H]⁺ C₁₂H₁₅: 159.1168

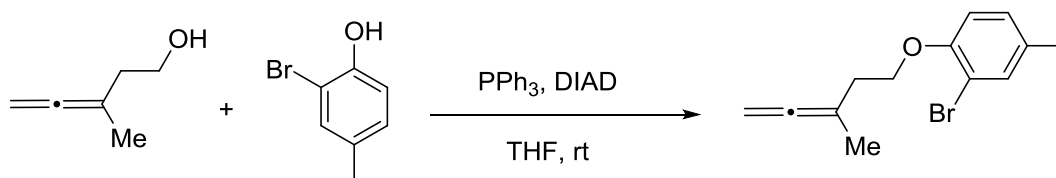
Found: 159.1168

Spectroscopic data are in agreement with those reported in the literature.⁴

2-Bromo-4-methyl-1-((3-methylpenta-3,4-dien-1-yl)oxy)benzene (3d)



This substrate was prepared via a Mitsunobu reaction according to the literature procedure.⁵



To a solution of 3-methylpenta-3,4-dien-1-ol⁶ (1.0 equiv, 5.0 mmol), 2-bromo-4-methylphenol (1.44 equiv, 7.2 mmol) and triphenylphosphine (1.5 equiv, 7.5 mmol) in THF (15 mL) was added diisopropyl azodicarboxylate (1.2 equiv, 6.0 mmol) dropwise at room temperature. The reaction mixture was stirred 14 h and the solvents were evaporated. The crude mixture was dissolved in DCM and filtered on a pad of silica (eluting with PE/Et₂O 97.5:2.5).

Purified by flash chromatography on silica gel (eluent: PE/Et₂O 99:1 to 98:2 to 97.5:2.5) afforded the pure product as a colourless oil (385 mg, 1.44 mmol, 29% yield).⁷

¹H NMR (δ, ppm) 7.35 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.03 (ddd, *J* = 8.2, 2.2, 0.8 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.65 (hex, *J* = 3.2 Hz, 2H), 4.09 (t, *J* = 7.0 Hz, 2H), 2.47 (tt, *J* = 6.7, 3.1 Hz, 2H), 2.27 (s, 3H), 1.79 (t, *J* = 3.2 Hz, 3H)

¹³C NMR (δ, ppm) 206.4, 153.3, 133.9, 131.6, 128.9, 113.5, 112.1, 95.2, 74.9, 67.9, 33.0, 20.3, 19.3

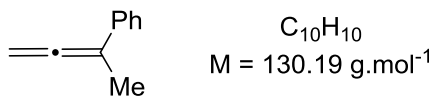
IR (cm⁻¹, neat) 2979, 2930, 2866, 1960, 1732, 1607, 1495, 1470, 1441, 1387, 1284, 1277, 1207, 1153, 1051, 1020, 901, 849, 802

MS
(HRMS APCI)

Calcd for [M+H]⁺ C₁₃H₁₆OBr: 267.0379

Found: 267.0378

Buta-2,3-dien-2-ylbenzene (3e)



Following procedure A starting with α -methylstyrene.

Flash chromatography: PE

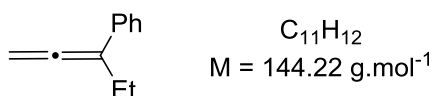
Overall yield: 69% of a colourless oil.

^1H NMR (δ , ppm) 7.43 – 7.40 (m, 2H), 7.36 – 7.30 (m, 2H), 7.23 – 7.18 (m, 1H), 5.03 (300 MHz, CDCl_3) (q, $J = 3.2 \text{ Hz}$, 2H), 2.10 (t, $J = 3.2 \text{ Hz}$, 3H)

^{13}C NMR (δ , ppm) 209.1, 136.8, 128.5, 126.7, 125.8, 99.9, 77.1, 16.8 (75 MHz, CDCl_3)

Spectroscopic data are in agreement with those reported in the literature⁸

Penta-1,2-dien-3-ylbenzene (3f)



Following procedure A starting with α -ethylstyrene.³

Flash chromatography: PE

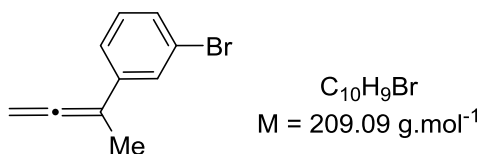
Overall yield: 29% of a colourless oil.

^1H NMR (δ , ppm) 7.44 – 7.40 (m, 2H), 7.36 – 7.30 (m, 2H), 7.23 – 7.18 (m, 1H), 5.11 (300 MHz, CDCl_3) (t, $J = 3.7 \text{ Hz}$, 2H), 2.44 (ddt, $J = 7.4, 6.8, 3.7 \text{ Hz}$, 2H), 1.16 (td, $J = 7.4, 0.7 \text{ Hz}$, 3H)

^{13}C NMR (δ , ppm) 208.5, 136.7, 128.5, 126.7, 126.0, 106.8, 78.9, 22.5, 16.2 (75 MHz, CDCl_3)

Spectroscopic data are in agreement with those reported in the literature.⁹

1-Bromo-3-(buta-2,3-dien-2-yl)benzene (3g)



Following procedure A starting with 1-bromo-3-(prop-1-en-2-yl)benzene.³

Flash chromatography: PE

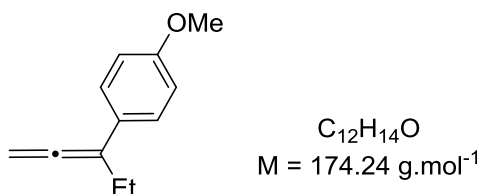
Overall yield: 65% of a colourless oil.

¹H NMR (δ , ppm) 7.53 (t, $J = 3.0$ Hz, 1H), 7.29 – 7.33 (m, 2H), 7.16 (dd, $J = 6.0, 3.0$ Hz, 1H), 5.05 (q, $J = 3.0$ Hz, 2H), 2.05 (t, $J = 3.0$ Hz, 3H)

¹³C NMR (δ , ppm) 209.1, 139.2, 129.8, 129.5, 128.8, 124.3, 122.8, 99.1, 77.7, 16.6 (75 MHz, CDCl_3)

Spectroscopic data are in agreement with those reported in the literature.¹⁰

1-Methoxy-4-(penta-1,2-dien-3-yl)benzene (3h)



Following procedure A starting with 1-(but-1-en-2-yl)-4-methoxybenzene.³

Flash chromatography: PE

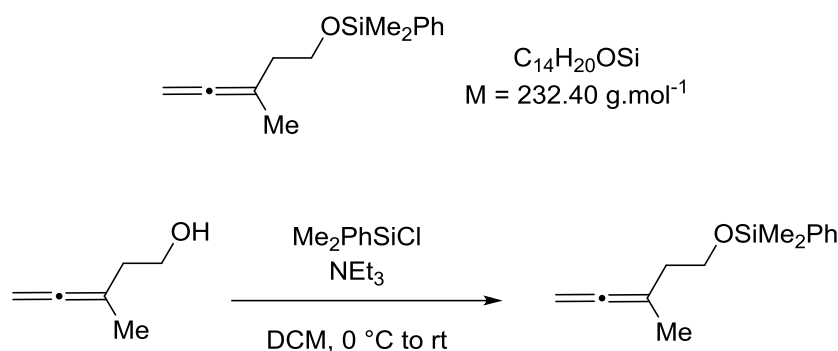
Overall yield: 47% of a colourless oil.

¹H NMR (δ , ppm) 7.32 (d, $J = 9.0$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.07 (t, $J = 3.0$ Hz, 2H), 3.79 (s, 3H), 2.34 – 2.44 (m, 2H), 1.14 (t, $J = 6.0$ Hz, 3H)

¹³C NMR (δ , ppm) 208.1, 158.5, 128.9, 127.1, 113.9, 106.3, 78.8, 55.4, 22.7, 12.6 (75 MHz, CDCl_3)

MS (HRMS APCI) Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{12}\text{H}_{15}\text{O}$: 175.1117 Found: 175.1117

Dimethyl((3-methylpenta-3,4-dien-1-yl)oxy)(phenyl)silane (3i)



To a solution of 3-methylpenta-3,4-dien-1-ol^{Erreur ! Signet non défini.} (1.0 equiv, 5.0 mmol) and triethylamine (2.0 equiv, 10.0 mmol) in DCM (25 mL) at 0 °C was added chloro(dimethyl)phenylsilane (1.5 equiv, 7.5 mmol) dropwise. The mixture was stirred 14 h while warming up at room temperature. The reaction was quenched by the addition of water, extracted with DCM (x3), washed successively with $\text{NH}_4\text{Cl}_{(\text{sat})}$, water, $\text{NaHCO}_3_{(\text{sat})}$, dried over Na_2SO_4 and concentrated under reduced pressure.

Purified by flash chromatography on silica gel (eluent: PE/ Et_2O 99:1 to 97:3) afforded the pure product as a colourless oil (952 mg, 4.10 mmol, 82% yield).

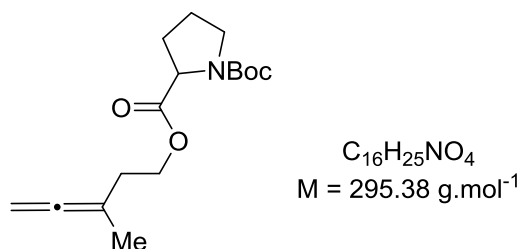
^1H NMR (δ , ppm) 7.60 – 7.57 (m, 2H), 7.41 – 7.36 (m, 3H), 4.56 (hex, $J = 3.1$ Hz, 2H), 3.70 (t, $J = 7.1$ Hz, 2H), 2.18 (dq, $J = 6.9, 3.0$ Hz, 2H), 1.67 (t, $J = 3.1$ Hz, 3H), 0.38 (s, 6H)

^{13}C NMR (δ , ppm) 206.5, 138.1, 133.6, 129.7, 127.9, 95.4, 74.2, 61.6, 36.6, 19.2, -1.6 (75 MHz, CDCl_3)

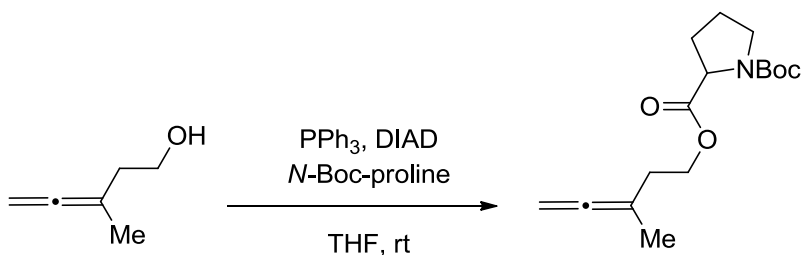
IR (cm^{-1} , neat) 2957, 2923, 2868, 2370, 2311, 1959, 1772, 1717, 1591, 1427, 1394, 1369, 1308, 1250, 1215, 1188, 1171, 1117, 1090, 997, 916, 825, 785

MS Calcd for $[\text{M}+\text{H}]^+ \text{C}_{14}\text{H}_{21}\text{O}^{28}\text{Si}$: 233.1355 Found: 233.1355 (HRMS APCI)

1-(tert-butyl) 2-(3-methylpenta-3,4-dien-1-yl) pyrrolidine-1,2-dicarboxylate (3j)



This substrate was prepared via a Mitsunobu reaction according to the literature procedure.⁵



To a solution of 3-methylpenta-3,4-dien-1-ol^{Erreur ! Signet non défini.} (1.0 equiv, 3.6 mmol), N-Boc-proline (1.5 equiv, 5.4 mmol) and triphenylphosphine (1.5 equiv, 5.4 mmol) in THF (10 mL) was added diisopropyl azodicarboxylate (1.2 equiv, 4.3 mmol) dropwise at room temperature. The reaction mixture was stirred 6 h and filtered over silica (Et₂O). The solvents were then evaporated and purification by flash chromatography on silica gel (eluent: PE/Et₂O 7:3 to 6:4) afforded the pure product as a mixture of rotamers (colourless oil, 775 mg, 2.62 mmol, 73 % yield).

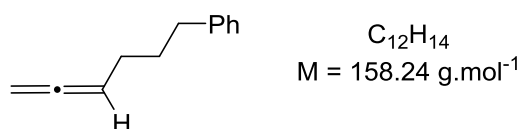
¹H NMR (δ, ppm) 4.68 – 4.60 (m, 2H), 4.29 – 4.18 (m, 3H), 3.59 – 3.35 (m, 2H), 2.30 – 2.15 (m, 3H), 1.99 – 1.82 (m, 3H), 1.72 – 1.69 (m, 3H), 1.46 – 1.41 (m, 9H)

¹³C NMR (δ, ppm) 206.3, 206.3, 173.2, 173.0, 154.5, 153.9, 94.8, 94.6, 79.9, 79.8, 75.0, 74.9, 63.0, 59.3, 59.0, 46.6, 46.4, 32.6, 32.6, 31.0, 30.0, 28.5, 28.4, 24.4, 23.7, 18.9, 18.9

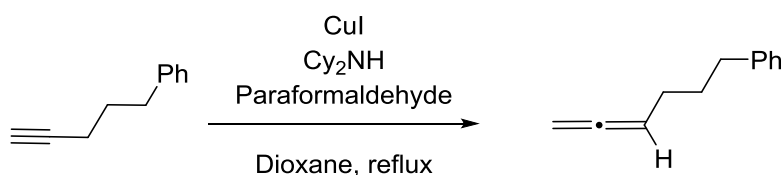
IR (cm⁻¹, neat) 2974, 2959, 2881, 1962, 1747, 1697, 1477, 1454, 1396, 1366, 1275, 1256, 1157, 1119, 1088, 1032, 988, 974, 918, 889, 851

MS (HRMS APCI) Calcd for [M+H]⁺ C₁₆H₂₆O₄N: 296.1856 Found: 296.1857

Hexa-4,5-dien-1-ylbenzene (3k)



This substrate was prepared via a Crabbé reaction according to a literature procedure.¹¹



Pent-4-yn-1-ylbenzene (1.0 equiv, 34.9 mmol, 5.00 g, 5.3 mL), dicyclohexylamine (1.8 equiv, 62.8 mmol, 11.39 g, 12.5 mL), copper(I) iodide (0.5 equiv, 17.45 mmol, 3.32 g) and

paraformaldehyde (2.5 equiv, 87.25 mmol, 2.62 g) were added sequentially in dioxane (150 mL). This mixture was stirred at 100 °C during 17 h. The reaction mixture was cooled down to room temperature and was filtered over silica (eluting with PE). The solvents were removed under reduced pressure. The crude was filtered again over silica (eluting with PE) and the solvents were evaporated.

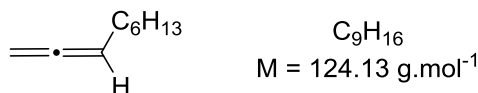
Purified by flash chromatography (PE) afforded the pure product as a colourless oil (3.58g, 22.6 mmol, 65% yield).

¹H NMR (δ, ppm) 7.30 – 7.25 (m, 2H), 7.19 – 7.15 (m, 3H), 5.12 (p, *J* = 6.7 Hz, 1H), (300 MHz, CDCl₃) 4.68 (dt, *J* = 6.6, 3.3 Hz, 2H), 2.68 – 2.62 (m, 2H), 2.09 – 1.99 (m, 2H), 1.80 – 1.69 (m, 2H)

¹³C NMR (δ, ppm) 208.7, 142.5, 128.6, 128.4, 125.8, 89.8, 75.0, 35.4, 30.9, 27.8 (75 MHz, CDCl₃)

Spectroscopic data are in agreement with those reported in the literature.¹²

Nona-1,2-diene (3l)



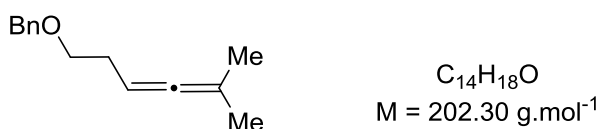
This substrate was prepared as described in the literature.^{Erreur ! Signet non défini.}

¹H NMR (δ, ppm) 5.09 (p, *J* = 6.8 Hz, 1H), 4.65 (dt, *J* = 6.6, 3.2 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.41 – 1.26 (m, 8H), 0.91 – 0.85 (m, 3H) (300 MHz, CDCl₃)

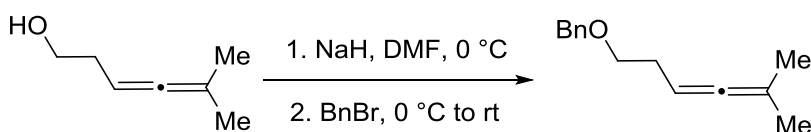
¹³C NMR (δ, ppm) 208.6, 90.3, 74.6, 31.8, 29.3, 28.9, 28.4, 22.8, 14.2 (75 MHz, CDCl₃)

Spectroscopic data are in agreement with those reported in the literature.¹²

(((5-Methylhexa-3,4-dien-1-yl)oxy)methyl)benzene (3m)



This substrate was prepared according to a literature procedure.¹³



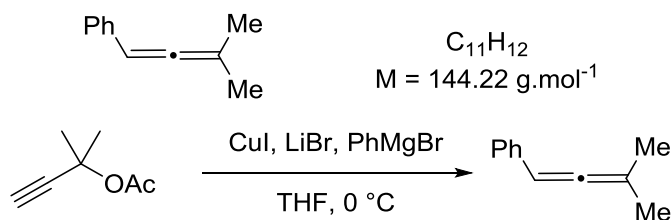
To a solution of NaH (60% in grease, 1.5 equiv, 2.67 mmol, 106.8 mg) in DMF (10 mL) was added 5-methylhexa-3,4-dien-1-ol (1.0 equiv, 1.78 mmol, 200.0 mg, 0.23 mL) dropwise at 0 °C. After stirring 20 min at 0 °C, benzyl bromide (1.5 equiv, 1.78 mmol, 456.7 mg, 0.32 mL) dropwise and the reaction mixture was stirred overnight while warming up to room temperature. The reaction was quenched by saturated NH₄Cl solution, and extracted with diethyl ether (x3). The organic layers were washed with brine (x3) and dried over Na₂SO₄. The solvents were then evaporated and purification by flash chromatography on silica gel (eluent: PE/Et₂O 97.5/2.5) afforded the pure product as a colourless oil (282.8 mg, 1.40 mmol, 79% yield).

¹H NMR (δ, ppm) 7.36 – 7.26 (s, 5H), 5.02 – 4.94 (m, 1H), 4.52 (s, 2H), 3.53 (t, *J* = 6.9 Hz, 2H), 2.28 (q, *J* = 6.8 Hz, 2H), 1.67 (d, *J* = 2.9 Hz, 6H)

¹³C NMR (δ, ppm) 202.5, 138.7, 128.5, 127.8, 127.6, 95.4, 85.4, 73.0, 70.3, 29.9, 20.8 (75 MHz, CDCl₃)

Spectroscopic data are in agreement with those reported in the literature.¹³

(3-Methylbuta-1,2-dien-1-yl)benzene (3n)



To a solution of CuI (3 equiv, 28 mmol, 5.33 g) and LiBr (3 equiv, 28 mmol, 2.43 g) in THF (60 mL) at 0 °C was added dropwise phenylmagnesium bromide (2.8 mol.L⁻¹ in Et₂O, 3 equiv, 28 mmol, 10 mL). After 25 min stirring at 0 °C, 2-methylbut-3-yn-2-yl acetate (1 equiv, 9.33 mmol, 1.18 g) in solution in THF (15 mL) was added dropwise and the reaction mixture was stirred 2 h at the same temperature. The reaction was quenched by saturated NH₄Cl solution, and extracted with diethyl ether (x3). The organic layers were washed successively with HCl 1 mol.L⁻¹ and water, and were then dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash chromatography on silica gel (eluent: pure PE) followed by Kugelrohr distillation (19 mbar, 120 °C) afforded the desired product as a colourless oil (94% purity (biphenyl as by-product), 736 mg, 5.11 mmol, 55% yield).

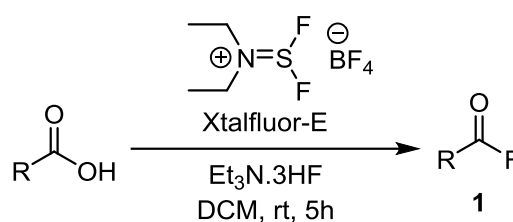
¹H NMR (δ, ppm) 7.28 – 7.24 (m, 4H), 7.18 – 7.12 (m, 1H), 5.98 (hept, *J* = 2.9 Hz, 1H), 1.81 (d, *J* = 2.9 Hz, 6H)

^{13}C NMR (δ , ppm) 203.3, 136.1, 128.6, 126.7, 126.5, 99.3, 92.7, 20.4
(75 MHz, CDCl_3)

Spectroscopic data are in agreement with those reported in the literature.¹⁴

Preparation of the acyl fluorides

Procedure B:

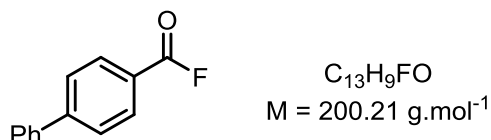


All acid fluorides were synthesized using a literature procedure¹⁵ with little modification.

To a stirred suspension of diethylaminodifluorosulfonium tetrafluoroborate (1.0 equiv) in dichloromethane (6.25 mL/mmol substrate) at room temperature was added the carboxylic acid (1.0 equiv) and triethylamine trihydrofluoride (1.0 equiv). The resulting mixture was stirred under nitrogen for 5 h at room temperature. The reaction was then quenched with a 5% NaHCO_3 aqueous solution, stirred for 15 minutes, until the effervescence ceased and the resulting mixture was extracted twice using DCM. The organic phases were combined, dried over Na_2SO_4 , filtered and concentrated. The crude mixture was purified by flash chromatography.

HRMS spectra of acyl fluorides could not be obtained using standard ionization methods due to the lack of stability of these compounds in these conditions.

[1,1'-Biphenyl]-4-carbonyl fluoride (1b)



Following procedure B starting with [1,1'-biphenyl]-4-carboxylic acid.

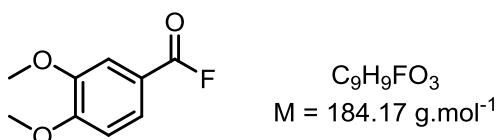
Flash chromatography: PE/EtOAc 95:5

Yield: 688 mg (86% yield) of a white solid.

^1H NMR (δ , ppm) 8.08 (d, $J = 9.0$ Hz, 2H), 7.70 – 7.75 (m, 2H), 7.59 – 7.63 (m, 2H),

(300 MHz, CDCl ₃)	7.41 – 7.50 (m, 3H)
¹³C NMR (δ, ppm) (75 MHz, CDCl ₃)	157.5 (d, J_{C-F} = 341.2 Hz), 148.2, 139.4, 132.1 (d, J_{C-F} = 3.7 Hz), 129.2, 128.9, 127.8, 127.5, 123.6 (d, J_{C-F} = 60.7 Hz)
¹⁹F NMR (δ, ppm) (282 MHz, CDCl ₃ , C ₆ F ₆)	14.9
IR (cm ⁻¹ , neat)	1936, 1927, 1767, 1720, 1607, 1566, 1487, 1450, 1406, 1342, 1277, 1254, 1200, 1182, 1173, 1126, 1076, 1028, 1001, 910.

3,4-Dimethoxybenzoyl fluoride (1c)



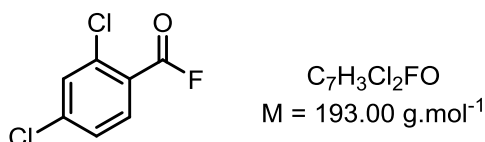
Following procedure B starting with 3,4-dimethoxybenzoic acid.

Flash chromatography: PE/Et₂O 95:5 to 9:1 to 8:2

Yield: 560 mg (61% yield) of a white solid.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	7.71 (dd, J = 8.5, 2.0 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	157.5 (d, J_{C-F} = 340.0 Hz), 155.1, 149.2, 126.4 (d, J_{C-F} = 2.9 Hz), 117.0 (d, J_{C-F} = 62.1 Hz), 113.2 (d, J_{C-F} = 4.5 Hz), 110.8, 56.3, 56.2
¹⁹F NMR (δ, ppm) (282 MHz, CDCl ₃ , C ₆ F ₆)	12.5
IR (cm ⁻¹ , neat)	2841, 1782, 1596, 1515, 1464, 1439, 1418, 1354, 1275, 1246, 1209, 1190, 1167, 1142, 1132, 1065, 1038, 1013, 901, 879, 858, 820

2,4-Dichlorobenzoyl fluoride (1d)



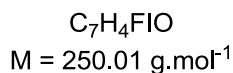
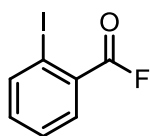
Following procedure B starting with 2,4-dichlorobenzoic acid.

Flash chromatography: PE/EtOAc 95:5

Yield: 645 mg (84% yield) of a white solid.

¹H NMR (δ, ppm) (500 MHz, CDCl ₃)	7.94 (d, <i>J</i> = 10.0 Hz, 1H), 7.55 (t, <i>J</i> = 5.0 Hz, 1H), 7.37 (dd, <i>J</i> = 10.0, 5.0 Hz, 1H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	153.8 (d, <i>J</i> _{C-F} = 341.2 Hz), 141.8, 138.1 (d, <i>J</i> _{C-F} = 4.5 Hz), 134.6 (d, <i>J</i> _{C-F} = 2.2 Hz), 132.14 (d, <i>J</i> _{C-F} = 3.7 Hz), 127.8, 122.1 (d, <i>J</i> _{C-F} = 62.2 Hz)
¹⁹F NMR (δ, ppm) (282 MHz, CDCl ₃ , C ₆ F ₆)	28.8
IR (cm ⁻¹ , neat)	1816, 1730, 1697, 1585, 1555, 1470, 1375, 1261, 1225, 1203, 1153, 1109, 1074, 999, 870

2-Iodobenzoyl fluoride (1e)



Following procedure B starting with 2-iodobenzoic acid.

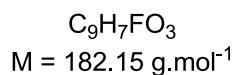
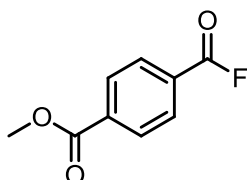
Flash chromatography: PE/EtOAc 95:5

Yield: 610 mg (61% yield) of a white solid.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	8.10 (d, <i>J</i> = 6.0 Hz, 1H), 7.99 (d, <i>J</i> = 9.0 Hz, 1H), 7.48 (t, <i>J</i> = 9.0 Hz, 1H), 7.24-7.30 (m, 1H)
¹³C NMR (δ, ppm) (75 MHz, CDCl ₃)	155.4 (d, <i>J</i> _{C-F} = 343.5 Hz), 142.8 (d, <i>J</i> _{C-F} = 3.7 Hz), 135.3, 133.5, 128.54, 128.48 (d, <i>J</i> _{C-F} = 58.5 Hz), 97.3

Spectroscopic data are in agreement with those reported in the literature¹⁶

Methyl 4-(fluorocarbonyl)benzoate (1f)



Following procedure B starting with 4-(methoxycarbonyl)benzoic acid.

Flash chromatography: PE/Et₂O 9:1 to 1:1

Yield: 422 mg (46% yield) of a white solid.

¹H NMR (δ, ppm)	8.18 – 8.15 (m, 2H), 8.11 – 8.09 (m, 2H), 3.96 (s, 3H)
-----------------------------------	--

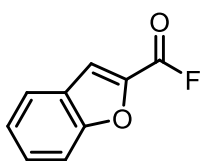
(300 MHz, CDCl₃)

¹³C NMR (δ, ppm) 165.7, 156.6 (d, J_{C-F} = 345.7 Hz), 136.1, 131.5 (d, J_{C-F} = 3.5 Hz),
(125 MHz, CDCl₃) 130.2, 128.7 (d, J_{C-F} = 61.7 Hz), 52.8

¹⁹F NMR (δ, ppm) 16.9
(282 MHz, CDCl₃,
C₆F₆)

IR 1811, 1717, 1612, 1578, 1502, 1441, 1410, 1256, 1238, 1196, 1109,
(cm⁻¹, neat) 1024, 1011, 959, 874, 831

Benzofuran-2-carbonyl fluoride (1g)



C₉H₅FO₂
M = 164.14 g.mol⁻¹

Following procedure B starting with benzo-furan-2-carboxylic acid.

Flash chromatography: PE/Et₂O 95:5

Yield: 597 mg (73% yield) of a white solid.

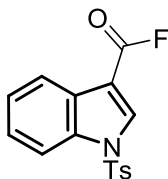
¹H NMR (δ, ppm) 7.76 – 7.74 (m, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2,
(500 MHz, CDCl₃) 1.2 Hz, 1H), 7.40 – 7.36 (m, 1H)

¹³C NMR (δ, ppm) 157.0, 149.5 (d, J_{C-F} = 329.9 Hz), 139.9 (d, J_{C-F} = 89.5 Hz), 129.6,
(125 MHz, CDCl₃) 126.4, 124.7, 123.7, 119.5, 112.7

¹⁹F NMR (δ, ppm) 14.2
(282 MHz, CDCl₃,
C₆F₆)

IR 1801, 1738, 1699, 1614, 1556, 1541, 1477, 1443, 1350, 1327, 1294,
(cm⁻¹, neat) 1275, 1209, 1161, 1136, 1047, 929, 885, 862, 837, 806

1-Tosyl-1H-indole-3-carbonyl fluoride (1h)



C₁₆H₁₂FNO₃S
M = 317.33 g.mol⁻¹

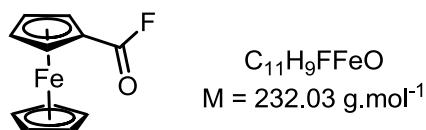
Following procedure B starting with 1-tosyl-1H-indole-3-carboxylic acid.

Flash chromatography: PE/EtOAc 85:15 to 65:35

Yield: 431 mg (34% yield) of a colorless crystals.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	8.38 (s, 1H), 8.07 – 8.04 (m, 1H), 7.99 (dd, <i>J</i> = 6.0, 3.0 Hz, 1H), 7.86 (d, <i>J</i> = 9.0 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.31 (d, <i>J</i> = 9.0 Hz, 2H), 2.39 (s, 3H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	153.4 (d, <i>J</i> _{C-F} = 330.7 Hz), 146.6, 135.0, 134.2, 130.6, 127.5, 127.4, 127.3, 126.4, 125.2, 121.7, 113.7, 107.9 (d, <i>J</i> _{C-F} = 69 Hz), 21.8
¹⁹F NMR (δ, ppm) (282 MHz, CDCl ₃ , C ₆ F ₆)	27.1
IR (cm ⁻¹ , neat)	1801, 1699, 1595, 1541, 1481, 1446, 1379, 1294, 1170, 1134, 1085, 1047, 993, 968, 937, 910, 831

Ferrocenoyl fluoride (*II*)



Following procedure B starting with ferrocenecarboxylic acid.

Flash chromatography: PE/EtOAc 95:5

Yield: 1.78 g (93%) of a red color solid.

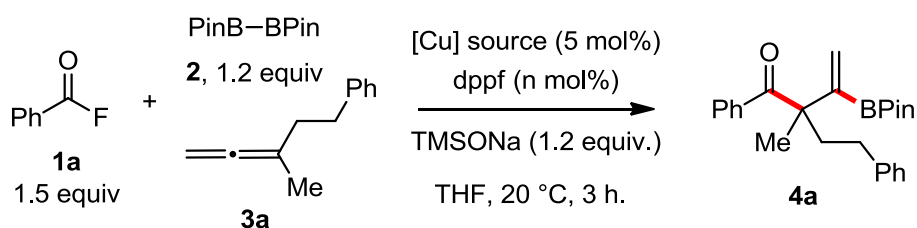
¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	4.83 (t, <i>J</i> = 3.0 Hz, 2H), 4.54 (q, <i>J</i> = 3.0 Hz, 2H), 4.28 (s, 5H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	163.2 (d, <i>J</i> _{C-F} = 332.2 Hz), 73.4, 71.3 (d, <i>J</i> _{C-F} = 2.2 Hz), 70.6, 63.8 (d, <i>J</i> _{C-F} = 70.5 Hz)
¹⁹F NMR (δ, ppm) (282 MHz, CDCl ₃ , C ₆ F ₆)	24.4
IR (cm ⁻¹ , neat)	1798, 1452, 1411, 1375, 1354, 1317, 1267, 1142, 1107, 1072, 1030, 1001, 912, 893, 825

Copper-catalyzed boroacylation of allenes

Standard procedure for the optimization of the reaction conditions

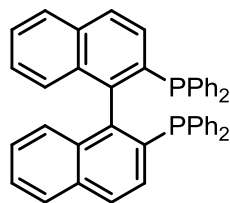
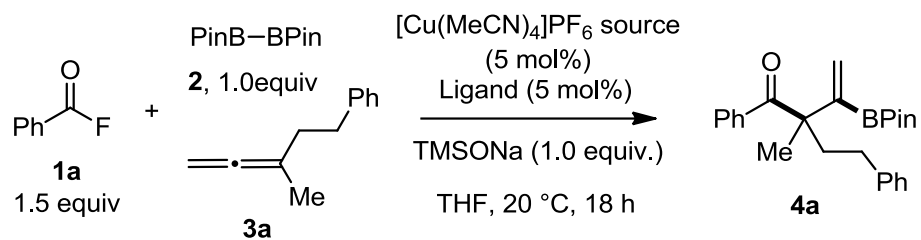
A flame-dried Schlenk was loaded with the copper catalyst (0.05 equiv, 0.015 mmol) and the ligand. After 3 vacuum/argon cycles, THF (0.5 mL) was added until the solids were dissolved. To the obtained blue/green solution was added TMSONa (1 M in THF, 1.0/1.2 equiv, 0.30/0.36 mmol). Bispinacolatodiboron **2** (1.0/1.2 equiv (same than TMSONa), 0.30/0.36 mmol) in solution in THF (0.5 mL) was added to the resulting yellow solutions and the mixture immediately turned into a brown slurry. The allene **3** (1.0 equiv, 0.3 mmol) and the acyl fluoride **1** (1.5 equiv, 0.45 mmol) were simultaneously added in solution in THF (0.5 mL). The mixture was stirred for 3 h at room temperature. The reaction mixture was filtered through silica (eluent: Et₂O + 1% NEt₃) and the solvents were removed under reduced pressure. 3,4,5-trimethoxybenzaldehyde was added as an internal standard and the yield was determined using ¹H NMR spectroscopy.

Optimization of the copper source

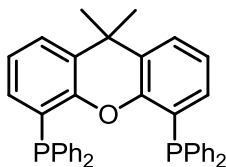


Entry	[Cu] source	n	Yield (%)
1	[Cu(MeCN) ₄]PF ₆	5	61
2	CuOAc	5	< 3
3	Cu(OAc) ₂	7.5	73
4	CuI	5	< 3
5	CuF(PPh ₃) ₃ ·2MeOH	5	73
6	(dppe)CuDBM	0	5
7	[(dppe)CuCl] ₂	0	55

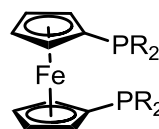
Optimization of the ligand with [Cu(MeCN)₄]PF₆ as a standard copper source



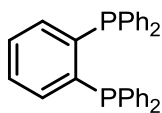
rac-binap (**L1**)



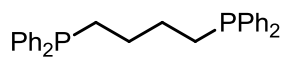
Xantphos (**L2**)



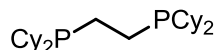
dppf (**L3**), R = Ph
L4, R = Cy



L5



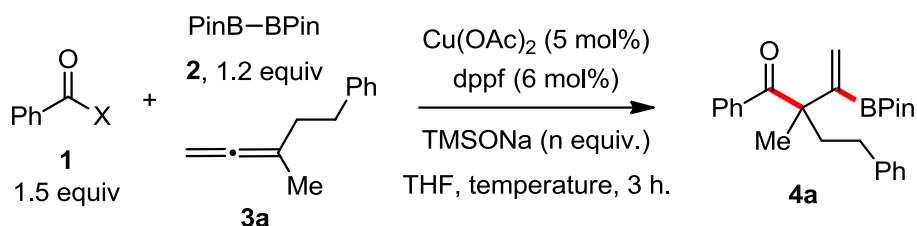
L6



L7

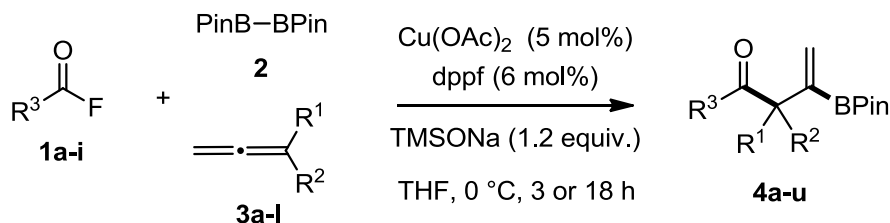
Entry	Ligand	Time (h)	Yield (%)
1	<i>rac</i> -binap L1	18	37
2	xantphos L2	18	< 3
3	dppf L3	18	58
4	L4	3	5
5	L5	3	10
6	L6	3	15
7	L7	3	30
8	PPh ₃ (10 mol%)	3	< 3
9	PCy ₃ (10 mol%)	3	5

Test of the other parameters



Entry	T (°C)	n	X	Comment	Yield (%)
1	20 °C	1.2	F	/	62
2	20 °C	1.2	F	B ₂ Pin ₂ was added at the end	< 3
3	0 °C	1.2	F	The reaction was cooled down to 0 °C after the addition of TMSNa	87
4	0 °C	0.2	F		11
5	0 °C	0	F		< 3
6	0 °C	0	Cl		10
7	0 °C	0	OBz		44

Scope of the reaction: procedure C:



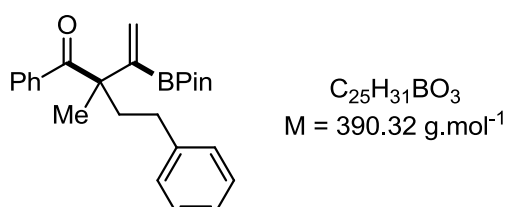
A flame-dried Schlenk was loaded with anhydrous copper(II) acetate (0.05 equiv, 0.025 mmol, 4.5 mg) and 1,1'-bis(diphenylphosphino)ferrocene (0.06 equiv, 0.030 mmol, 16.6 mg). After 3 vacuum/argon cycles, THF (0.8 mL) was added until the solids were dissolved. To the obtained blue/green solution was added TMSNa (1 M in THF, 1.2 equiv, 0.6 mmol, 0.6 mL). The resulting yellow solution was cooled down to 0 °C in a water/ice bath. Bispinacolotodiboron **2** (1.2 equiv, 0.6 mmol, 152.4 mg) in solution in THF (0.8 mL) was added and the mixture immediately turned into a brown slurry. The allene **3** (1.0 equiv, 0.5 mmol) and the acyl fluoride **1** (1.5 equiv, 0.75 mmol) were simultaneously added in solution in THF (0.8 mL).

Procedure C₁: The mixture was stirred for 3 h at 0 °C.

Procedure C₂: The mixture was stirred for 18 h while warming up to room temperature.

The reaction mixture was filtered through silica (eluent: Et₂O + 1% NEt₃) and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel afforded the desired product **4**.

2-Methyl-2-phenethyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4a)



Following procedure C₁ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 155.1 mg (80% yield) of a slightly yellow oil.

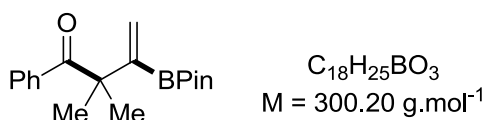
¹H NMR (δ, ppm) 7.93 – 7.91 (m, 2H), 7.44 – 7.41 (m, 1H), 7.35 – 7.32 (m, 2H), 7.25 – 7.22 (m, 2H), 7.15 – 7.10 (m, 3H), 6.10 (d, *J* = 2.2 Hz, 1H), 5.90 (d, *J* = 2.2 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.39 – 2.33 (m, 1H), 2.27 – 2.21 (m, 2H), 1.52 (s, 3H), 1.00 (s, 6H), 1.00 (s, 6H)

¹³C NMR (δ, ppm) 203.9, 142.9, 137.7, 131.7, 129.6, 128.5, 128.4, 128.0, 127.8, 125.8, 81.7, 54.8, 40.2, 31.1, 24.6, 24.4, 24.0
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2978, 2928, 1680, 1597, 1578, 1497, 1447, 1412, 1371, 1354, 1315, 1271, 1242, 1213, 1167, 1140, 1103, 1029, 1003, 967, 945

MS (HRMS APCI) Calcd for [M+H]⁺ C₂₅H₃₂O₃B: 391.2439 Found: 391.2440

2,2-Dimethyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4b)



Following procedure C₁ starting with 0.5 mmol 3-methyl-1,2-butadiene (**3b**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 107.5 mg (72% yield) of a yellow oil.

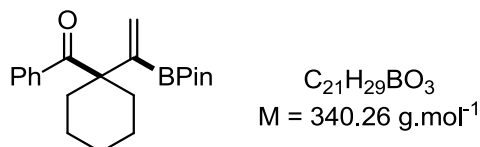
¹H NMR (δ, ppm) 7.91 – 7.88 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.29 (m, 2H), 5.98 (d, *J* = 2.3 Hz, 1H), 5.89 (d, *J* = 2.1 Hz, 1H), 1.45 (s, 6H), 0.97 (s, 12H)

¹³C NMR (δ, ppm) 204.6, 137.2, 131.6, 129.7, 127.9, 126.3, 83.7, 51.4, 26.8, 24.5
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2976, 1682, 1597, 1578, 1466, 1447, 1410, 1371, 1352, 1313, 1256, 1213, 1167, 1140, 1103, 1013, 1003, 968, 937, 876, 849

MS (HRMS APCI) Calcd for [M+H]⁺ C₁₈H₂₆O₃B: 301.1970 Found: 301.1969

Phenyl(1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexyl)methanone (4c)



Following procedure C₁ starting with 0.5 mmol vinylidenecyclohexane (**3c**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 124.6 mg (73%) of a colourless oil.

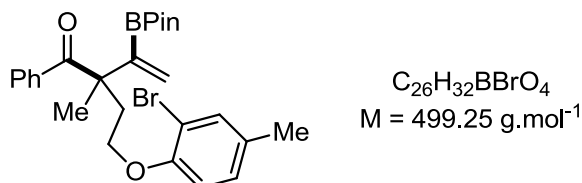
¹H NMR (δ, ppm) 7.80 – 7.77 (m, 2H), 7.43 – 7.37 (m, 1H), 7.35 – 7.28 (m, 2H), 5.96 (d, *J* = 2.0 Hz, 1H), 5.77 (d, *J* = 1.8 Hz, 1H), 2.28 – 2.22 (m, 2H), 1.80 – 1.71 (m, 2H), 1.57 – 1.24 (m, 6H), 1.18 (s, 12H)

¹³C NMR (δ, ppm) 205.3, 138.4, 131.1, 129.3, 129.1, 127.8, 83.7, 56.1, 34.8, 26.0, 24.7, 23.2
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2955, 1674, 1597, 1578, 1447, 1421, 1371, 1346, 1310, 1275, 1225, 1197, 1134, 1076, 1051, 1030, 987, 968, 951, 876, 851

MS (HRMS ESI) Calcd for [M+Na]⁺ C₂₁H₂₉O₃NaB: 363.2102 Found: 363.2099

2-(2-(2-Bromo-4-methylphenoxy)ethyl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4d)



Following procedure C₁ starting with 0.5 mmol 2-bromo-4-methyl-1-((3-methylpenta-3,4-dien-1-yl)oxy)benzene (**3d**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 199.7 mg (79%) of a slightly yellow oil.

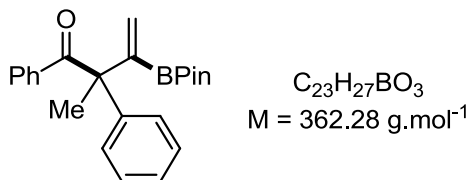
¹H NMR (δ, ppm) 7.96 – 7.92 (m, 2H), 7.43 – 7.35 (m, 1H), 7.35 – 7.26 (m, 3H), 6.99 (ddd, *J* = 8.3, 2.2, 0.8 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.12 (d, *J* = 2.1 Hz, 1H), 5.97 (d, *J* = 2.1 Hz, 1H), 4.07 (ddd, *J* = 9.7, 8.1, 5.8 Hz, 1H), 3.92 (ddd, *J* = 9.7, 8.0, 6.9 Hz, 1H), 2.54 – 2.38 (m, 2H), 2.24 (s, 3H), 1.60 (s, 3H), 0.97 (s, 6H), 0.95 (s, 6H)

¹³C NMR (δ, ppm) 203.2, 153.3, 136.9, 133.7, 131.9, 131.2, 129.8, 128.8, 128.4, 128.1, 113.2, 111.8, 83.8, 66.3, 53.5, 37.5, 24.6, 24.5, 24.4, 20.3
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2976, 2935, 1678, 1605, 1578, 1495, 1468, 1447, 1412, 1371, 1354, 1316, 1275, 1252, 1213, 1182, 1140, 1103, 1049, 1003, 966, 866, 851, 800

MS Calcd for [M+H]⁺ C₂₆H₃₃O₄BBr: 499.1651 Found: 499.1653
(HRMS APCI)

2-Methyl-1,2-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4e)



Following procedure C₁ starting with 0.5 mmol buta-2,3-dien-2-ylbenzene (**3e**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

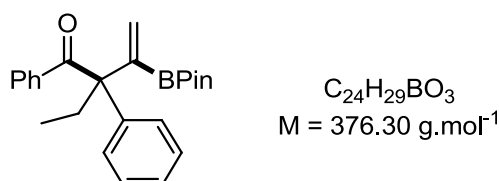
Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 120.1 mg (66% yield) of a white solid.

¹H NMR (δ, ppm) 7.45 – 7.20 (m, 10H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.79 (d, *J* = 2.5 Hz,

(300 MHz, CDCl ₃)	1H), 1.87 (s, 3H), 1.32 (s, 6H), 1.31 (s, 6H)
¹³C NMR (δ, ppm) (75 MHz, CDCl ₃)	204.2, 141.6, 137.2, 131.6, 129.5, 128.7, 128.3, 128.0, 127.2, 127.0, 83.4, 61.3, 25.2, 24.6, 24.2 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	2982, 1672, 1614, 1597, 1578, 1458, 1447, 1410, 1371, 1350, 1304, 1248, 1215, 1143, 1113, 1099, 1068, 1028, 1001, 968
MS (HRMS APCI)	Calcd for [M+H] ⁺ C ₂₃ H ₂₈ O ₃ B: 363.2126 Found: 363.2123

2-Ethyl-1,2-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4f)



Following procedure C₁ starting with 0.5 mmol penta-1,2-dien-3-ylbenzene (**3f**),

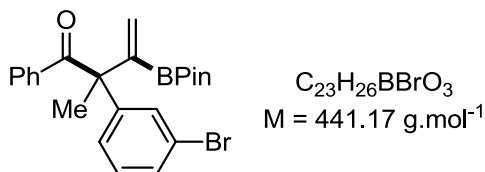
bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 114.9 mg (61%) of a slightly yellow oil.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	7.43 – 7.17 (m, 10H), 5.83 (d, <i>J</i> = 2.3 Hz, 1H), 5.05 (d, <i>J</i> = 2.2 Hz, 1H), 2.43 (dq, <i>J</i> = 14.5, 7.3 Hz, 1H), 2.29 (dq, <i>J</i> = 14.9, 7.5 Hz, 1H), 1.30 (s, 6H), 1.30 (s, 6H), 0.87 (t, <i>J</i> = 7.4 Hz, 3H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	203.8, 141.7, 137.4, 131.6, 129.5, 128.7, 128.6, 128.0, 127.6, 127.0, 83.2, 65.5, 28.2, 25.0, 24.8, 10.5 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	2976, 1668, 1614, 1597, 1578, 1447, 1408, 1371, 1352, 1296, 1273, 1234, 1215, 1180, 1138, 1111, 1082, 1081, 1034, 1009, 968, 881, 860, 841
MS (HRMS ESI)	Calcd for [M+H] ⁺ C ₂₄ H ₃₀ O ₃ B: 377.2283 Found: 377.2282

2-(3-Bromophenyl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4g)



Following procedure C₁ starting with 0.5 mmol 1-bromo-3-(buta-2,3-dien-2-yl)benzene (**3g**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 112.4 mg (51% yield) of a white solid.

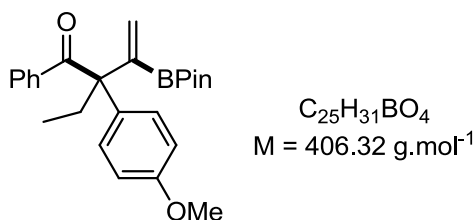
¹H NMR (δ, ppm) 7.54 – 7.53 (m, 1H), 7.46 – 7.37 (m, 4H), 7.27 – 7.19 (m, 4H), 5.76 (d, *J* = 2.2 Hz, 1H), 4.81 (d, *J* = 2.2 Hz, 1H), 1.85 (s, 3H), 1.30 (s, 6H), 1.29 (s, 6H)

¹³C NMR (δ, ppm) 203.4, 144.2, 136.8, 131.8, 131.1, 130.4, 130.2, 129.4, 128.2, 127.3, 127.1, 123.0, 83.5, 61.1, 25.2, 25.0, 24.2
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 1674, 1614, 1593, 1564, 1474, 1447, 1410, 1371, 1348, 1306, 1271, 1244, 1215, 1163, 1142, 1107, 1059, 997, 912, 912, 868, 847

MS (HRMS APCI) Calcd for [M+H]⁺ C₂₃H₂₇O₃BBr: 441.1232 Found: 440.1231

2-Ethyl-1-(4-methoxyphenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4h)



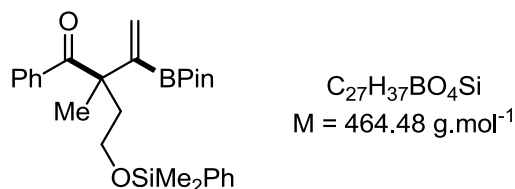
Following procedure C₁ starting with 0.5 mmol 1-methoxy-4-(penta-1,2-dien-3-yl)benzene (**3h**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 120.2 mg (60%) of a yellow oil.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	7.42 – 7.20 (m, 7H), 6.89 – 6.84 (m, 2H), 5.83 (d, <i>J</i> = 2.3 Hz, 1H), 5.08 (d, <i>J</i> = 2.3 Hz, 1H), 3.80 (s, 3H), 2.45 – 2.20 (m, 2H), 1.32 (s, 6H), 1.31 (s, 6H), 0.86 (t, <i>J</i> = 7.4 Hz, 3H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	204.1, 158.5, 137.7, 133.4, 131.4, 129.9, 129.5, 128.0, 127.5, 114.0, 83.2, 64.9, 55.3, 28.1, 25.0, 24.8, 10.5 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	2982, 2939, 2839, 1666, 1609, 1578, 1510, 1464, 1447, 1410, 1371, 1354, 1296, 1252, 1111, 1034, 1011, 968, 945, 881, 864, 825
MS (HRMS ESI)	Calcd for [M+H] ⁺ C ₂₅ H ₃₂ O ₄ B: 407.2389 Found: 407.2389

2-(2-((Dimethyl(phenyl)silyl)oxy)ethyl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4i)



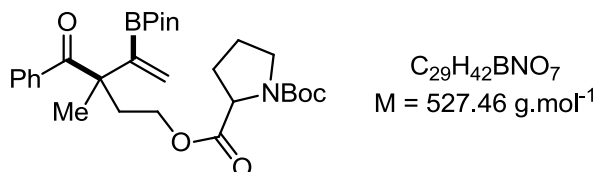
Following procedure C₁ starting with 0.5 mmol dimethyl((3-methylpenta-3,4-dien-1-yl)oxy)(phenyl)silane (**3i**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 133.7 mg (58% yield) of a yellow oil.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	7.90 – 7.86 (m, 2H), 7.53 – 7.51 (m, 2H), 7.45 – 7.29 (m, 6H), 6.02 (d, <i>J</i> = 2.2 Hz, 1H), 5.84 (d, <i>J</i> = 2.2 Hz, 1H), 3.64 (dt, <i>J</i> = 10.3, 7.2 Hz, 1H), 3.51 (dt, <i>J</i> = 10.3, 7.5 Hz, 1H), 2.27 – 2.22 (m, 2H), 1.43 (s, 3H), 0.97 (s, 6H), 0.97 (s, 6H), 0.31 (s, 6H)
¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	203.2, 138.1, 137.3, 133.6, 131.6, 129.6, 129.6, 127.9, 127.9, 127.5, 83.7, 60.0, 53.3, 40.7, 24.5 (2C), 24.4, -1.73, -1.66 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	2970, 2332, 1680, 1597, 1578, 1447, 1427, 1412, 1371, 1354, 1315, 1252, 1215, 1188, 1142, 1115, 1084, 1043, 1003, 966, 949, 849, 827
MS (HRMS APCI)	Calcd for [M+H] ⁺ C ₂₇ H ₃₈ O ₄ BSi: 465.2628 Found: 465.2632

2-(3-Benzoyl-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl) 1-tert-butyl pyrrolidine-1,2-dicarboxylate (4j)



Following procedure C₁ starting with 0.5 mmol 1-(tert-butyl) 2-(3-methylpenta-3,4-dien-1-yl) pyrrolidine-1,2-dicarboxylate (**3j**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 8:2 + 1% Et₃N.

Yield: 113.3 mg (43% yield) of a yellow oil.

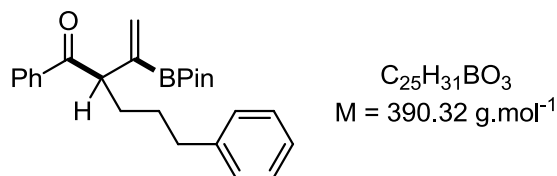
¹H NMR (δ, ppm) 7.90 – 7.87 (m, 2H), 7.45 – 7.30 (m, 3H), 6.12 – 6.09 (m, 1H), 5.91 – 5.90 (m, 1H), 4.23 – 4.01 (m, 3H), 3.53 – 3.33 (m, 2H), 2.30 – 2.06 (m, 3H), 1.94 – 1.81 (m, 3H), 1.52 (s, 3H, major), 1.50 (s, 3H, minor), 1.44 – 1.39 (m, 9H), 0.97 (s, 12H, minor), 0.96 (s, 12H, major)

¹³C NMR (δ, ppm) 202.9, 173.2 (major, C_a), 172.9 (minor, C_a), 154.5 (minor, C_b), 154.0 (major, C_b), 137.0 (major, C_c), 137.0 (minor, C_c), 131.9 (major, C_d), 131.8 (minor, C_d), 129.7, 128.5 – 128.4 (m), 128.0, 83.9 (major, C_e), 83.8 (minor, C_e), 79.9 (major, C_f), 79.8 (minor, C_f), 62.4 (major, C_g), 62.3 (minor, C_g), 59.3 (major, C_h), 59.0 (minor, C_h), 53.4 (minor, C_i), 53.3 (major, C_i), 46.7 (minor, C_j), 46.4 (major, C_j), 36.9 (minor, C_k), 36.8 (major, C_k), 30.9, 29.9, 28.6 (minor, C_l), 28.5 (major, C_l), 24.6 – 24.3, 23.9 – 23.8 (m)
 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2989, 1745, 1682, 1597, 1578, 1539, 1447, 1393, 1354, 1317, 1260, 1165, 1088, 1093, 996, 918, 878, 851

MS (HRMS ESI) Calcd for [M+H]⁺ C₂₉H₄₃O₇NB: 528.3129 Found: 528.3128

1,5-Diphenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pentan-1-one (4k)



Following procedure C₁ starting with 0.5 mmol hexa-4,5-dien-1-ylbenzene (**3k**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Only a small fraction of the product could be obtained pure after flash chromatography over silica. An NMR yield using 3,4,5-trimethoxybenzaldehyde was determined (see spectrum below).

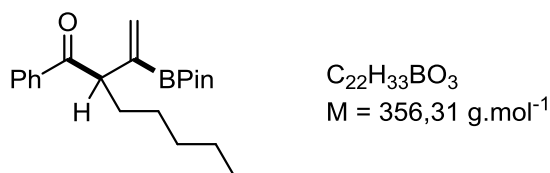
¹H NMR (δ, ppm) 7.98 – 7.95 (m, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.37 (m, 2H), 7.27 – 7.23 (m, 2H), 7.18 – 7.15 (m, 3H), 5.92 (d, *J* = 2.4 Hz, 1H), 5.67 (d, *J* = 2.0 Hz, 1H), 4.29 – 4.25 (m, 1H), 2.68 – 2.60 (m, 2H), 2.00 – 1.95 (m, 1H), 1.73 – 1.63 (m, 3H, H), 1.27 (s, 6H), 1.25 (s, 6H)

¹³C NMR (δ, ppm) 200.8, 142.6, 137.1, 132.7, 131.9, 128.8, 128.5, 128.4, 128.3, 125.7, 84.0, 50.1, 36.0, 32.5, 29.6, 24.9, 24.8
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

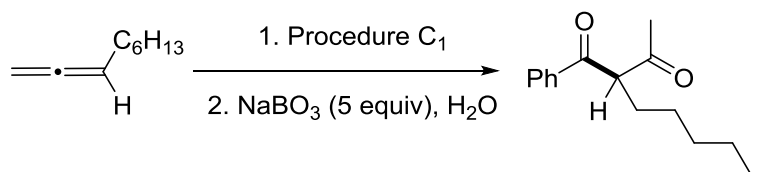
IR (cm⁻¹, neat) 3057, 2964, 2920, 2851, 1718, 1684, 1597, 1446, 1356, 1343, 1250, 1217, 1134, 1078, 966

MS (HRMS ESI) Calcd for [M+H]⁺ C₂₅H₃₂O₃B: 391.2439 Found: 391.2441

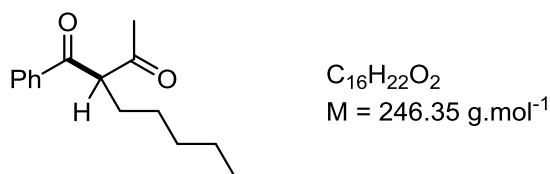
1-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)octan-1-one (4l)



Because of the low stability of this compound in the presence of silica gel or alumina, a modified procedure was used: the obtained product was directly oxidized into the corresponding ketone, which was isolated and characterized.



2-Hexyl-1-phenylbutane-1,3-dione (5l)



A flame-dried Schlenk was loaded with anhydrous copper(II) acetate (0.05 equiv, 0.025 mmol, 4.5 mg) and 1,1'-bis(diphenylphosphino)ferrocene (0.06 equiv, 0.030 mmol, 16.6 mg).

After 3 vacuum/argon cycles, THF (0.8 mL) was added until the solids were dissolved. To the obtained blue/green solution was added TMSNa (1 M in THF, 1.2 equiv, 0.6 mmol, 0.6 mL). The resulting yellow solution was cooled down to 0 °C in a water/ice bath. Bispinacolatodiboron **2** (1.2 equiv, 0.6 mmol, 152.4 mg) in solution in THF (0.8 mL) was added and the mixture immediately turned into a brown slurry. Nona-1,2-diene **3I** (1.0 equiv, 0.5 mmol, 62.1 mg) and benzoyl fluoride (1.5 equiv, 0.75 mmol, 81 µL) were simultaneously added in solution in THF (0.8 mL). After 3 h stirring at 0 °C, water (2.4 mL) and NaBO₃ (5 equiv, 2.5 mmol, 249.5 mg) were added and the mixture was vigorously stirred at room temperature for 3 h. Et₂O and NH₄Cl_(sat) were added and the layers were separated. After extraction with Et₂O, the organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash column chromatography (PE/Et₂O 95 : 5) afforded the pure product as a slightly yellow oil (88.5 mg, 0.362 mmol, 72% yield).

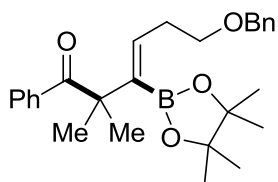
¹H NMR (δ, ppm) 7.99 – 7.97 (m, 2H), 7.59 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 4.42 (t, *J* = 7.1 Hz, 1H), 2.13 (s, 3H), 2.05 – 1.97 (m, 1H), 1.97 – 1.90 (m, 1H), 1.30 – 1.22 (m, 8H), 0.86 – 0.83 (m, 3H)

¹³C NMR (δ, ppm) 204.6, 196.6, 136.7, 133.8, 129.0, 128.8, 63.7, 31.6, 29.3, 29.2, 27.9, 27.8, 22.6, 14.1

IR (cm⁻¹, neat) 2959, 2928, 2856, 1720, 1674, 1597, 1580, 1448, 1356, 1283, 1265, 1211, 1180, 1161, 1117, 1076, 1001, 970, 914

MS (HRMS ESI) Calcd for [M+H]⁺ C₁₆H₂₃O₂: 247.1693 Found: 247.1691

(E)-6-(Benzyloxy)-2,2-dimethyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-1-one (4m)



C₂₇H₃₅BO₄
M = 434.38 g.mol⁻¹

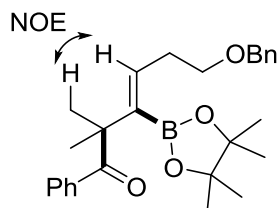
Following procedure C₁ starting with 0.5 mmol (((5-Methylhexa-3,4-dien-1-yl)oxy)methyl)benzene (**3m**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 55.8 mg (26% yield) of a colourless oil.

The stereochemistry was determined by H-H NOESY correlation.

For the only observed isomer, the NOESY spectrum showed a correlation between the vinylic proton and the *gem*-dimethyl protons. This product was assigned to the (*E*)-isomer.



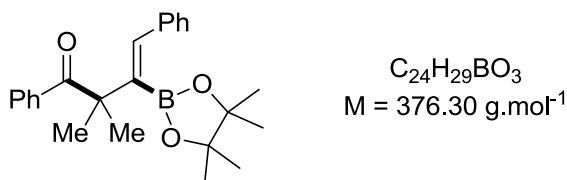
¹H NMR (δ, ppm) 7.92 – 7.89 (m, 2H), 7.41 – 7.25 (m, 8H), 6.24 (t, *J* = 7.4 Hz, 1H), 4.52 (s, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.71 (q, *J* = 6.8 Hz, 2H), 1.42 (s, 6H), 1.07 (s, 12H)

¹³C NMR (δ, ppm) 205.0, 138.9, 138.8, 137.1, 131.4, 129.9, 128.5, 127.8, 127.7, 127.6, 83.4, 72.8, 70.2, 52.0, 31.9, 27.5, 24.8
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2978, 2928, 2893, 1722, 1678, 1624, 1597, 1466, 1447, 1416, 1371, 1360, 1304, 1250, 1213, 1169, 1140, 1099, 1018, 970, 910

MS (HRMS APCI) Calcd for [M+H]⁺ C₂₇H₃₆O₄B: 435.2702 Found: 435.2703

(*E*)-2,2-Dimethyl-1,4-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4n)



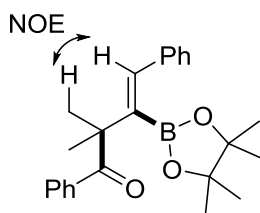
Following procedure C₁ starting with 0.5 mmol (3-methylbuta-1,2-dien-1-yl)benzene (**3n**), bis(pinacolato)diboron (**2**) and benzoyl fluoride (**1a**).

Flash chromatography: pentane/Et₂O 97.5 : 2.5 + 1% Et₃N.

Yield: 30.0 mg (16% yield) of a colourless oil.

The stereochemistry was determined by H-H NOESY correlation.

For the only observed isomer, the NOESY spectrum showed a correlation between the vinylic proton and the *gem*-dimethyl protons. This product was assigned to the (*E*)-isomer.



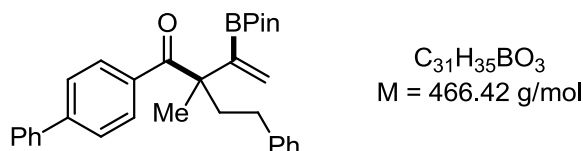
¹H NMR (δ, ppm) 8.00 – 7.98 (m, 2H), 7.46 – 7.42 (m, 1H), 7.39 – 7.36 (m, 2H), 7.32 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 6.88 (s, 1H), 1.50 (s, 6H), 1.18 (s, 12H)

¹³C NMR (δ, ppm) 204.6, 139.0, 138.4, 136.6, 131.7, 130.1, 128.2, 128.1, 128.0, 127.5, 84.1, 52.4, 27.5, 25.1
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 3026, 2976, 2939, 2930, 1724, 1674, 1609, 1597, 1576, 1495, 1464, 1447, 1389, 1373, 1348, 1310, 1252, 1211, 1167, 1140, 1111, 1076, 1011, 974, 920, 883, 854, 829

MS (HRMS APCI) Calcd for [M+H]⁺ C₂₄H₃₀O₃B: 377.2883 Found: 377.2883

1-([1,1'-Biphenyl]-4-yl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4o)



Following procedure C₁ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and [1,1'-biphenyl]-4-carbonyl fluoride (**1b**).

Flash chromatography: PE / EtOAc 95 : 5 + 1% Et₃N

Yield: 184.0 mg (79% yield) of a white solid.

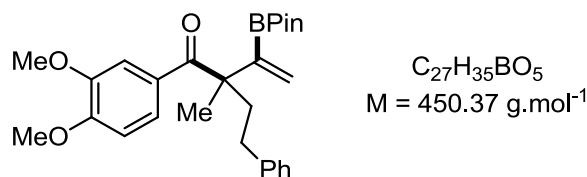
¹H NMR (δ, ppm) 8.06 – 8.03 (m, 2H), 7.63 – 7.59 (m, 4H), 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 6.15 (d, *J* = 2.2 Hz, 1H), 5.95 (d, *J* = 2.2 Hz, 1H), 2.59 (ddd, *J* = 12.4, 9.7, 7.2 Hz, 1H), 2.46 – 2.24 (m, 3H), 1.57 (s, 3H), 1.03 (s, 6H), 1.03 (s, 6H)

¹³C NMR (δ, ppm) 203.3, 144.3, 142.9, 140.2, 136.3, 130.2, 129.0, 128.5, 128.4, 128.1, 127.9, 127.3, 126.6, 125.8, 83.7, 54.8, 40.3, 31.1, 24.6, 24.4, 24.0.
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2974, 2926, 1676, 1603, 1560, 1485, 1448, 1412, 1354, 1313, 1273, 1248, 1215, 1178, 1167, 1140, 1113, 1030, 1007, 966, 912, 878, 851, 835

MS (HRMS ESI) Calcd for [M+H]⁺ C₃₁H₃₆O₃B: 467.2754 Found: 467.2755

1-(2,3-Dimethoxyphenyl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4p)



Following procedure C₁ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and 3,4-dimethoxybenzoyl fluoride (**1c**).

Flash chromatography: Pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 122.7 mg (55% yield) of a white solid.

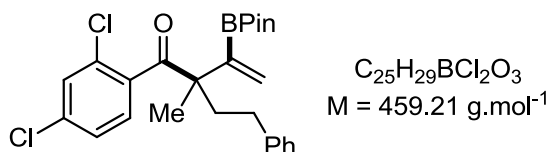
¹H NMR (δ, ppm) (300 MHz, CDCl₃) 7.66 – 7.60 (m, 2H), 7.24 – 7.12 (m, 5H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 5.86 (d, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.61 – 2.52 (m, 1H), 2.37 – 2.19 (m, 3H), 1.50 (s, 3H), 1.00 (s, 6H), 1.00 (s, 6H)

¹³C NMR (δ, ppm) (125 MHz, CDCl₃) 201.8, 152.1, 148.5, 143.0, 130.2, 128.5, 128.4, 126.9, 125.7, 124.1, 112.5, 109.5, 83.7, 56.1, 56.0, 54.4, 40.7, 31.1, 24.6, 24.5, 24.4 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2976, 1799, 1668, 1595, 1583, 1514, 1456, 1412, 1371, 1352, 1315, 1259, 1225, 1213, 1165, 1138, 1024, 968, 947, 866, 847, 816

MS (HRMS ESI) Calcd for [M+H]⁺ C₂₇H₃₆O₅B: 451.2651 Found: 451.2651

1-(2,4-Dichlorophenyl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4q)



Following procedure C₂ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and 2,4-dichlorobenzoyl fluoride (**1d**).

Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 97.1 mg (42%) of a yellow oil.

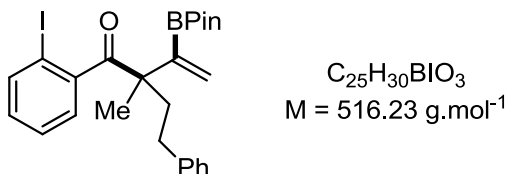
¹H NMR (δ, ppm) 7.39 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.14 (m, 7H), 6.09 (d, *J* = 2.1 Hz, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 2.51 – 2.39 (m, 3H), 2.08 – 1.99 (m, 1H), 1.44 (s, 3H), 1.23 (s, 6H), 1.23 (s, 6H)

¹³C NMR (δ, ppm) 206.2, 142.6, 138.0, 135.4, 132.0, 130.2, 129.9, 129.0, 128.5, 128.4, 126.1, 125.9, 83.8, 57.0, 38.9, 30.8, 24.8, 24.7, 21.1
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 2980, 1693, 1583, 1553, 1497, 1456, 1418, 1371, 1350, 1311, 1265, 1229, 1215, 1167, 1136, 1105, 1059, 962, 851, 824

MS (HRMS ESI) Calcd for [M+H]⁺ C₂₅H₃₀O₃BCl₂: 459.1661 Found: 459.1661

1-(2-Iodophenyl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4r)



Following procedure C₂ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and 2-iodobenzoyl fluoride (**1e**).

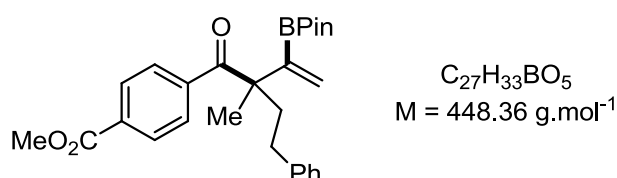
Flash chromatography: pentane/Et₂O 95:5 + 1% Et₃N.

Yield: 128.0 mg (50% yield) of a colourless sticky oil.

¹H NMR (δ, ppm) 7.87 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.20 – 7.15 (m, 3H), 7.04 – 7.01 (m, 1H), 6.06 (d, *J* = 2.1 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 1H), 2.55 – 2.45 (m, 3H), 2.16 – 2.07 (m, 1H), 1.47 (s, 3H), 1.24 (s, 6H), 1.23 (s, 6H)

¹³C NMR (δ, ppm) (125 MHz, CDCl ₃)	208.1, 144.9, 142.9, 140.5, 130.5, 129.4, 128.6, 128.4, 127.7, 127.0, 125.8, 93.1, 83.8, 56.6, 39.6, 31.1, 24.9, 24.8, 21.5 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	2324, 1690, 1607, 1558, 1541, 1497, 1456, 1418, 1371, 1352, 1313, 1275, 1259, 1140, 1016, 966, 851, 764
MS (HRMS ESI)	Calcd for [M+H] ⁺ C ₂₅ H ₃₁ O ₃ BI: 517.1407 Found: 517.1409

Methyl-4-(2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoyl)benzoate (4s)



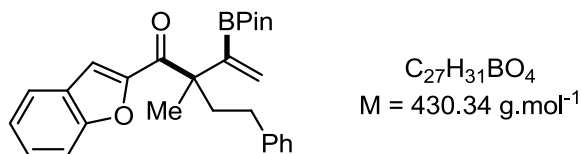
Following procedure C₂ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and methyl 4-(fluorocarbonyl)benzoate (**1f**).

Flash chromatography: PE/Et₂O 9 :1 + 1% Et₃N.

Yield: 101.8 mg (45%) of a yellow solid.

¹H NMR (δ, ppm) (300 MHz, CDCl ₃)	8.03 – 8.00 (m, 2H), 7.97 – 7.94 (m, 2H), 7.27 – 7.09 (m, 5H), 6.14 (d, $J = 2.1$ Hz, 1H), 5.92 (d, $J = 2.0$ Hz, 1H), 3.93 (s, 3H), 2.58 – 2.48 (m, 1H), 2.40 – 2.31 (m, 1H), 2.28 – 2.19 (m, 2H), 1.52 (s, 3H), 1.03 (s, 6H), 1.02 (s, 6H)
¹³C NMR (δ, ppm) (75 MHz, CDCl ₃)	203.6, 166.6, 142.7, 141.4, 132.4, 129.3, 129.2, 128.6, 128.5, 128.5, 125.8, 83.9, 55.0, 52.5, 40.1, 31.0, 24.6, 24.5, 23.7 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)
IR (cm ⁻¹ , neat)	3078, 3030, 2976, 2935, 1726, 1682, 1605, 1568, 1497, 1454, 1434, 1414, 1353, 1315, 1275, 1238, 1215, 1190, 1167, 1138, 1105, 1030, 1018, 966, 906, 878
MS (HRMS ESI)	Calcd for [M+H] ⁺ C ₂₇ H ₃₄ O ₅ B: 449.2495 Found: 449.2495

1-(Benzofuran-2-yl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4t)



Following procedure C₂ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and benzofuran-2-carboxylic acid (**1g**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 83.4 mg (39% yield) of a white solid.

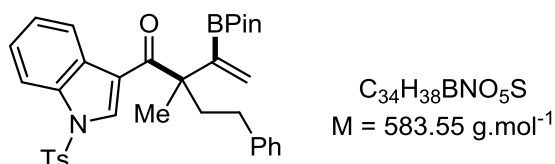
¹H NMR (δ, ppm) 7.66 – 7.63 (m, 1H), 7.58 – 7.55 (m, 1H), 7.46 – 7.40 (m, 2H), 7.30 – 7.23 (m, 3H), 7.18 – 7.13 (m, 3H), 6.19 (d, *J* = 2.2 Hz, 1H), 5.98 (d, *J* = 2.1 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.48 – 2.38 (m, 1H), 2.30 – 2.24 (m, 2H), 1.55 (s, 3H), 1.02 (s, 6H), 1.01 (s, 6H)

¹³C NMR (δ, ppm) 194.0, 154.9, 151.8, 142.8, 128.5, 128.4, 128.3, 127.8, 127.1, 125.8, 123.7, 123.2, 114.0, 112.4, 83.8, 54.2, 39.4, 31.0, 24.5, 24.5, 23.2 (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm⁻¹, neat) 3078, 3057, 3032, 2976, 2935, 2928, 1732, 1676, 1612, 1545, 1497, 1447, 1412, 1371, 1354, 1315, 1271, 1213, 1157, 1136, 1115, 1030, 991, 966, 949, 918, 876

MS (HRMS ESI) Calcd for [M+Na]⁺ C₂₇H₃₁O₄BNa: 453.2209 Found: 453.2209

2-Methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(1-tosyl-1H-indol-3-yl)but-3-en-1-one (4u)



Following procedure C₂ starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and 1-Tosyl-1H-indole-3-carbonyl fluoride (**1h**).

Flash chromatography: (PE/EtOAc 95:5 to 85:15) + 1% Et₃N.

Yield: 134.4 mg (46% yield) of semi solid.

¹H NMR (δ, ppm) 8.38 – 8.35 (m, 1H), 8.17 (s, 1H), 7.93 – 7.90 (m, 1H), 7.77 (d, *J* = 6.0 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.21 (m, 4H), 7.18 – 7.09

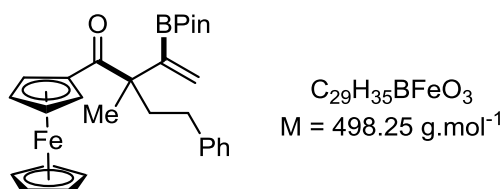
(m, 3H), 6.19 (d, $J = 3.0$ Hz, 1H), 6.00 (d, $J = 3.0$ Hz, 1H), 2.59 – 2.49 (m, 1H), 2.43 – 4.37 (m, 1H), 2.34 (s, 3H), 2.29 – 2.22 (m, 2H), 1.53 (s, 3H), 0.86 (s, 6H), 0.85 (s, 6H)

^{13}C NMR (δ , ppm) 199.7, 145.6, 142.8, 135.0, 134.1, 131.5, 130.3, 129.5, 128.5, 128.4, 128.1, 127.2, 125.8, 125.5, 124.7, 123.7, 119.3, 112.9, 83.7, 55.4, 39.8, 30.9, 24.34, 24.28, 23.5, 21.7
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm^{-1} , neat) 1718, 1666, 1596, 1535, 1444, 1411, 1377, 1353, 1313, 1210, 1174, 1135, 1099, 1085, 983, 968, 910, 871, 846, 811

MS (HRMS ESI) Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{34}\text{H}_{39}\text{BNO}_5\text{S}$: 584.2637 Found: 584.2641

2-Methyl-2-phenethyl-1-ferrocenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4v)



Following procedure **C₂** starting with 0.5 mmol (3-methylpenta-3,4-dien-1-yl)benzene (**3a**), bis(pinacolato)diboron (**2**) and ferrocenoyl fluoride (**1i**).

Flash chromatography: PE/Et₂O 95:5 + 1% Et₃N.

Yield: 153.6 mg (62% yield) of an orange-red solid.

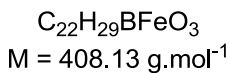
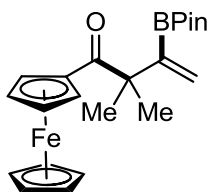
^1H NMR (δ , ppm) 7.26 – 7.23 (m, 2H), 7.16 – 7.13 (m, 3H), 6.01 (d, $J = 2.4$ Hz, 1H), 5.76 (d, $J = 2.4$ Hz, 1H), 4.90 (dt, $J = 2.6, 1.3$ Hz, 1H), 4.72 (dt, $J = 2.5, 1.2$ Hz, 1H), 4.39 (dtd, $J = 7.0, 2.5, 1.4$ Hz, 2H), 4.19 (s, 5H), 2.45 – 2.40 (m, 2H), 2.26 – 2.20 (m, 1H), 2.17 – 2.11 (m, 1H), 1.62 (s, 3H), 1.13 (s, 6H), 1.11 (s, 6H)

^{13}C NMR (δ , ppm) 209.0, 143.2, 128.5, 128.4, 126.2, 125.6, 83.4, 78.2, 71.6, 71.2, 71.1, 70.9, 70.0, 55.7, 39.3, 31.0, 24.8, 24.7, 24.0
(quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR (cm^{-1} , neat) 1663, 1607, 1497, 1454, 1439, 1412, 1371, 1354, 1313, 1298, 1259, 1215, 1165, 1140, 1107, 1053, 1028, 1003, 968, 947, 891, 870, 847, 824

MS (HRMS ESI) Calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{29}\text{H}_{36}\text{O}_3\text{BFe}$: 499.2103 Found: 499.2105

2,2-Dimethyl-1-ferrocenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one
(**4w**)



Following procedure C₂ starting with 1.5 mmol 3-methyl-1,2-butadiene (**3b**), bis(pinacolato)diboron (**2**) and ferrocenoyl fluoride (**1i**).

Flash chromatography: (PE/Et₂O 9:1 to 85:15) + 1% Et₃N.

Yield: 481.2 mg (79% yield) of an orange-red solid.

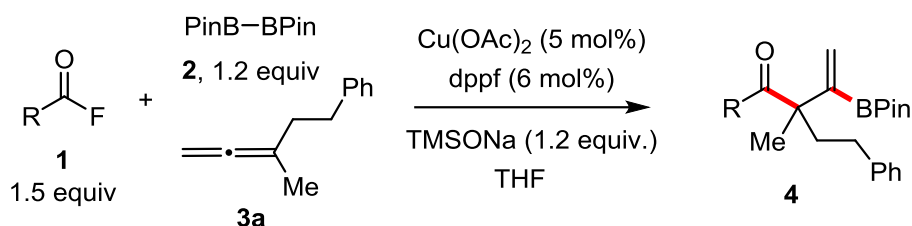
¹H NMR (δ, ppm) 5.87 (d, $J = 2.4$ Hz, 1H), 5.77 (d, $J = 2.4$ Hz, 1H), 4.77 – 4.76 (m, 2H), 4.36 – 4.35 (m, 2H), 4.16 (s, 5H), 1.46 (s, 6H), 1.04 (s, 12H)
(500 MHz, CDCl₃)

¹³C NMR (δ, ppm) 209.2, 125.1, 83.4, 78.1, 71.4, 70.9, 69.9, 51.8, 26.5, 24.7
(125 MHz, CDCl₃) (quaternary carbon next to boron could not be observed because of quadrupolar coupling effects)

IR 2972, 1734, 1668, 1466, 1439, 1412, 1371, 1352, 1313, 1267, 1211, 1142, 1107, 1055, 1003, 968, 943, 891, 862, 843, 822
(cm⁻¹, neat)

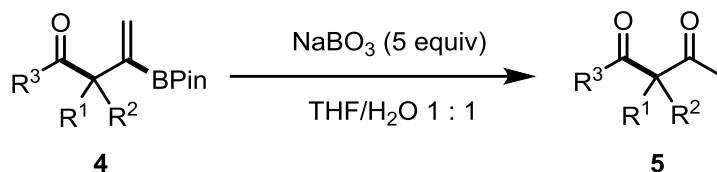
MS Calcd for [M+H]⁺ C₂₂H₃₀O₃BFe: 409.1632 Found: 409.1633
(HRMS ESI)

Tests with aliphatic acyl fluorides



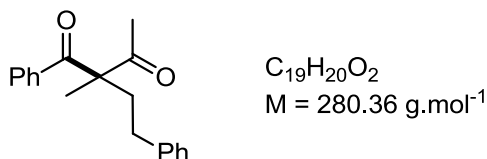
Entry	Acyl fluoride (R =)	Conditions	Results	
			Conversion of 3a	Products
1	-Cy	0 °C, 3 h	Complete	Only hydroboration product observed
2	-CH ₂ CH ₂ Ph	0 °C, 3 h	~ 60-70%	Ratio product / hydroboration product 1 : 0.6
3		0 °C to rt, 18 h	~ 40-50%	Hydroboration product mainly observed

Oxidation of the vinylboron moiety: procedure D:



To a solution of **4** (1 equiv, 0.2 mmol) in THF/H₂O 1 : 1 was added NaBO₃ (5 equiv, 1.0 mmol, 99.8 mg) and the mixture was vigorously stirred at room temperature for 2 h. Et₂O and NH₄Cl_(sat) were added and the layers were separated. After extraction with Et₂O, the organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Purification by flash column chromatography (PE/Et₂O) afforded the pure product.

2-Methyl-2-phenethyl-1-phenylbutane-1,3-dione (**5a**)



Following procedure D starting with 0.2 mmol 2-methyl-2-phenethyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (**4a**).

Flash chromatography: PE/Et₂O 9 : 1 to 8 : 2

Yield: 44.0 mg (78% yield) of a slightly yellow oil.

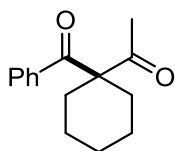
¹H NMR (δ, ppm) 7.83 – 7.79 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.41 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 7.09 – 7.06 (m, 2H), 2.48 – 2.20 (m, 4H), 2.13 (s, 3H), 1.56 (s, 3H)

¹³C NMR (δ, ppm) 208.1, 199.3, 141.6, 136.0, 133.2, 129.0, 128.9, 128.6, 128.4, 126.2, 65.0, 37.6, 30.3, 27.3, 20.1

IR (cm⁻¹, neat) 2918, 2849, 1712, 1670, 1597, 1580, 1497, 1447, 1375, 1356, 1246, 1205, 1180, 1157, 1097, 1078, 1001, 986, 955

MS Calcd for [M+H]⁺ C₁₉H₂₁O₂: 281.15266 Found: 281.1535 (HRMS APCI)

1-(1-Benzoylcyclohexyl)ethan-1-one (5c)



C₁₅H₁₈O₂
M = 230.31 g.mol⁻¹

Following procedure D starting with 0.2 mmol phenyl(1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexyl)methanone (**4c**).

Flash chromatography: Pentane/Et₂O 96 : 4

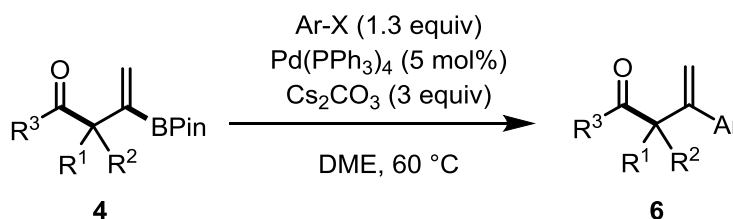
Yield: 40.6 mg (88% yield) of a slightly yellow oil.

¹H NMR (δ, ppm) 7.72 – 7.70 (m, 2H), 7.51 – 7.48 (m, 1H), 7.40 – 7.37 (m, 2H), 2.25 – 2.20 (m, 2H), 2.11 (s, 3H), 1.95 – 1.89 (m, 2H), 1.60 – 1.54 (m, 2H), 1.50 – 1.30 (m, 4H)

¹³C NMR (δ, ppm) 208.4, 200.6, 137.0, 132.7, 128.6, 128.6, 66.6, 31.9, 26.8, 25.6, 22.5 (125 MHz, CDCl₃)

Spectroscopic data are in agreement with those reported in the literature.¹⁷

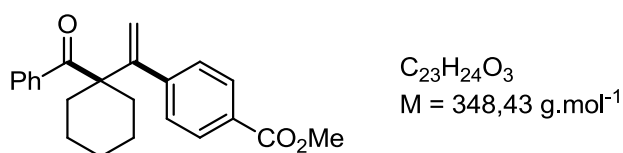
Suzuki coupling: procedure E:



The Suzuki coupling was carried out according to a literature procedure.¹⁸

A flame-dried Schlenk was loaded with Pd(PPh₃)₄ (0.05 equiv, 0.01 mmol, 11.6 mg), aryl halide (1.3 equiv, 0.26 mmol) and Cs₂CO₃ (3 equiv, 0.6 mmol, 195.5 mg). After 3 vacuum/argon cycles, dried and degassed DME (2.0 mL) was added, followed by vinylboron **4** (1 equiv, 0.2 mmol) in solution in DME (0.5 mL). The reaction mixture was stirred at 60 °C for the indicated time. After dilution with EtOAc, the reaction mixture was filtrated on silica (EtOAc) and concentrated under reduced pressure. Purification by flash chromatography afforded the desired coupling product.

Methyl 4-(1-(1-benzoylcyclohexyl)vinyl)benzoate (6c)



Following procedure E starting with 0.2 mmol phenyl(1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexyl)methanone **4c** and methyl 4-bromobenzoate.

Flash chromatography: PE/Et₂O 95 : 5

Yield: 50.7 mg (73% yield) of a colourless oil.

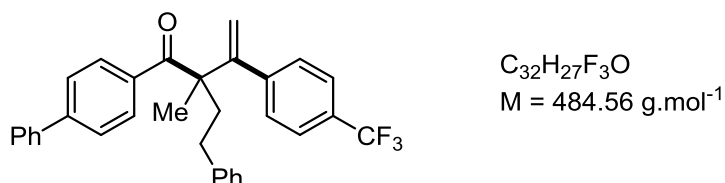
¹H NMR (δ, ppm) 7.94 – 7.91 (m, 4H), 7.51 – 7.46 (m, 1H), 7.41 – 7.36 (m, 2H), 7.24 – 7.20 (m, 2H), 5.55 (s, 1H), 5.34 (s, 1H), 3.89 (s, 3H), 2.30 – 2.26 (m, 2H), 1.67 – 1.52 (m, 4H), 1.43 – 1.18 (m, 4H)

¹³C NMR (δ, ppm) 204.3, 167.0, 153.1, 146.4, 139.0, 131.7, 129.3, 129.1, 128.9, 128.7, 128.4, 118.1, 57.2, 52.2, 34.9, 25.8, 22.8

IR (cm⁻¹, neat) 2918, 2856, 1720, 1676, 1607, 1597, 1578; 1504, 1452, 1435, 1400, 1311, 1275, 1227, 1180, 1155, 1115, 1053, 1030, 1018, 986, 970, 912, 883, 862, 833, 814

MS (HRMS APCI) Calcd for [M+H]⁺ C₂₃H₂₅O₃: 349.1798 Found: 349.1798

1-([1,1'-Biphenyl]-4-yl)-2-methyl-2-phenethyl-3-(4-(trifluoromethyl)phenyl)but-3-en-1-one (6o)



Following procedure E starting with 0.135 mmol 1-([1,1'-biphenyl]-4-yl)-2-methyl-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one **4o** and 4-bromobenzotrifluoride.

Flash chromatography: PE/Et₂O 98 : 2

Yield: 51 mg (78% yield) of a colourless sticky oil.

¹H NMR (δ, ppm) 8.17 (d, *J* = 9 Hz, 2H), 7.66 – 7.60 (m, 4H), 7.52 – 7.31 (m, 7H), 7.24 – 7.14 (m, 3H), 7.01 – 6.98 (m, 2H), 5.62 (s, 1H), 5.48 (s, 1H), 2.64 – 2.53 (m, 1H), 2.45 – 2.33 (m, 2H), 2.16 – 2.06 (m, 1H), 1.59 (s, 3H)

¹³C NMR (δ, ppm) 202.1, 152.6, 145.1, 145.0, 142.1, 139.9, 136.2, 130.0, 129.5, 129.1, 128.5, 128.4, 128.3, 127.3, 127.0, 126.1, 125.3 (q, *J*_{C-F} = 3.75 Hz), 122.4, 118.1, 56.4, 40.4, 30.8, 24.2

¹⁹F NMR (δ, ppm) -62.7
(282 MHz, CDCl₃, C₆F₆)

IR (cm⁻¹, neat) 1672, 1602, 1487, 1456, 1404, 1325, 1242, 1166, 1122, 1066, 1016, 973, 916, 848

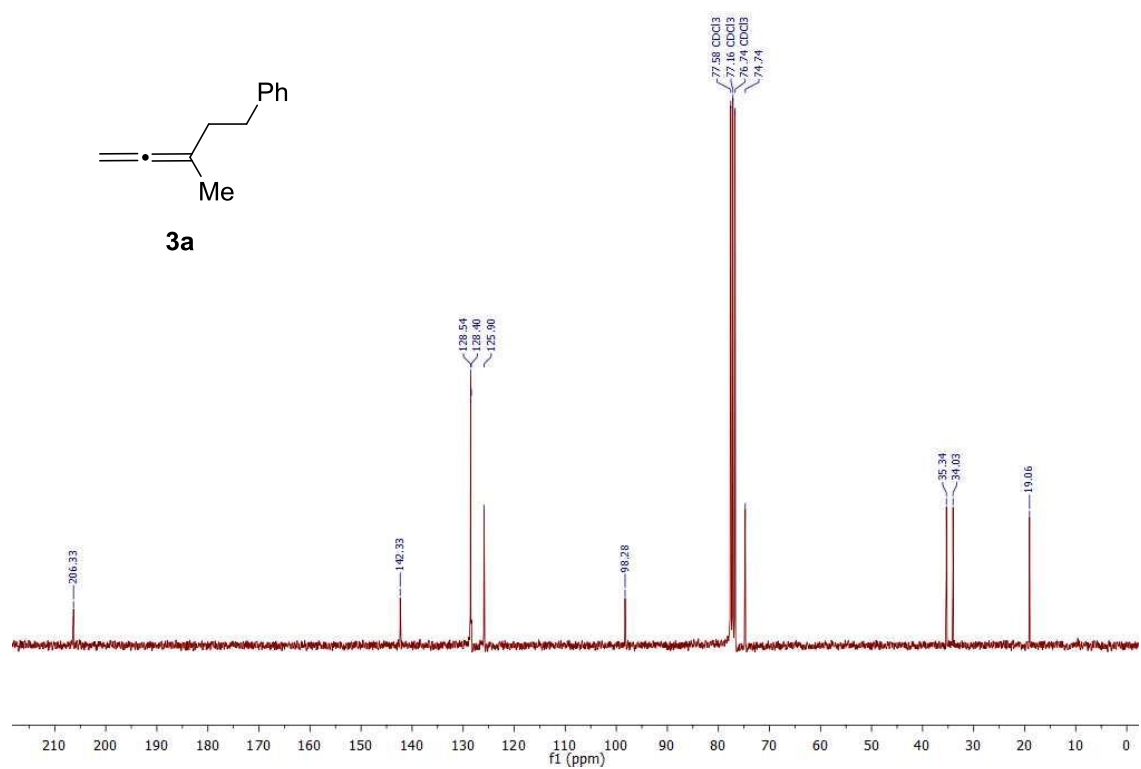
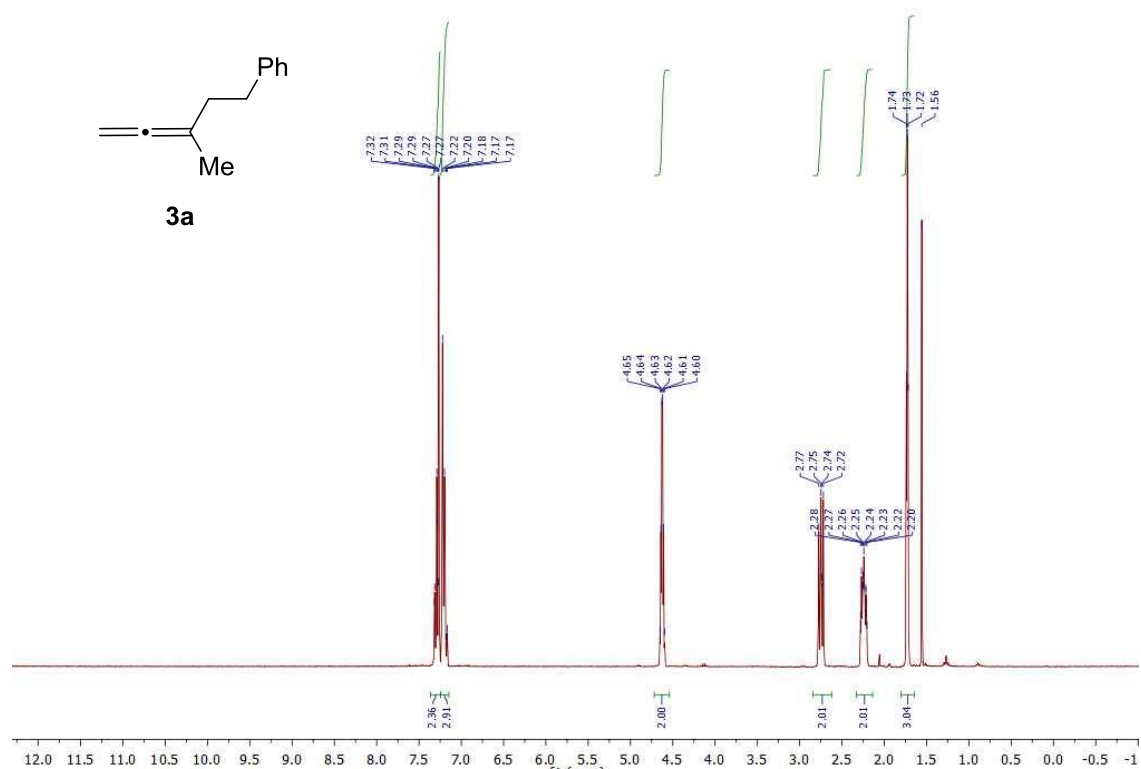
MS Calcd for [M+H]⁺ C₃₂H₂₈F₃O: 485.2087 Found: 485.2085
(HRMS APCI)

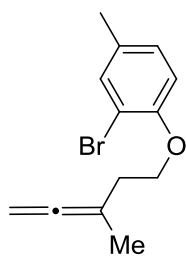
References

- (1) Edwards, A.; Ryabchuk, P.; Barkov, A.; Rubina, M.; Rubin, M. *Tetrahedron: Asymmetry*, **2014**, 25, 1537–1549.
- (2) Yang, X.; She, Y.; Chong, Y.; Zhai, H.; Zhu, H.; Chen, B.; Huang, G.; Yan, R. *Adv. Synth. Catal.* **2016**, 358, 3130–3134.
- (3) Prepared via a Wittig reaction from the corresponding ketone. Standard Wittig procedure: Movahhed, S.; Westphal, J.; Dindaroglu, M.; Falk, A.; Schmalz, H.-G. *Chem. Eur. J.* **2016**, 22, 7381–7384.
- (4) Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, 130, 83, 15254–15255.
- (5) Tani, Y.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2014**, 136, 17706–17709.
- (6) This allenol was prepared according to a literature procedure: Stoll, A. H.; Blakey, S. B. *J. Am. Chem. Soc.* **2010**, 132, 2108–2109.
- (7) The low yield of this reaction is not due to the reaction itself but to the difficulties in separating the desired product from the other components of the crude mixture.
- (8) Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, 13, 3864–3867.
- (9) Li, Q.-H.; Liao, J.-W.; Huang, Y.-L.; Chiang, R.-T.; Gau, H.-M. *Org. Biomol. Chem.* **2014**, 12, 7634–7642.

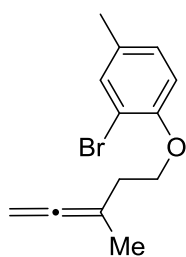
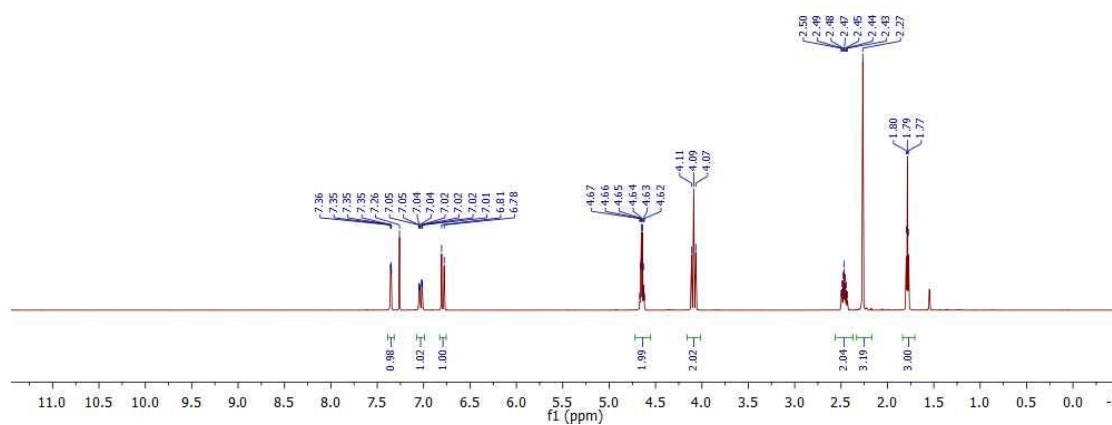
- (10) Jang, H.; Jung, B.; Hoveyda, A. H. *Org. Lett.* **2014**, *16*, 4658–4661.
- (11) Kuang, J.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1763–1765.
- (12) Song, G.; Wang, B.; Nishiura, M.; Hou, Z. *Chem. Eur. J.* **2015**, *21*, 8394–8398.
- (13) Wang, H.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 7318–7322.
- (14) Zhang, H.; Fu, X.; Chen, J.; Wang, E.; Liu, Y.; Li, Y. *J. Org. Chem.* **2009**, *74*, 9351–9358.
- (15) Beaulieu, F.; Beauregard, L.-P.; Courchesne, G.; Couturier, M.; LaFlamme, F.; L'Heureux, A., *Org. Lett.* **2009**, *11*, 5050–5053.
- (16) Stanek, K.; Koller, R.; Togni, A. *J. Org. Chem.* **2008**, *73*, 7678–7685.
- (17) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis*, **1995**, *9*, 1163–1170.
- (18) Moure, A. L.; Mauleón, P.; Arrayás, R. G.; Carretero, J. C. *Org. Lett.* **2013**, *15*, 2054–2057.

NMR spectra

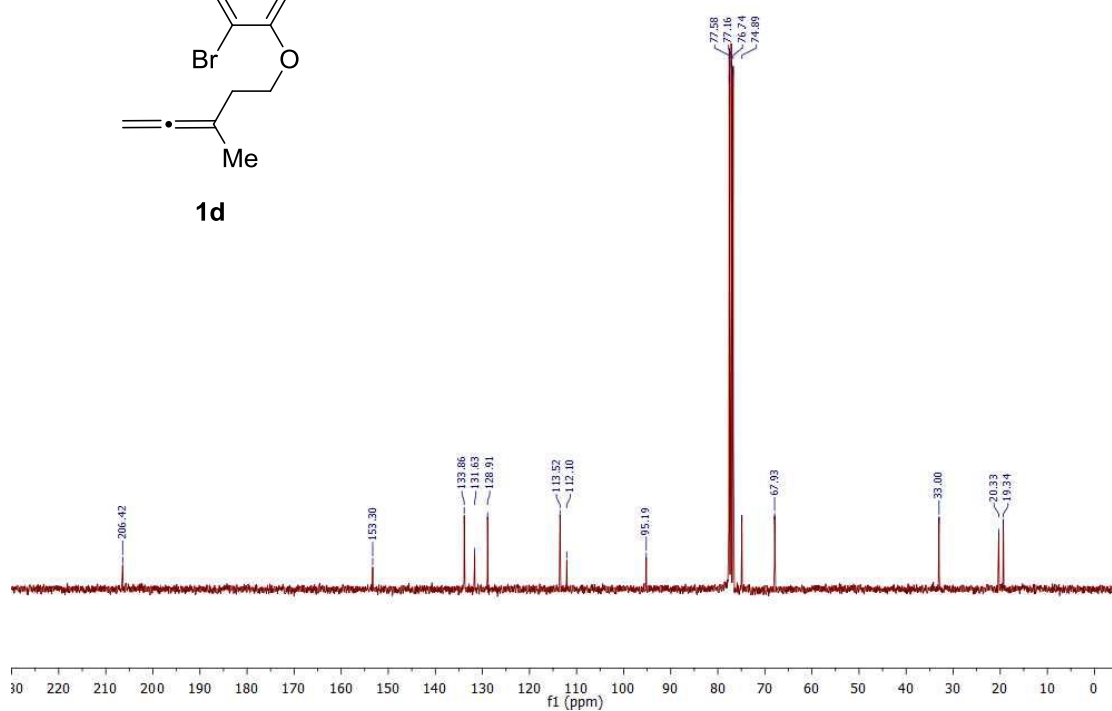


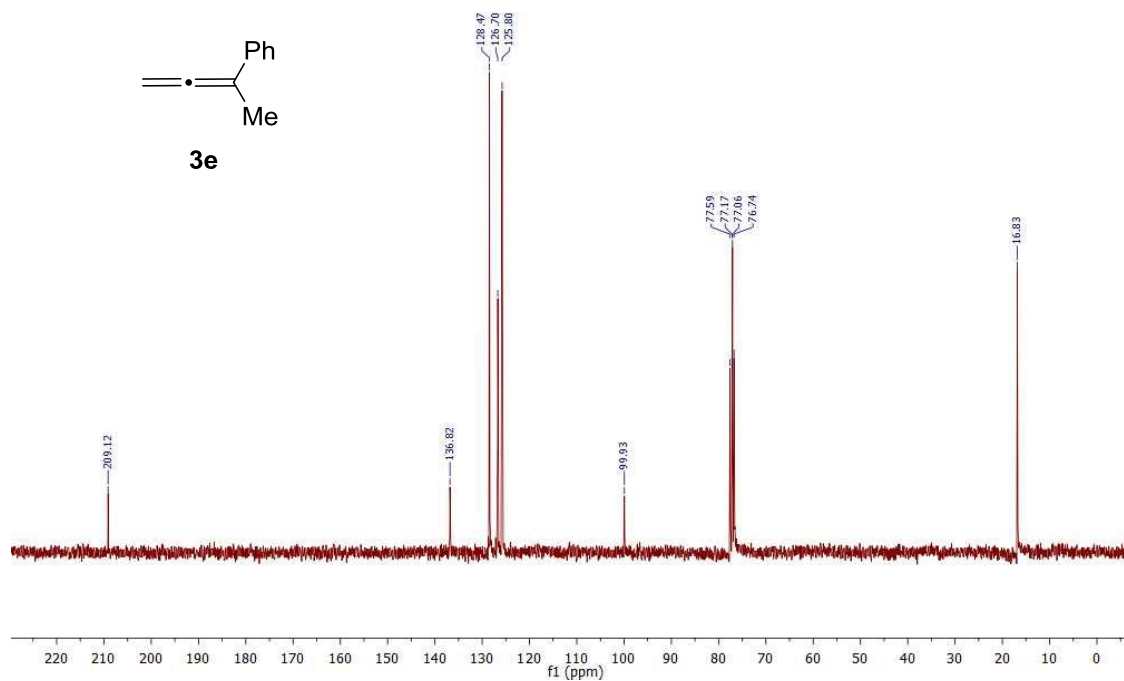
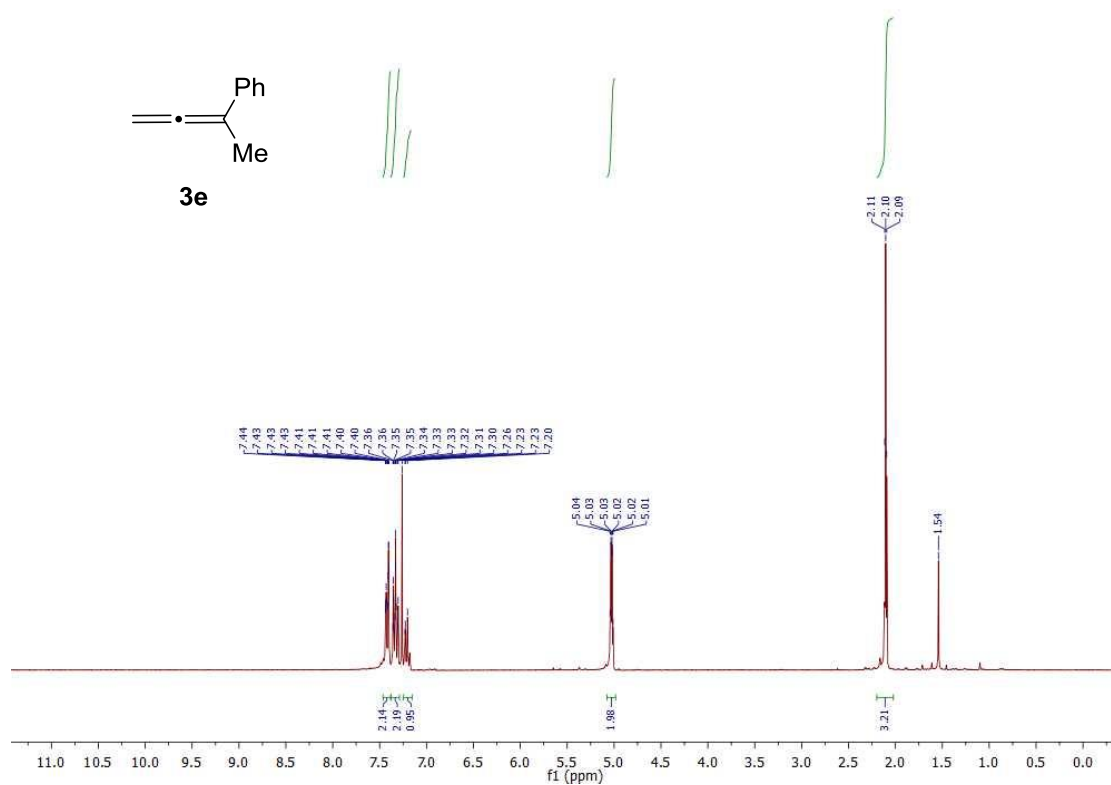


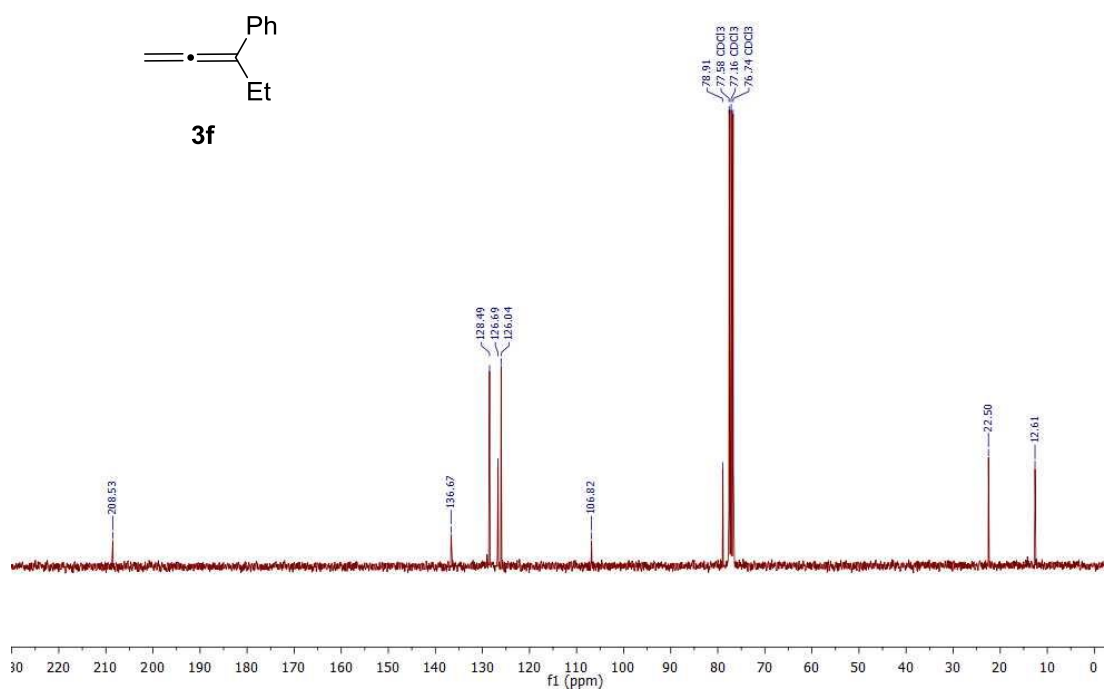
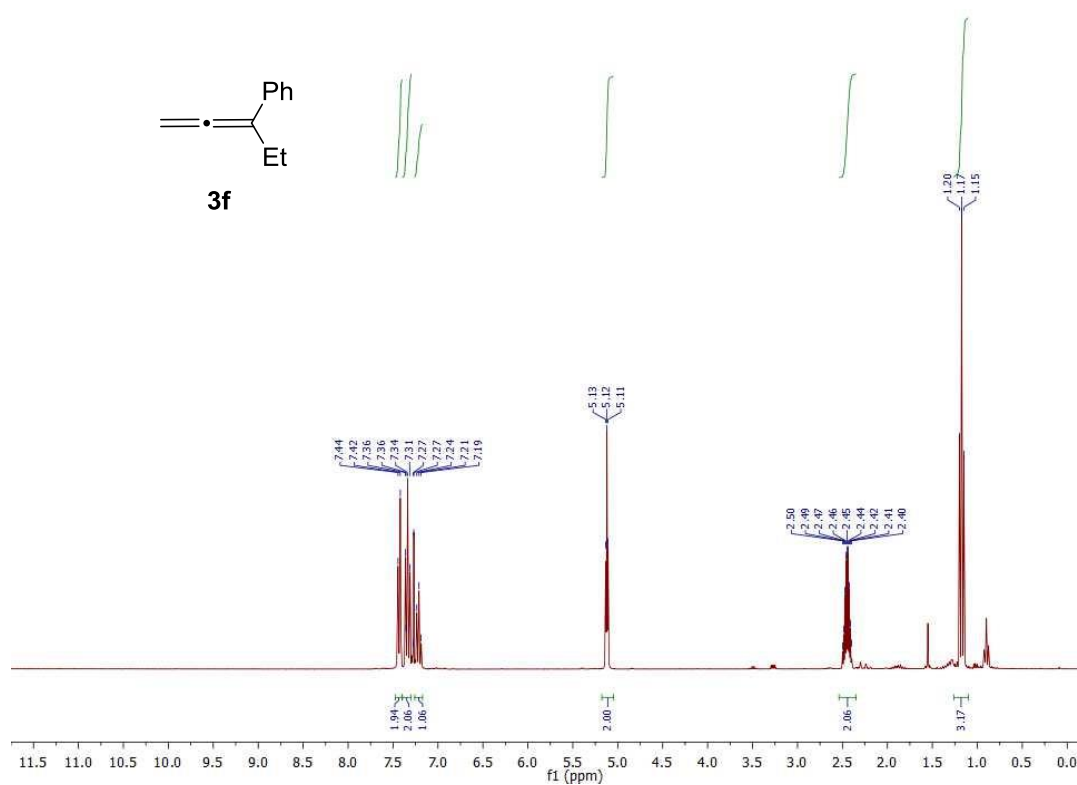
1d

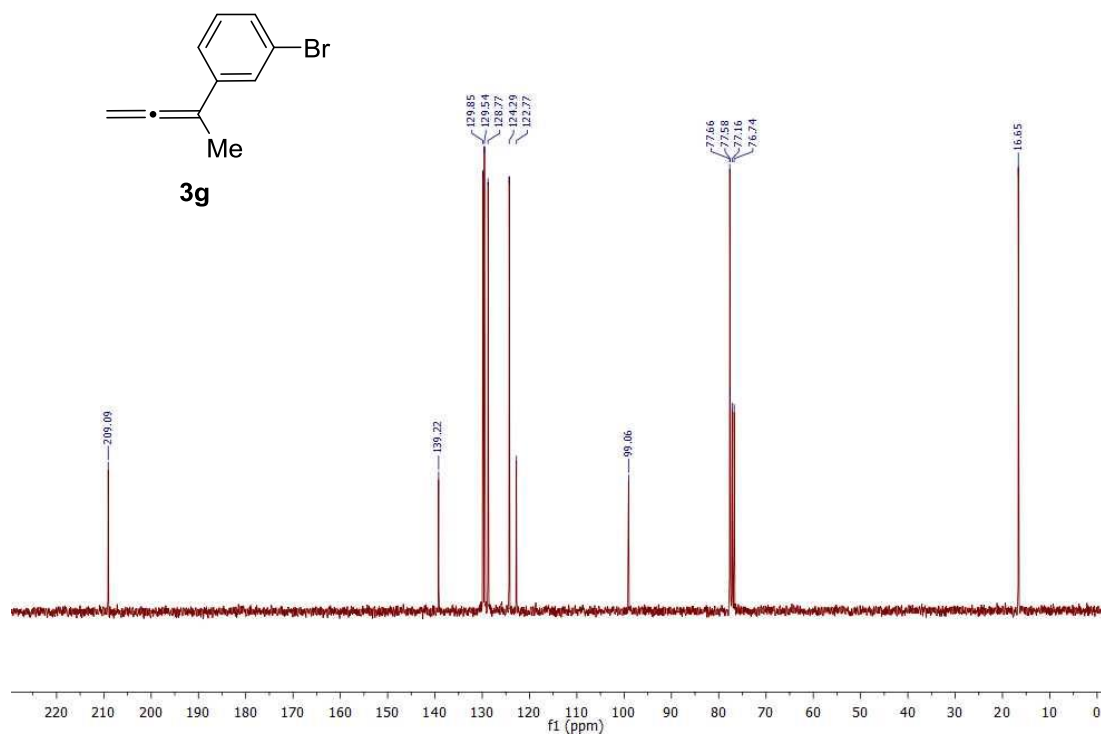
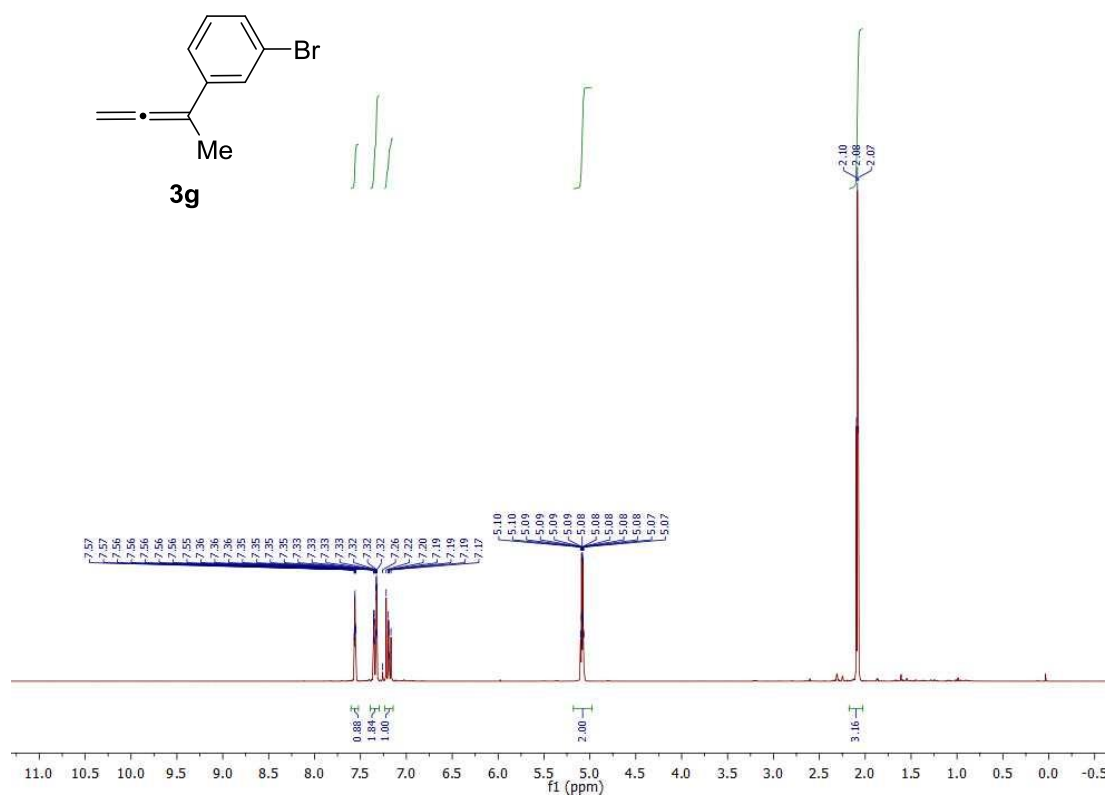


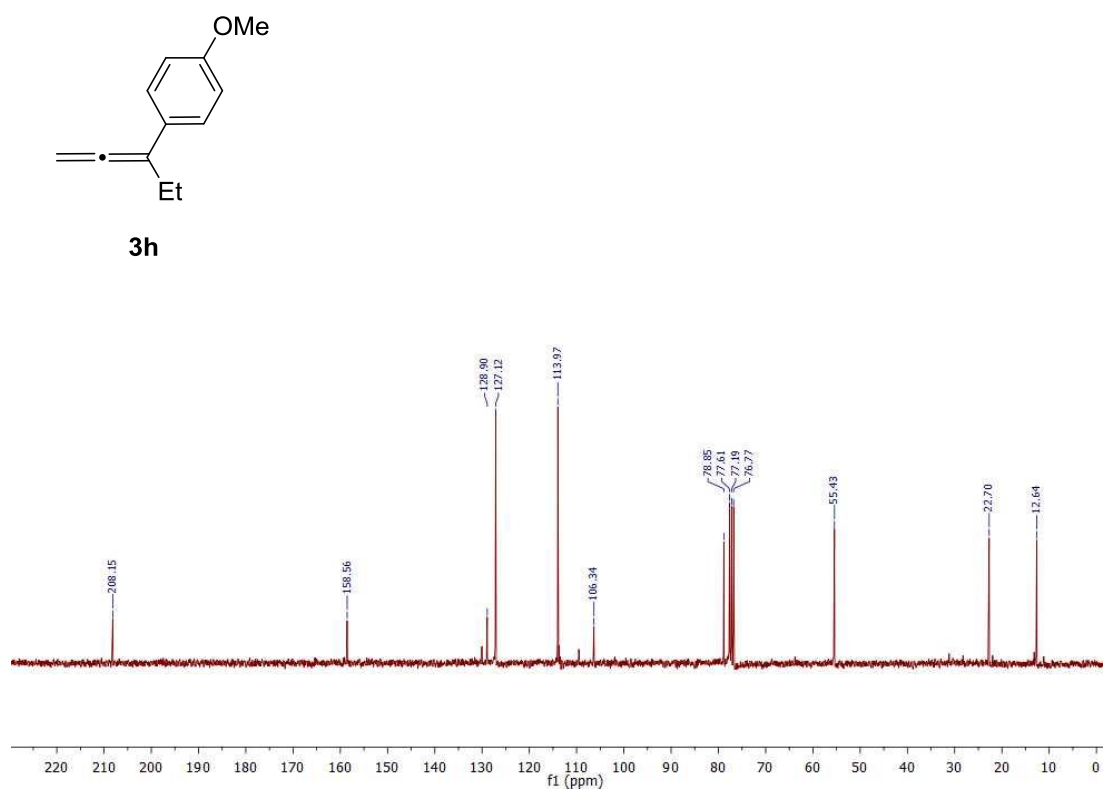
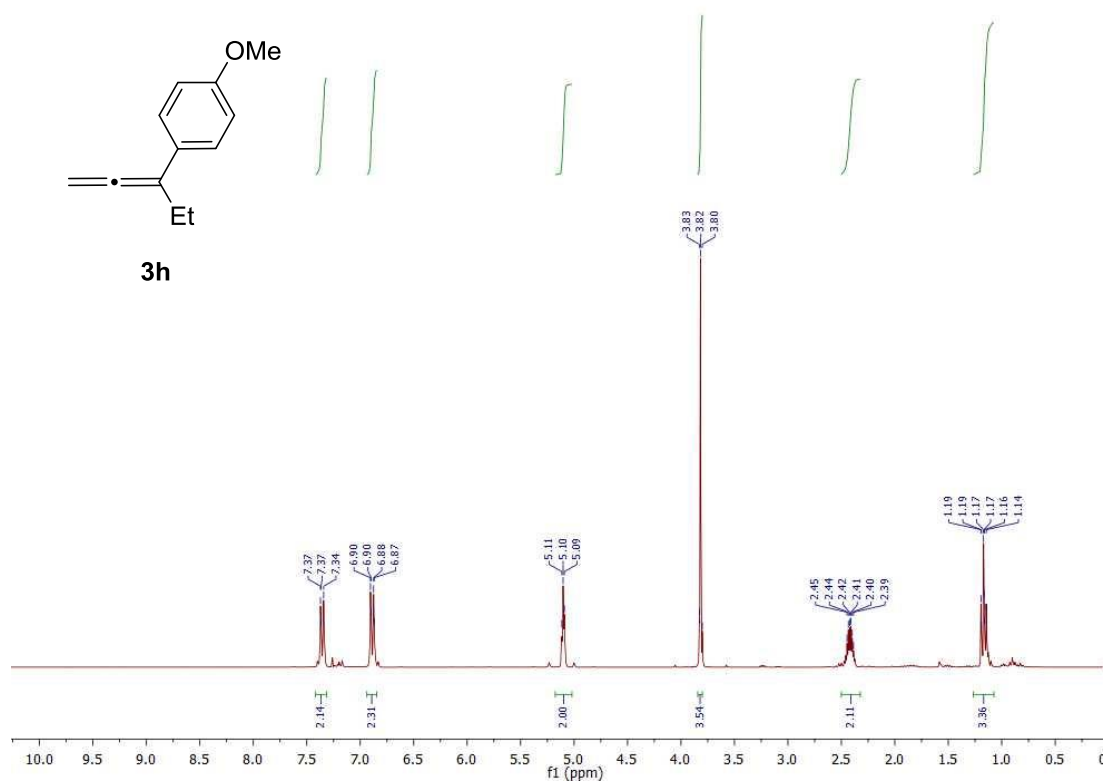
1d

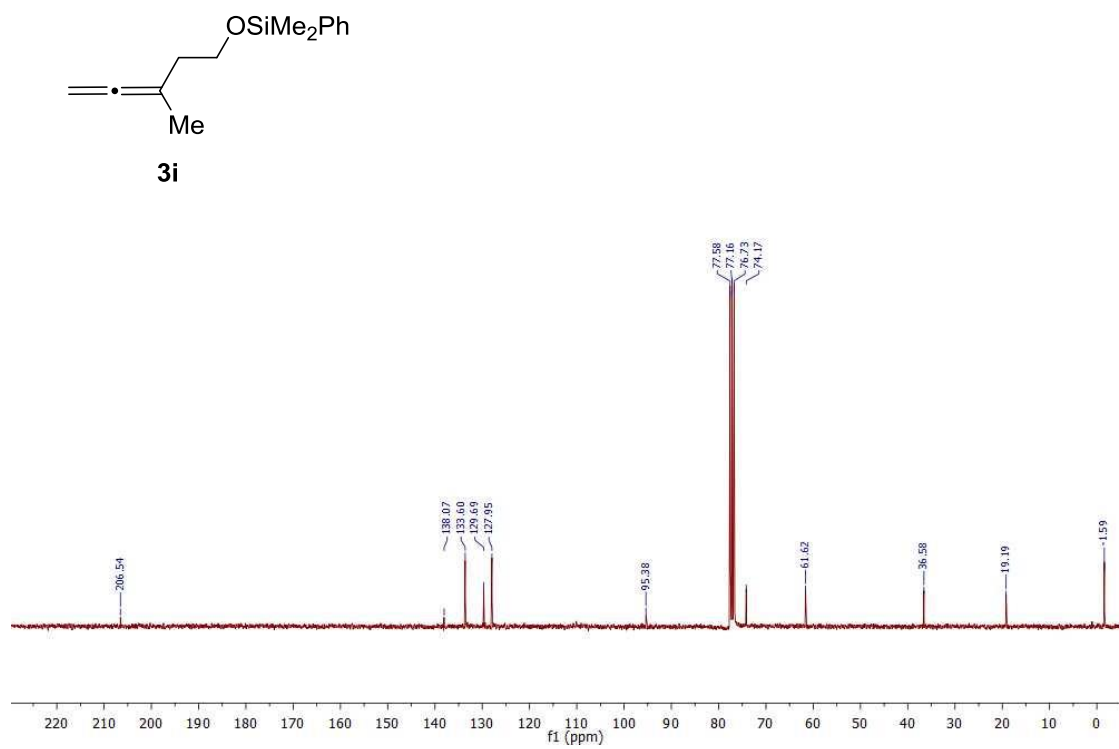
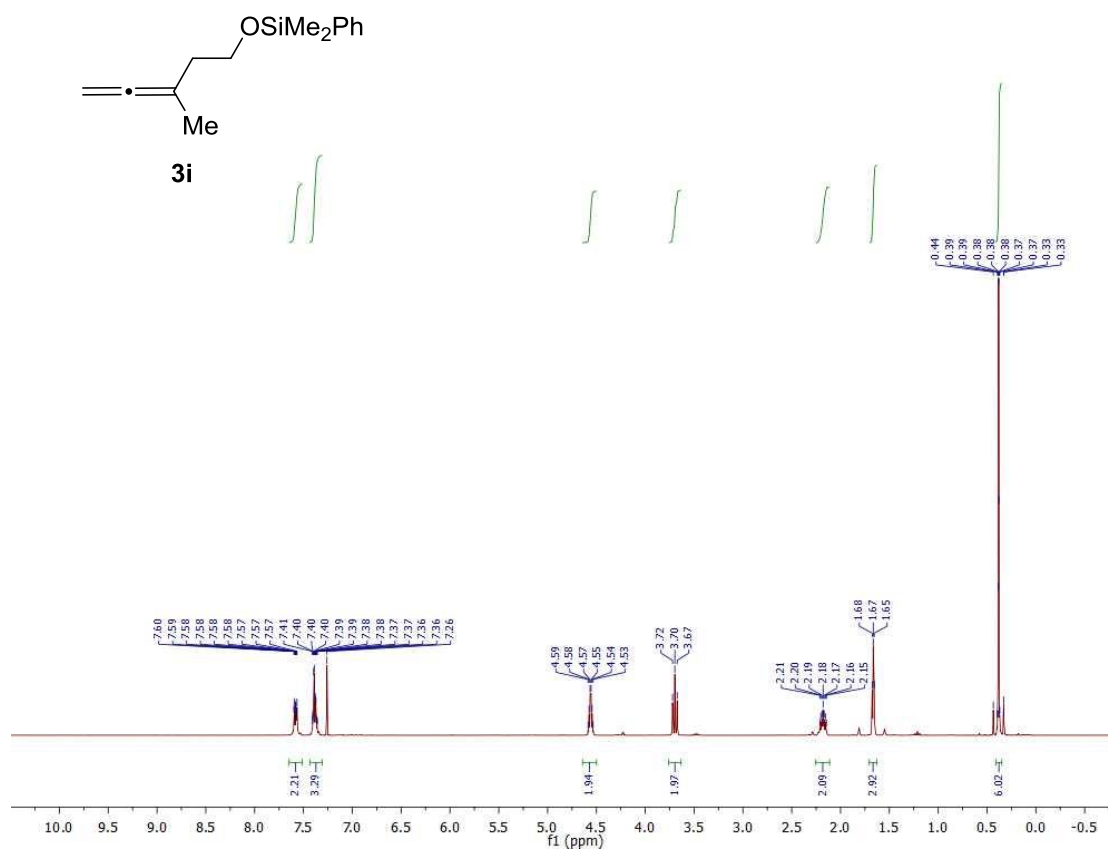


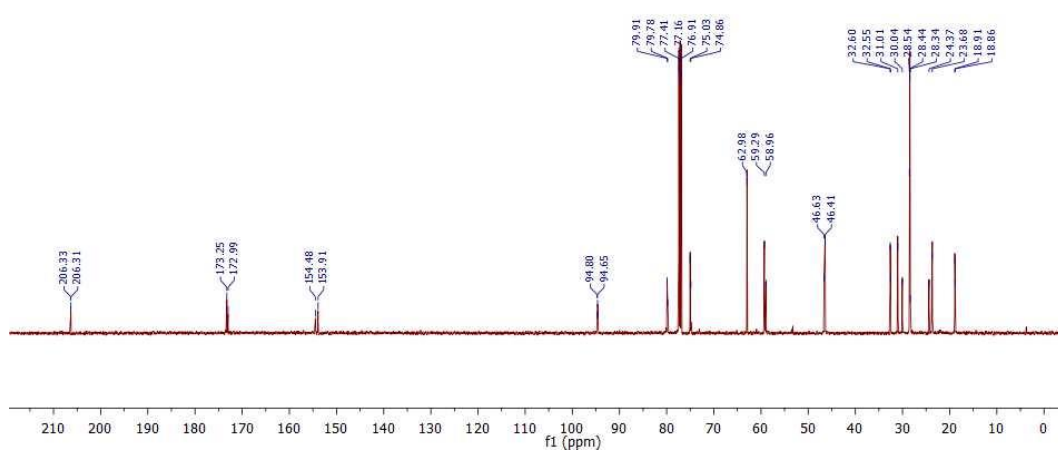
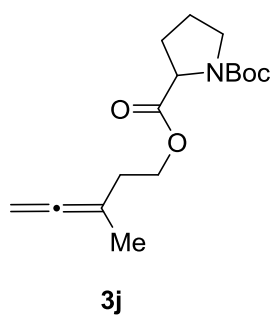
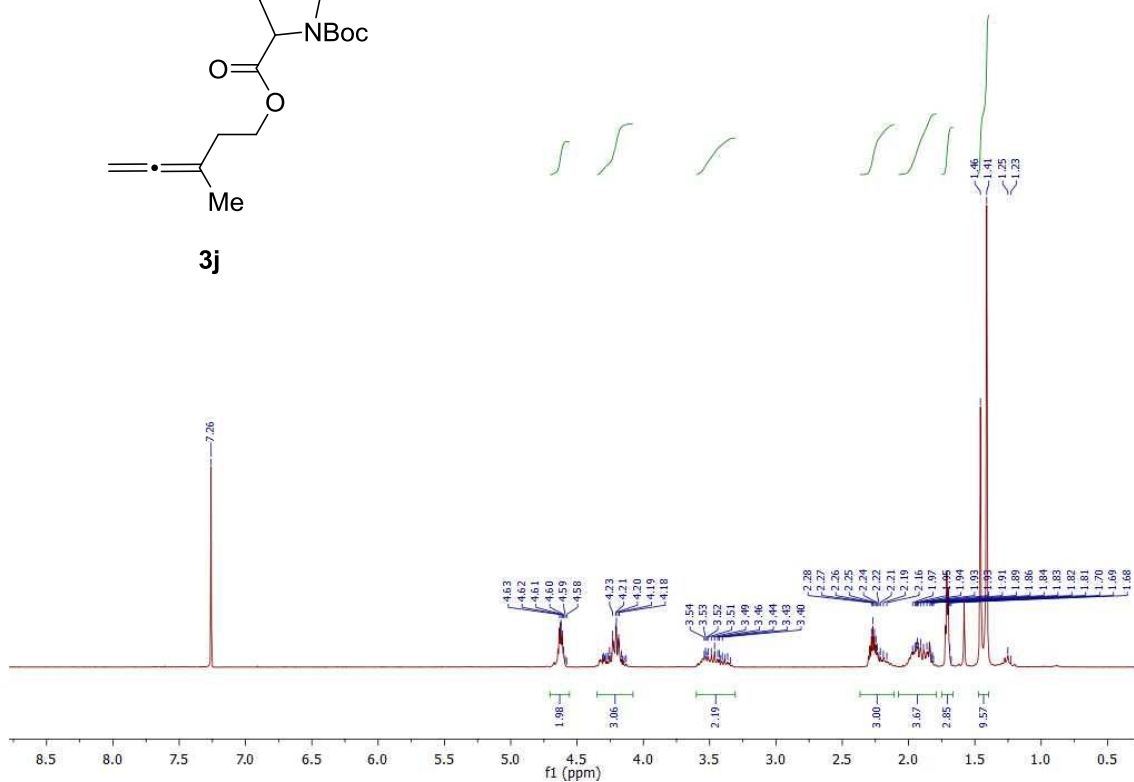
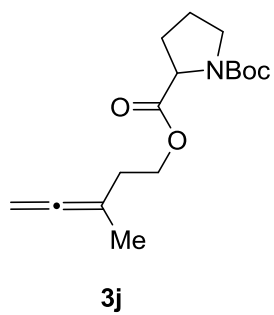


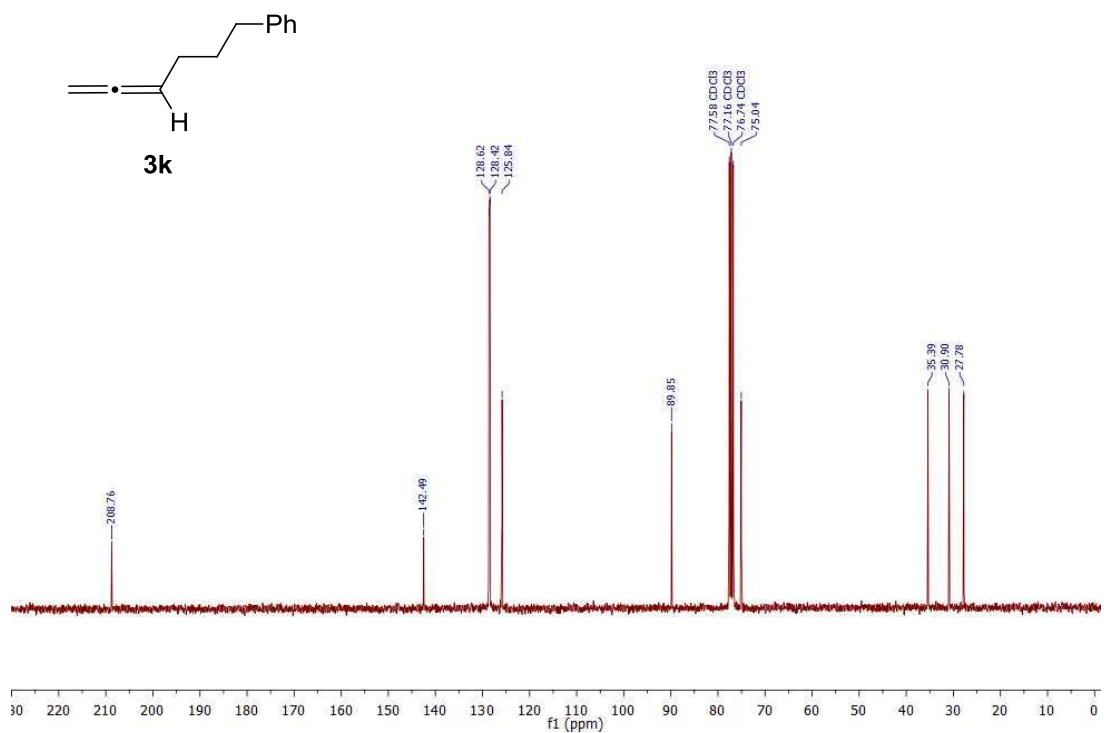
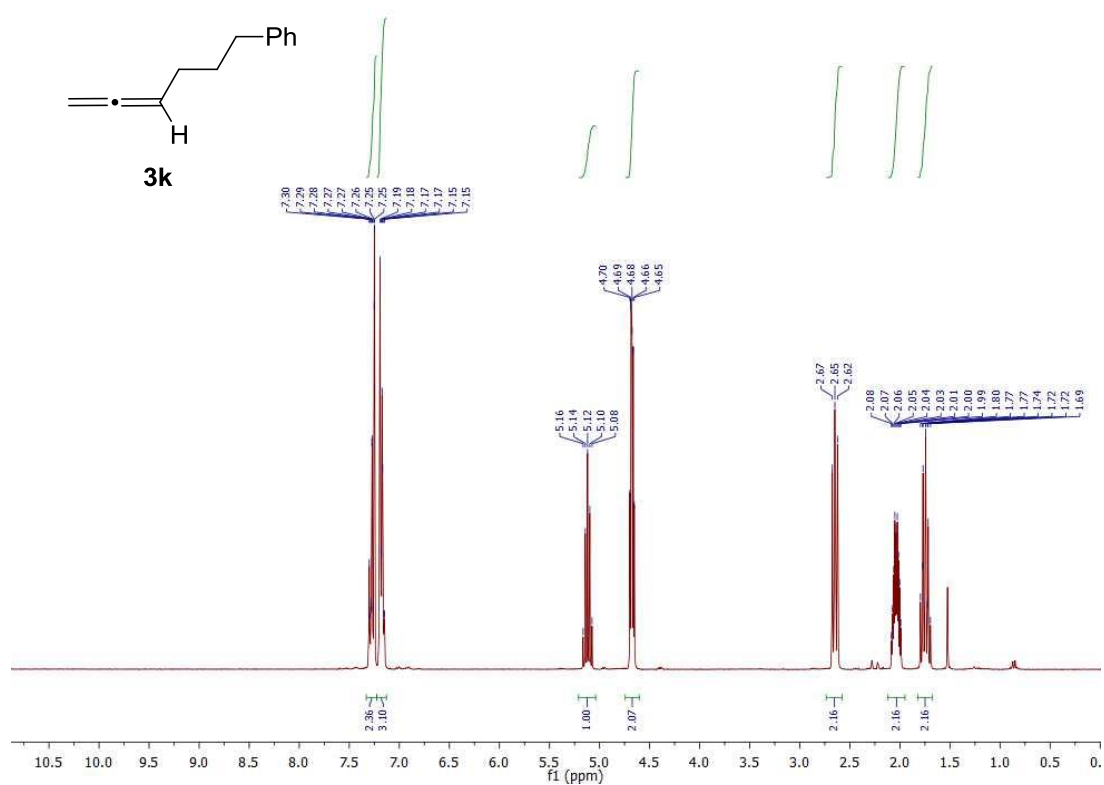


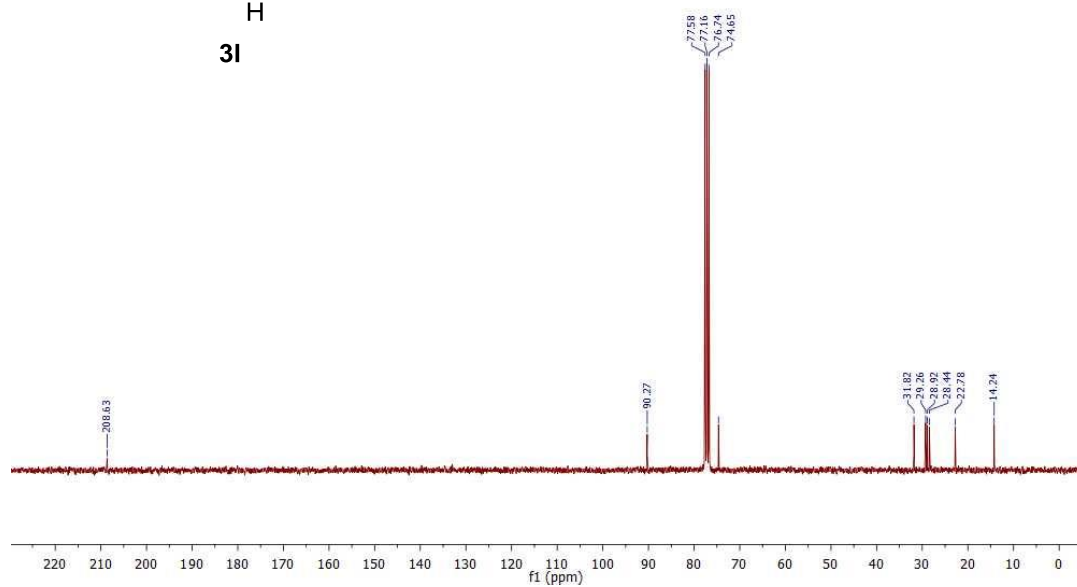
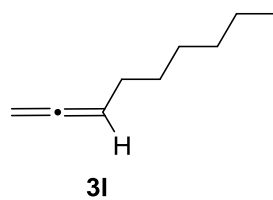
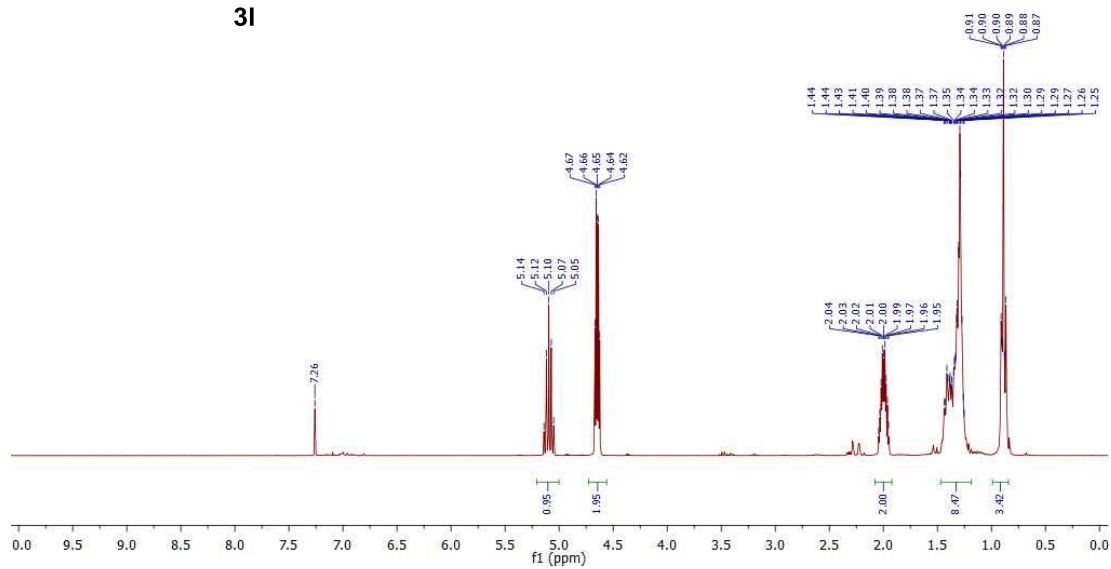
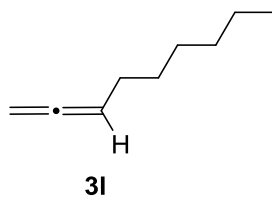


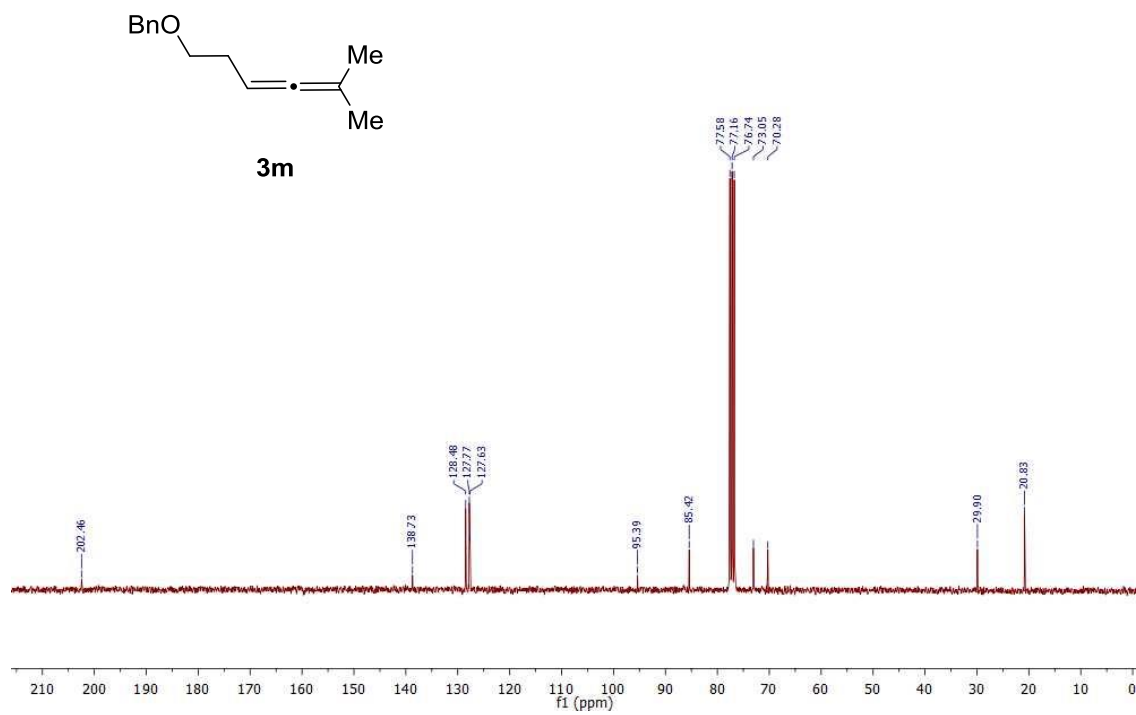
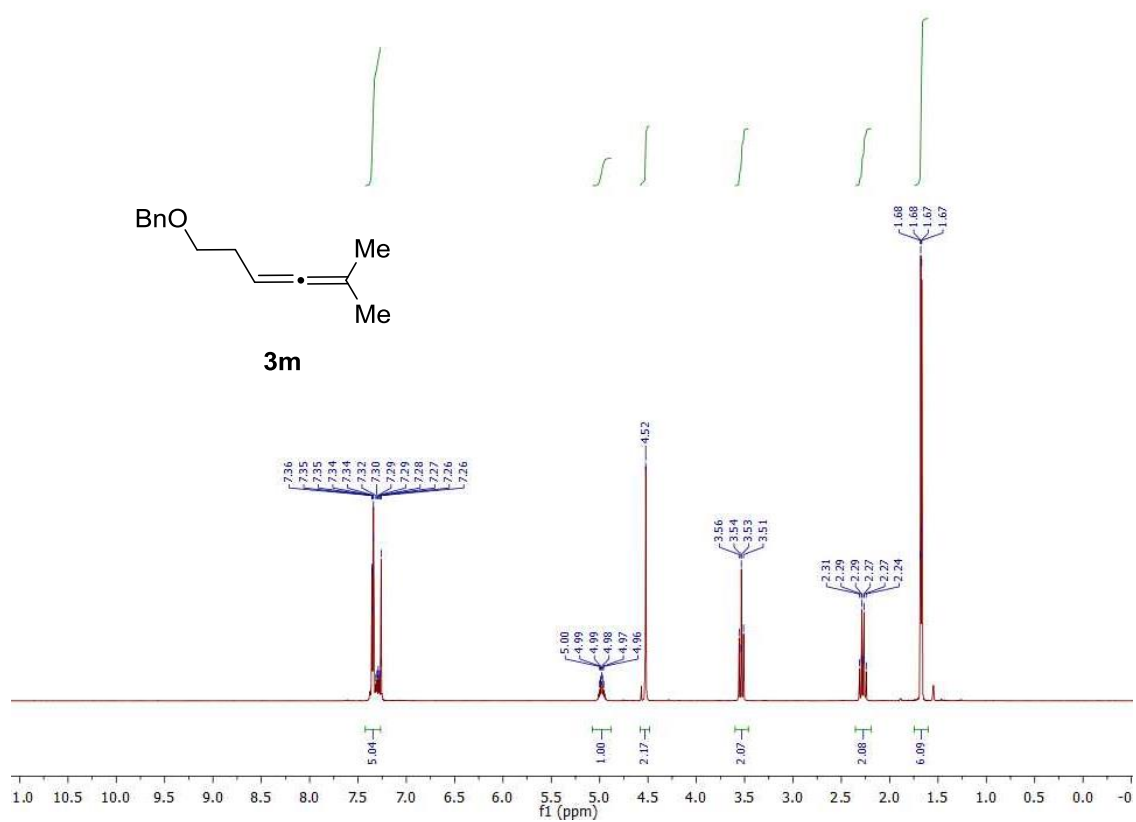


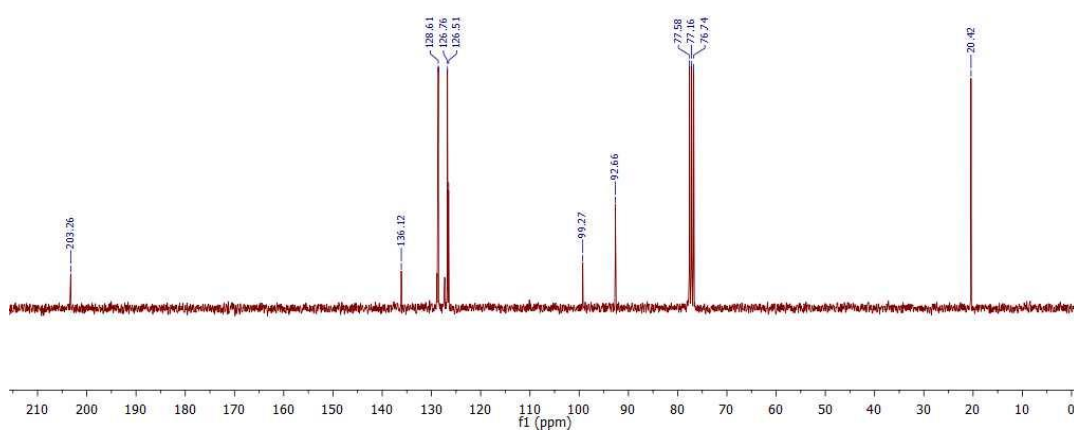
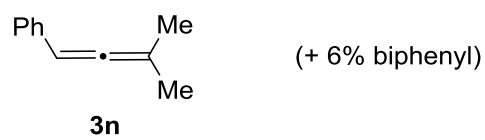
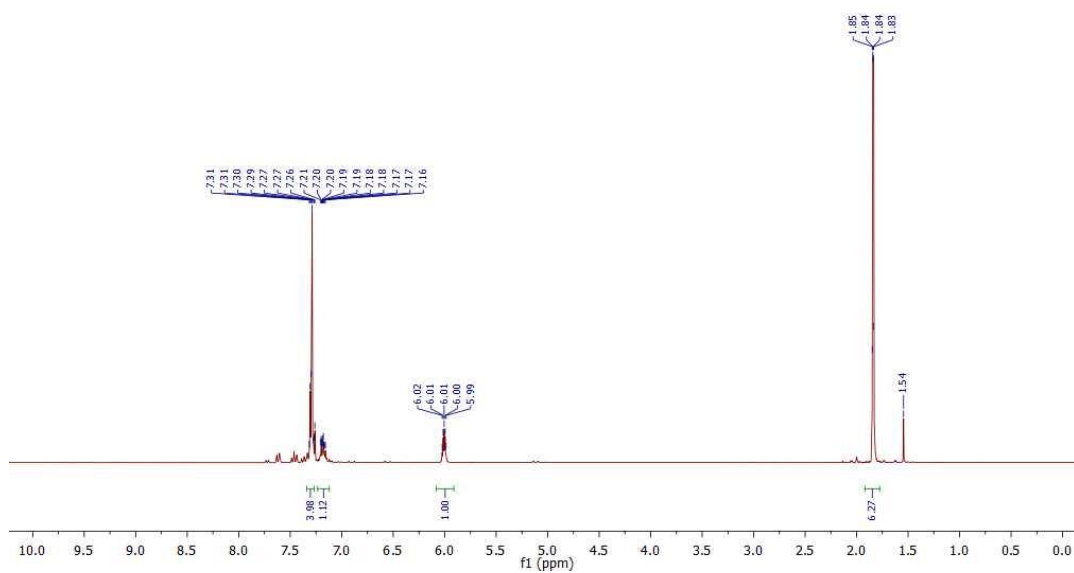
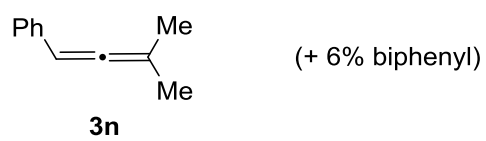


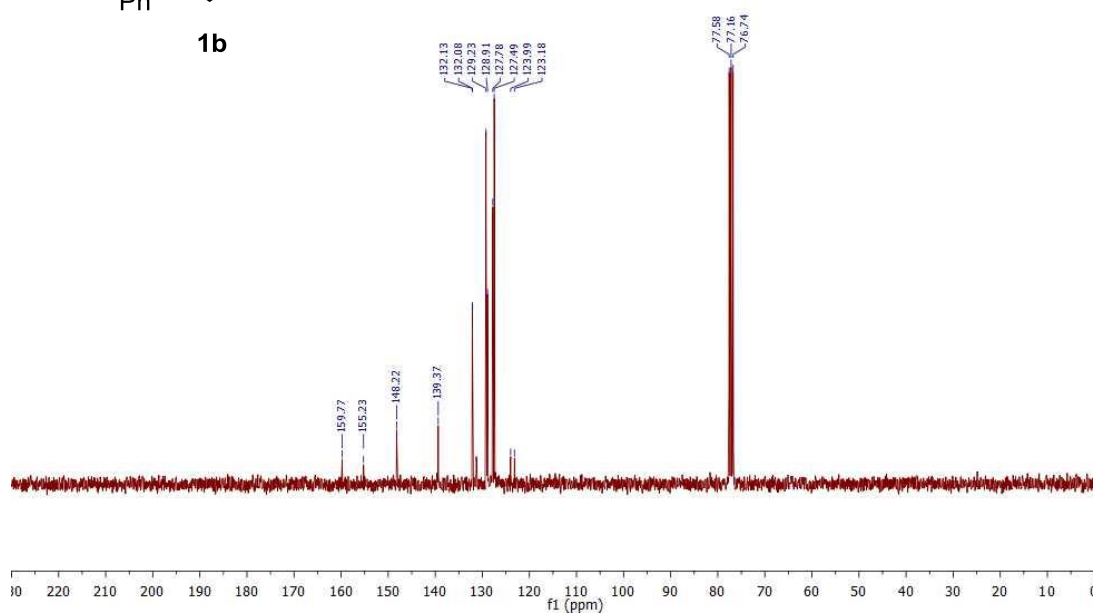
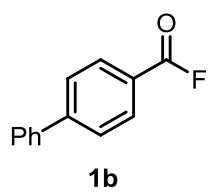
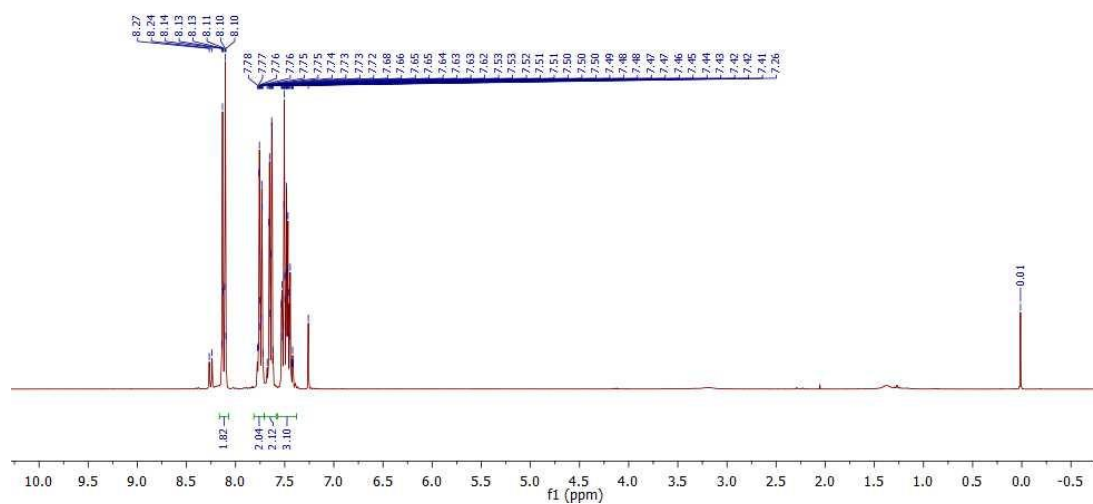
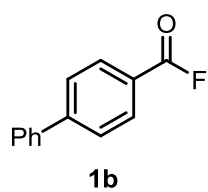
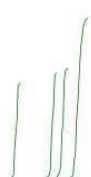


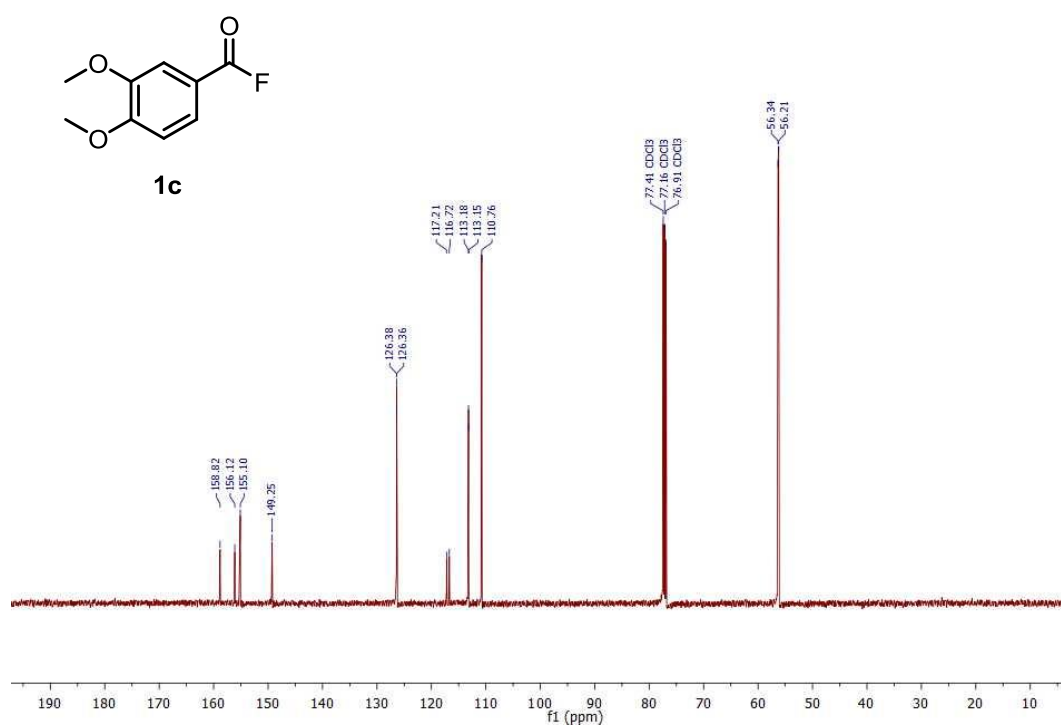
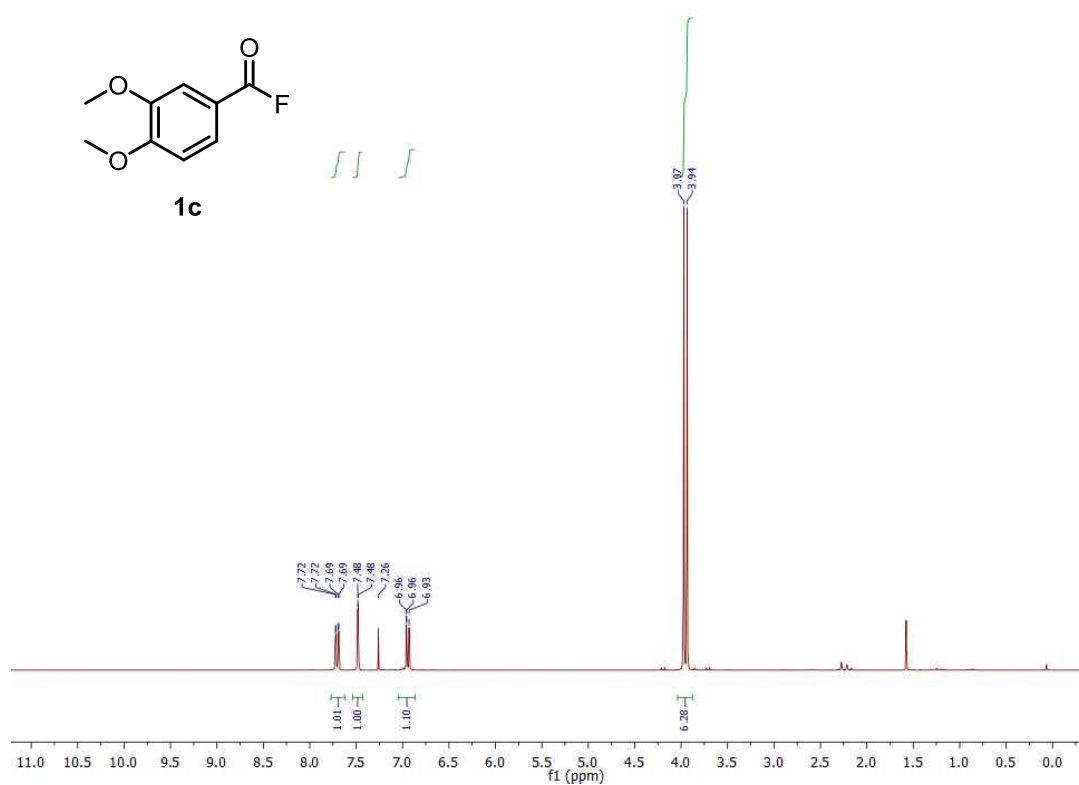


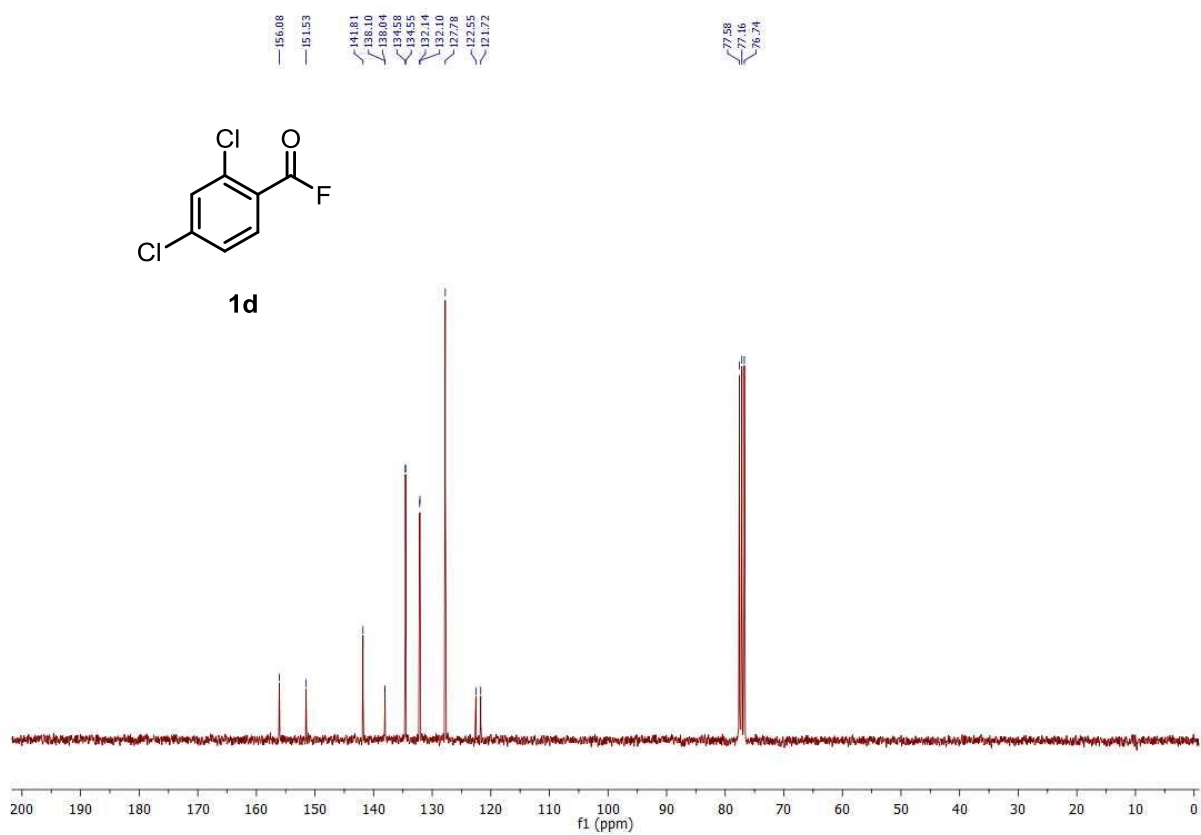
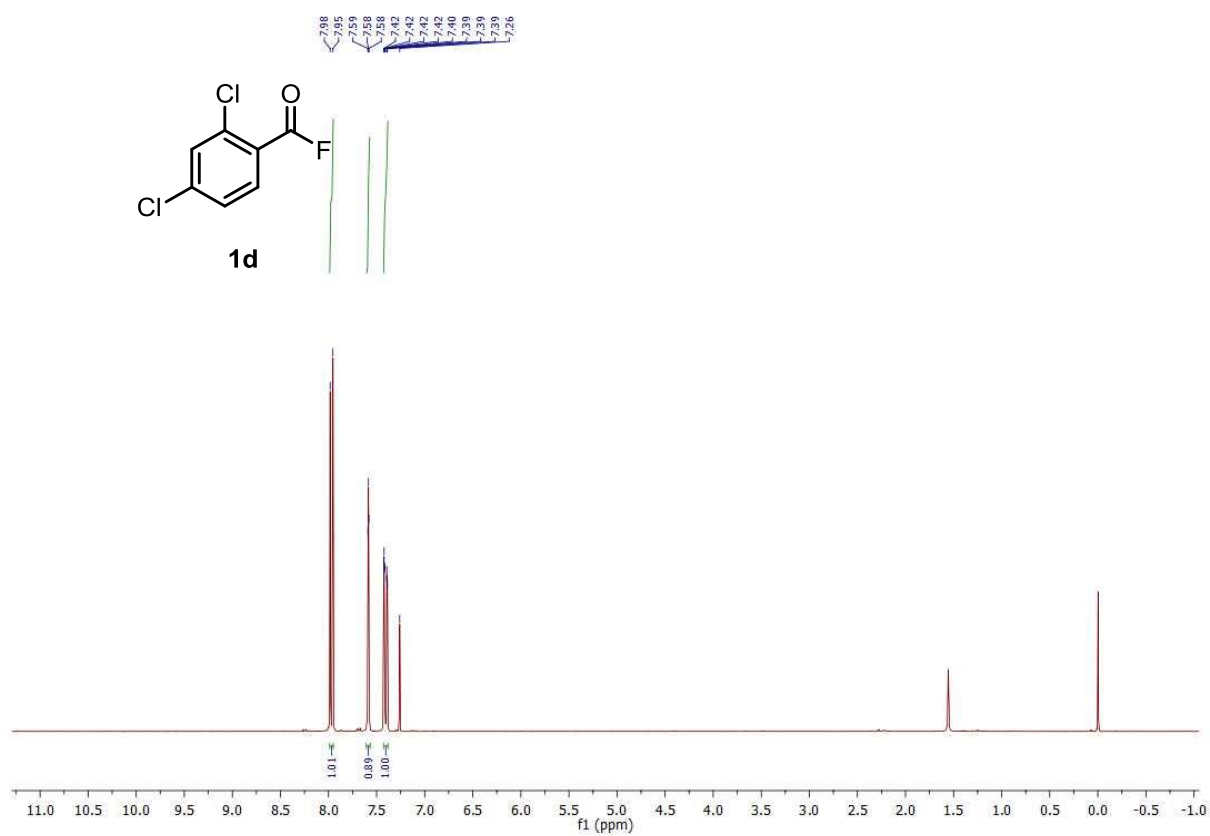


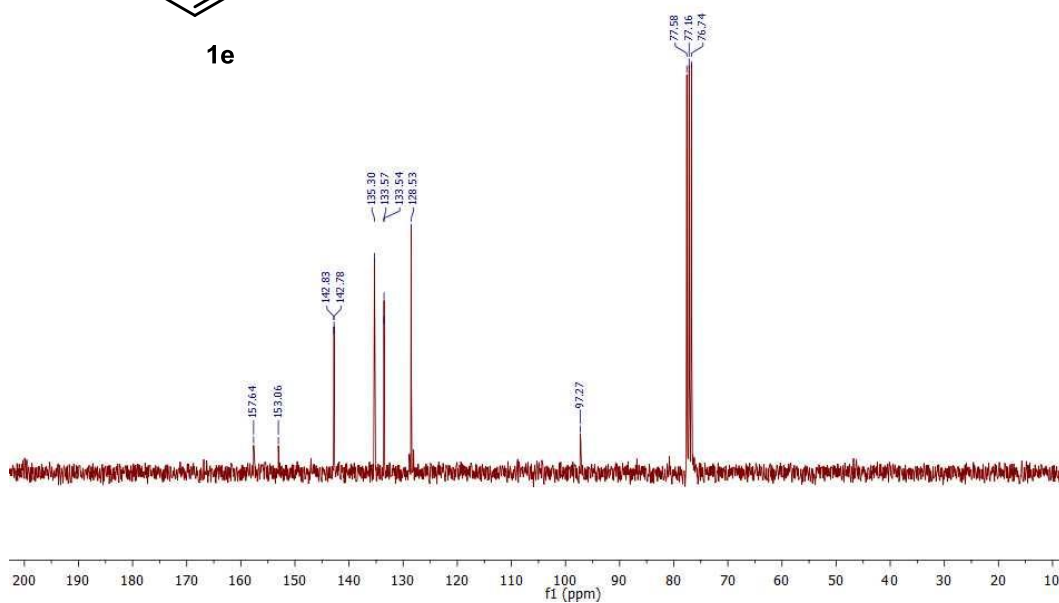
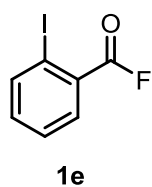
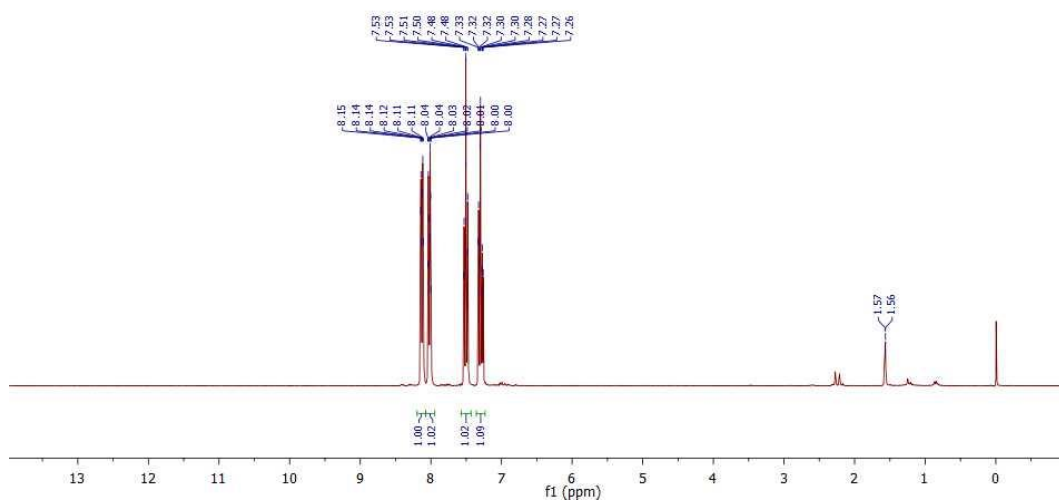
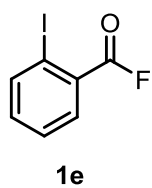


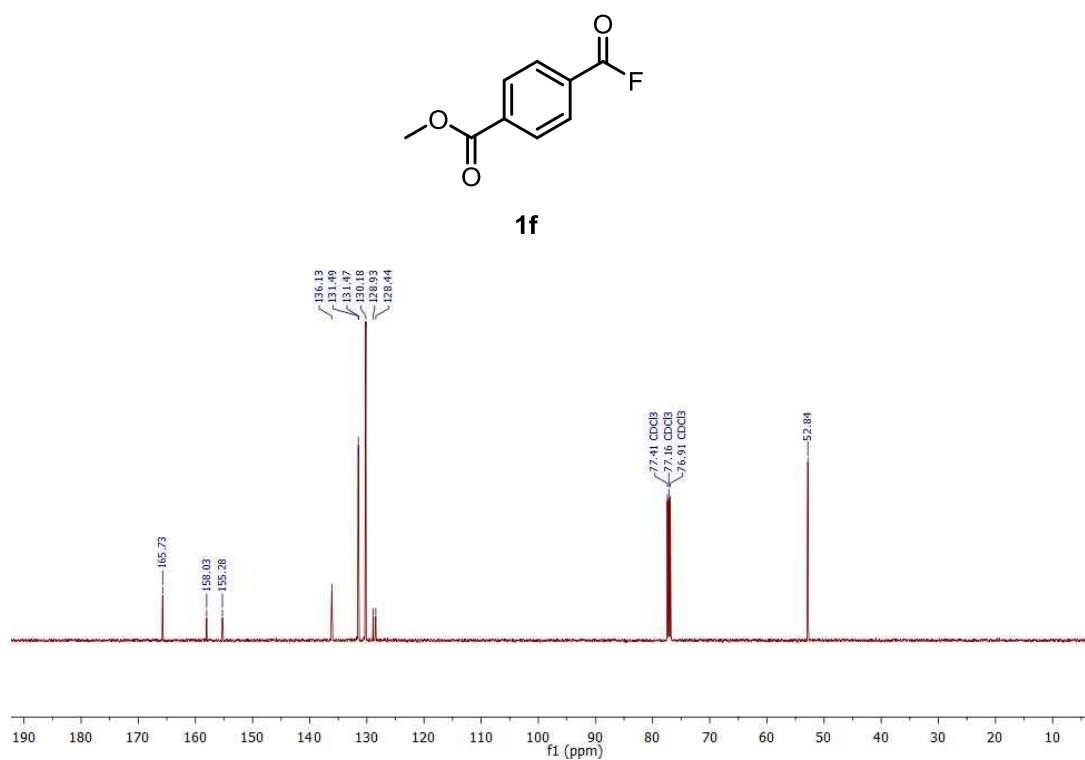
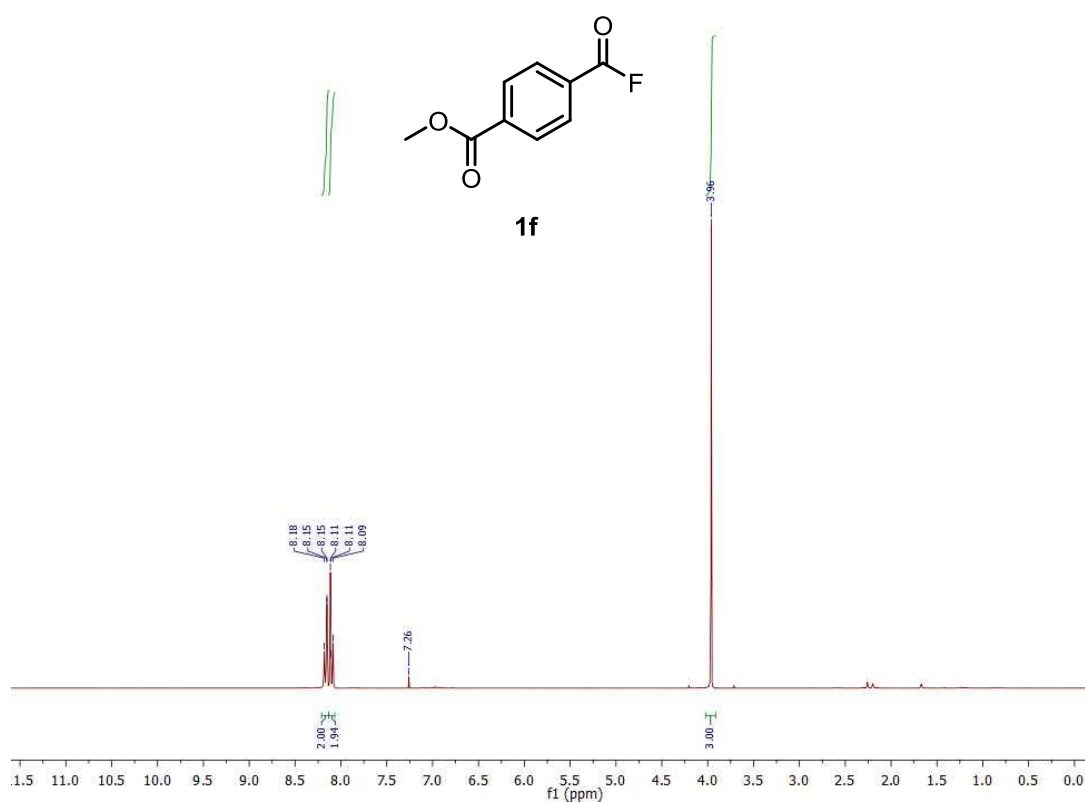


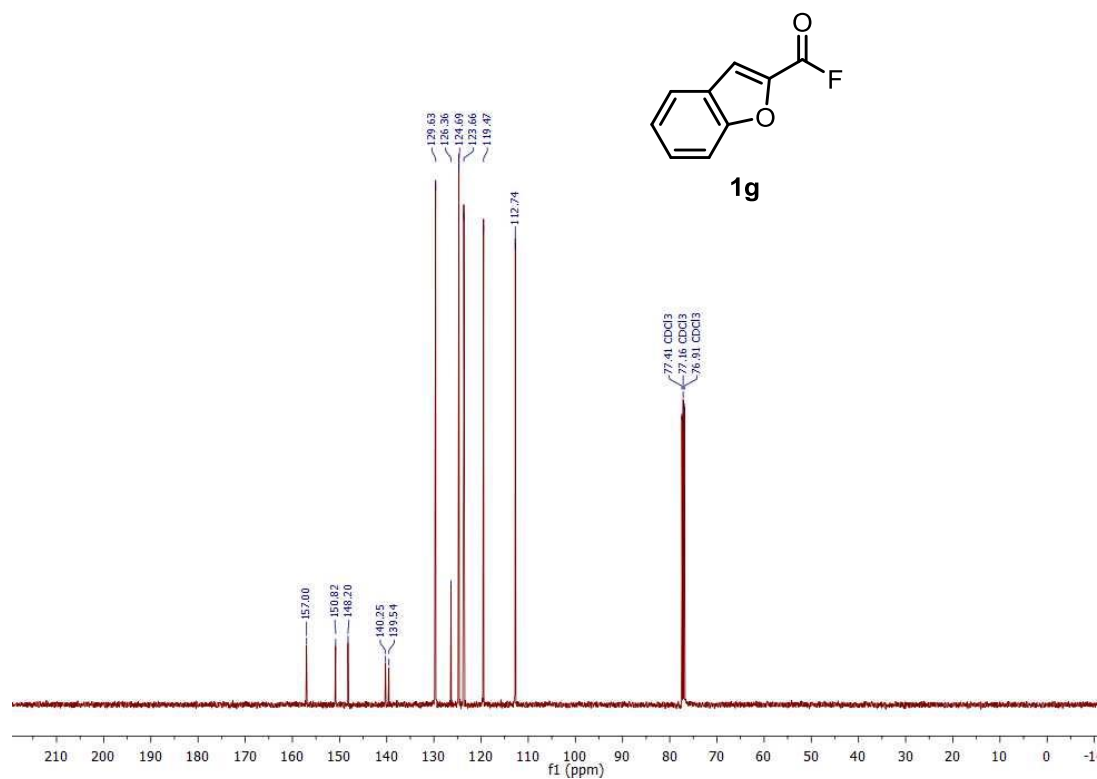
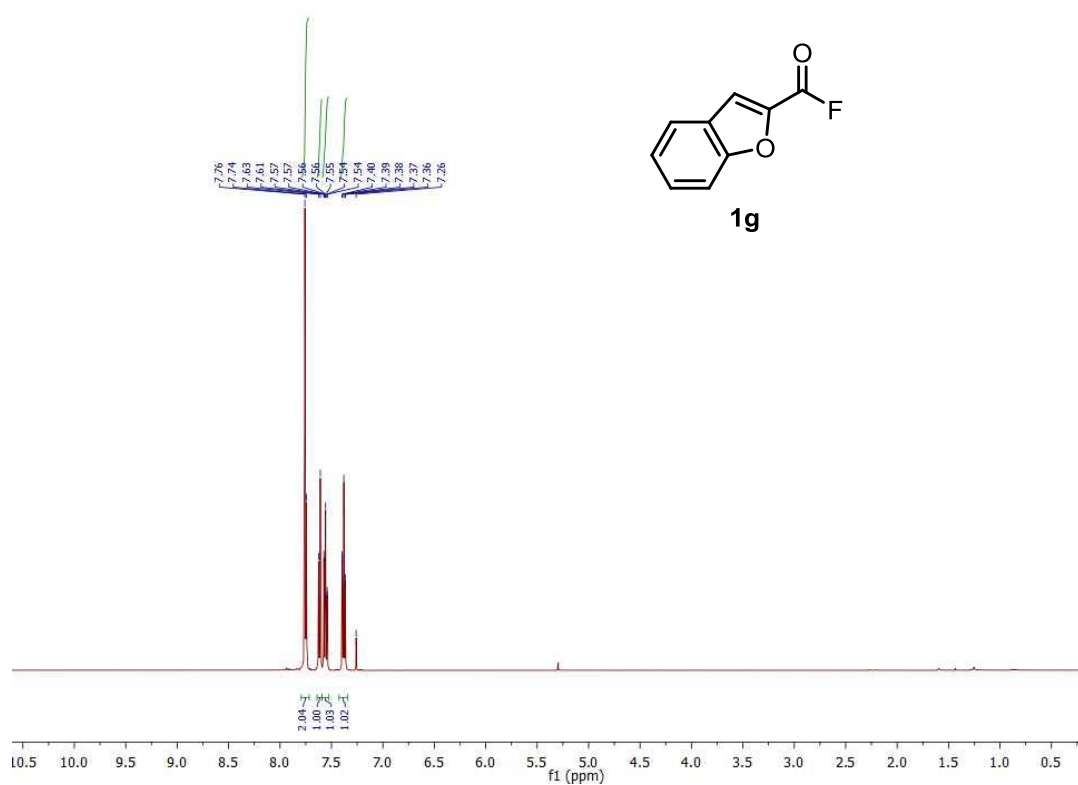


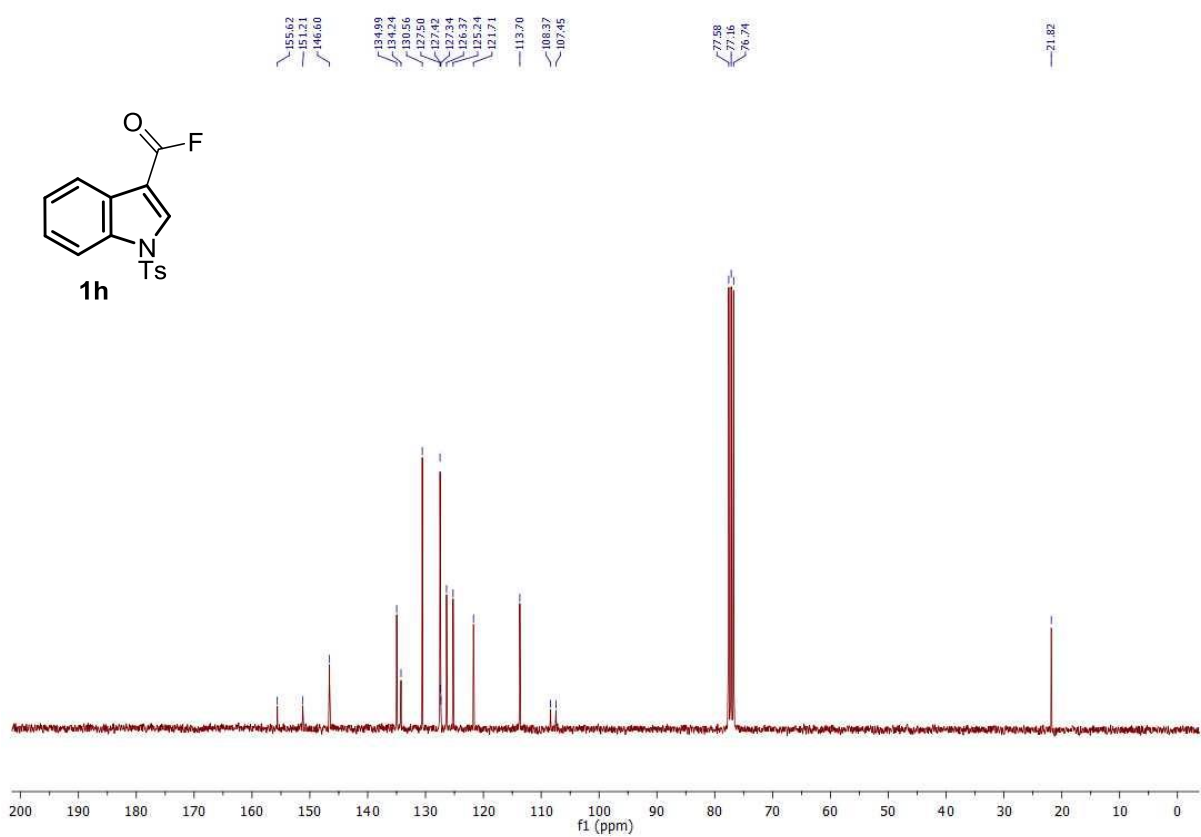
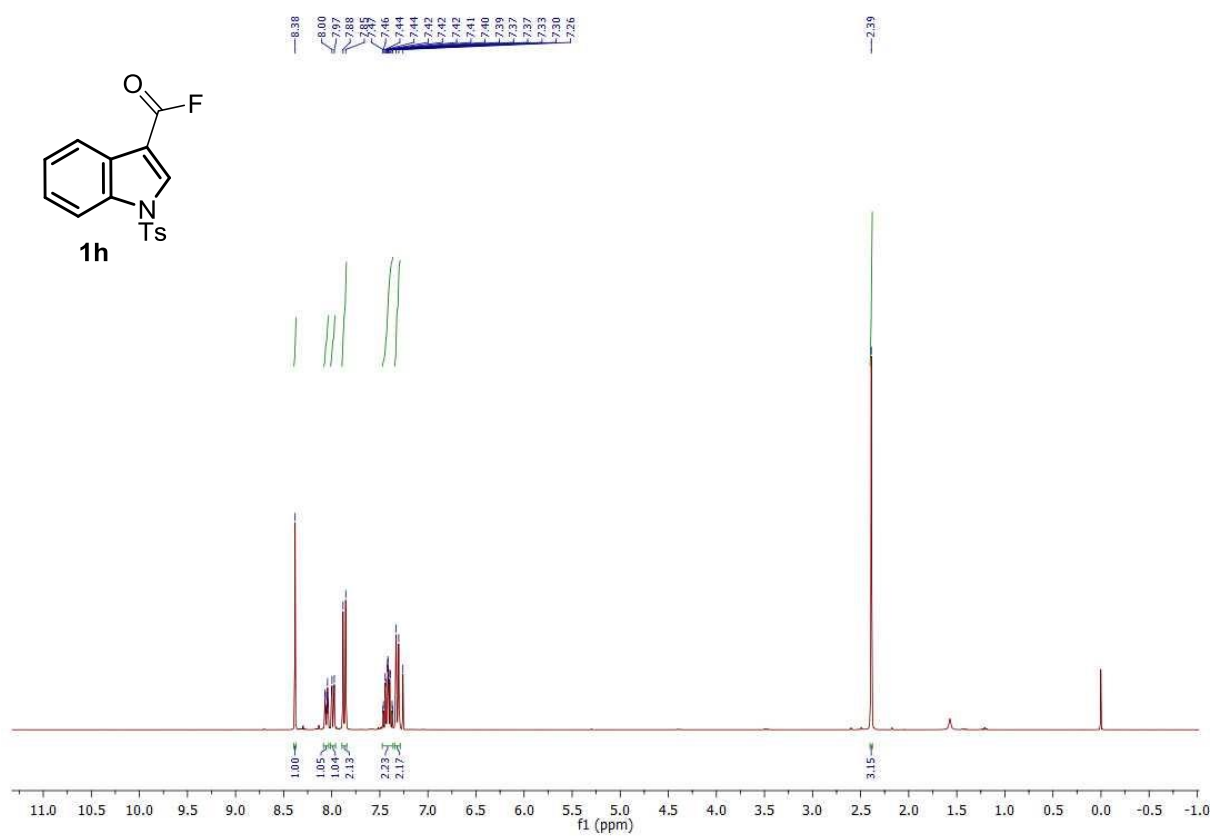


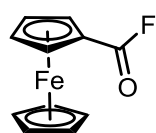




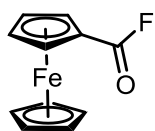
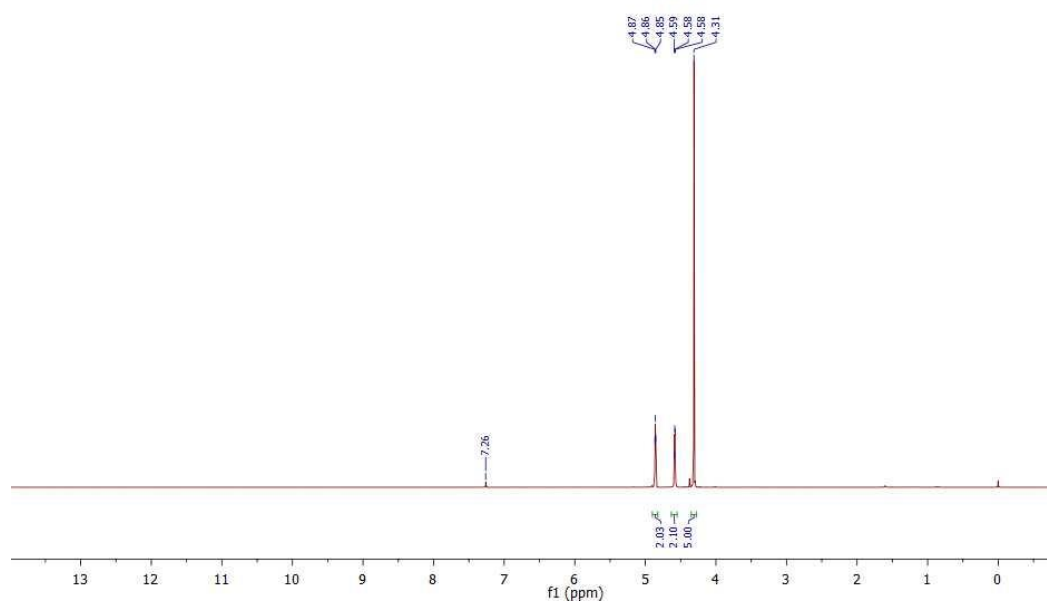








1i



1i

