Electronic Supplementary Material (ESI) for Chemical Science

Carbon-carbon bond construction using boronic acids and aryl methyl sulfides: Orthogonal reactivity in Suzuki-type couplings

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Supplementary Information

Experimental – Organic synthesis

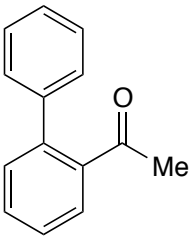
General experimental methods

Reactions were performed under inert atmosphere of nitrogen with anhydrous solvent unless otherwise stated. All glassware was oven dried at >80 °C, and allowed to cool to room temperature under a positive nitrogen pressure. Reactions were monitored by TLC until deemed complete using aluminium backed silica plates. Plates were visualised under ultraviolet light and/or by staining with $KMnO_4$. Reagents were purchased from Sigma-Aldrich Chemical Co. Ltd., Acros Organics Ltd., Lancaster Synthesis Ltd, or Strem Chemicals Inc. and were used as supplied unless otherwise stated. Anhydrous acetonitrile, diethyl ether, dichloromethane, toluene and tetrahydrofuran were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. Acetone was distilled from Drierite®. 1,2-Dichloroethane was distilled from calcium hydride. Petrol refers to the fractions obtained between 30 and 40 °C. Ether refers to diethyl ether. Flash chromatography was carried out using matrix 60 silica.

^{1}H NMR spectra were obtained on a Bruker DQX-400 (400 MHz) or Bruker AVC-500 (500 MHz) spectrometer using the residual solvent as an internal standard. ^{13}C NMR spectra were obtained on a Bruker DQX-400 (100 MHz) or Bruker AVC-500 (125 MHz) spectrometer using the residual solvent as an internal standard. Chemical shifts were reported in parts per million (ppm) with the multiplicities of the spectra reported as following: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Low resolution ESI mass spectra were recorded on a Fisons Platform spectrometer. High resolution ESI mass spectrometry measurements were recorded on a Brucker Daltronics microTOF (ESI) spectrometer by the internal service at the Department of Organic Chemistry, University of Oxford. Infra-red spectra were recorded as thin films on a Bruker Tensor 27 FT-IR spectrometer. Melting points were determined using a Stuart Scientific Melting Point Apparatus SMP1.

Rh(I)-catalysed Suzuki Couplings

1-([1,1'-Biphenyl]-2-yl)ethanone (3a)



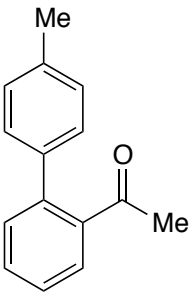
General Procedure A

To a flask containing [Rh(^{i}Pr$_2$PCH$_2$P^{i}Pr$_2$)(C$_6$H$_5$F)][BAr$^{F}_4$] **A** (10 mg, 0.0075 mmol), 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) phenylboronic acid (28 mg, 0.23 mmol) and Ag_2CO_3 (41 mg, 0.15 mmol) under an atmosphere of N_2 was added anhydrous acetone (2 mL). The suspension was heated to 55 °C for 16 h, allowed to cool to room temperature, filtered through a small plug of silica and concentrated *in vacuo*. The product was purified by silica gel chromatography, eluted with 5% ether/petrol to yield the biaryl **3a** as a colourless oil (28 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5 1.5 Hz, 1H), 7.52 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45-7.40 (m, 7H), 7.37-7.35 (m, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 140.7, 140.5, 130.7, 130.2, 128.87, 128.69, 127.90, 127.87, 127.5, 30.4; ν_{max} (film)/cm^{-1}1686, 1268, 1233, 759, 743, 702; MS (ESI^{+}) *m/z* (rel intensity) 197 [35, (M+H)$^{+}$], 219 [100, (M+Na)$^{+}$].

These data are consistent with previously reported values.[1]

1-(4'-Methyl-[1,1'-biphenyl]-2-yl)ethanone (3b)

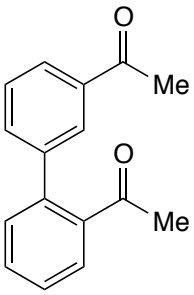


Compound **3b** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and *p*-tolylboronic acid (16 mg, 0.11 mmol) to give the product as a colourless oil (13 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 2H), 7.42-7.37 (m, 2H), 7.23 (br s, 4H), 2.41 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 140.9, 137.8, 130.7, 130.2, 129.4, 128.7, 127.8, 127.2, 30.5, 21.2 ; ν_{max} (film)/cm^{-1} 1683, 1441, 1353, 1266, 1231, 821, 761; MS (ESI$^+$) *m/z* (rel intensity) 233 [95, (M+Na)$^+$], 249 [100, (M+K)$^+$].

These data are consistent with previously reported values.[2]

1,1'-([1,1'-Biphenyl]-2,3'-diyl)diethanone (3c)

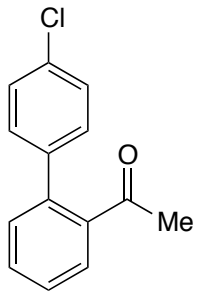


Compound **3c** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 3-acyl(phenyl)boronic acid (18 mg, 0.11 mmol.) to give the product as a colourless oil (17 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (ddd, *J* = 5.5, 3.5, 2 Hz, 1H), 7.94 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.56-7.51 (m, 3H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39 (dd, *J* = 7.5, 0.5 Hz, 1H), 2.63 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 197.8, 141.4, 140.4, 139.6, 137.4, 133.5, 131.0, 130.5, 128.9, 128.5, 128.13, 127.94, 127.6, 30.4, 26.8; ν_{max} (film)/cm^{-1} 1686, 1421, 1229, 910, 731; MS (ESI$^+$) *m/z* (rel intensity) 261 [100, (M+Na)$^+$], 499 [40, (2M+Na)$^+$]; HRMS (ESI$^+$) 261.0878 (261.0886 calc. for $C_{16}H_{14}NaO_2$ (M+Na)$^+$).

These data are consistent with previously reported values.[3]

1-(4'-Chloro-[1,1'-biphenyl]-2-yl)ethanone (3d)

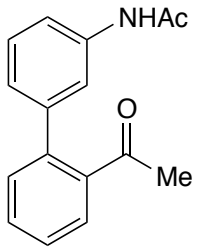


Compound **3d** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 4-chloro(phenyl)boronic acid (17 mg, 0.11 mmol.) to give the product as a colourless oil (15 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5, 1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42-7.40 (m, 2H), 7.36 (dd, *J* = 7.5, 1 Hz, 1H), 7.29 -7.27(m, 2H), 2.10 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 140.6, 139.25, 139.22, 134.1, 130.9, 130.26, 130.09, 128.9, 128.0, 127.8, 30.5; ν_{max} (film)/cm^{-1} 1688, 1495, 1265, 1232, 1091, 833, 761; MS (ESI^{+}) *m/z* (rel intensity) 231 [35, (M+H)$^{+}$], 253 [100, (M+Na)$^{+}$].

These data are consistent with previously reported values.[2]

***N*-(2'-Acetyl-[1,1'-biphenyl]-3-yl)acetamide (3e)**

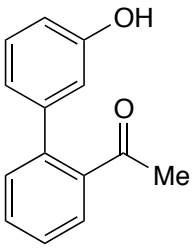


Compound **3e** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 3-acetamido(phenyl) boronic acid (20 mg, 0.11 mmol.) to give the product as a colourless oil (17 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.59 (dd, *J* = 8, 1 Hz, 1H), 7.54 (dd, *J* = 7.5, 1 Hz, 1H), 7.51-7.46 (m, 2H), 7.40 (td, *J* = 7.5, 1 Hz, 1H), 7.37-7.31 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 168.8, 141.4, 140.6, 140.0, 138.4,

130.8, 130.3, 129.3, 127.8, 127.6, 124.6, 120.0, 119.2, 30.5, 24.6; ν_{max} (film)/cm^{-1} 3307, 1671, 1551, 1420, 1272, 759; MS (ESI$^+$) *m/z* (rel intensity) 254 [20, (M+H)$^+$], 276 [100, (M+Na)$^+$]; HRMS (ESI$^+$) 276.0991 (276.0995calc. for $C_{16}H_{15}NNaO_2$ (M+Na)$^+$).

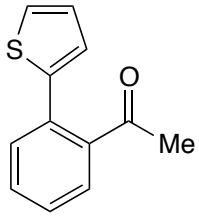
1-(3'-Hydroxy-[1,1'-biphenyl]-2-yl)ethanone (3f)



Compound **3f** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 3-hydroxy(phenyl) boronic acid (15 mg, 0.11 mmol.), columned with 20 % ether/petrol to give the product as a colourless oil (11 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ) 7.53-7.48 (m, 2H), 7.43-7.37 (m, 2H), 7.29 (t, *J* = 8 Hz, 1H), 6.92-6.87 (m, 2H), 6.81 (t, *J* = 2 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 156.0, 142.1, 140.7, 140.2, 130.8, 130.1, 127.78, 127.59, 121.2, 115.9, 115.1, 30.5; ν_{max} (film)/cm^{-1} 3343 br, 1672, 1591, 1446, 1241, 758; MS (ESI$^+$) *m/z* (rel intensity) 213 [20, (M+H)$^+$], 235 [100, (M+Na)$^+$].

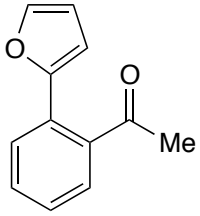
1-(2-(Thiophen-2-yl)phenyl)ethanone (3g)



Compound **3g** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 2-thiophene boronic acid (14 mg, 0.11 mmol.) to give the product as a colourless oil (14 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.44-7.40 (m, 3H), 7.25 (dd, *J* = 3, 1.5 Hz, 1H), 7.13 (dd, *J* = 4.5, 1.5 Hz, 1H), 2.11 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 141.0, 134.7, 130.6, 129.9, 128.3, 127.53, 127.50, 126.3, 123.4, 30.2; ν_{max} (film)/cm^{-1} 2360, 2341, 1710, 1220, 760; MS (ESI$^+$) *m/z* (rel intensity) 203 [30, $(M+H)^+$], 225 [100, $(M+Na)^+$]; HRMS (ESI$^+$) 225.0336 (225.0345 calc. for $C_{12}H_{10}NaOS$ $(M+Na)^+$).

1-(2-(Furan-2-yl)phenyl)ethanone (3h)

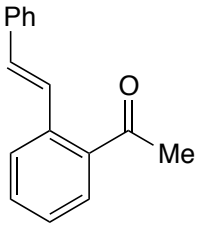


Compound **3h** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and 2-furanylboronic acid (14 mg, 0.11 mmol.) to give the product as a colourless oil (13 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.48-7.45 (m, 2H), 7.39-7.38 (m, 1H), 7.38-7.35 (m, 1H), 6.50 (dd, *J* = 2, 1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 143.3, 140.8, 140.1, 130.6, 130.3, 129.9, 127.4, 127.3, 124.9, 111.3, 30.5; ν_{max} (film)/cm^{-1} 1765, 1683, 1358, 1258, 1113, 1022, 961, 763; MS (ESI$^+$) *m/z* (rel intensity) 187 [10, $(M+H)^+$], 209 [40, $(M+Na)^+$], 239 [100, $(M+K)^+$].

These data are consistent with previously reported values.[2]

(*E*)-1-(2-Styrylphenyl)ethanone (3i)

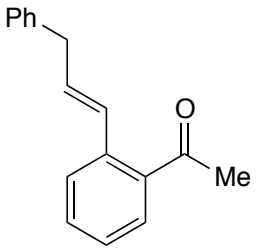


Compound **3i** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and (*E*)-styrylboronic acid (16 mg, 0.11 mmol.) to give the product as a colourless oil (18 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ) 7.72-7.66 (m, 3H), 7.55-7.52 (m, 2H), 7.50 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38-7.33 (m, 3H), 7.29-7.25 (m, 1H), 6.99 (d, *J* = 16 Hz, 1H), 2.62 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 137.42, 137.33, 137.28, 131.66,, 131.63 129.1, 128.7, 127.9, 127.39, 127.21, 126.8, 29.9; ν_{max} (film)/cm^{-1} 1768, 1684, 1254, 761, 699; MS (ESI^{+}) *m/z* (rel intensity) 130 [100], 245 [35, $(M+Na)^{+}$].

These data are consistent with previously reported values.[4]

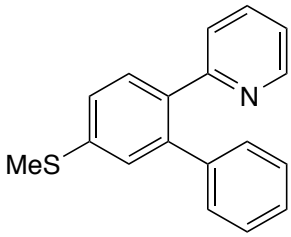
(*E*)-1-(2-(3-Phenylprop-1-en-1-yl)phenyl)ethanone (3j)



Compound **3j** was synthesised according to General Procedure A, using 1-(2-(methylthio)phenyl)ethanone **1** (13 mg, 0.075 mmol) and (*E*)-(3-phenylprop-1-en-1-yl)boronic acid (18 mg, 0.11 mmol.) to give the product as a colourless oil (16 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.5, 1 Hz, 1H), 7.53 (dd, *J* = 8, 0.5 Hz, 1H), 7.44-7.40 (m, 1H), 7.35-7.27 (m, 5H), 7.25-7.21 (m, 1H), 6.98 (d, *J* = 15.5 Hz, 1H), 6.25 (dt, *J* = 15.5, 7 Hz, 1H), 3.59 (d, *J* = 7 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 137.3, 132.3, 131.5, 129.8, 128.71, 128.52, 127.7, 126.8, 126.2, 39.6, 30.0; MS (ESI^{+}) *m/z* (rel intensity) 237 [30, $(M+H)^{+}$], 259 [100, $(M+Na)^{+}$].

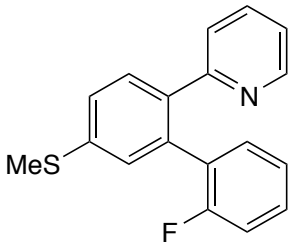
2-(5-(Methylthio)-[1,1'-biphenyl]-2-yl)pyridine (5)



Compound **5** was synthesised according to General Procedure A, using 2-(2,4-bis(methylthio)phenyl)pyridine **4** (19 mg, 0.075 mmol) and phenylboronic acid (14 mg, 0.11 mmol.) to give the product as a colourless oil (17 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 5, 2, 1 Hz, 1H), 7.67 (d, *J* = 8 Hz, 1H), 7.40-7.35 (m, 2H), 7.30 (d, *J* = 2 Hz, 1H), 7.19-7.16 (m, 2H), 7.11 (ddd, *J* = 7.5, 5, 1 Hz, 1H), 6.85 (dt, *J* = 8, 1 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 149.2, 141.1, 140.9, 139.3, 135.9, 135.4, 131.0, 129.6, 128.18, 128.04, 127.0, 125.45, 125.41, 121.3, 15.6; ν_{max} (film)/cm^{-1} 1589, 1459, 1442, 1150, 770, 701; MS (ESI$^+$) *m/z* (rel intensity) 278 [100, $(M+H)^+$]; HRMS (ESI$^+$) 278.0995 (278.0998 calc. for $C_{18}H_{16}NS$ $(M+H)^+$).

2-(2'-Fluoro-5-(methylthio)-[1,1'-biphenyl]-2-yl)pyridine (6)

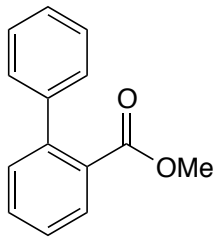


Compound **6** was synthesised according to General Procedure A, using 2-(2,4-bis(methylthio)phenyl)pyridine **4** (19 mg, 0.075 mmol) and (*o*-fluorophenyl)boronic acid (15 mg, 0.11 mmol.) to give the product as a colourless oil (18 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H), 7.69 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.43-7.37 (m, 2H), 7.28-7.23 (m, 2H), 7.19 (td, *J* = 7.5, 2.0 Hz, 1H), 7.10-7.05 (m, 2H), 6.97-6.92 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 158.2, 149.2, 139.1, 137.0, 135.5, 134.8, 131.9, 130.5, 129.3, 128.7, 128.5, 126.1, 124.0, 121.5, 115.7, 115.5, 15.6 ; ν_{max}

(film)/cm^{-1} 1590, 1484, 1429, 1077, 788, 761; MS (ESI^+) *m/z* (rel intensity) 296 [100, $(M+H)^+$]; HRMS (ESI^+) 296.0907 (296.0904 calc. for $C_{18}H_{15}FNS$ $(M+H)^+$).

Methyl [1,1'-biphenyl]-2-carboxylate (8)

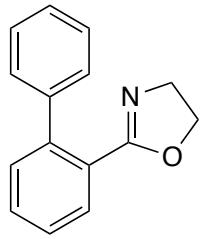


Compound **8** was synthesised according to General Procedure A, using methyl 2-(methylthio)benzoate **7** (14 mg, 0.075 mmol) and phenylboronic acid (14 mg, 0.11 mmol.) to give the product as a colourless oil (14 mg, 95%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddd, *J* = 7.5, 1.5, 0.5 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45-7.37 (m, 5H), 7.34 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 142.5, 141.3, 131.3, 130.85, 130.71, 129.8, 128.3, 128.1, 127.23, 127.17, 52.0; ν_{max} (film)/cm^{-1}; MS (ESI^+) *m/z* (rel intensity) 213 [30, $(M+H)^+$], 235 [100, $(M+Na)^+$].

These data are consistent with previously reported values.[5]

2-([1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (10)



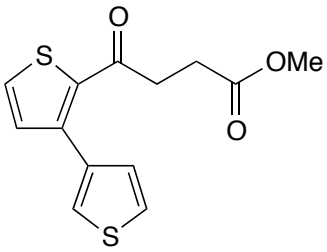
Compound **10** was synthesised according to General Procedure A, using 2-(2-(methylthio)phenyl)-4,5-dihydrooxazole (16 mg, 0.075 mmol) and phenylboronic acid (14 mg, 0.11 mmol.) to give the product as a colourless oil (9 mg, 54%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43-7.39 (m, 1H), 7.32-7.29 (m, 5H), 7.29-7.24 (m, 2H), 4.03 (td, *J* = 9.5, 1.0 Hz, 2H), 3.86-3.81 (m, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 166.3, 141.9, 141.3, 130.6, 130.4, 130.2, 128.3, 128.1, 127.5, 127.23, 127.15, 67.9, 54.9; ν_{max} (film)/cm^{-1} 1652, 1355, 1115, 1079, 974, 771, 743, 698; MS (ESI^+) *m/z* (rel intensity) 224 [100, $(M+H)^+$].

These data are consistent with previously reported values.[6]

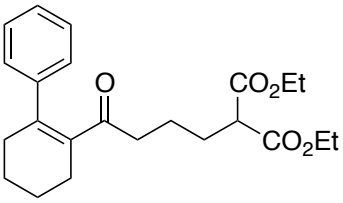
Methyl 4-([3,3'-bithiophen]-2-yl)-4-oxobutanoate (12)



Compound **12** was synthesised according to General Procedure A, using methyl 4-(3-(methylthio)thiophen-2-yl)-4-oxobutanoate **11** (30 mg, 0.12 mmol) and 3-thiophene boronic acid (23 mg, 0.18 mmol.) to give the product as a colourless oil (31 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 5.0 Hz, 1H), 7.41 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.31 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.14 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 3.59 (s, 3H), 2.88 (t, *J* = 6.5 Hz, 2H), 2.56 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 173.2, 141.2, 137.8, 136.1, 132.1, 130.6, 128.8, 125.5, 124.6, 51.8, 36.0, 28.2; ν_{max} (film)/cm^{-1} 1735, 1651, 1402, 1214, 1165, 854, 736; MS (ESI^+) *m/z* (rel intensity) 281 [100, $(M+H)^+$], 303 [75, $(M+Na)^+$]; HRMS (ESI^+) 303.0106 (303.0120 calc. for $C_{13}H_{12}O_3S_2$ $(M+H)^+$).

Diethyl 2-(4-oxo-4-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)butyl)malonate (14)



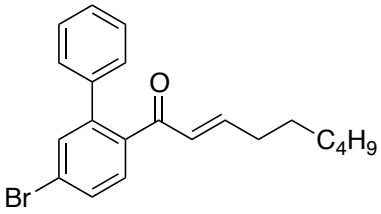
Compound **14** was synthesised according to General Procedure A, using diethyl 2-(4-(2-(methylthio)cyclohex-1-en-1-yl)-4-oxobutyl)malonate **11** (27 mg, 0.075 mmol),

phenylboronic acid (14 mg, 0.11 mmol) and Cu(OAc) (13 mg, 0.11 mmol) to give the product as a colourless oil (22 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 3H), 7.14-7.11 (m, 2H), 4.14 (qd, *J* = 7, 1 Hz, 4H), 3.10 (t, *J* = 7.5 Hz, 1H), 2.41-2.37 (m, 2H), 2.34-2.31 (m, 2H), 1.93 (t, *J* = 7.5 Hz, 2H), 1.77-1.67 (m, 5H), 1.57-1.52 (m, 2H), 1.36-1.29 (m, 2H), 1.23 (t, *J* = 7 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 169.3, 142.4, 141.5, 137.8, 128.5, 127.82, 127.71, 61.3, 51.8, 42.1, 31.7, 28.0, 26.9, 22.7, 22.03, 22.01, 14.1; ν_{max} (film)/cm^{-1} 2937, 1730, 1677, 1149, 1028, 716, 703; MS (ESI$^+$) *m/z* (rel intensity) 204 [100], 409 [75, $(M+Na)^+$]; HRMS (ESI$^+$) 409.1981 (409.1985 calc. for $C_{23}H_{30}O_5Na$ $(M+Na)^+$).

Tandem Hydroacylation / Suzui Coupling Reactions

(*E*)-1-(5-Bromo-[1,1'-biphenyl]-2-yl)non-2-en-1-one (16a)

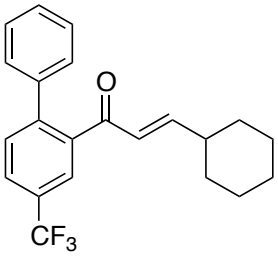


General Procedure B

To a solution of 4-bromo-2-(methylthio)benzaldehyde **15a** (17 mg, 0.075 mmol) and [Rh(^{i}Pr$_2$PCH$_2$P^{i}Pr$_2$)(C$_6$H$_5$F)][BAr$^{F}_4$] **A** (9 mg, 0.0065 mmol) in acetone (20 μL) was added 1-octyne (16 μL, 0.11 mmol) and the solution stirred at rt for 5 min. The solution was diluted with acetone (1 mL) and was transferred by cannula to a flask containing phenylboronic acid (28 mg, 0.23 mmol) and Ag_2CO_3 (41 mg, 0.15 mmol). The resulting suspension was heated to 55 °C for 16 h, allowed to cool to room temperature, filtered through a small plug of silica and concentrated *in vacuo*. The product was purified by silica gel chromatography, eluted with 5% ether/petrol to yield to title compound (20 mg, 72%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2 Hz, 1H), 7.56 (dd, *J* = 8, 2 Hz, 1H), 7.40-7.35 (m, 4H), 7.30-7.27 (m, 2H), 6.53 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.89 (dt, *J* = 15.5, 1.5 Hz, 1H), 1.95 (qd, *J* = 7, 1 Hz, 2H), 1.30-1.21 (m, 2H), 1.11-1.09 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 150.7, 142.5, 139.1, 138.5, 132.8, 130.36, 130.29, 130.20, 128.9, 128.6, 128.1, 124.5, 32.4, 31.5, 28.7, 27.8, 22.5, 14.1; ν_{max} (film)/cm^{-1} 2927, 1653, 1583, 1288, 701; MS (ESI$^+$) *m/z* (rel intensity) 370 [40, (M+H)$^+$], 393 [100, (M+Na)$^+$]; HRMS (ESI$^+$) 393.0821 (393.0824 calc. for C$_{21}$H$_{24}$^{79}BrONa (M+Na)$^+$).

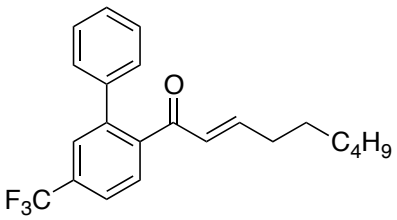
(*E*)-3-Cyclohexyl-1-(4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)prop-2-en-1-one (16b)



Compound **16b** was synthesised according to General Procedure A, using 2-(methylthio)-5-(trifluoromethyl)benzaldehyde **15b** (17 mg, 0.075 mmol), phenylboronic acid (14 mg, 0.11 mmol) and cyclohexylacetylene (14 μL, 0.11 mmol) to give the product as a colourless oil (22 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.55-7.52 (m, 1H), 7.33-7.29 (m, 3H), 7.24-7.22 (m, 2H), 6.33 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.78 (dd, *J* = 16.0, 1.5 Hz, 1H), 1.86-1.76 (m, 1H), 1.58-1.50 (m, 3H), 1.38-1.34 (m, 2H), 1.14-0.96 (m, 3H), 0.75 (qd, *J* = 11.9, 2.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ196.9, 156.1, 142.8, 141.2, 140.3, 139.2, 132.1 (q, J = 26 Hz), 129.11, 129.05, 128.7, 128.3, 127.8, 126.8 (m), 124.2 (m), 122.7 (q, J = 216 Hz), 40.6, 31.4, 25.8, 25.5; MS (ESI^+) *m/z* (rel intensity) 116 [100], 359 [10, $(M+H)^+$].

(*E*)-1-(5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)non-2-en-1-one (16c)

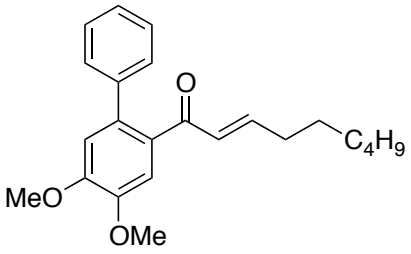


Compound **16c** was synthesised according to General Procedure A, using 4-trifluoromethyl-2-(methylthio)benzaldehyde **15a** (17 mg, 0.075 mmol), phenylboronic acid (14 mg, 0.11 mmol) and 1-octyne (13 μL, 0.11 mmol) to give the product as a colourless oil (20 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.7 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.40-7.38 (m, 3H), 7.33-7.31 (m, 2H), 6.54 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.93 (dt, *J* = 15.5, 1.5 Hz, 1H), 1.97 (q, *J*

= 6.5 Hz, 2H), 1.28-1.09 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 151.4, 143.9, 140.2, 139.1, 130.5, 130.1, 129.5, 128.9, 128.7, 128.4, 126.89, 126.86, 125.6, 32.4, 31.5, 28.7, 27.8, 22.5, 14.0; ν_{max} (film)/cm^{-1} 2929, 1655, 1620, 1334, 1169, 1127; MS (ESI$^+$) *m/z* (rel intensity) 361 [100, (M+H)$^+$], 383 [60, (M+Na)$^+$]; HRMS (ESI$^+$) 361.1760 (361.1774 calc. for $C_{22}H_{24}F_3O$ (M+H)$^+$).

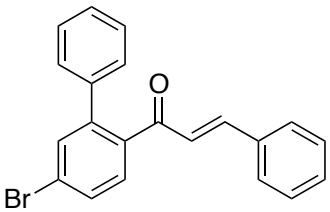
(*E*)-1-(4,5-dimethoxy-[1,1'-biphenyl]-2-yl)non-2-en-1-one (16d)



Compound **16d** was synthesised according to General Procedure A, using 4,5-dimethoxy-2-(methylthio)benzaldehyde **15d** (16 mg, 0.075 mmol), phenylboronic acid (14 mg, 0.11 mmol) and 1-octyne (13 μL, 0.11 mmol) to give the product as a colourless oil (16 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 4H), 7.16 (s, 1H), 6.88 (s, 1H), 6.59 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.82 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 1.91-1.87 (m, 2H), 1.27-1.09 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 150.6, 148.5, 148.1, 140.7, 134.9, 132.0, 130.3, 129.2, 128.4, 127.5, 112.6, 111.9, 56.1, 32.2, 31.6, 28.7, 27.8, 22.5, 14.1; ν_{max} (film)/cm^{-1} 2928, 1664, 1597, 1350, 1269, 1036, 766, 703; MS (ESI$^+$) *m/z* (rel intensity) 353 [100, (M+H)$^+$]; HRMS (ESI$^+$) 353.2096 (353.2096 calc. for $C_{23}H_{29}O_3$ (M+H)$^+$).

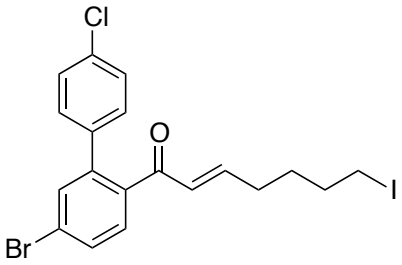
(*E*)-1-(5-bromo-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-en-1-one (16e)



Compound **16e** was synthesised according to General Procedure A, using 4-bromo-2-(methylthio)benzaldehyde **15a** (17 mg, 0.075 mmol), phenylboronic acid (14 mg, 0.11 mmol) and phenylacetylene (13 μL, 0.11 mmol) to give the product as a colourless oil (15 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2 Hz, 1H), 7.62-7.58 (m, 2H), 7.54 (d, *J* = 8 Hz, 1H), 7.39-7.27 (m, 8H), 7.24-7.21 (m, 2H), 6.49 (d, *J* = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 144.0, 139.0, 138.5, 135.7, 134.5, 133.0, 131.62, 131.56, 130.53, 130.45, 129.0, 128.8, 128.6, 128.4, 128.2, 126.3; ν_{max} (film)/cm^{-1} 1666, 1601, 1581, 825, 766, 699; MS (ESI$^+$) *m/z* (rel intensity) 363 [100, $(M+H)^+$], 387 [60, $(M+Na)^+$]; HRMS (ESI$^+$) 385.0190 (385.0198 calc. for $C_{21}H_{16}{}^{79}BrO$ $(M+H)^+$).

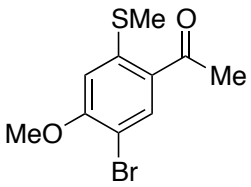
(*E*)-1-(5-bromo-4'-chloro-[1,1'-biphenyl]-2-yl)-9-iodonon-2-en-1-one (16f)



Compound **16f** was synthesised according to General Procedure A, using 4-bromo-2-(methylthio)benzaldehyde **15a** (17 mg, 0.075 mmol), (4-chlorophenyl)boronic acid (17 mg, 0.11 mmol) and 6-iodo-1-hexyne (16 μL, 0.11 mmol) to give the product as a colourless oil (21 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.48 (dd, *J* = 2.0, 0.5 Hz, 1H), 7.33-7.29 (m, 3H), 7.17-7.15 (m, 2H), 6.45 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.86 (d, *J* = 15.5 Hz, 1H), 3.04 (t, *J* = 7.0 Hz, 2H), 1.96 (qd, *J* = 7.0, 1.5 Hz, 2H), 1.58-1.51 (m, 2H), 1.30-1.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 149.6, 141.2, 138.3, 137.6, 134.5, 132.7, 130.83, 130.69, 130.35, 130.26, 129.0, 124.9, 32.4, 31.3, 28.7, 6.3; ν_{max} (film)/cm^{-1} 1651, 1582, 1287, 831; HRMS (FI$^+$) 503.9175 (503.9175 calc. for $C_{19}H_{17}{}^{81}BrIClO$ $(M)^+$).

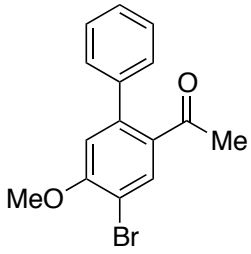
1-(5-bromo-4-methoxy-2-(methylthio)phenyl)ethanone (17)



To a solution of 1-(4-methoxy-2-(methylthio)phenyl)ethanone (2.0 g, 10.2 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added Br_2 (0.53 mL. 11 mmol) dropwise. The mixture was stirred at 0 °C for 2 h, concentrated *in vacuo* and purified by silica gel chromatography, eluted with 20% ether/petrol to yield the bromoarene **17** as a colourless solid (2.11 g, 75%).

M.p. = 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 6.75 (s, 1H), 4.01 (s, 3H), 2.59 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 158.6, 145.6, 136.3, 127.7, 107.4, 105.8, 56.3, 27.7, 16.0; ν_{max} (film)/cm^{-1} 1666, 1601, 1581, 1387, 766, 732, 699; ; HRMS (FI$^+$) 275.9643 (275.9663 calc. for $C_{10}H_{11}{}^{79}BrO_2S$ (M)$^+$)

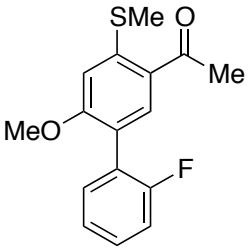
1-(4-Bromo-5-methoxy-[1,1'-biphenyl]-2-yl)ethanone (18)



Compound **18** was synthesised according to General Procedure A, using **17** (100 mg, 0.36 mmol) and phenylboronic acid (74 mg, 0.54 mmol) to give the product as a colourless oil (87 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.38-7.35 (m, 3H), 7.27-7.24 (m, 2H), 6.75 (s, 1H), 3.88 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 157.5, 142.5, 140.4, 133.8, 133.7, 128.78, 128.6, 128.3, 113.4, 110.8, 56.5, 30.1; ν_{max} (film)/cm^{-1} 1679, 1585, 1481, 1222, 1059, 733, 711; HRMS (ESI$^+$) 305.0166 (305.0172 calc. for $C_{15}H_{14}{}^{79}BrO_2$ (M+H)$^+$)

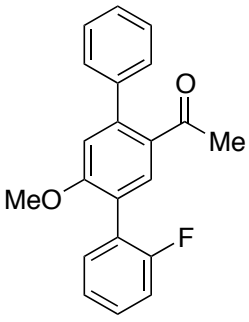
1-(2'-fluoro-6-methoxy-4-(methylthio)-[1,1'-biphenyl]-3-yl)ethanone (19)



A suspension of **17** (100 mg, 0.36 mmol), 2-fluorophenyl boronic acid (76 mg, 0.54 mmol), K_2CO_3 (74 mg, 0.54 mmol), Pd_2dba_3 (8 mg, 0.0009 mmol) and S-Phos (15 mg, 0.036 mmol) in toluene (2 mL) and water (0.5 mL) was heated to 100 °C for 1 h. The mixture was cooled to room temperature, and the organic phase was loaded directly onto a silica gel column, eluted with 10% ether/petrol to yield the product as a colourless oil (94 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.31-7.26 (m, 2H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07 (td, *J* = 9.5, 1.0 Hz, 1H), 6.78 (s, 1H), 3.83 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 160.1 (d, J = 247 Hz), 159.8, 146.3, 134.9, 131.8, (d, J = 3 Hz), 149.5, 149.4, 126.7, 124.8 (d, J = 8 Hz), 124.0, 120.0, 115.8, 115.5, 106.7, 55.8, 27.8, 16.0; ν_{max} (film)/cm^{-1} 1660, 1599, 1537, 1358, 1223, 1106, 762; MS (ESI$^+$) *m/z* (rel intensity) 291 [100, $(M+H)^+$], 313, [40, $(M+Na)^+$], 411 [50]; HRMS (ESI$^+$) 313.0655 (313.0669 calc. for $C_{16}H_{15}NaFSO_2$ $(M+Na)^+$).

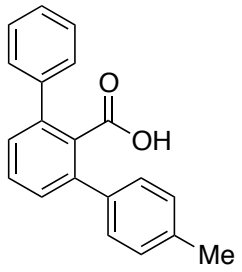
1-(2''-fluoro-5'-methoxy-[1,1':4',1''-terphenyl]-2'-yl)ethanone (20)



Compound **20** was synthesised according to General Procedure A, using **19** (20 mg, 0.065 mmol) and phenylboronic acid (12 mg, 0.98 mmol) to give the product as a colourless oil (19 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.40-7.25 (m, 6H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 7.06 (ddd, *J* = 10.0, 8.5, 1.0 Hz, 1H), 6.84 (s, 1H), 3.79 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 161.3, 158.9, 158.7, 143.4, 141.2, 132.7, 132.2, 131.8, 129.6, 129.5, 128.8, 128.7, 128.1, 124.2, 124.0, 115.7, 115.4, 112.8, 56.0, 30.3; ν_{max} (film)/cm^{-1} 1680, 1595, 1218, 821, 703; HRMS (ESI$^+$) 343.1089 (343.1105 calc. for $C_{21}H_{18}FO_2$ $(M+H)^+$).

4-methyl-[1,1':3',1''-terphenyl]-2'-carboxylic acid (21)

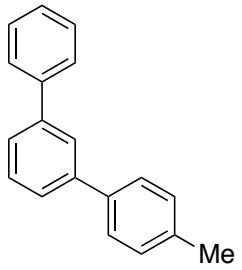


A solution of methyl [1,1'-biphenyl]-2-carboxylate (**8**) (50 mg, 0.025 mmol) and KOH (28 mg, 0.50 mmol) in MeOH (3 mL) was heated to reflux for 16 h. The solution was diluted with water (10 mL) and acidified to pH 2-3 by addition of 2 M HCl. The solution was extracted with EtOAc (3 × 5 mL) and concentrated *in vacuo* to give the crude carboxylic acid.

To the crude carboxylic acid was added $Pd(OAc)_2$ (6 mg, 0.025 mmol), cataxium A (18 mg, 0.05 mmol), Cs_2CO_3 (131 mg, 0.25 mmol) and 4-chlorotoluene (240 μL, 0.37 mmol) and DMF (2 mL). The mixture was heated to 140 °C for 16 h, allowed to cool to room temperature, diluted with water (15 mL) and extracted with EtOAc (3 × 10 mL). The extracts were concentrated *in vacuo* and purified by silica gel chromatography, eluted with 20% EtOAc/petrol to yield the product as a colourless oil (51 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.5 Hz, 1H), 7.33-7.22 (m, 9H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 140.40, 140.34, 140.24, 137.41, 137.34, 131.7, 129.6, 129.14, 129.07, 128.8, 128.46, 128.35, 128.32, 127.6, 21.3; ν_{max} (film)/cm^{-1} 2922 br, 1698, 1457, 1293, 806, 760, 700; HRMS (ESI$^-$) 287.1089 (287.1078 calc. for $C_{20}H_{15}O_2$ $(M-H)^-$).

4-Methyl-1,1':3',1''-terphenyl (22)



The carboxylic acid (**21**) (20 mg, 0.07 mmol), Ag_2CO_3 (19 mg, 0.07 mmol) and K_2CO_3 (19 mg, 0.14 mmol) in DMA (1 mL) were heated to 140 °C for 16 h. The solution was allowed to cool to room temperature and leaded directly onto a silica gel column, eluted with 5% Et_2O/petrol to give the product as a colourless solid (11 mg, 65%).

M.p. = 75-76 °C (lit. m.p. = 77-78 °C)[11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.71 (m, 1H), 7.58-7.56 (m, 2H), 7.48 (ddt, *J* = 6.5, 4.5, 2 Hz, 4H), 7.44-7.42 (m, 1H), 7.41-7.37 (m, 2H), 7.31-7.27 (m, 1H), 7.20 (dd, *J* = 8.5, 0.5 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.77, 141.72, 141.3, 138.3, 137.2, 129.6, 129.2, 128.8, 127.39, 127.29, 127.12, 125.99, 125.97, 125.89, 21.2; ; ν_{max} (film)/cm^{-1} 794, 755, 698.

These data are consistent with previously reported values.[11]

Experimental - Inorganic

General Experimental Procedures

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. Pentane, CH_2Cl_2 and MeCN were dried using a Grubbs type solvent purification system (MBraun SPS-800), acetone was twice dried over B_2O_3 and vacuum distilled and all solvents were degassed by successive freeze-pump-thaw cycles.[7] C_6H_5F was dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. $[Rh(^iPr_2PCH_2P^iPr_2)(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$[8] (**A**), $[Rh(Cy_2PCH_2PCy_2)(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$[9] (**B**) and $[Rh(^tBu_2PCH_2P^tBu_2)(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$[9] (**C**) were prepared as reported. All other chemicals are commercially available and were used as received. NMR spectra were recorded on a Varian

Mercury VX 300 MHz or Bruker Avance 500 MHz spectrometer at room temperature, unless otherwise stated. ^{1}H NMR spectra are referenced to residual solvent signals. ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3.OEt_2$ (external) respectively. Chemical shifts are reported in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument interfaced with a glovebox.[10] Concentrations of reagents and products used in kinetic plots were either derived from internal standards present in NMR samples or obtained using HPLC-UV-Vis (Zorbaz SB-C18 5 μm, column, 10×180 mm, 85% MeCN/H_2O, 1 mL/min).

$[Rh_2(Cy_2PCH_2PCy_2)_2(SMe)_2(C_6H_4(C(O)Me)_2][BAr^F{}_4]_2$ (E)

$[Rh(Cy_2PCH_2PCy_2)(C_6H_5F)][BAr^F{}_4]$ (**B**) (10.0 mg, 6.8x10^{-6} mol) was dissolved in acetone-d_6 (0.6 mL). To this solution was added 2-thiomethyl-acetophenone (**1**) (1.2 mg, 7.2x10^{-6} mol). The resultant solution was characterised by ^{1}H and ^{31}P NMR spectroscopies, and MS-ESI.

^{1}H NMR ($(CD_3)_2CO$): δ_H 8.25-8.07, 7.63-7.36 (m, 8H,C_6H_4(C(O)Me)), 7.84-7.75 (m, 16H, $BAr^F{}_4$), 7.70-7.66 (m, 8H, $BAr^F{}_4$), 3.55-3.29 (m, 4H, PCH_2P), 3.17 (s, 6H, C(O)Me), 3.00 (s, 6H, SMe), 2.28-0.34 (m, 88H, PCy_2); $^{31}P\{^{1}H\}$ NMR ($(CD_3)_2CO$): δ_P -5.7 (dd, 2P, $^{1}J_{PRh}$ = 122.5 Hz, $^{2}J_{PP}$ = 55.0 Hz), -14.8 (dd, 2P, $^{1}J_{PRh}$ = 89.7 Hz, $^{2}J_{PP}$ = 55.0 Hz); ESI-MS($(CD_3)_2CO$, 60 °C, 4.5 kV) *m/z*: 677.26 $[M_2]^{2+}$, calcd 677.26 (observed isotopic pattern agrees with calculated distribution for dication).

$[Rh(Cy_2PCH_2PCy_2)(\eta^6$-*Me*-$C_6$ $C_6H_4(B(OH)_2))][BAr^F{}_4]$ (G)

$[Rh(Cy_2PCH_2PCy_2)(C_6H_5F)][BAr^F{}_4]$ (**B**) (10.0 mg, 6.8x10^{-6} mol) was dissolved in acetone-d_6 (0.6 mL). To this solution was added 4-tolylboronic acid (**2b**) (1.0 mg, 7.4x10^{-6} mol in 0.2 mL $(CD_3)_2CO$). The resultant solution was characterised by ^{1}H and ^{31}P NMR spectroscopies, and MS-ESI.

^{1}H NMR ($(CD_3)_2CO$): δ_H 7.84-7.79 (m, 8H, $BAr^F{}_4$), 7.72-7.68 (m, 4H, $BAr^F{}_4$), 6.66 (ABq, 4H, δ_{AB} = 0.14, J_{HH} = 6.5 Hz, *Me*-$C_6H_4(B(OH)_2)$), 3.01 (t, 2H, $^{2}J_{HP}$ = 10.0 Hz, PCH_2P), 2.61 (s, 3H, *Me*-

$C_6H_4(B(OH)_2)$), 2.09-0.87 (m, 44H, PCy_2); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ_P -9.9 (d, 2P, $^1J_{PRh}$ = 171.9 Hz); ^{11}B NMR ($(CD_3)_2CO$): δ_B 20.1 (s, 1B); ESI-MS($(CD_3)_2CO$, 60 °C, 4.5 kV) *m/z*: 647.27 $[M]^+$, calcd 647.28 (observed isotopic pattern agrees with calculated distribution).

[Rh($Cy_2PCH_2PCy_2$)(η^6-*Me*-C_6H_4{B(O)(OH)}] (G-H^+)

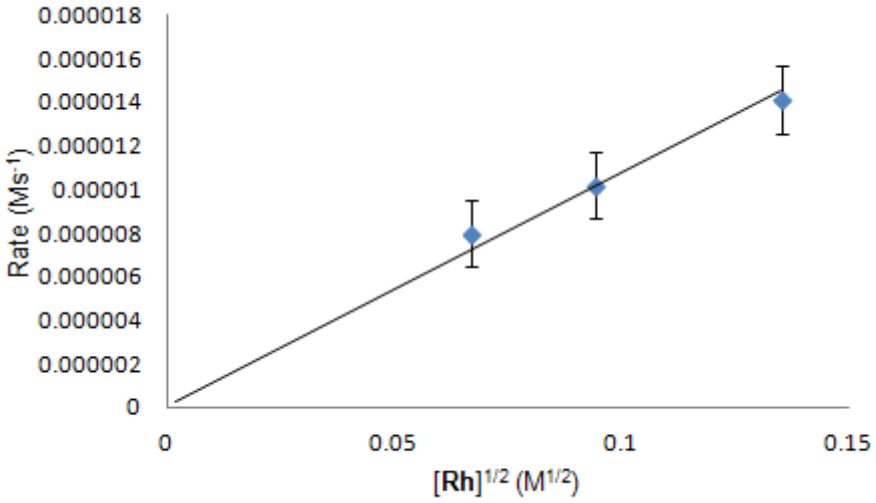
[Rh($Cy_2PCH_2PCy_2$)(C_6H_5F)][BAr^F_4] (**B**) (10.0 mg, 6.8x10^{-6} mol) was dissolved in acetone-d_6 (0.6 mL). To this solution was added 4-tolylboronic acid (**2b**) (10 mg, 7.4x10^{-5} mol in 0.2 mL $(CD_3)_2CO$). Ag_2CO_3 (30 mg, 1.1x10^{-4} mol) was added and the solution was left at room temperature for 7 days, after which time it was characterised by ^1H and ^{31}P NMR spectroscopies.

^1H NMR ($(CD_3)_2CO$): δ_H 7.84-7.79 (m, 8H, BAr^F_4), 7.71-7.68 (m, 4H, BAr^F_4), 6.85-6.64 (m, 4H, *Me*-C_6H_4{B(O)(OH)}), 3.02 (t, 2H, PCH_2P, $^2J_{HP}$ = 10.2 Hz), 2.52 (s, 3H, *Me*-C_6H_4{B(O)(OH)}), 2.05-0.87 (m, 44H, PCy_2); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ_P -9.4 (d, 2P, $^1J_{PRh}$ = 171.0 Hz); ^{11}B NMR ($(CD_3)_2CO$): δ_B 1.3 (s, 1B).

Kinetic plots

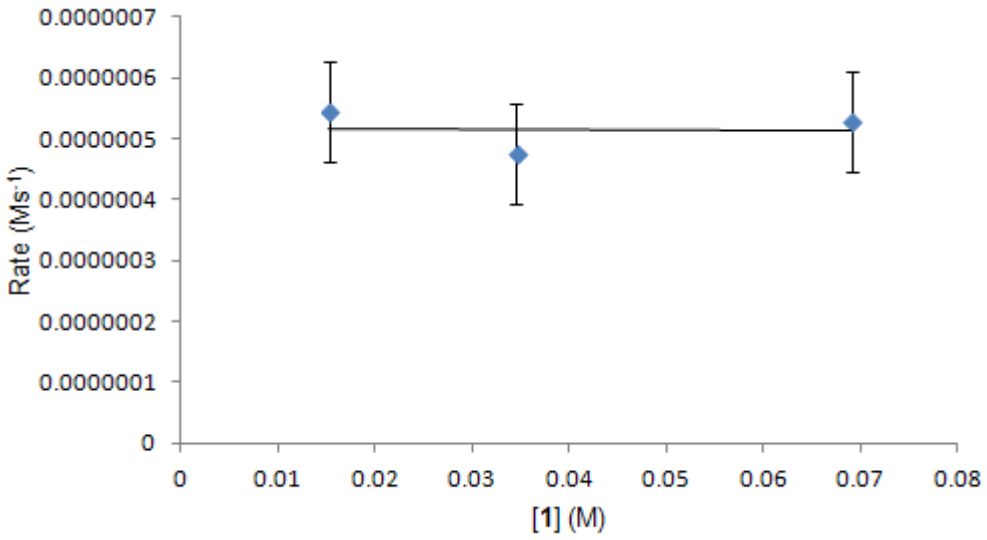
Order in [Rh]

Plot 1. Conditions: [**1**] = 33.4 mM, [**2b**] = 37.6 mM, Ag_2CO_3 = 15 mg in 0.6 mL acetone-d_6, T = 55 °C; Concentration [**Rh**] / mM: 4.5; 8.9; 18.3.



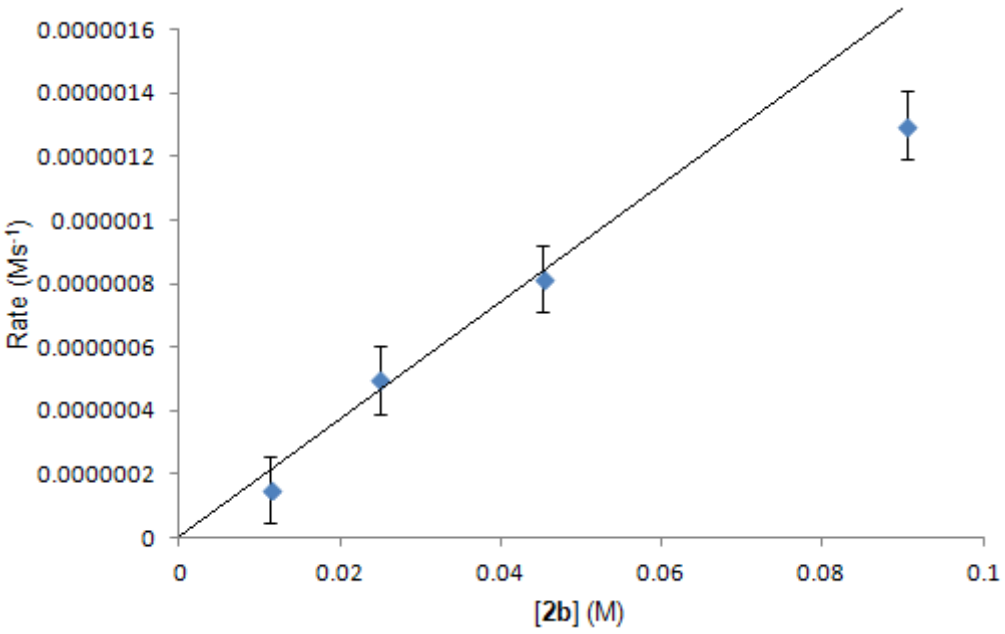
Order in [ketone 1]

Plot 2. Conditions: [**Rh**] = 8.4 mM, [**2b**] = 37.6 mM, Ag_2CO_3 = 20 mg in 0.75 mL acetone-d_6, T = 55 °C; Concentration [**1**] / mM: 15.3; 35.3; 69.1.

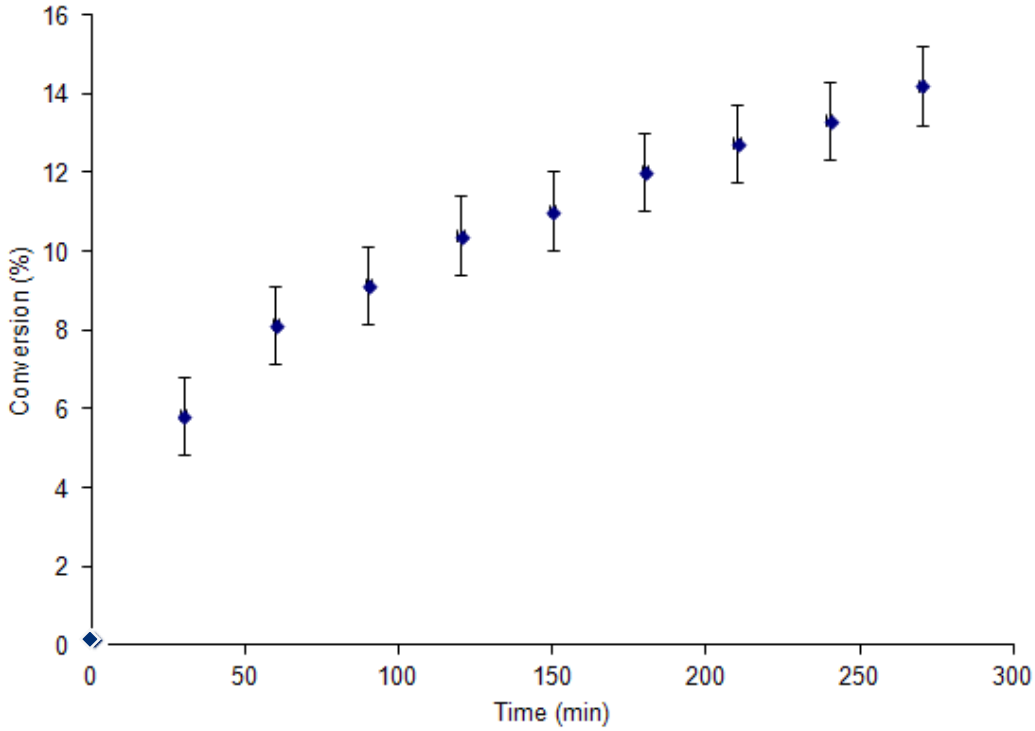


Order in Boronic acid 2b

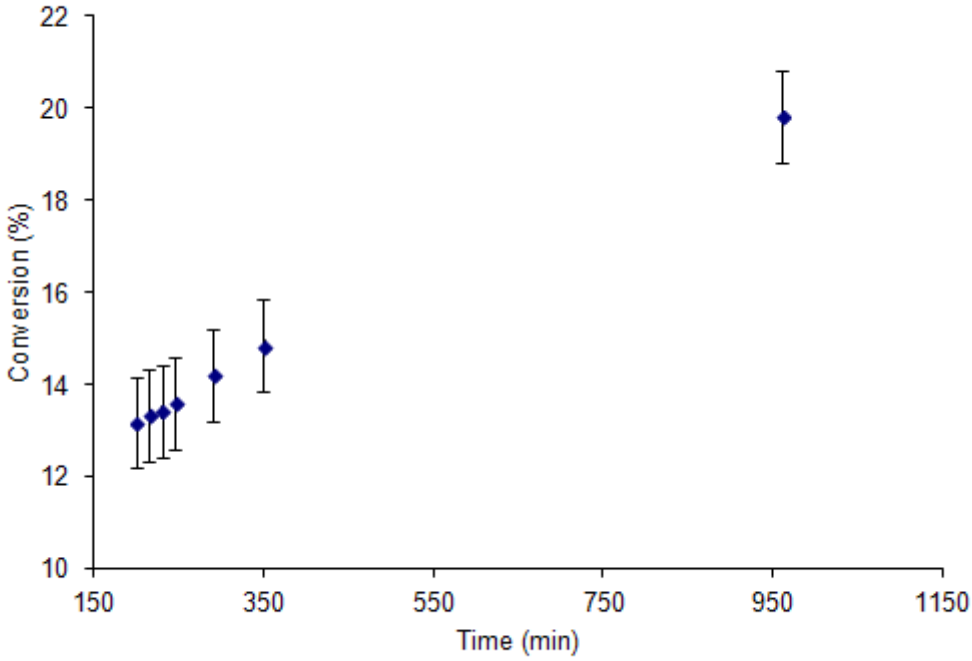
Plot 3. Conditions: [**Rh**] = 4.8 mM, [**1**] = 45.4 mM, Ag_2CO_3 = 15 mg in 0.65 mL acetone-d_6, T = 55 °C; Concentration [**2b**] / mM: 11.3; 24.9; 45.2; 90.5.



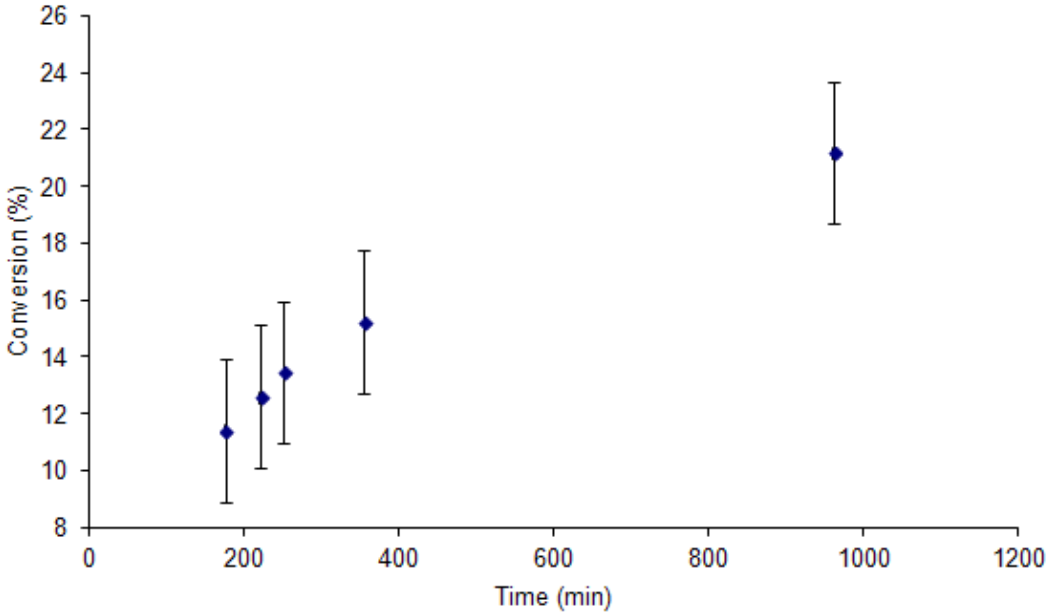
Plot 4. Reaction time profile displaying non-sinusoidal plot. Conditions: [**1**] = 12.0 mM, [**B**] = 10 mol%, [**2b**] = 1.1 eq., Ag_2CO_3 = 1.5 eq., T = 55 °C, reaction volume = 5 mL.



Plot 5. Reaction time profile displaying effect of added Hg (1 mL) to reaction after 175 minutes. Conditions: [**1**] = 12.0 mM, [**B**] = 10 mol%, [**2b**] = 1.1 eq., Ag_2CO_3 = 1.5 eq., T = 55 °C, reaction volume = 5 mL.



Plot 6. Reaction time profile displaying effect of filtering reaction mixture after 175 minutes through 0.22 µm PTFE syringe filters. Conditions: [**1**] = 12.0 mM, [**B**] = 10 mol%, [**2b**] = 1.1 eq., Ag_2CO_3 = 1.5 eq., T = 55 °C, reaction volume = 5 mL. Note: another 1.5 eq. of Ag_2CO_3 was added to the filtered reaction mixture to enable catalysis.



NMR Spectra of new organometallic compounds

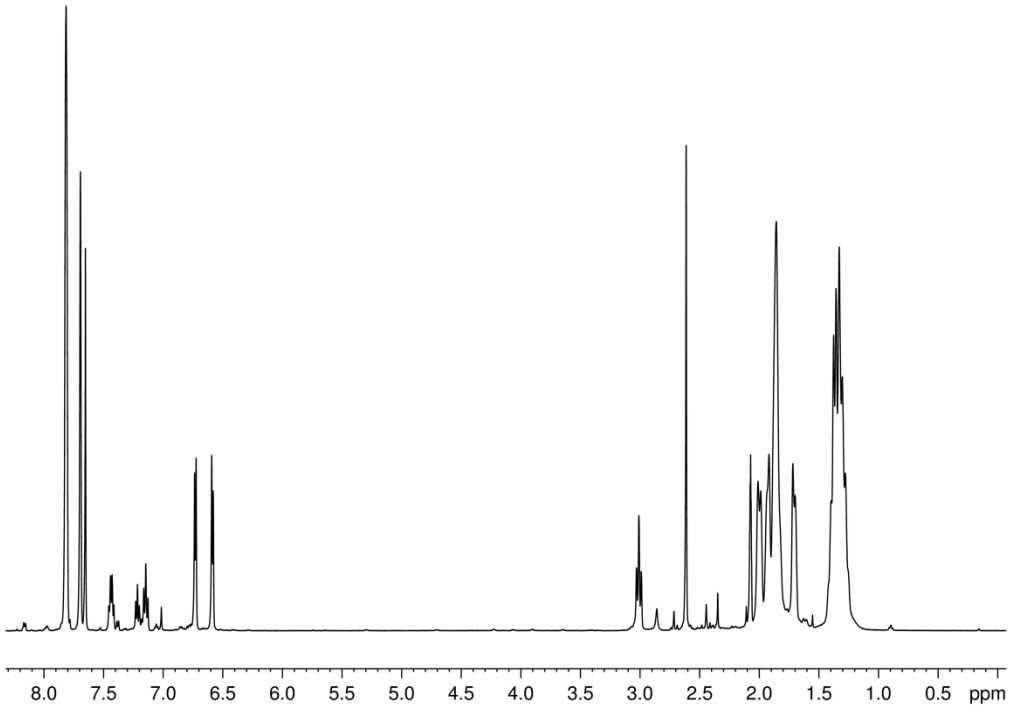


Figure 1. ^{1}H NMR spectrum of [**G**] in acetone-d_6 (298 K).

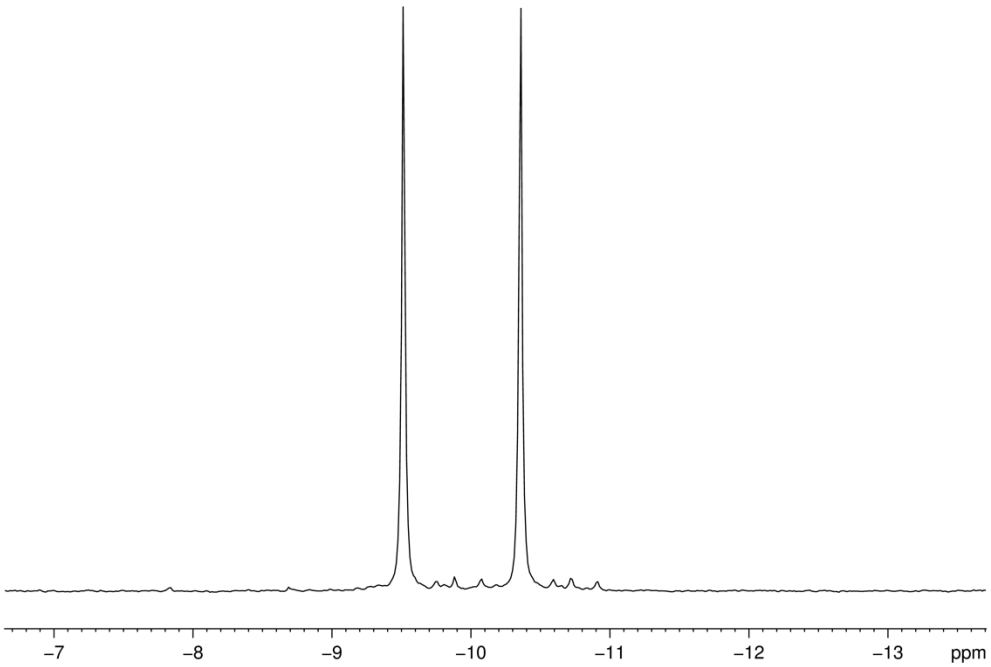


Figure 2. ^{31}P{^{1}H} NMR spectrum of [**G**] in acetone-d_6 (298 K).

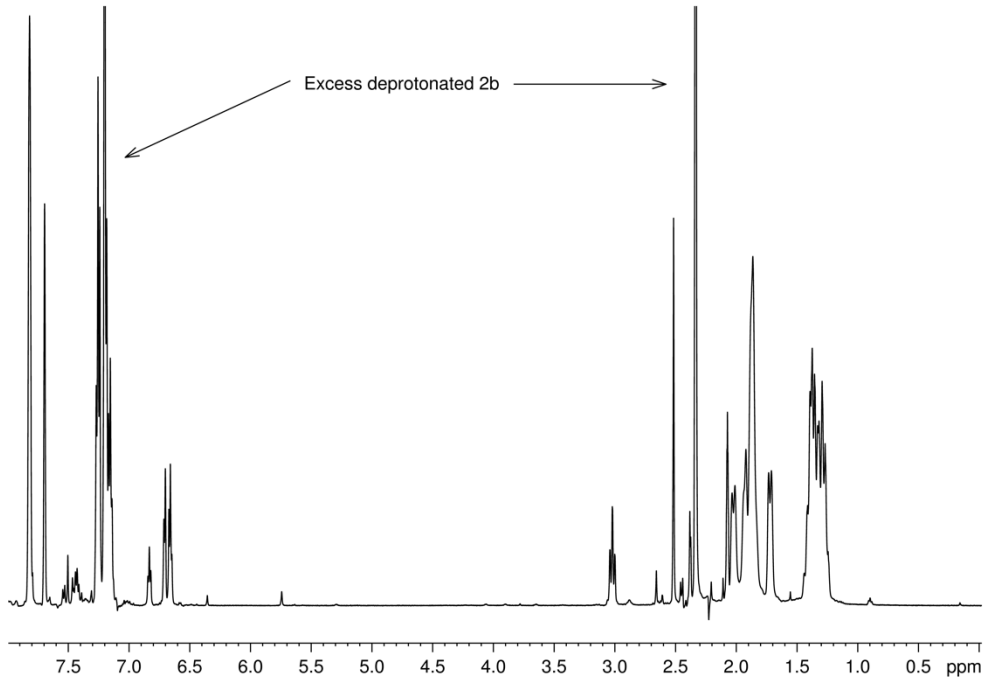


Figure 3. ^{1}H NMR spectrum of [**G-H**$^{+}$] in acetone-d$_6$ (298 K).

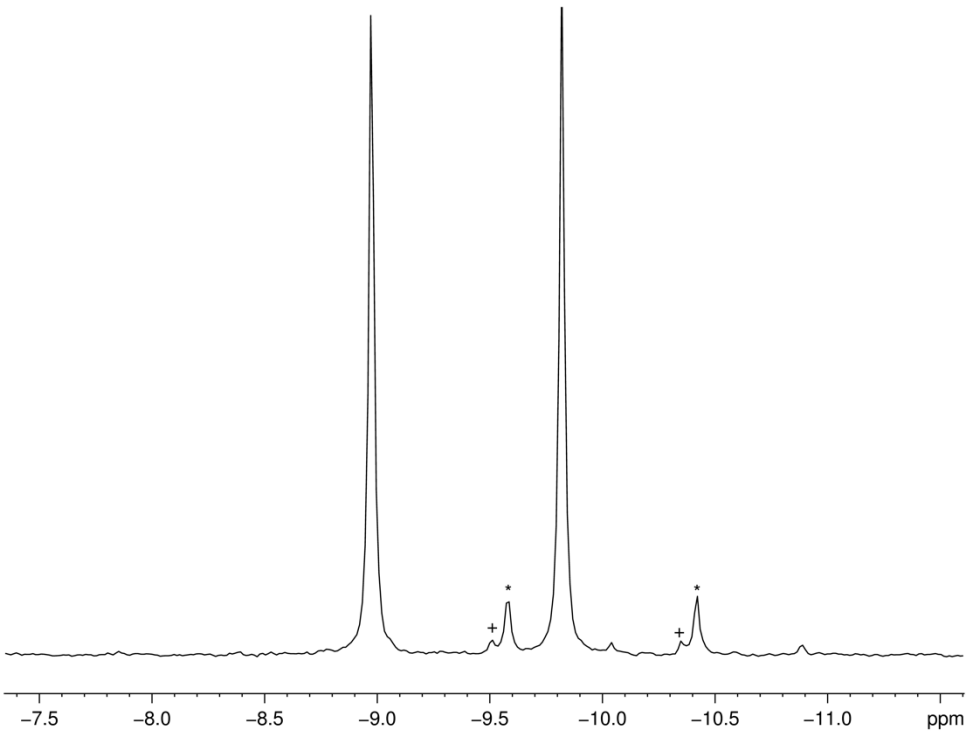


Figure 4. ^{31}P{^{1}H} NMR spectrum of [**G-H**$^{+}$] in acetone-d$_6$ (298 K).

XPS Data

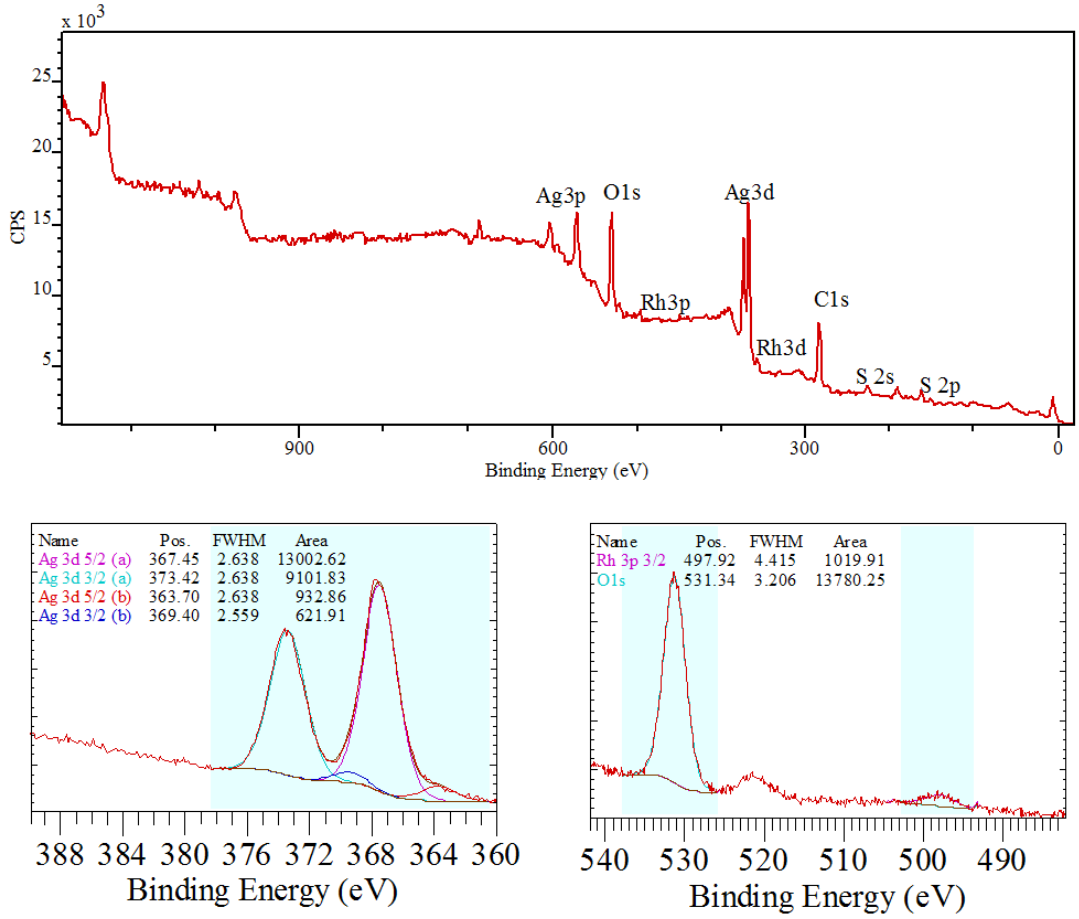
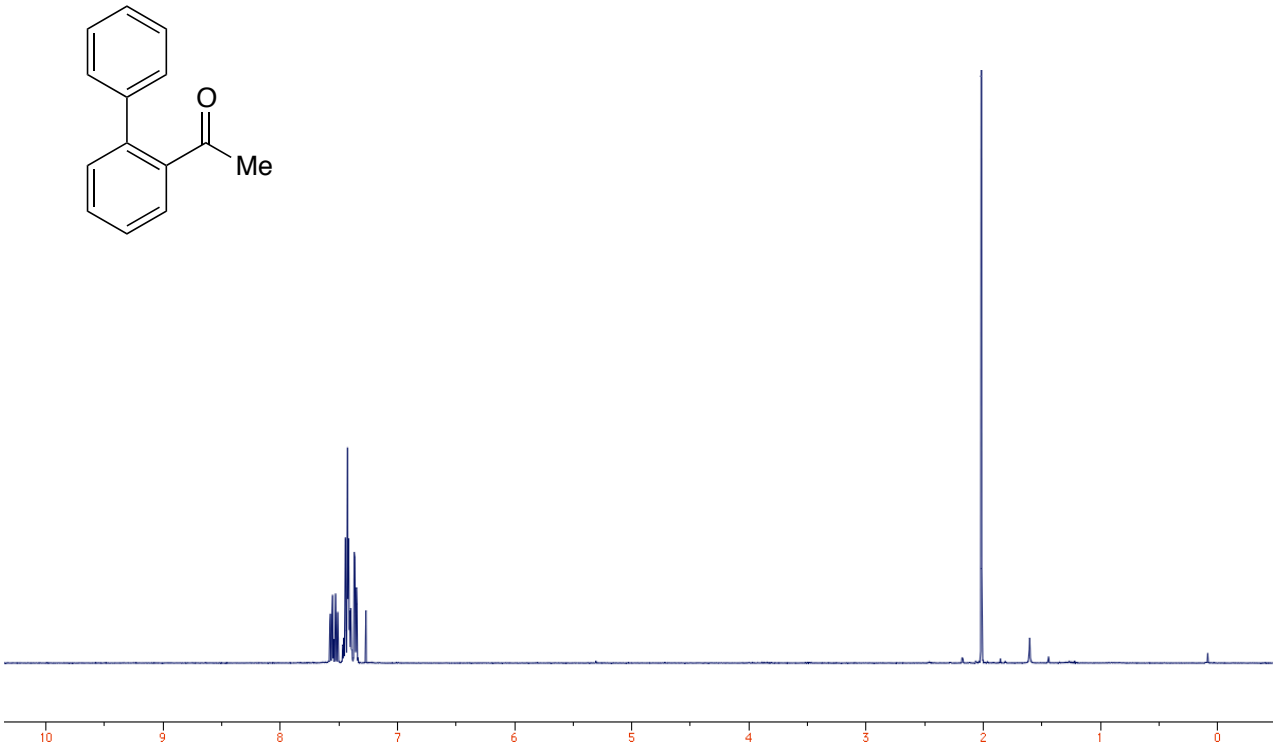


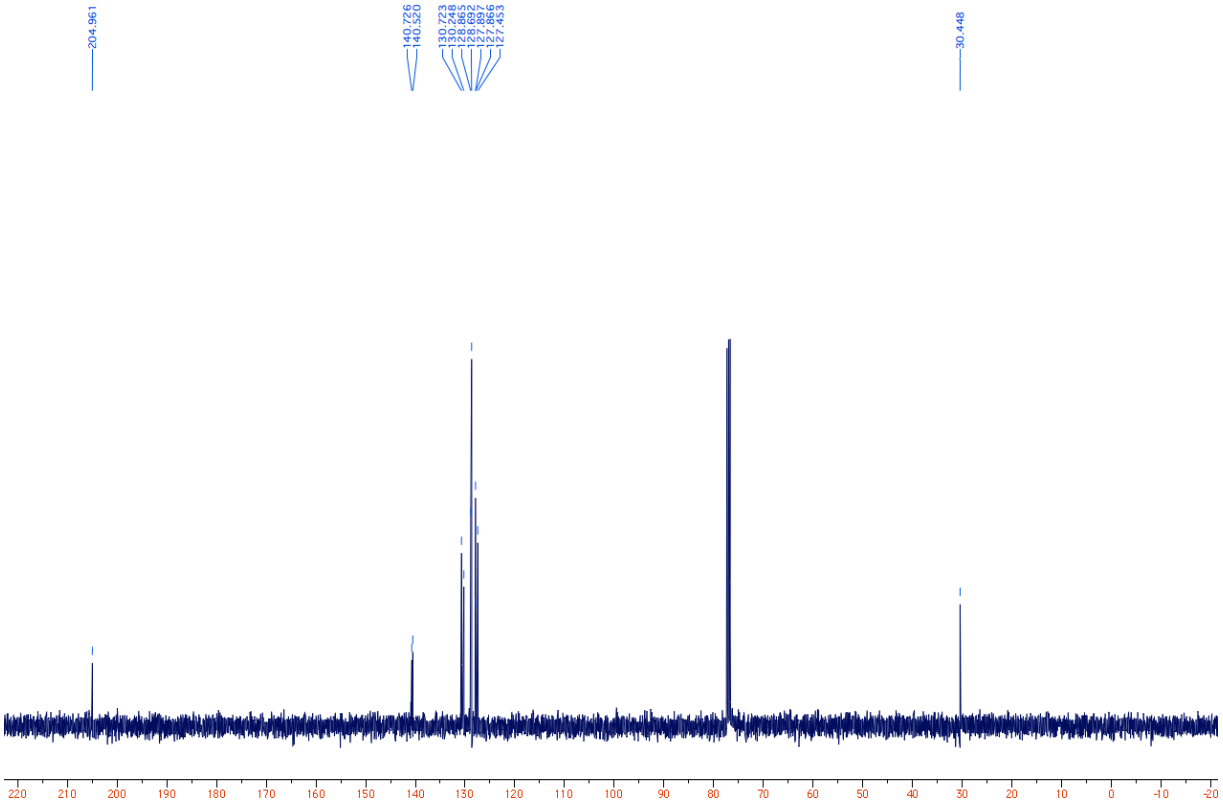
Figure 5. (above) XPS spectrum of colloidal material formed during reaction between **1** and **2b**, identifying the major composition of this material to be Ag. (Conditions: **B** 10 mol%, [**2b**] = 37.6 mM, Ag_2CO_3 = 20 mg in 1 mL acetone, T = 55 °C; [**1**] = 35.3 mM.) (below) Observed (red) and modelled traces of Ag 3d (left) and Rh 3p (right) emissions. The calculated ratio of Rh to Ag was approximately 1:9.

NMR Spectra of Organic Compounds

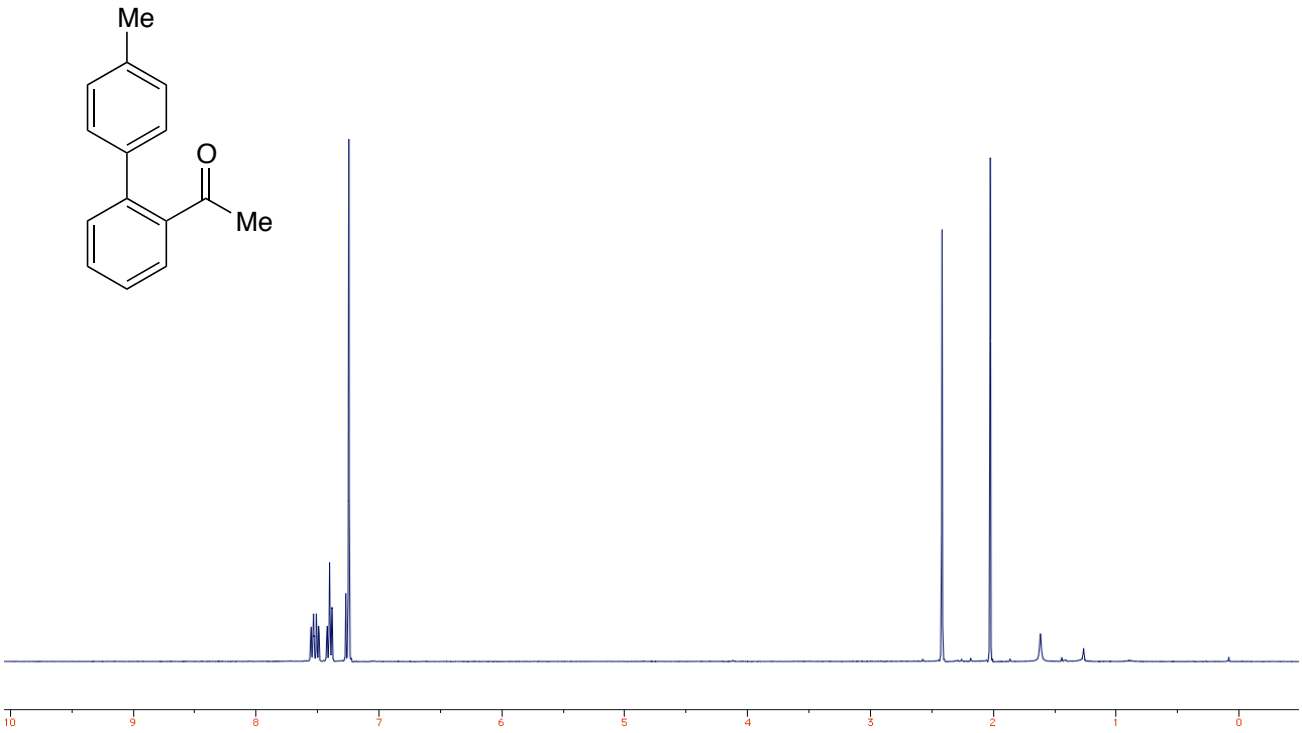
3a (^{1}H NMR, 400 MHz, $CDCl_3$)



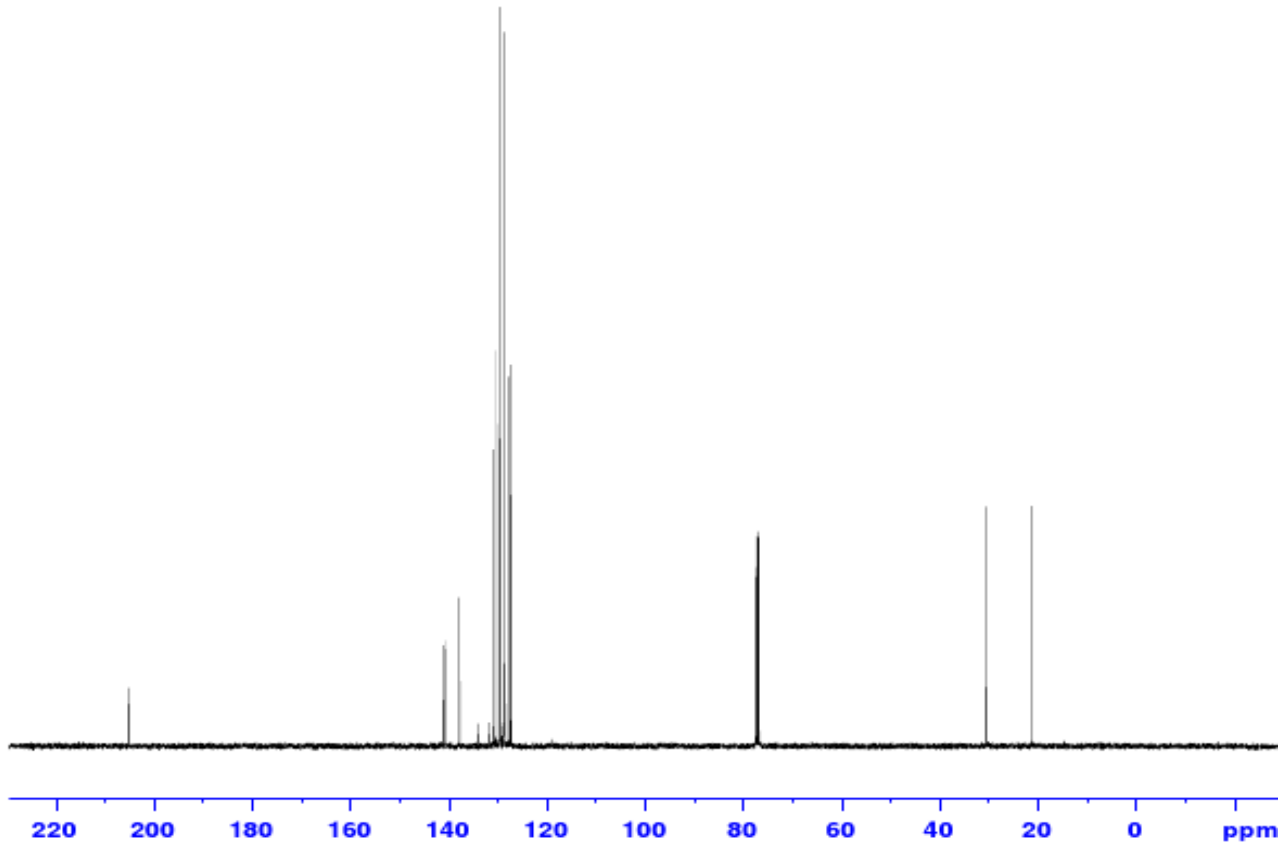
3a (^{13}C NMR, 100 MHz, $CDCl_3$)



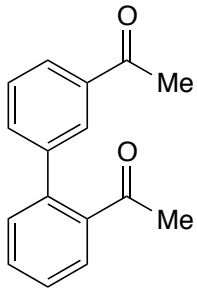
3b (^{1}H NMR, 400 MHz, $CDCl_3$)

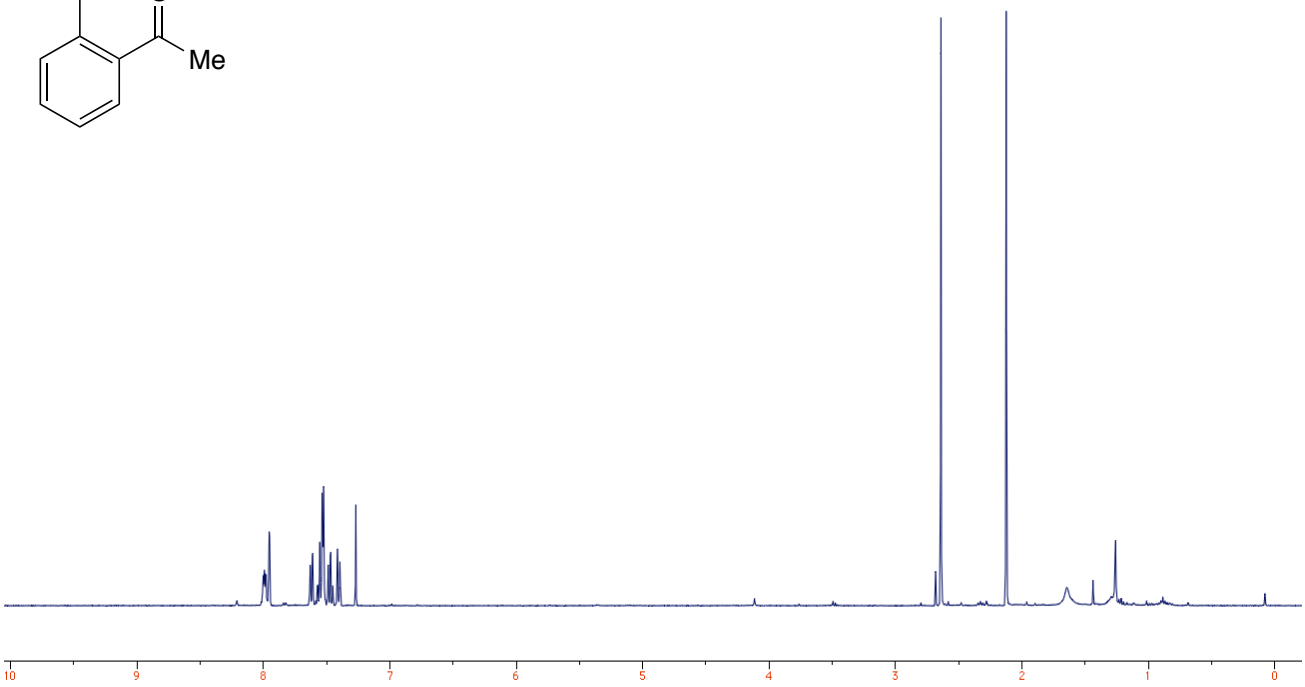


3b (^{13}C NMR, 100 MHz, $CDCl_3$)

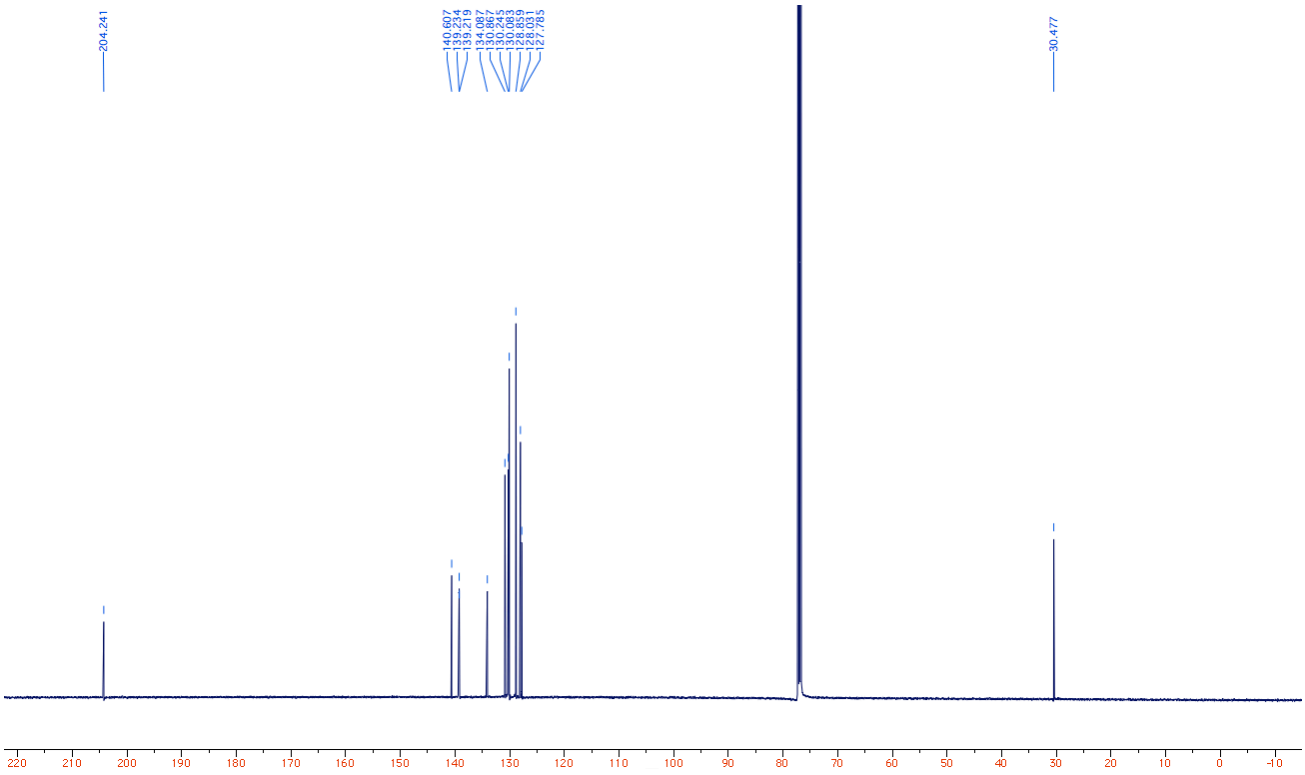


3c (^{1}H NMR, 400 MHz, $CDCl_3$)

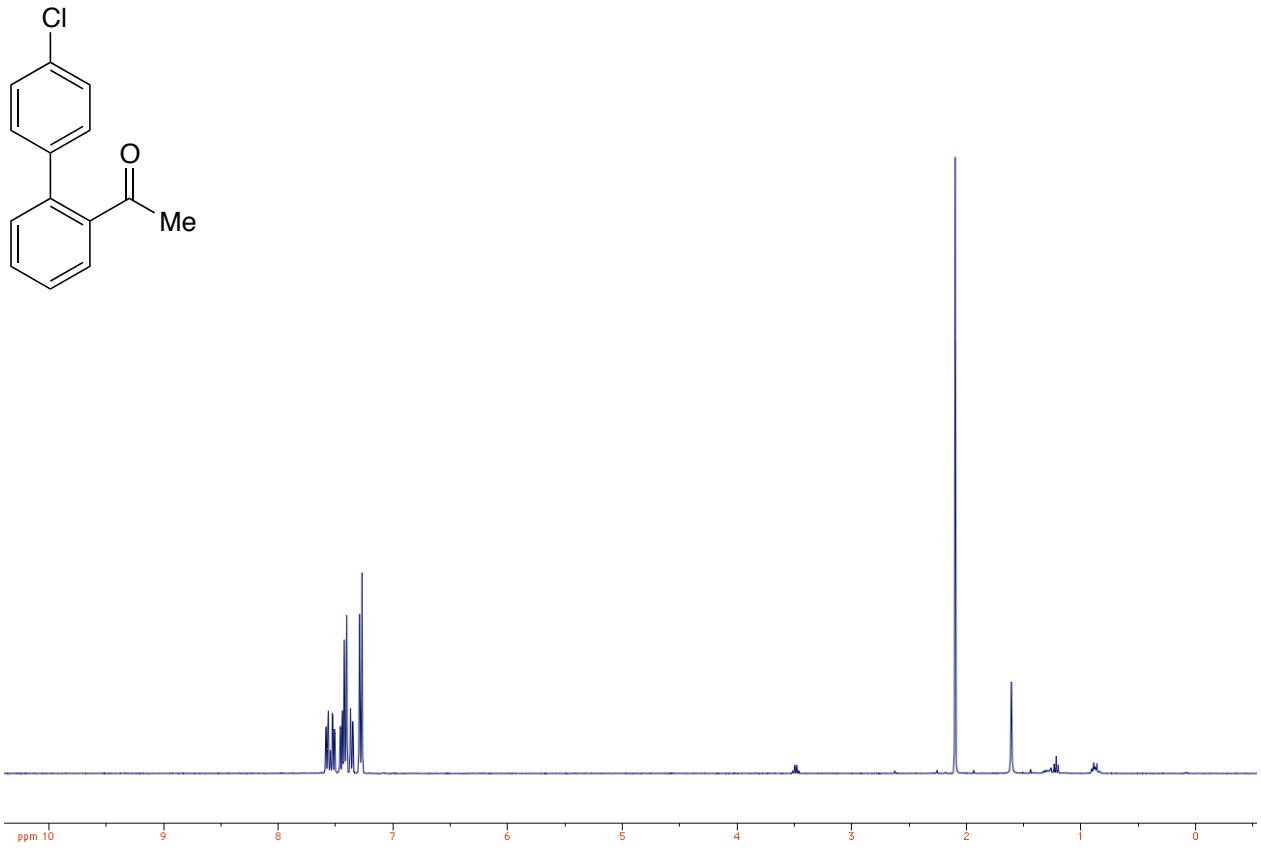




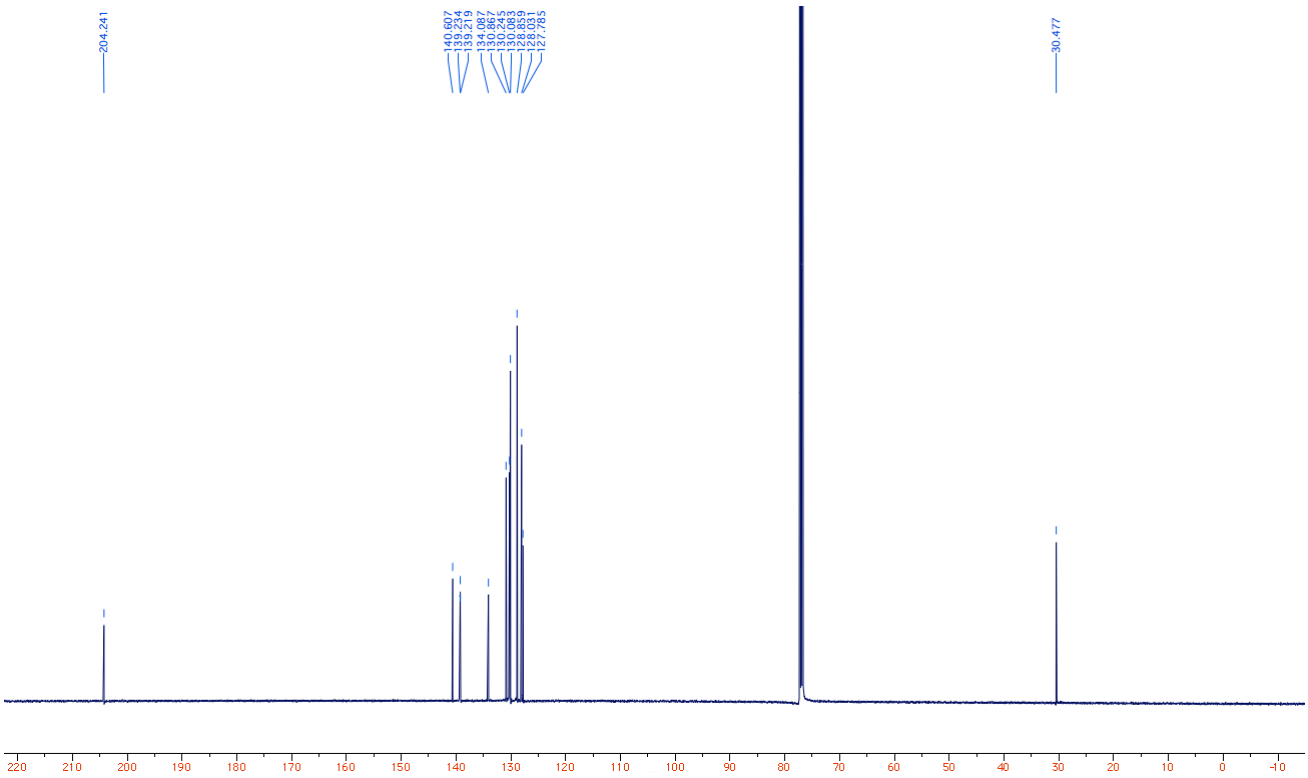
3c (^{13}C NMR, 100 MHz, $CDCl_3$)



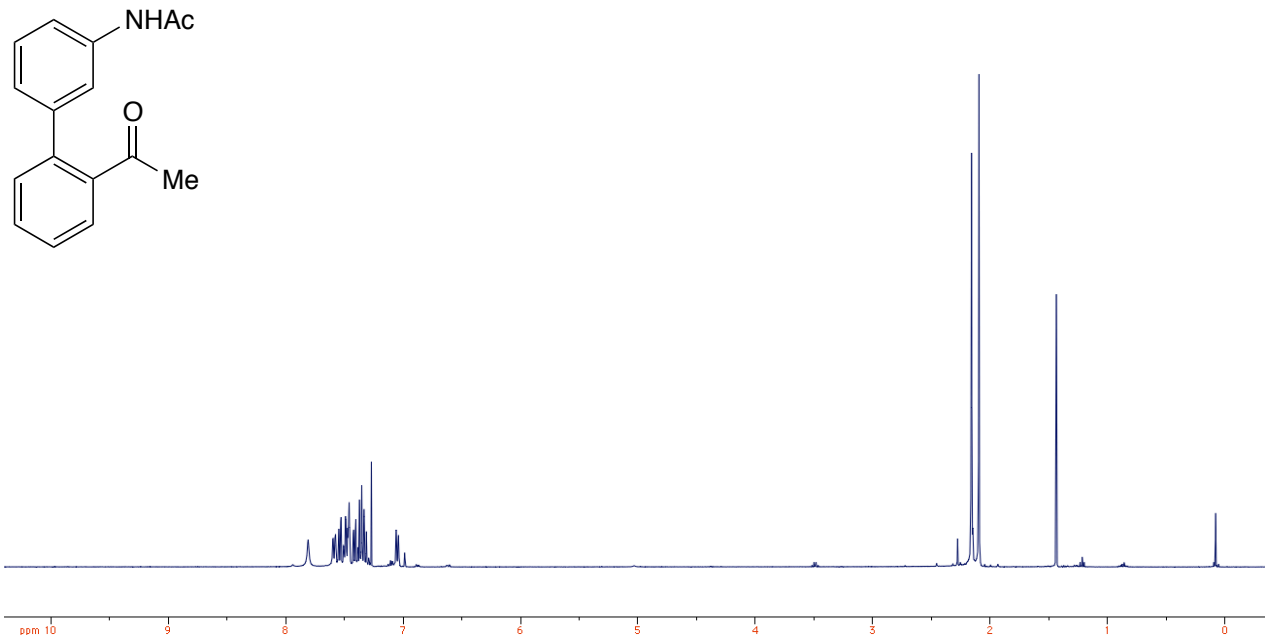
3d (^{1}H NMR, 400 MHz, $CDCl_3$)



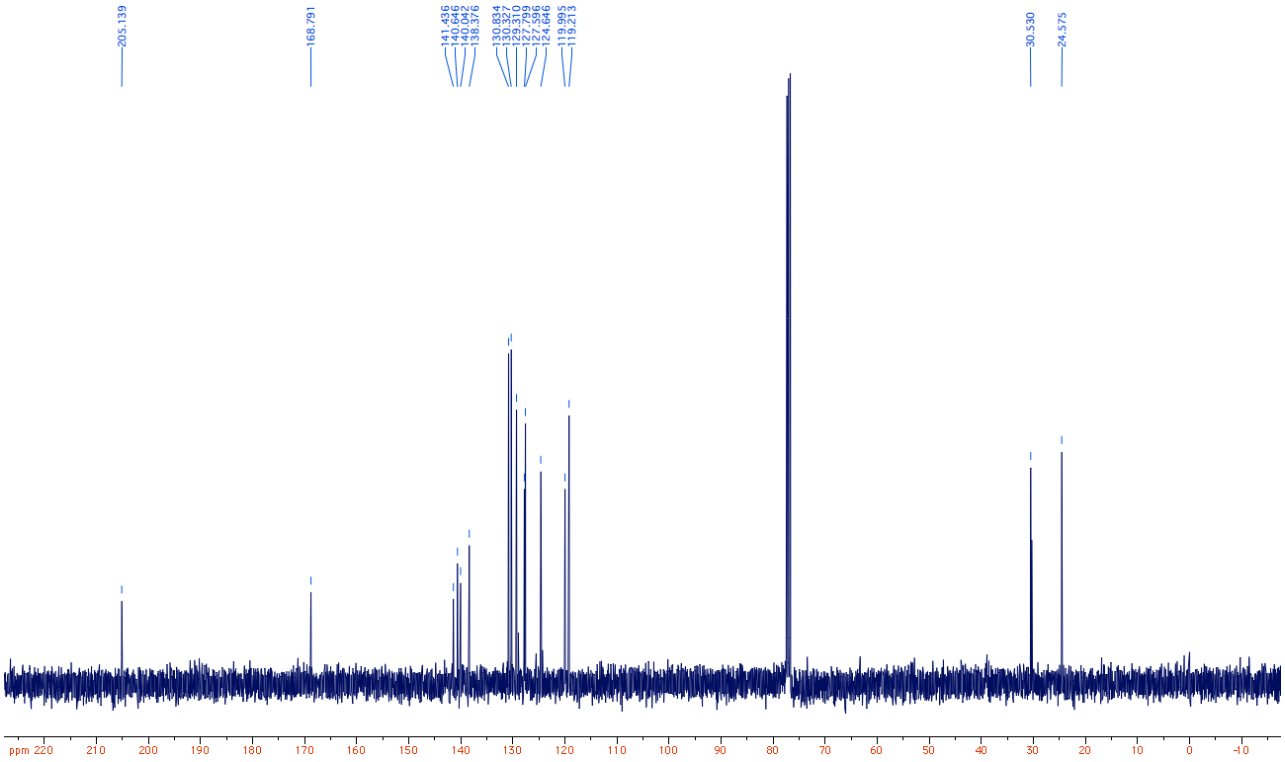
3d (^{13}C NMR, 100 MHz, $CDCl_3$)



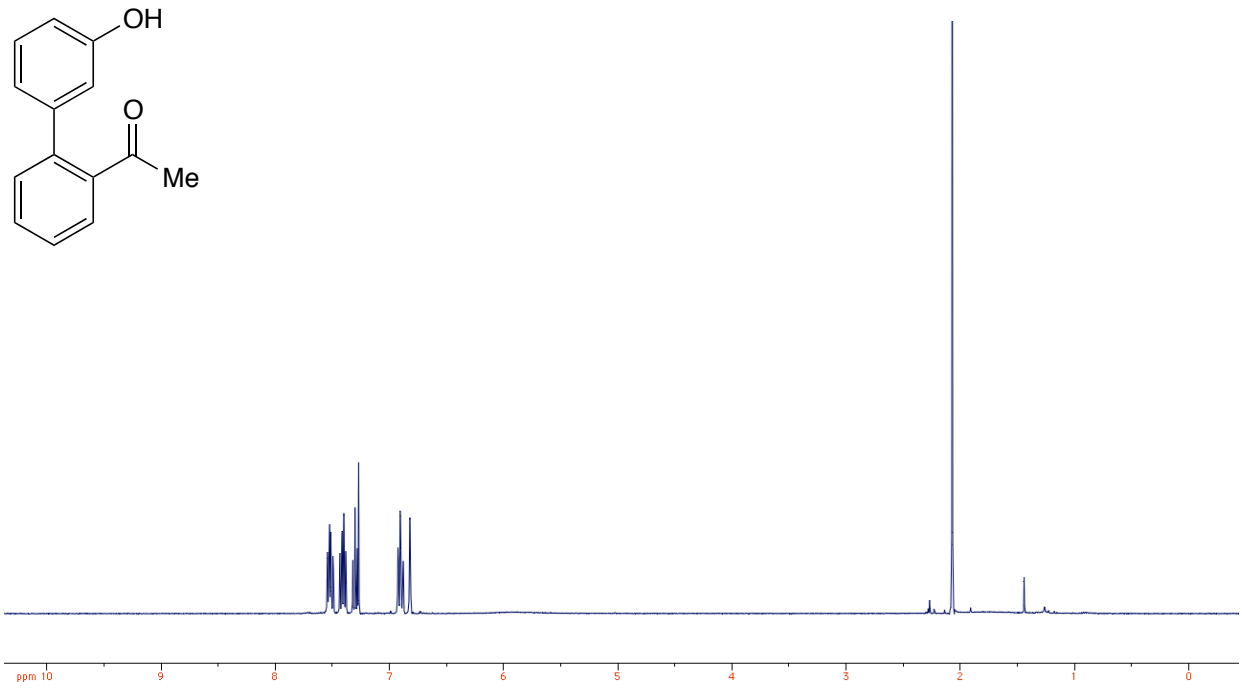
3e (^{1}H NMR, 400 MHz, $CDCl_3$)



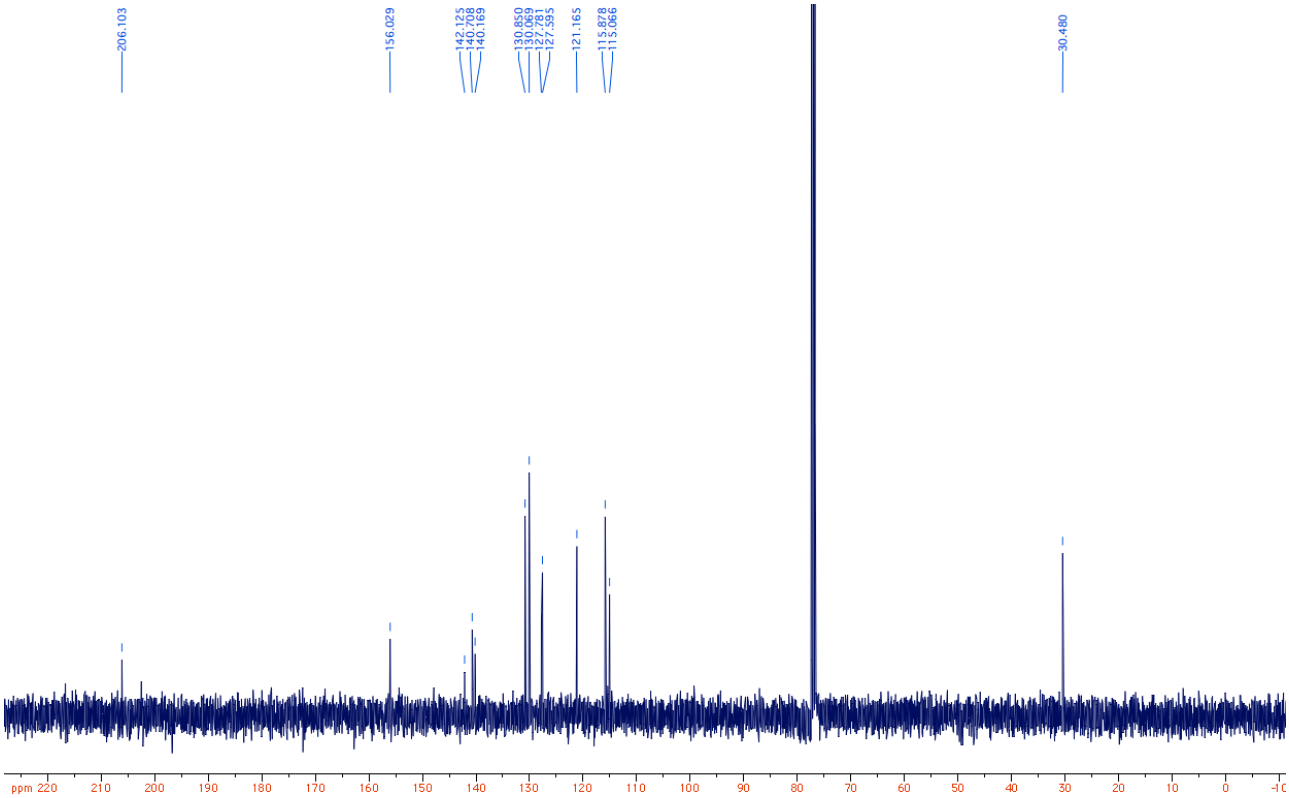
3e (^{13}C NMR, 100 MHz, $CDCl_3$)



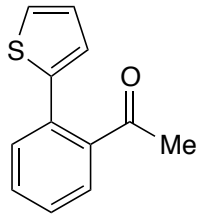
3f (^{1}H NMR, 400 MHz, $CDCl_3$)

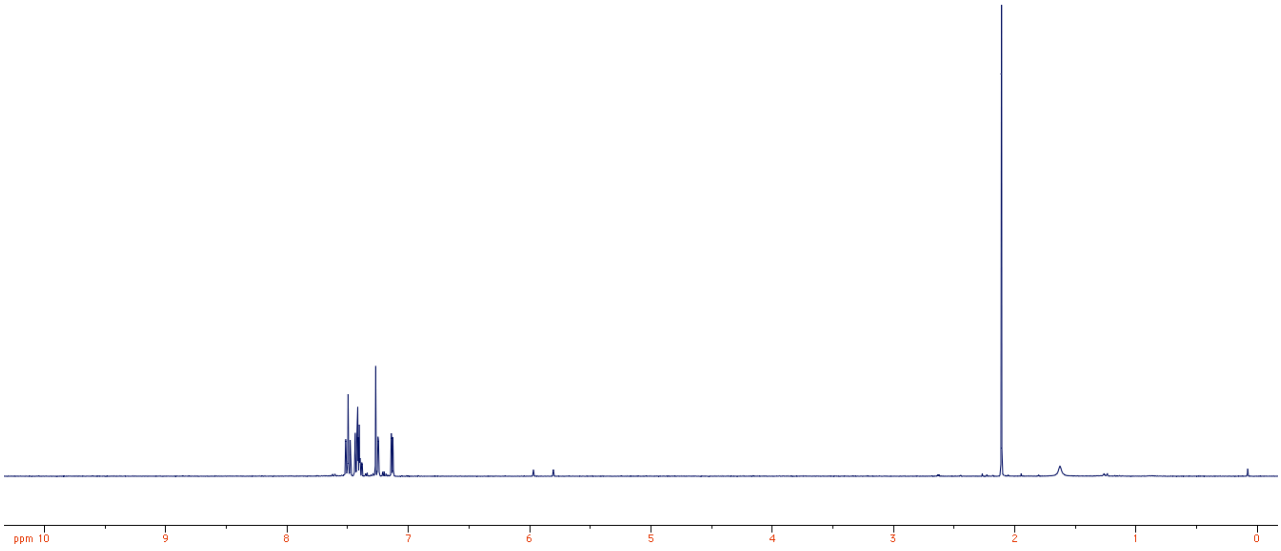


3f (^{13}C NMR, 100 MHz, $CDCl_3$)

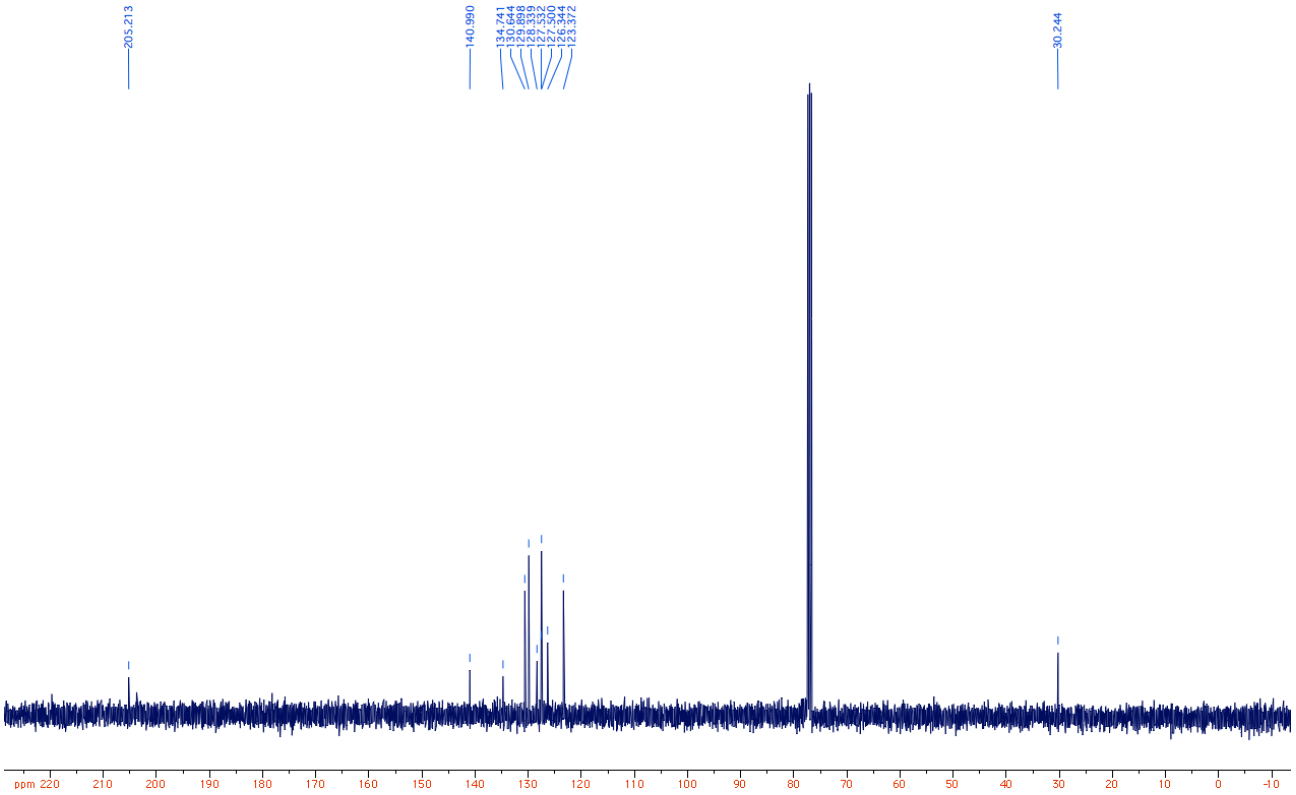


3g (^{1}H NMR, 400 MHz, $CDCl_3$)

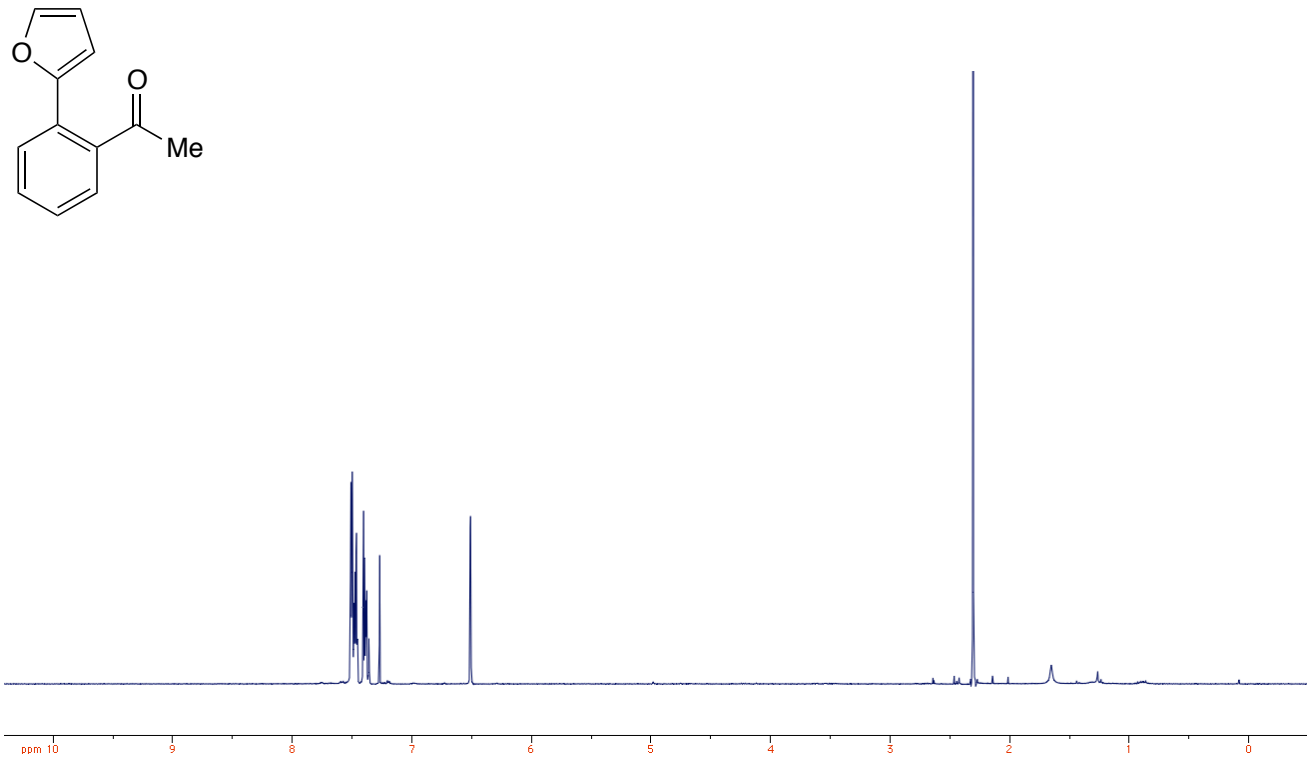




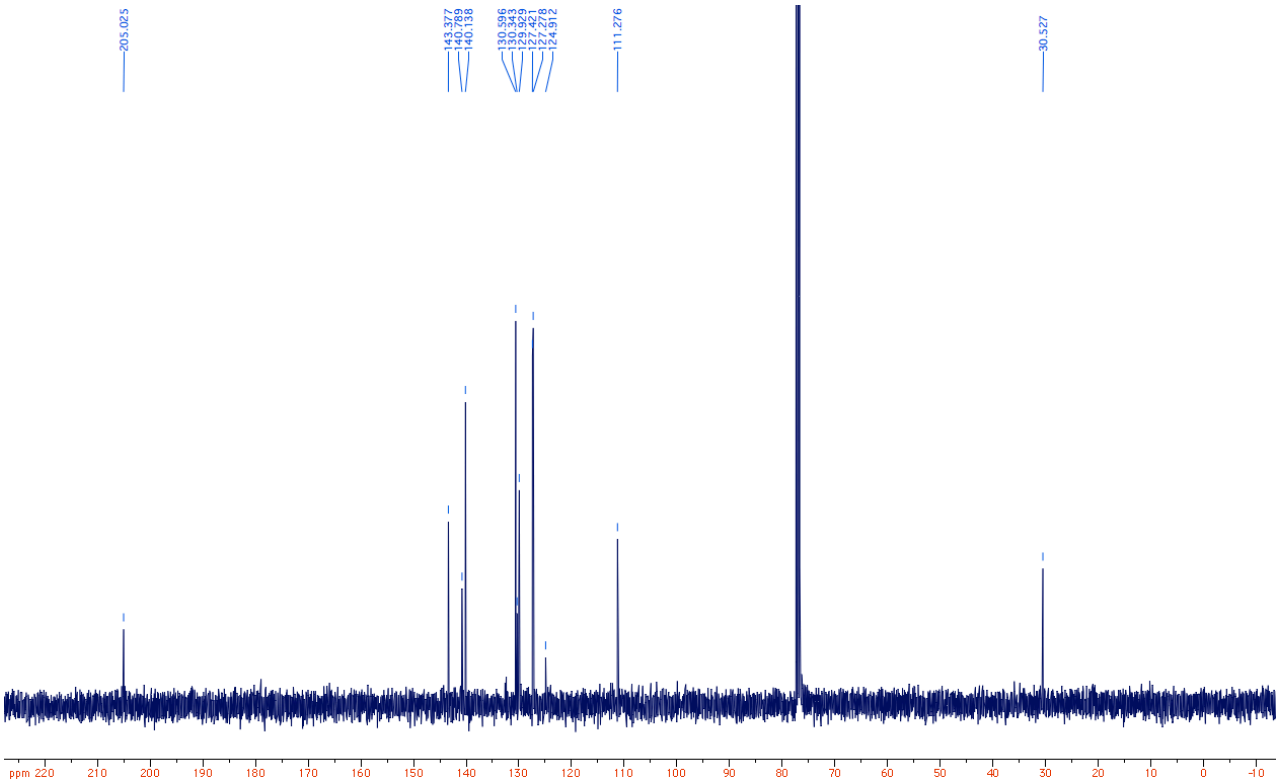
3g (^{13}H NMR, 100 MHz, $CDCl_3$)



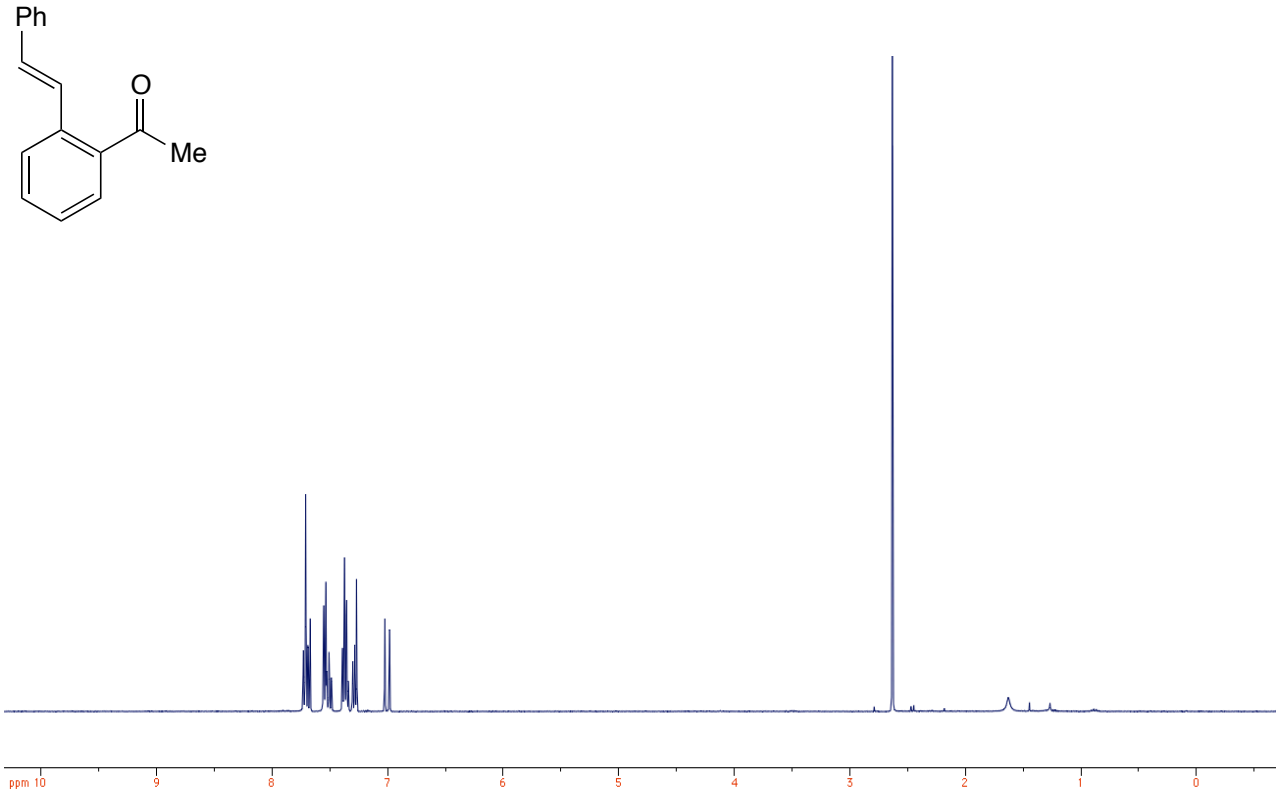
3h (^{1}H NMR, 400 MHz, $CDCl_3$)



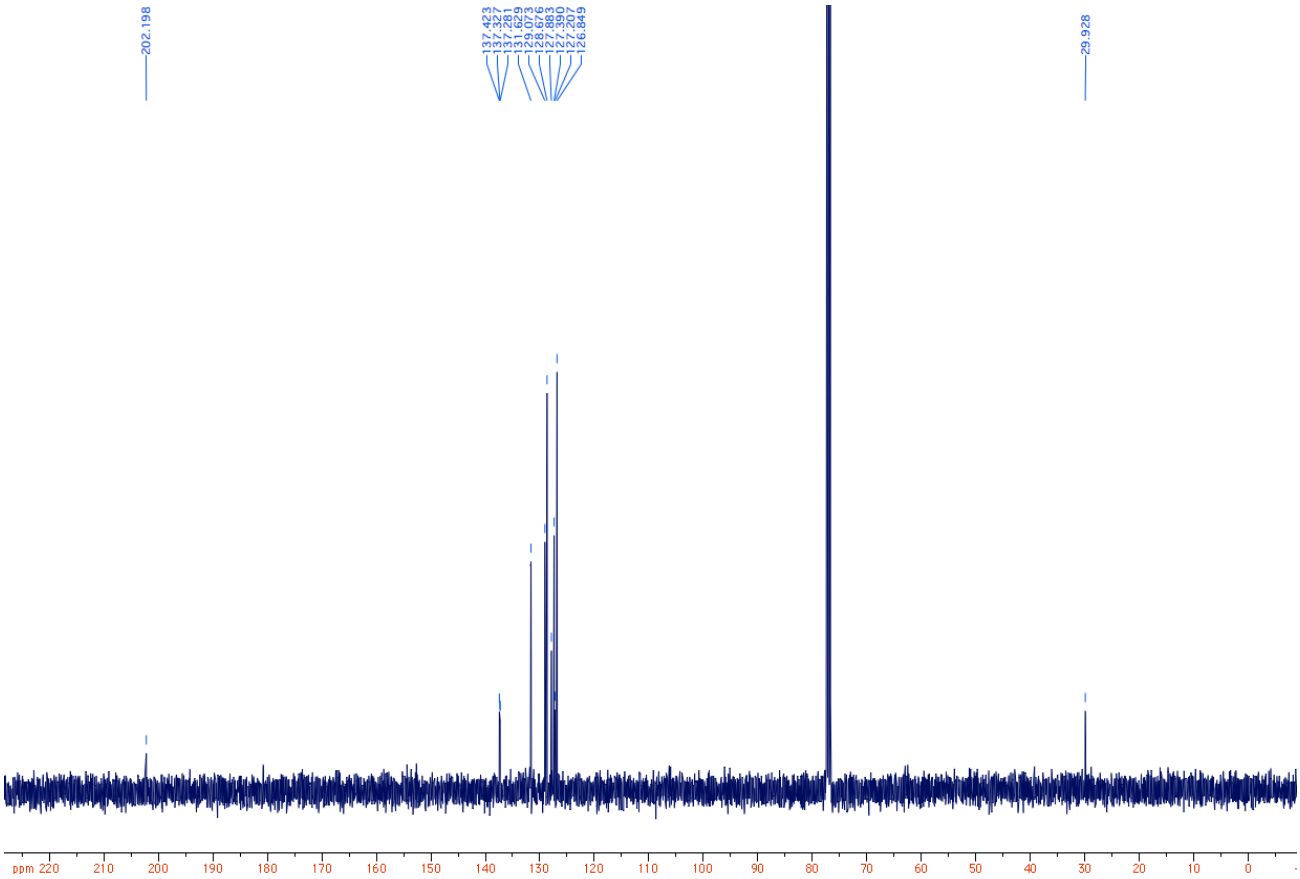
3h (^{13}H NMR, 100 MHz, $CDCl_3$)



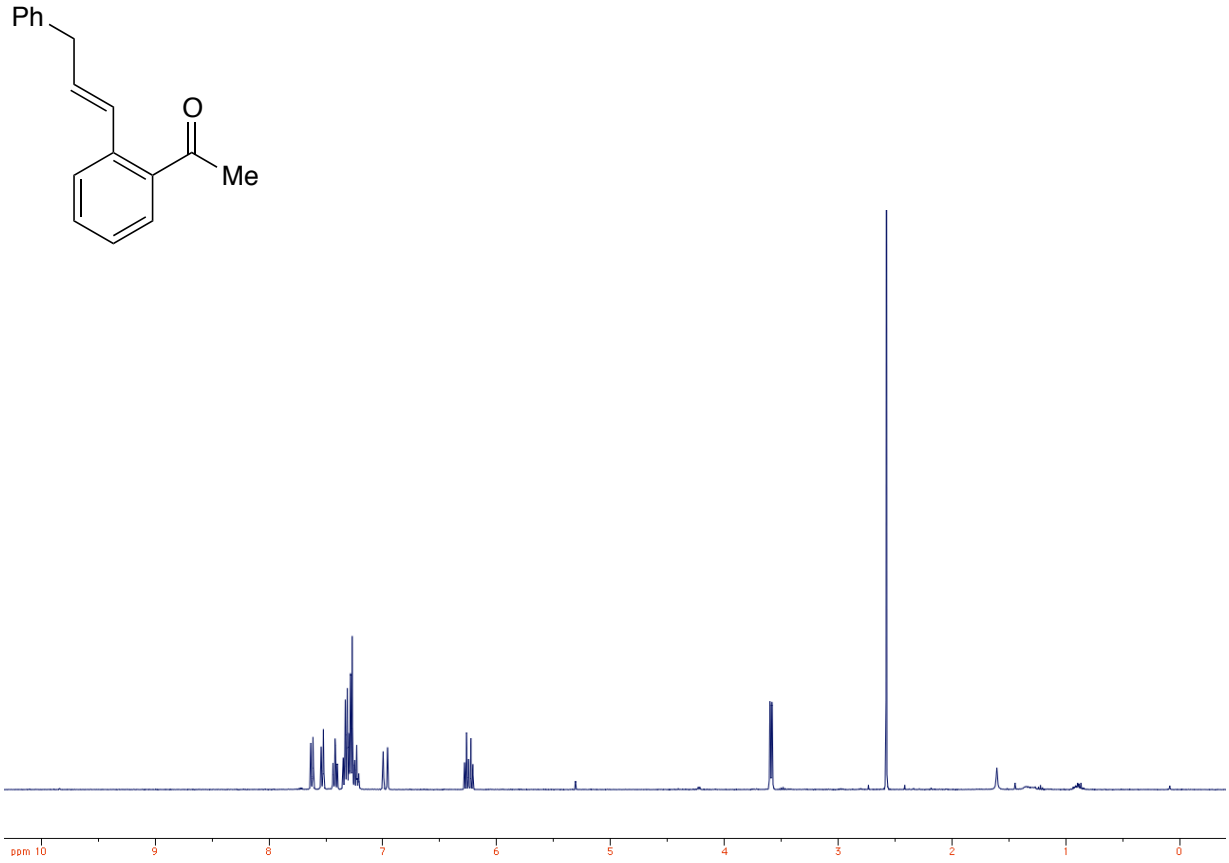
3i (^{1}H NMR, 400 MHz, $CDCl_3$)



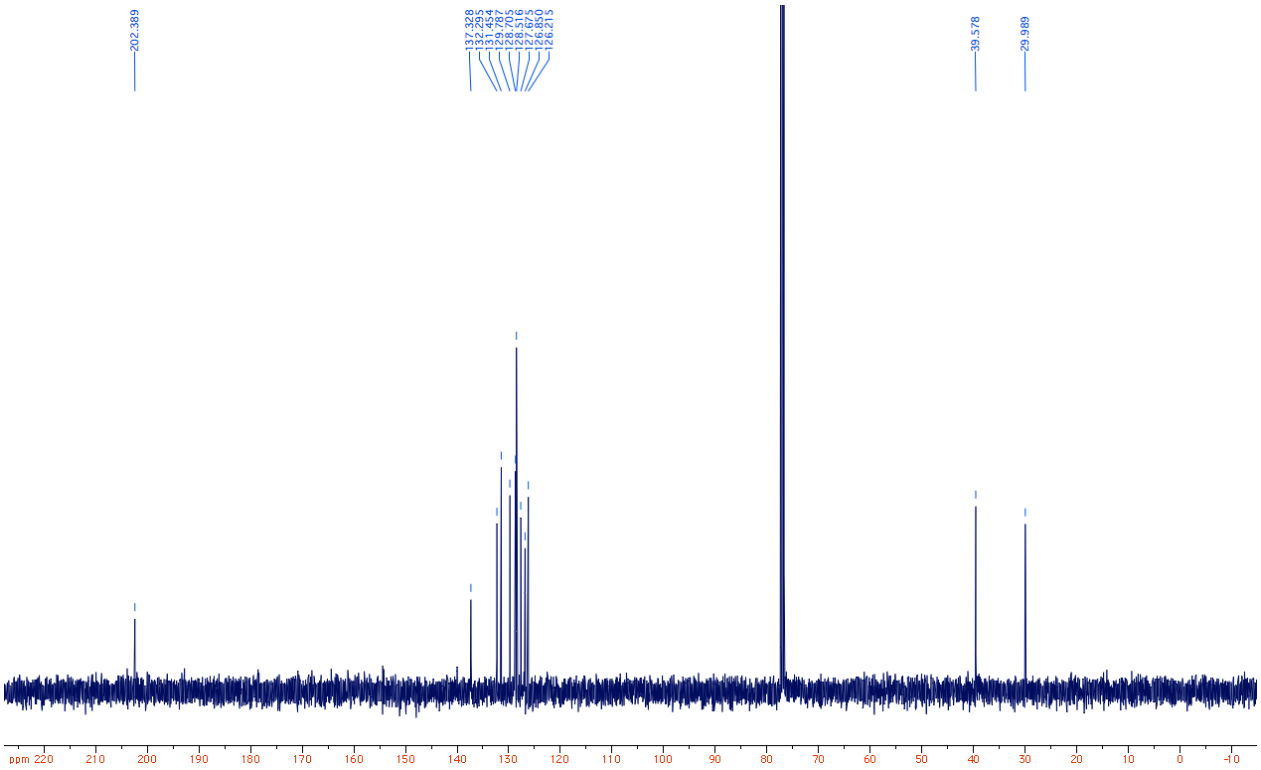
3i (^{13}C NMR, 100 MHz, $CDCl_3$)



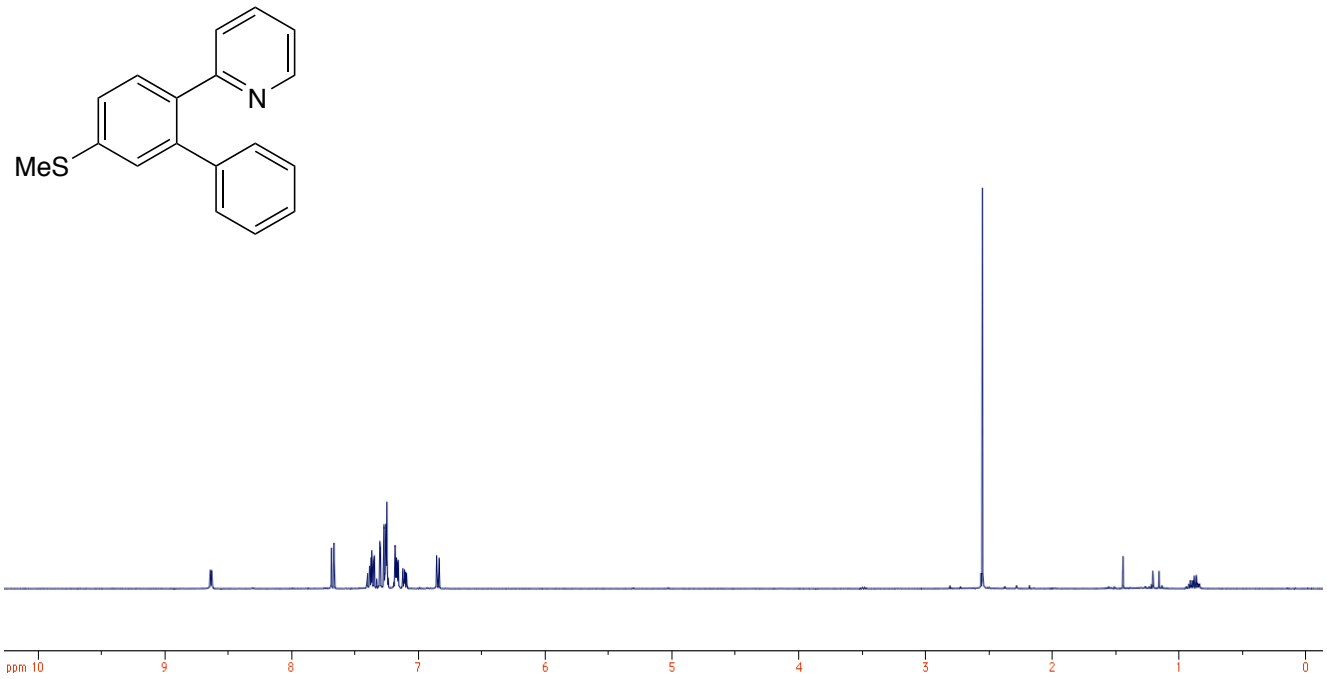
3j (^{1}H NMR, 400 MHz, $CDCl_3$)



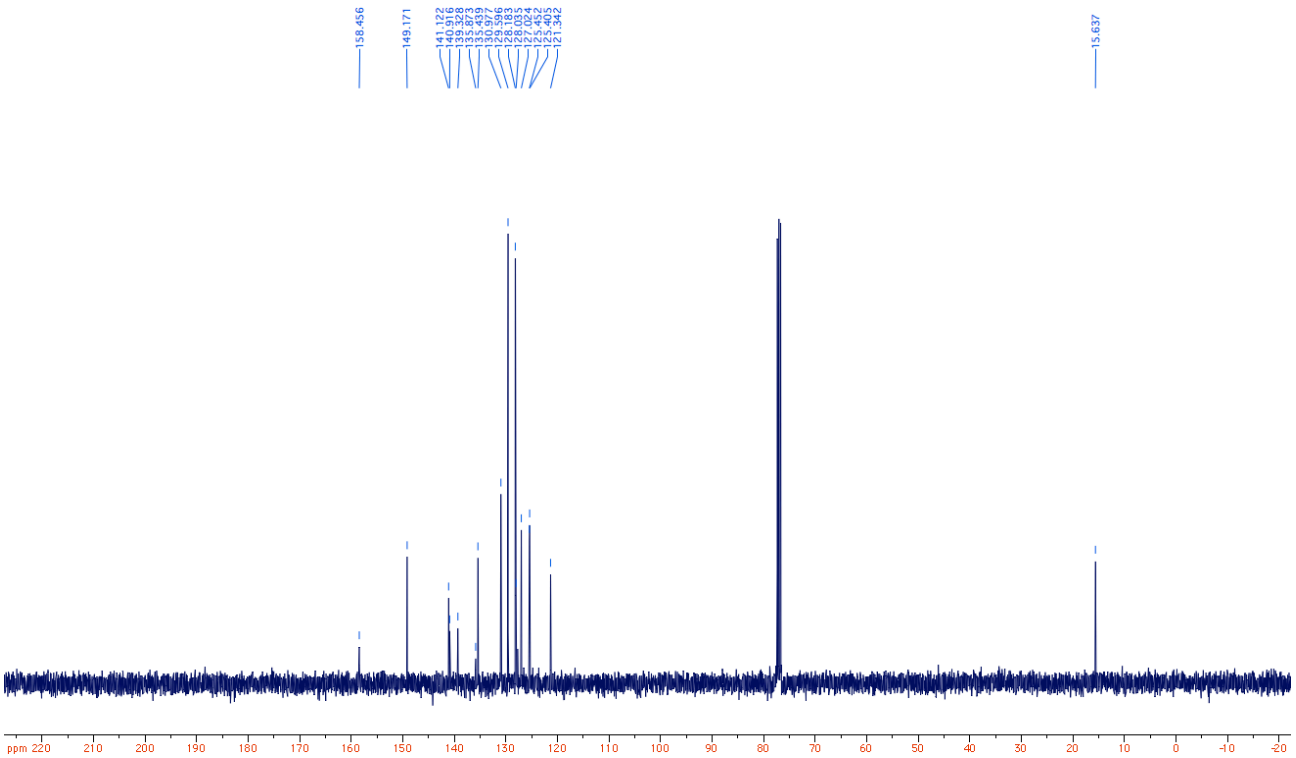
3j (^{13}C NMR, 100 MHz, $CDCl_3$)



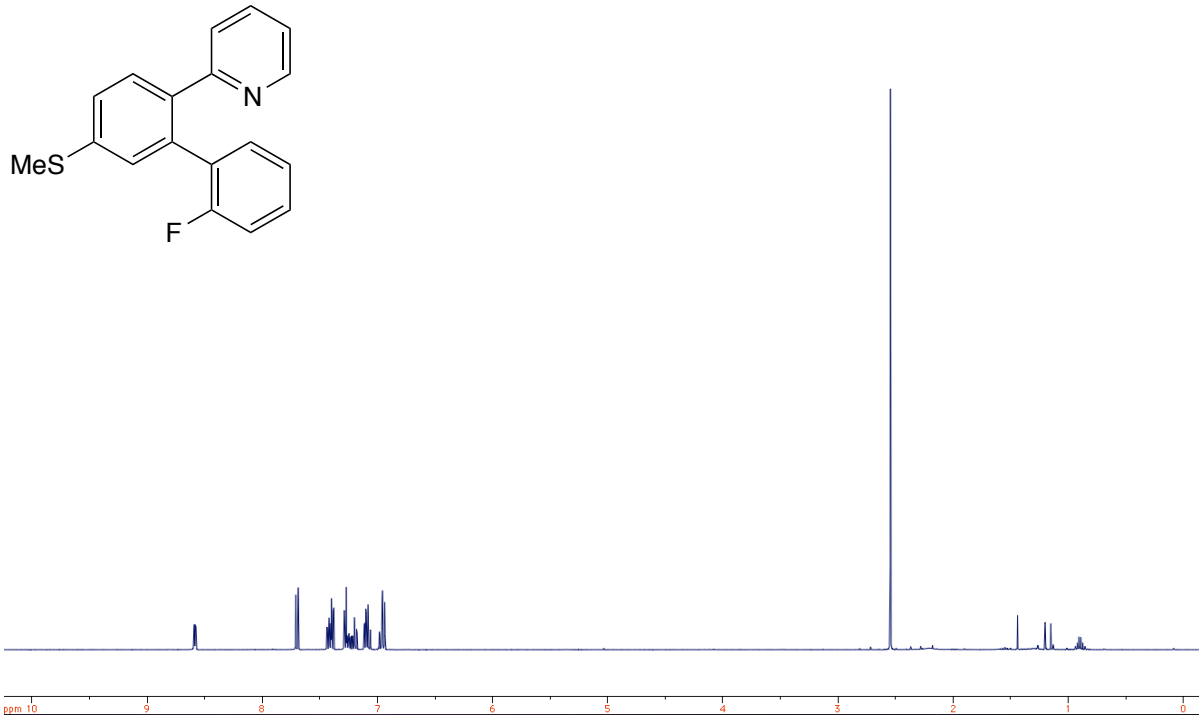
5 (^{1}H NMR, 400 MHz, $CDCl_3$)



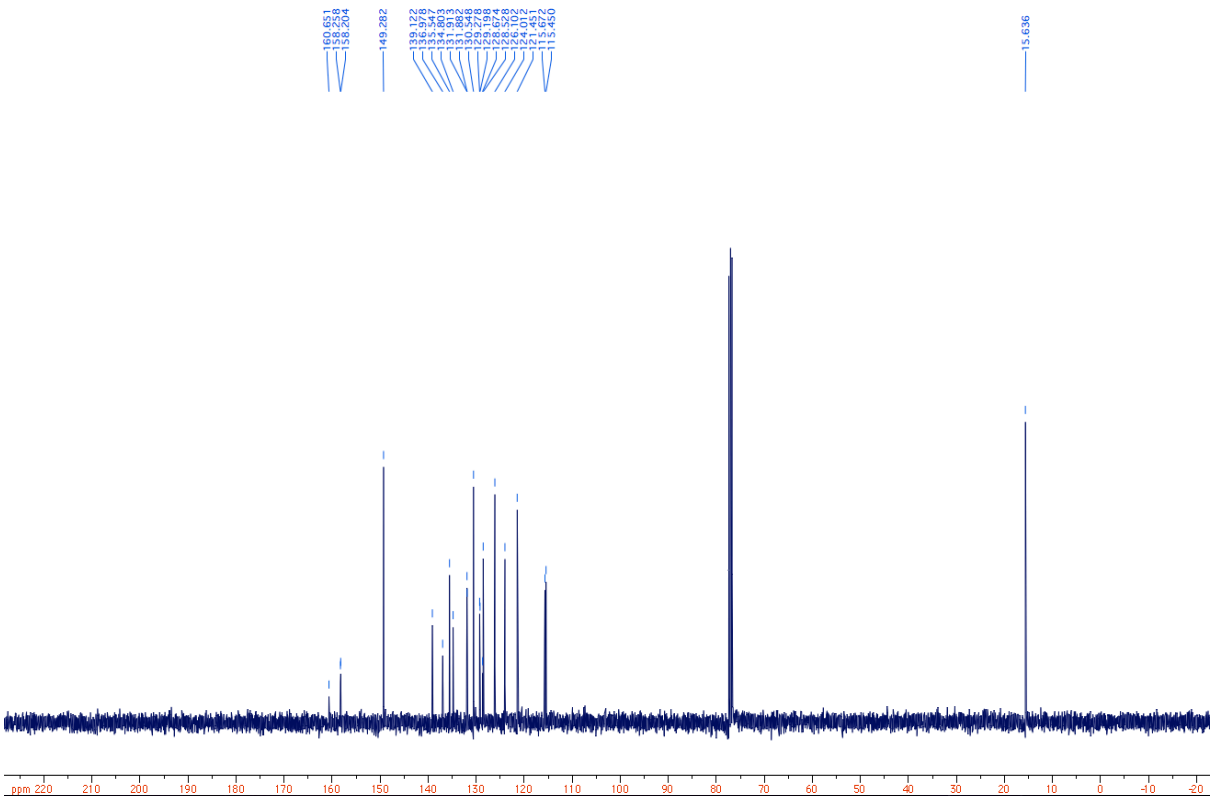
5 (^{13}C NMR, 100 MHz, $CDCl_3$)



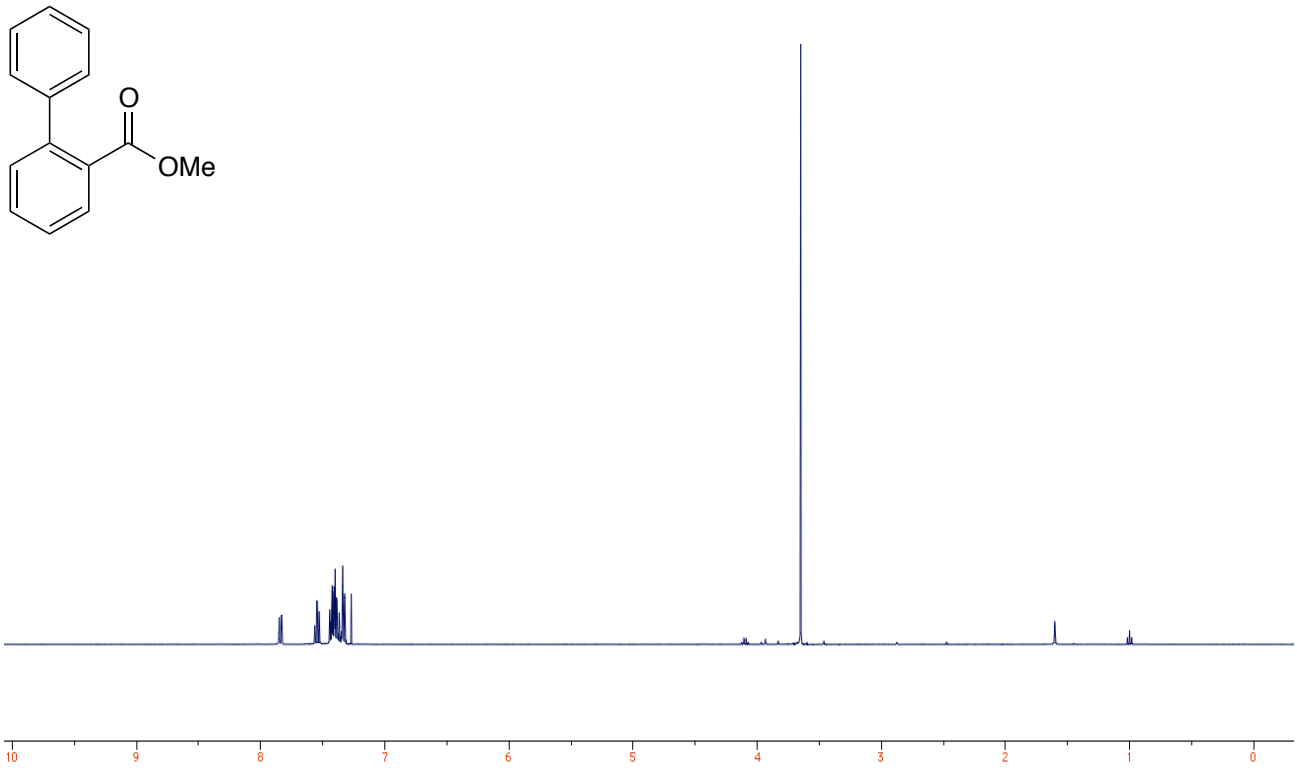
6 (^{1}H NMR, 400 MHz, $CDCl_3$)



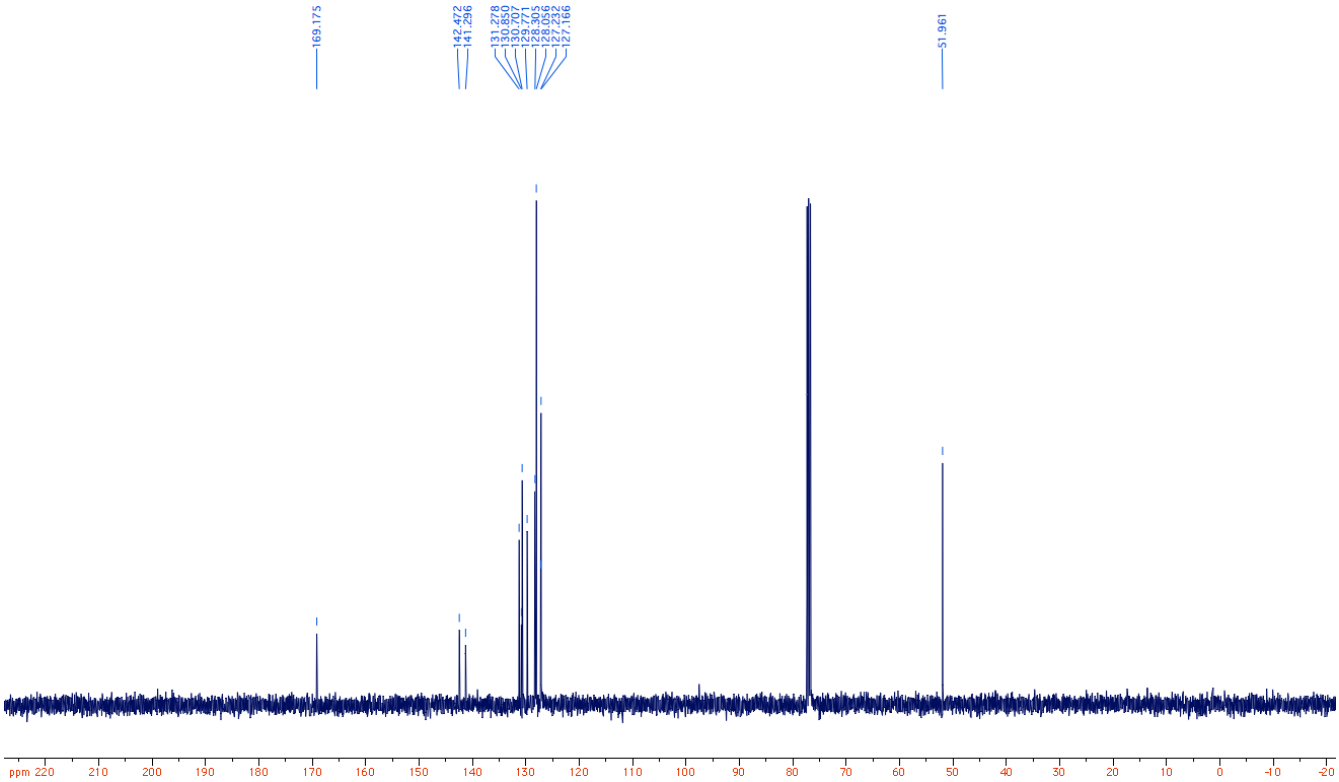
6 (^{13}C NMR, 100 MHz, $CDCl_3$)



8 (^{1}H NMR, 400 MHz, $CDCl_3$)



8 (^{13}C NMR, 100 MHz, $CDCl_3$)



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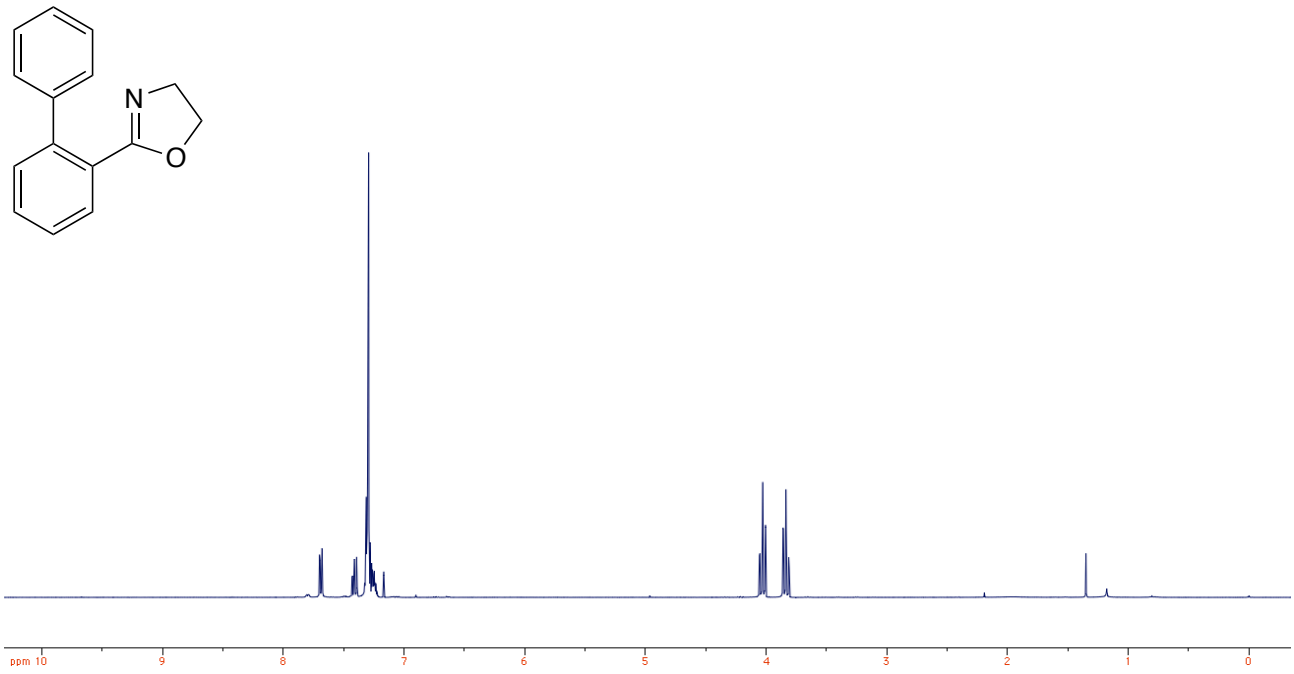

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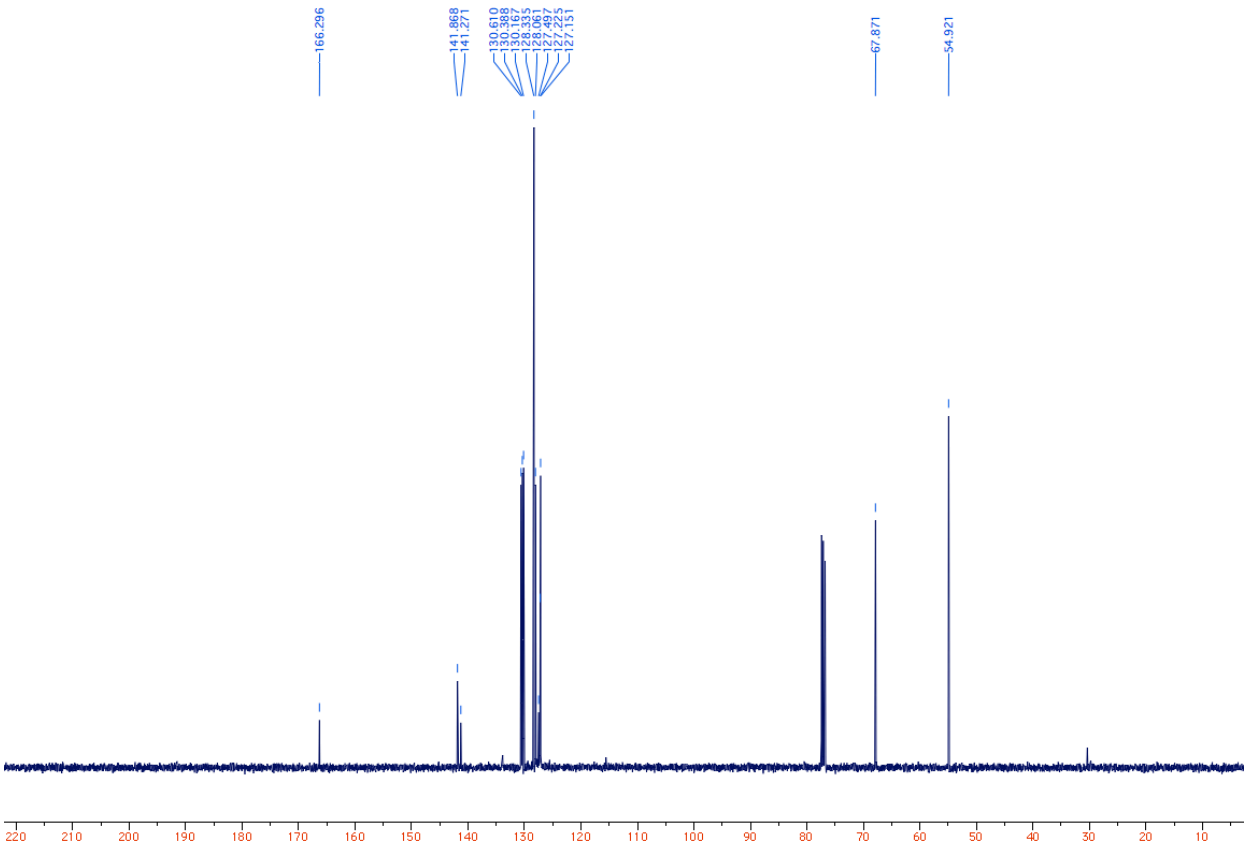

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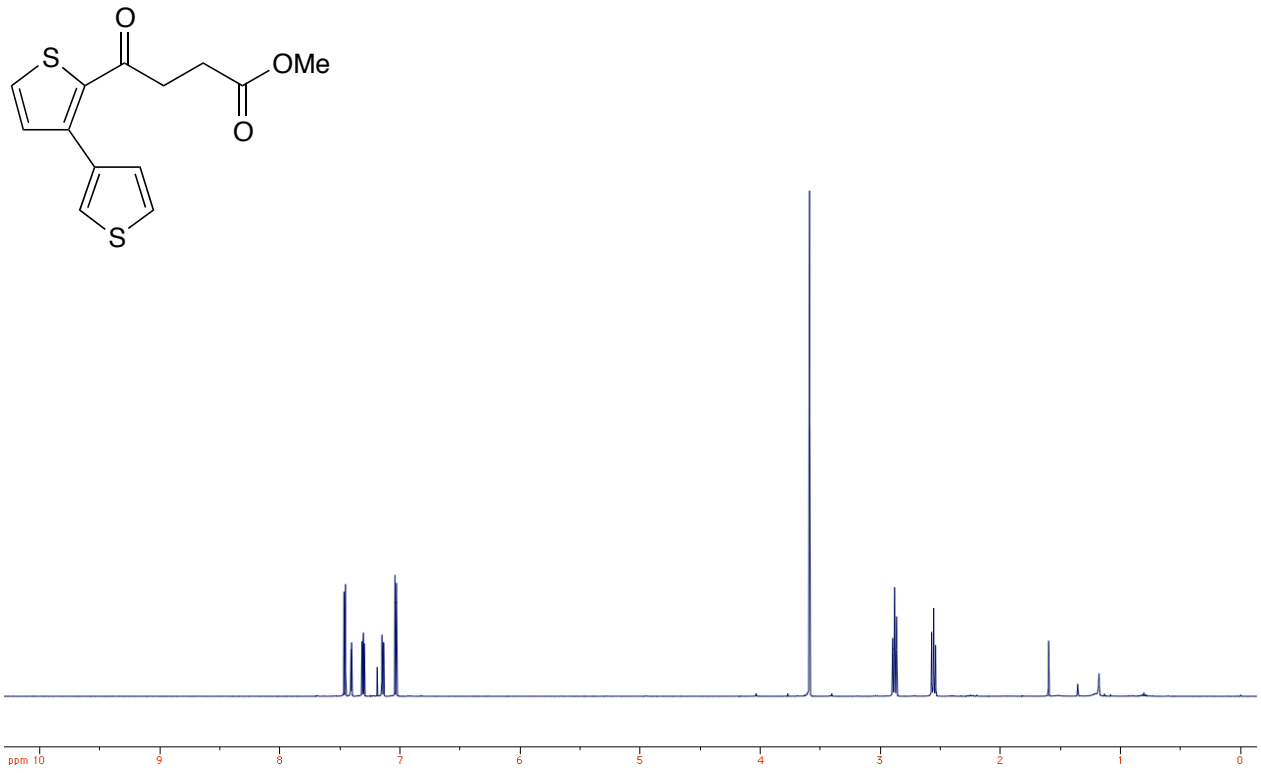

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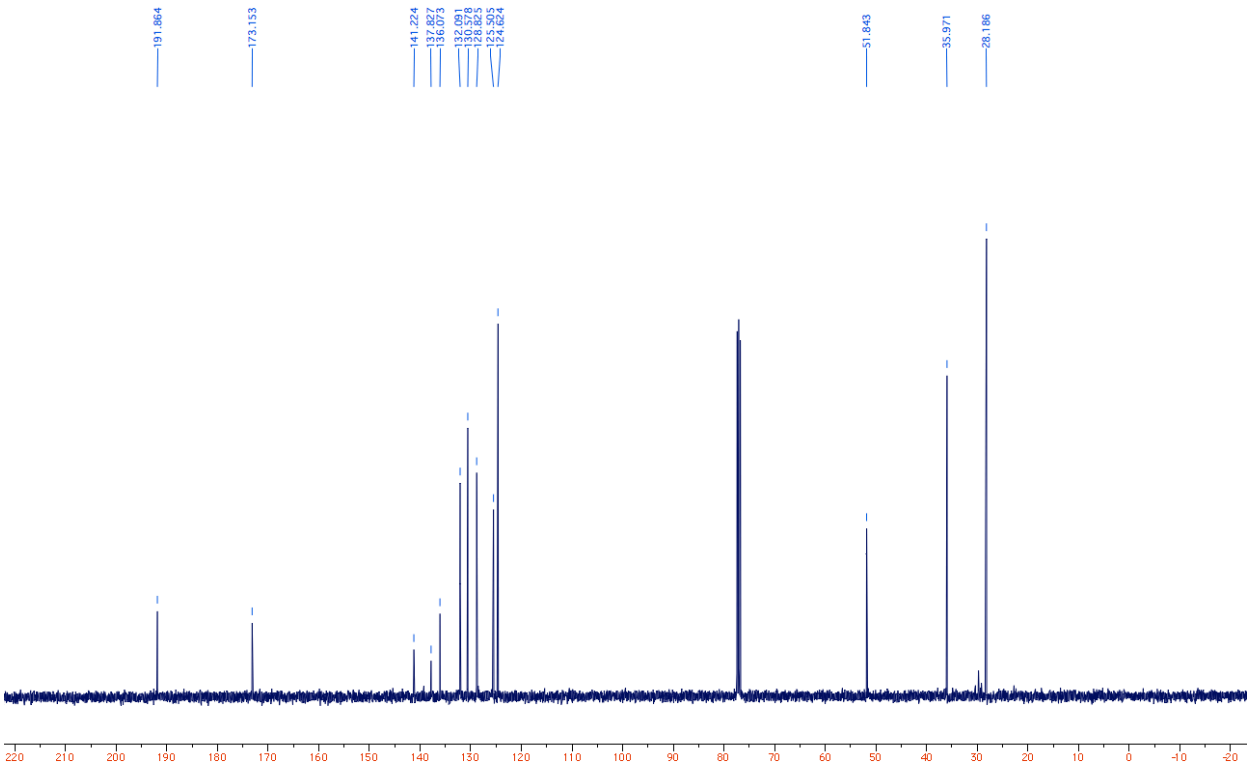
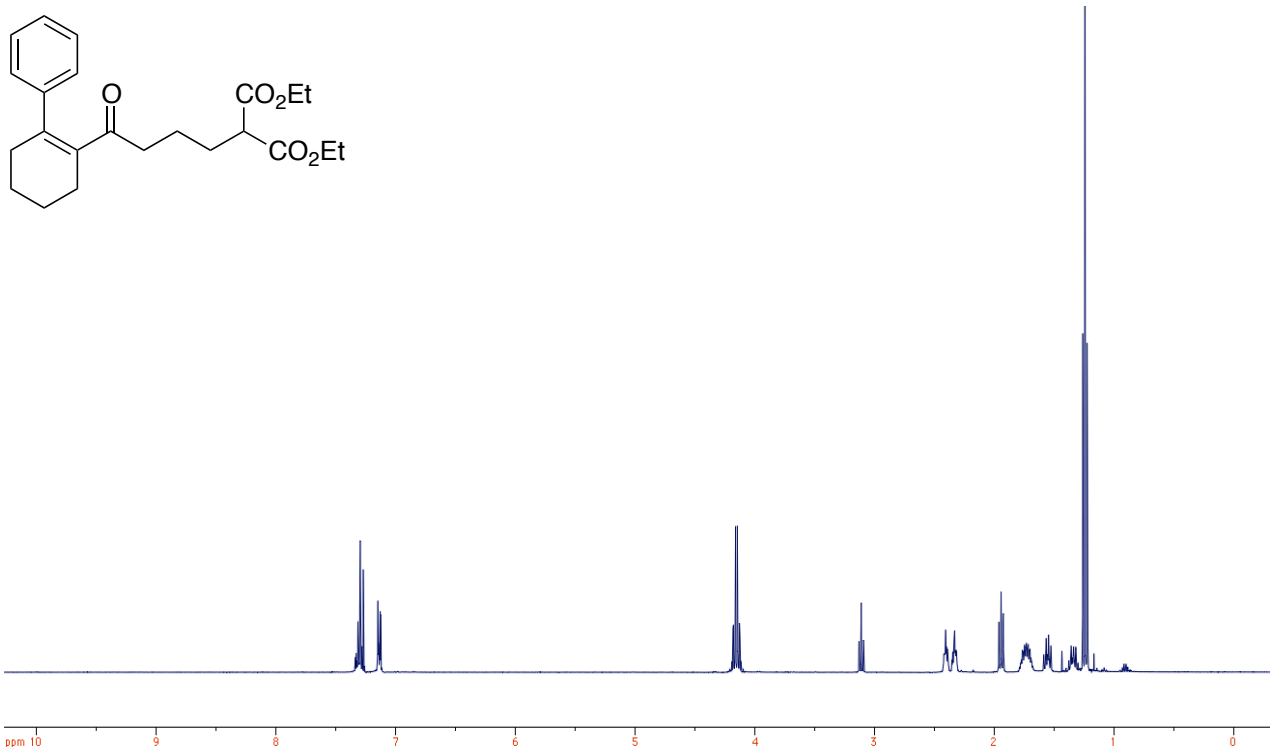
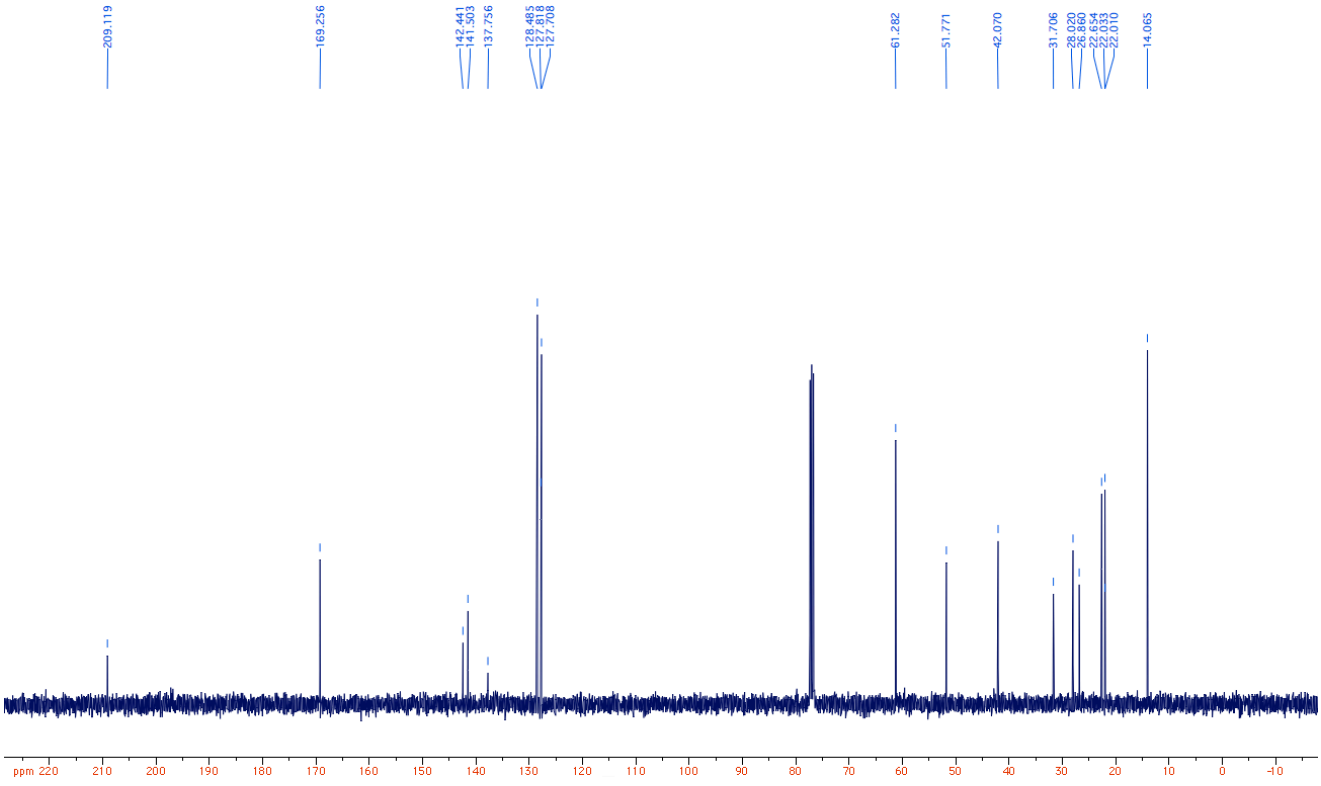


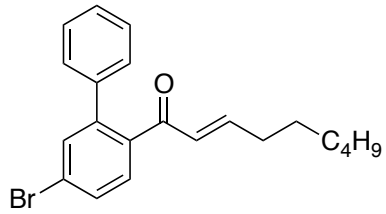
14 (^{1}H NMR, 400 MHz, $CDCl_3$)

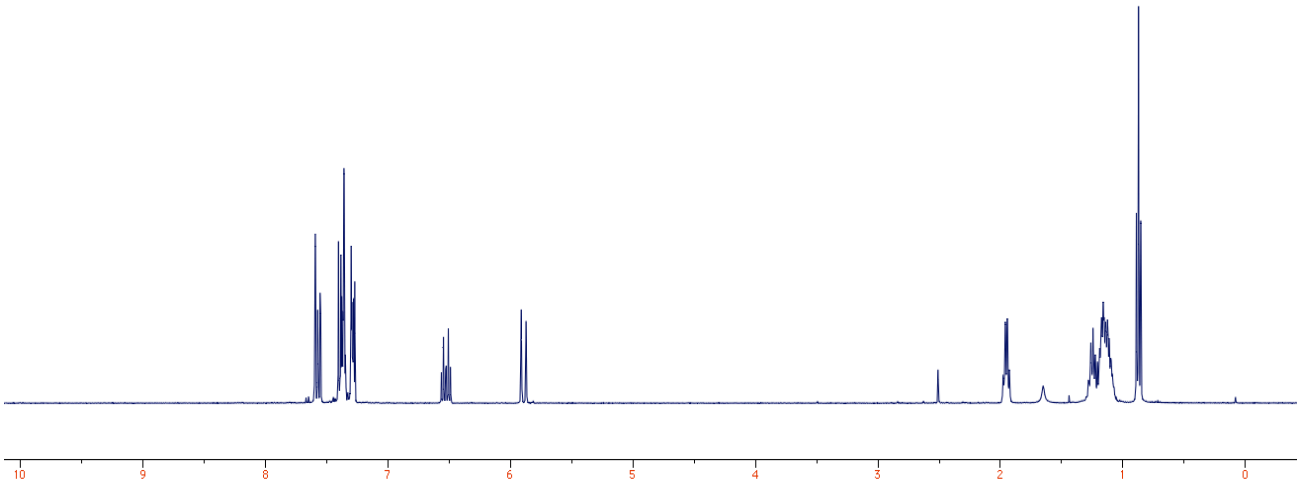


14 (^{13}C NMR, 100 MHz, $CDCl_3$)

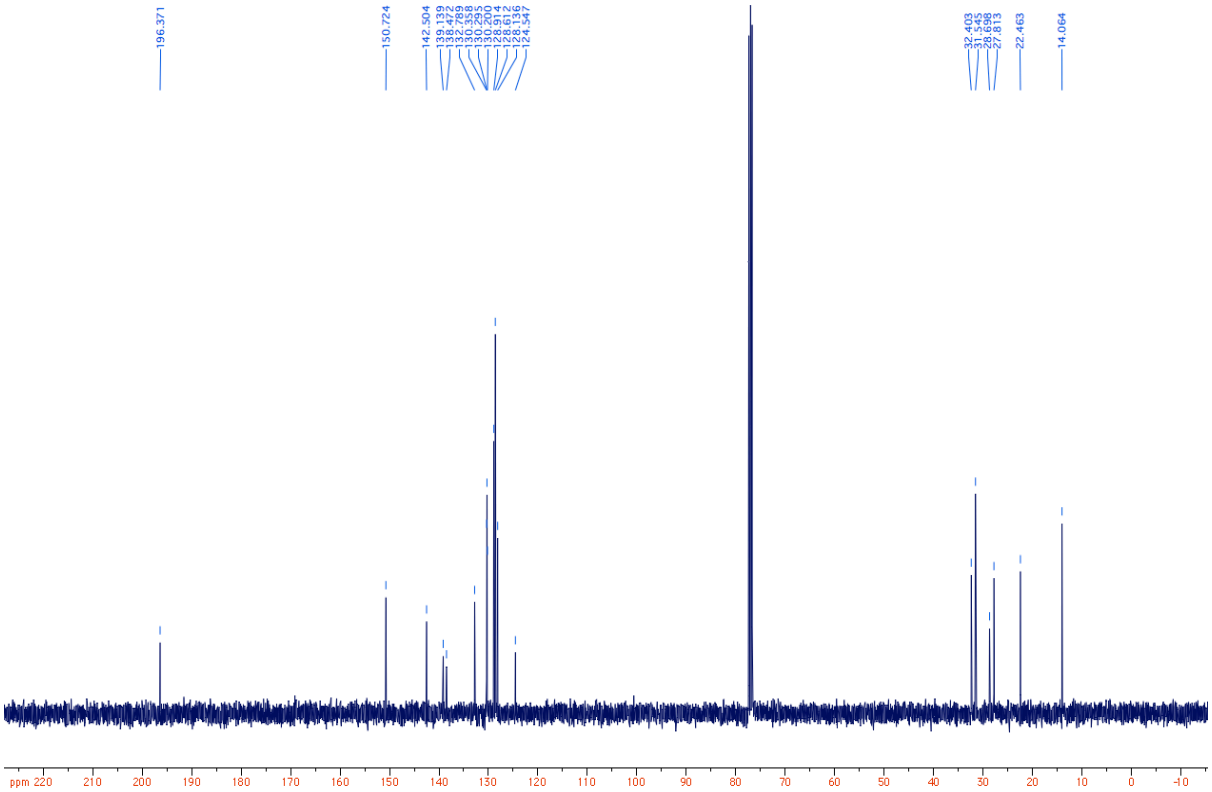


16a (^{1}H NMR, 400 MHz, $CDCl_3$)

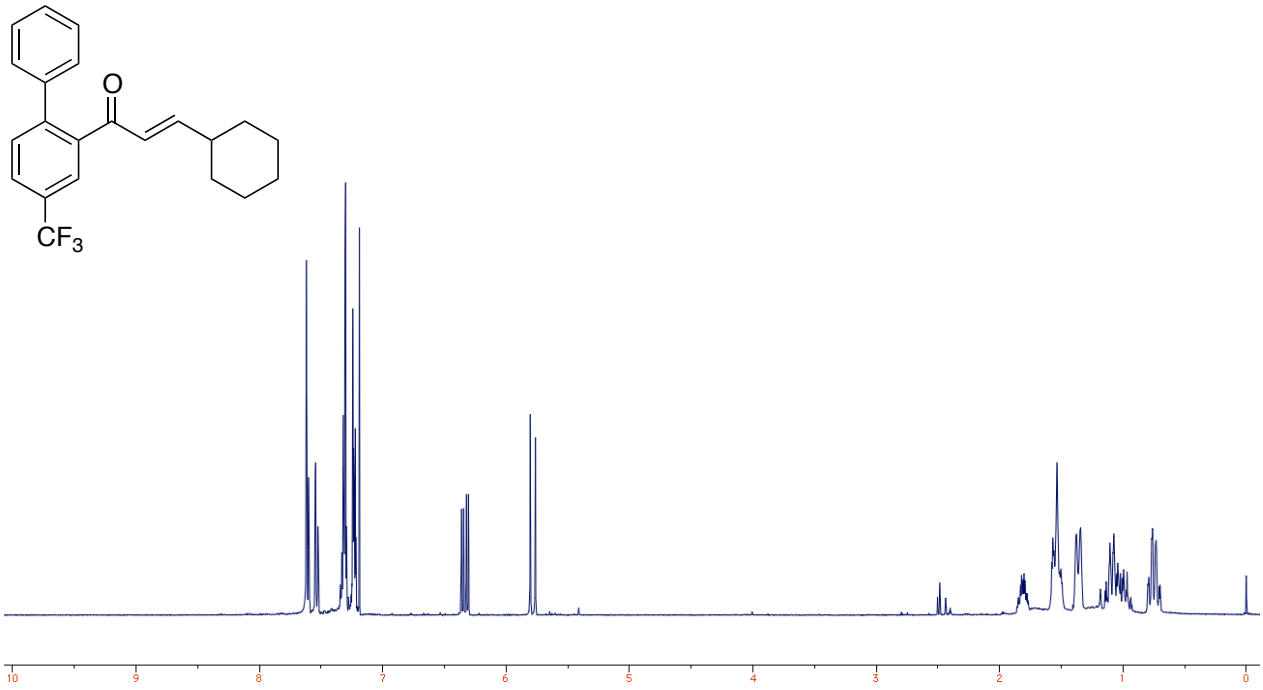




16a (^{13}C NMR, 100 MHz, $CDCl_3$)



16b (^{1}H NMR, 400 MHz, $CDCl_3$)



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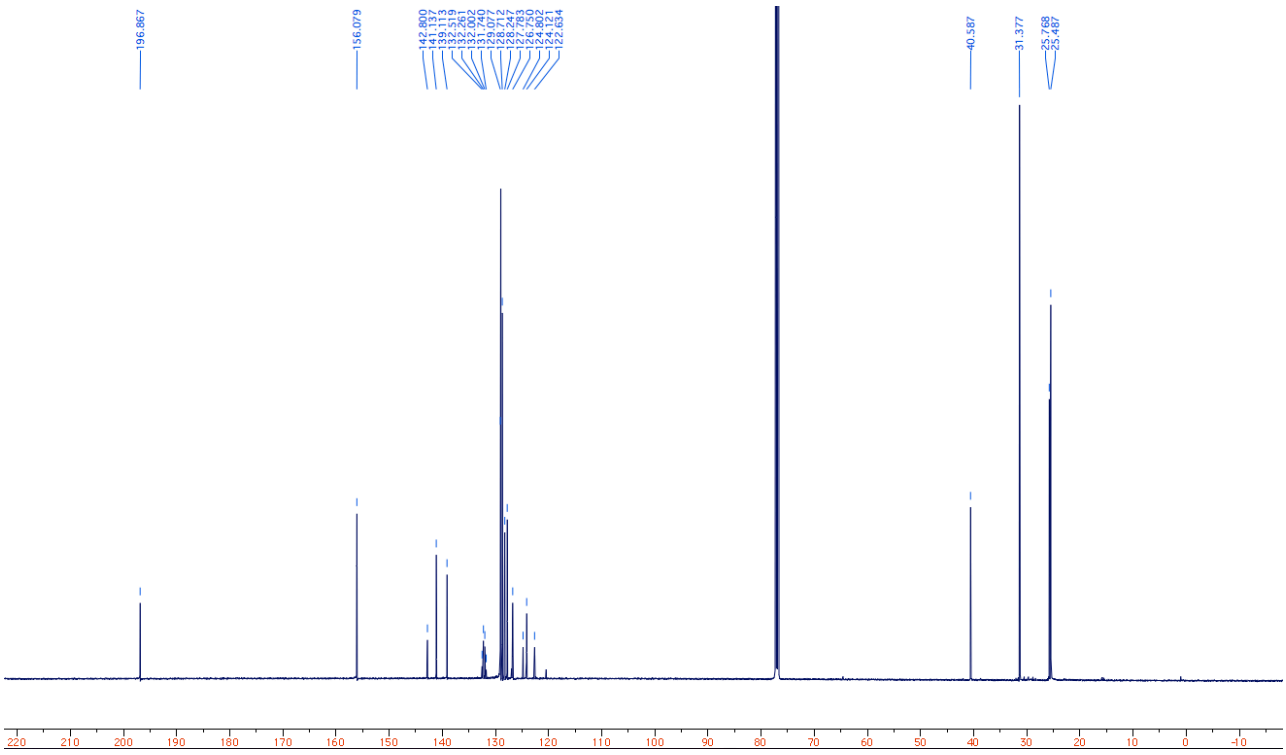
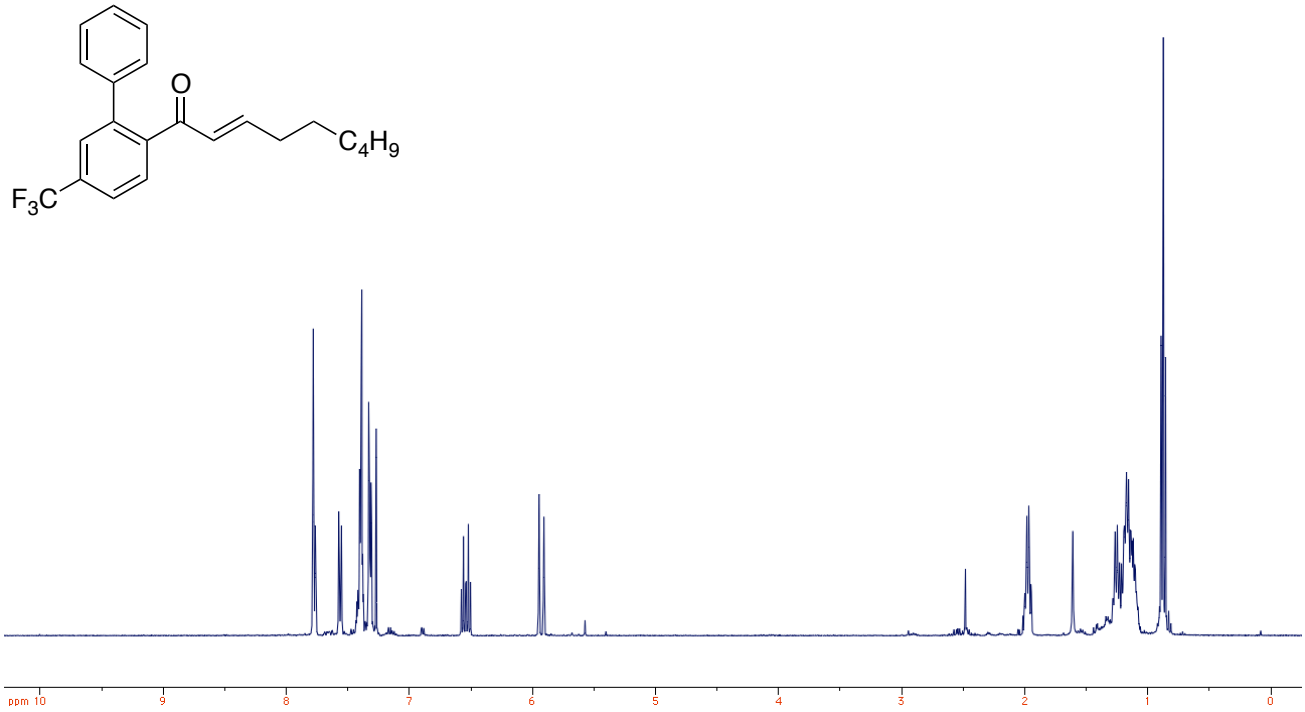


16c (^{1}H NMR, 400 MHz, $CDCl_3$)



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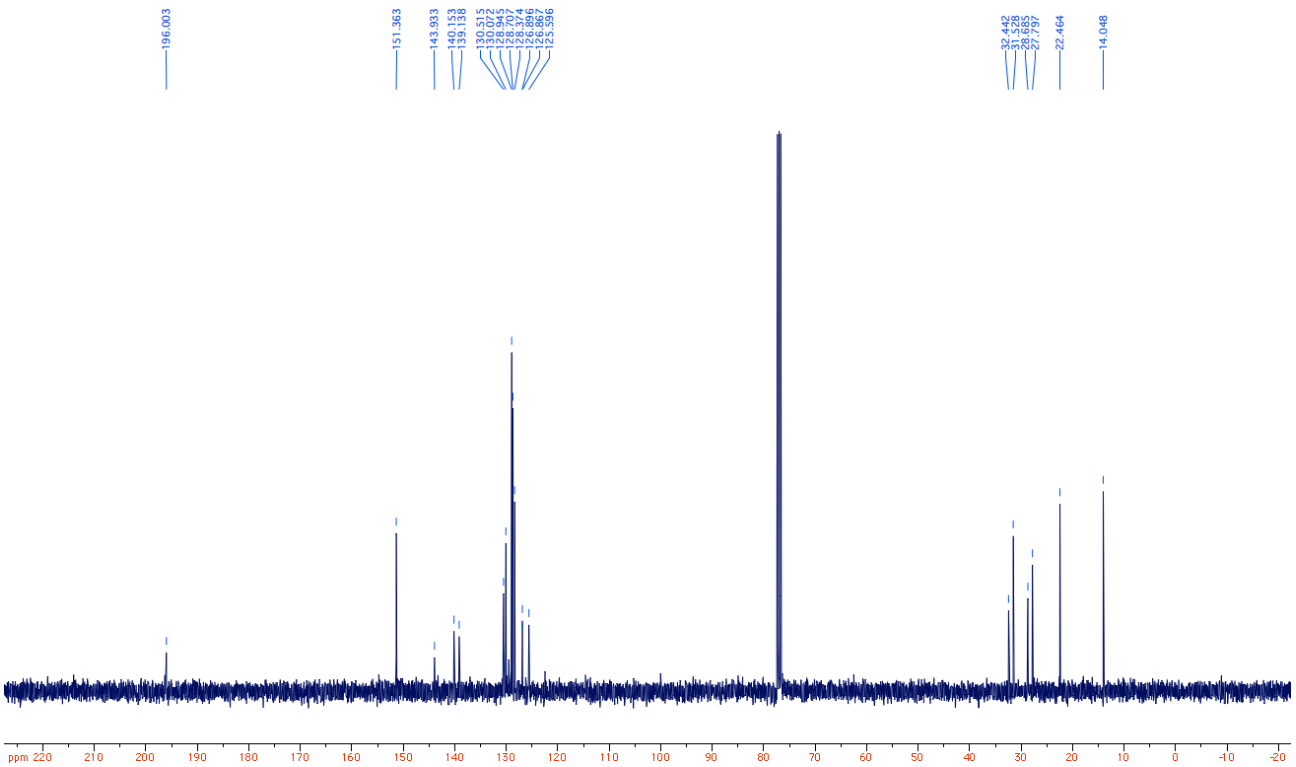

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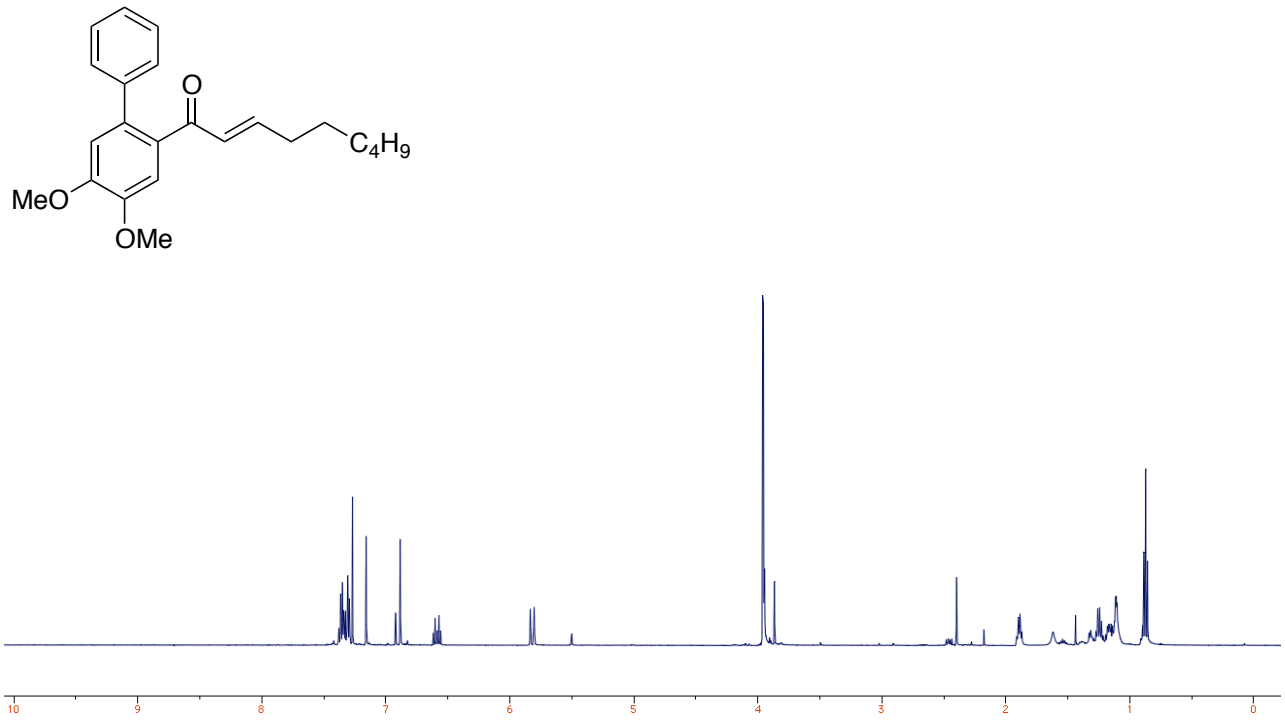

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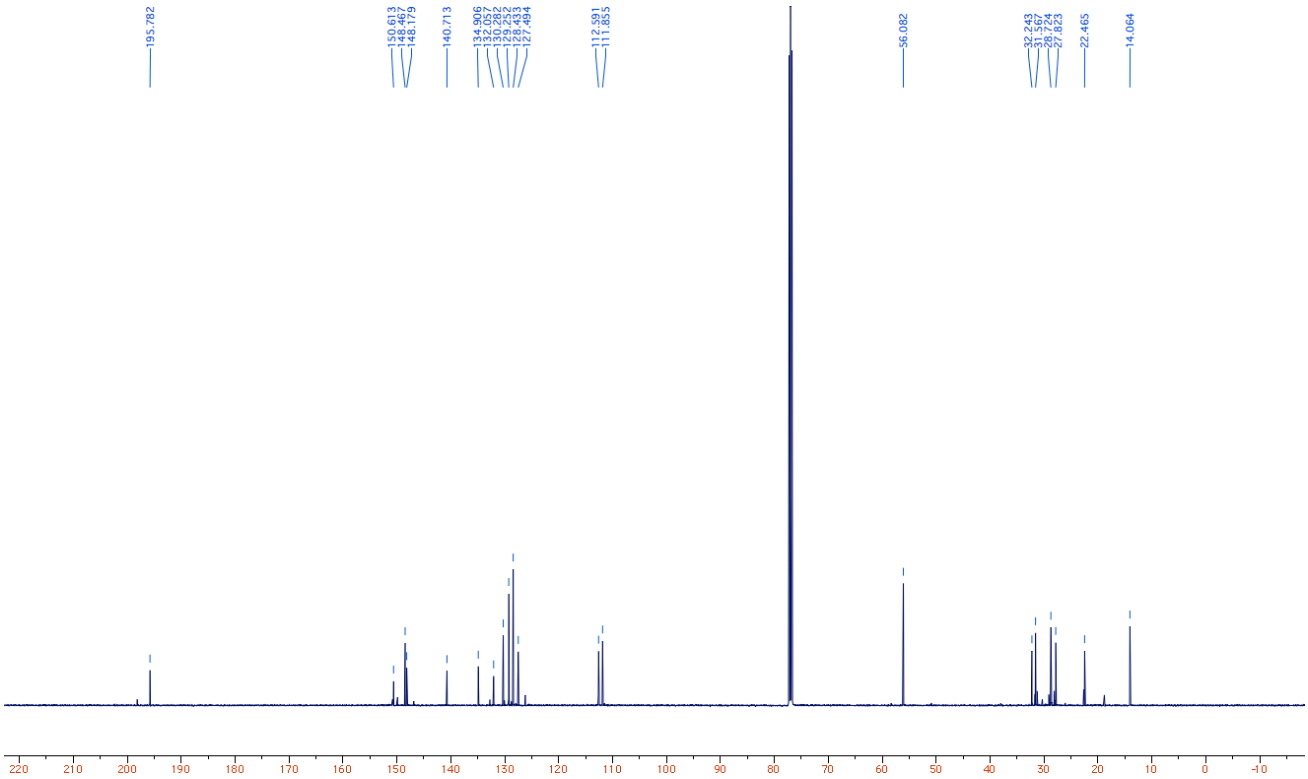

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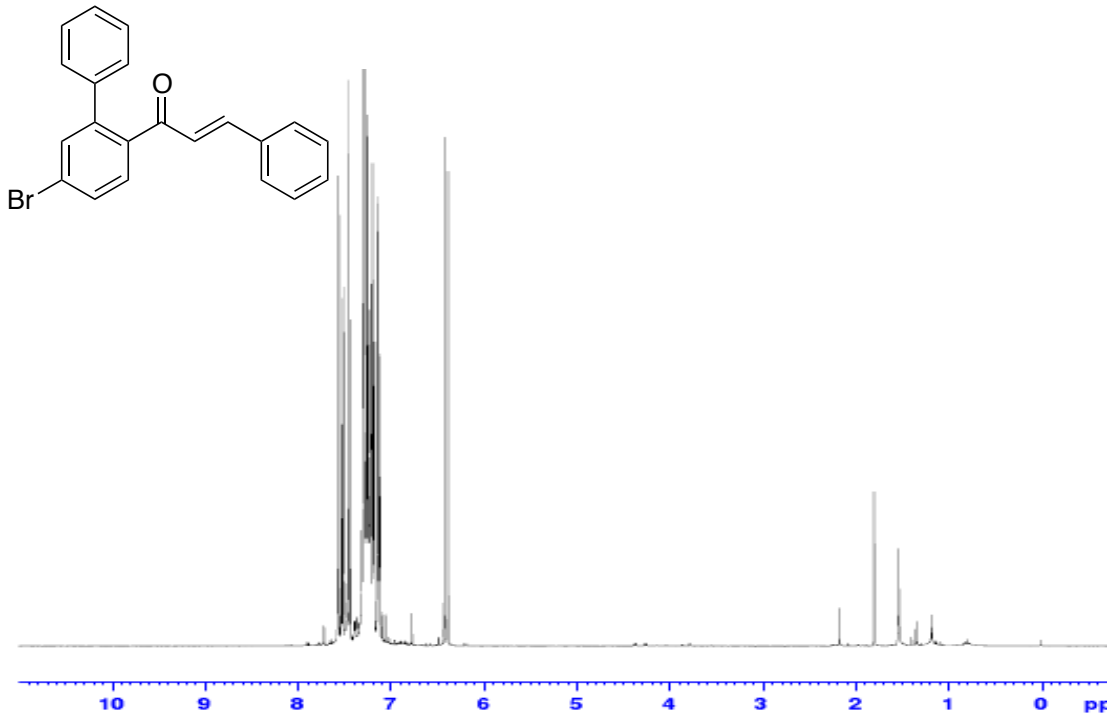
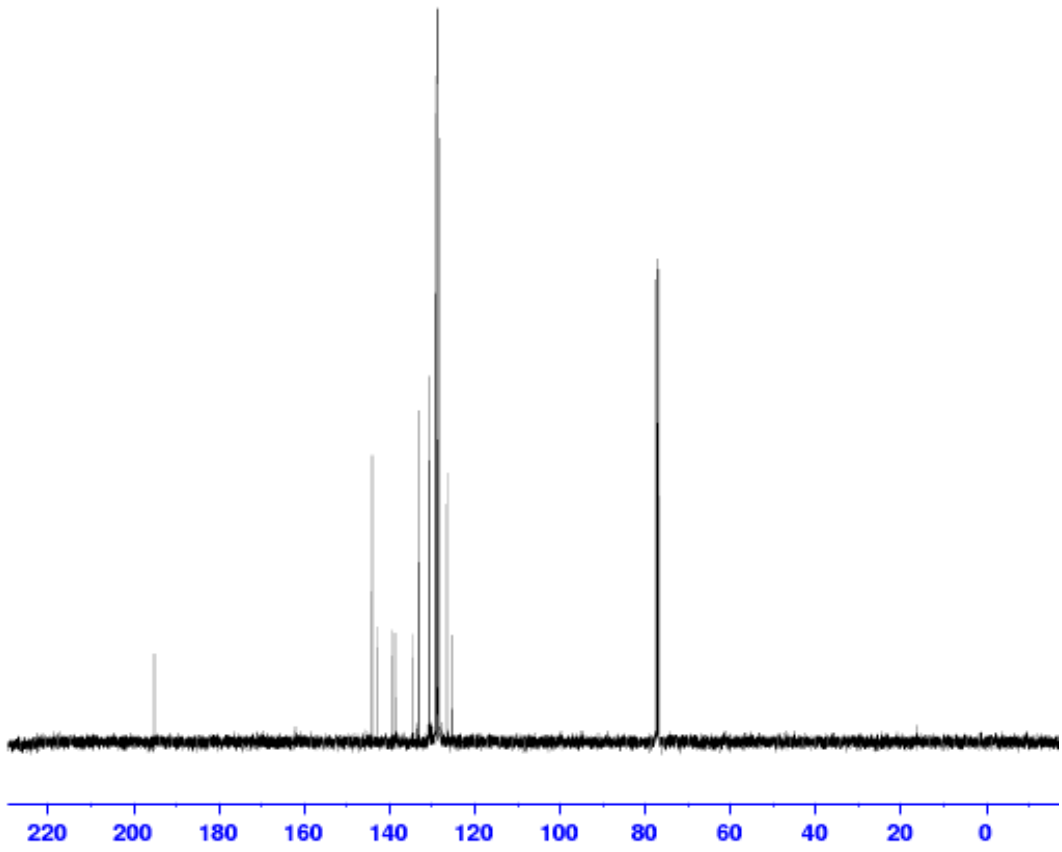


16e (^{13}C NMR, 100 MHz, $CDCl_3$)



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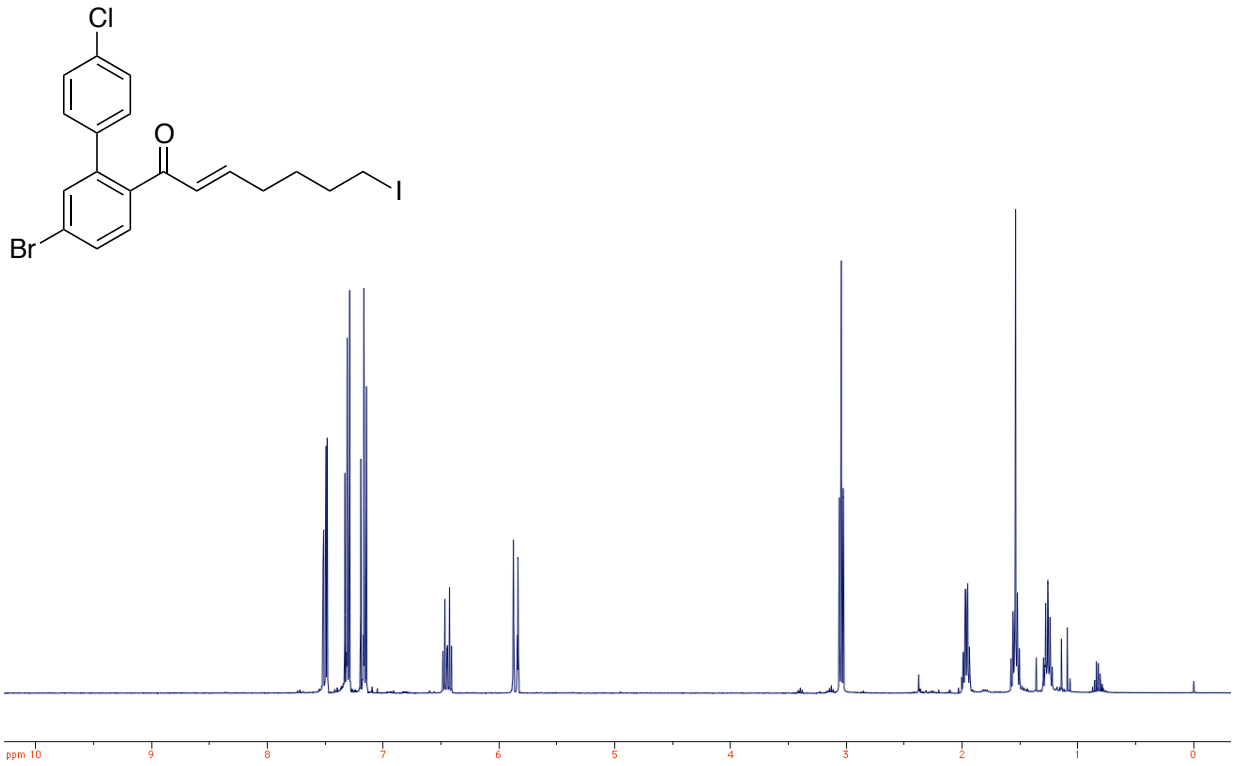
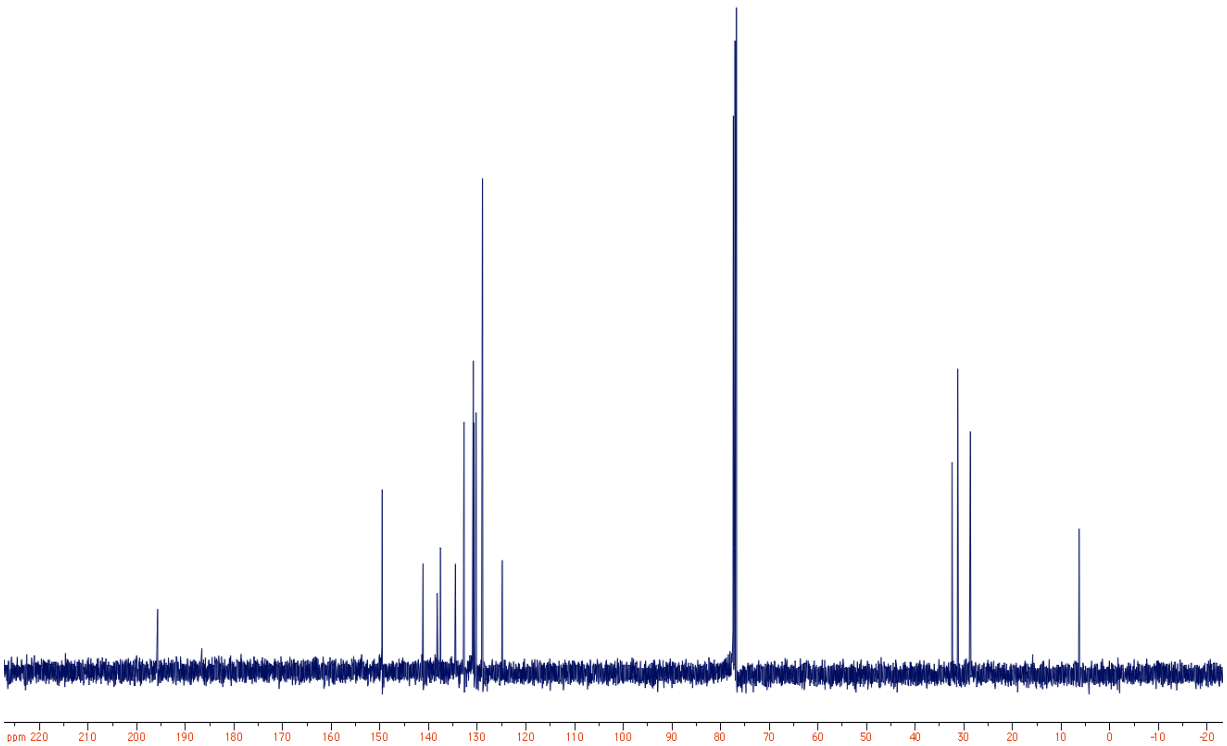


16f (^{13}C NMR, 100 MHz, $CDCl_3$)



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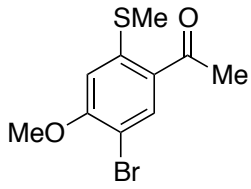
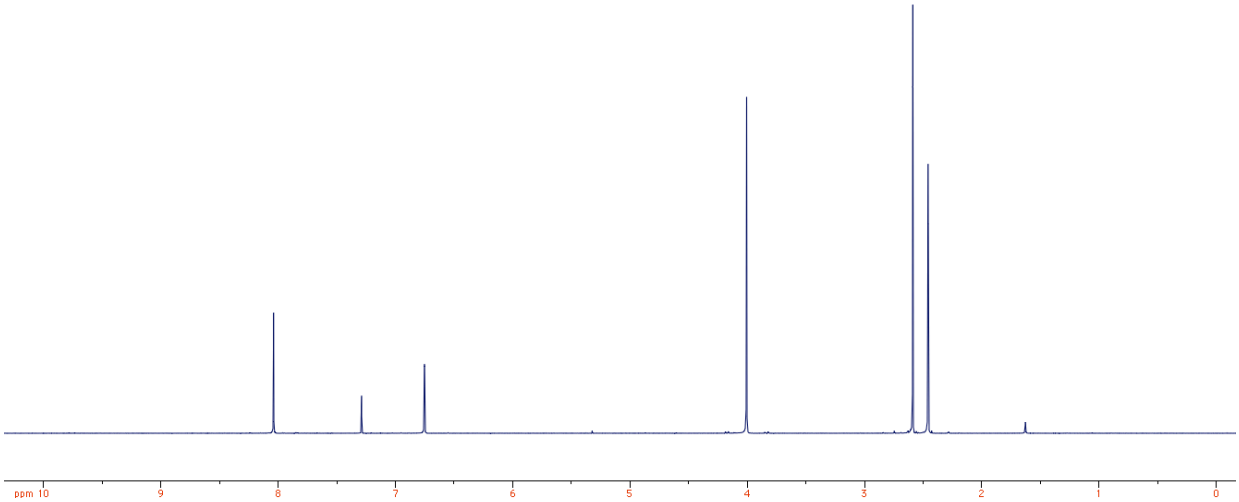
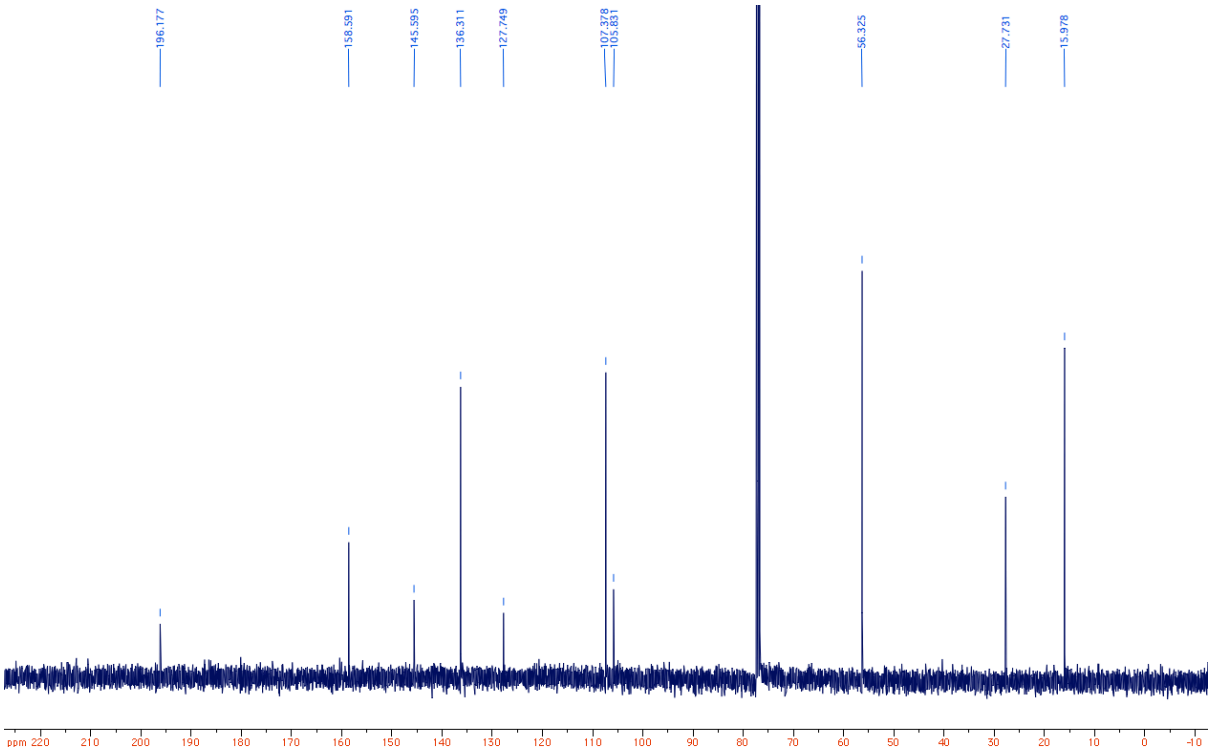




17 (^{13}C NMR, 100 MHz, $CDCl_3$)



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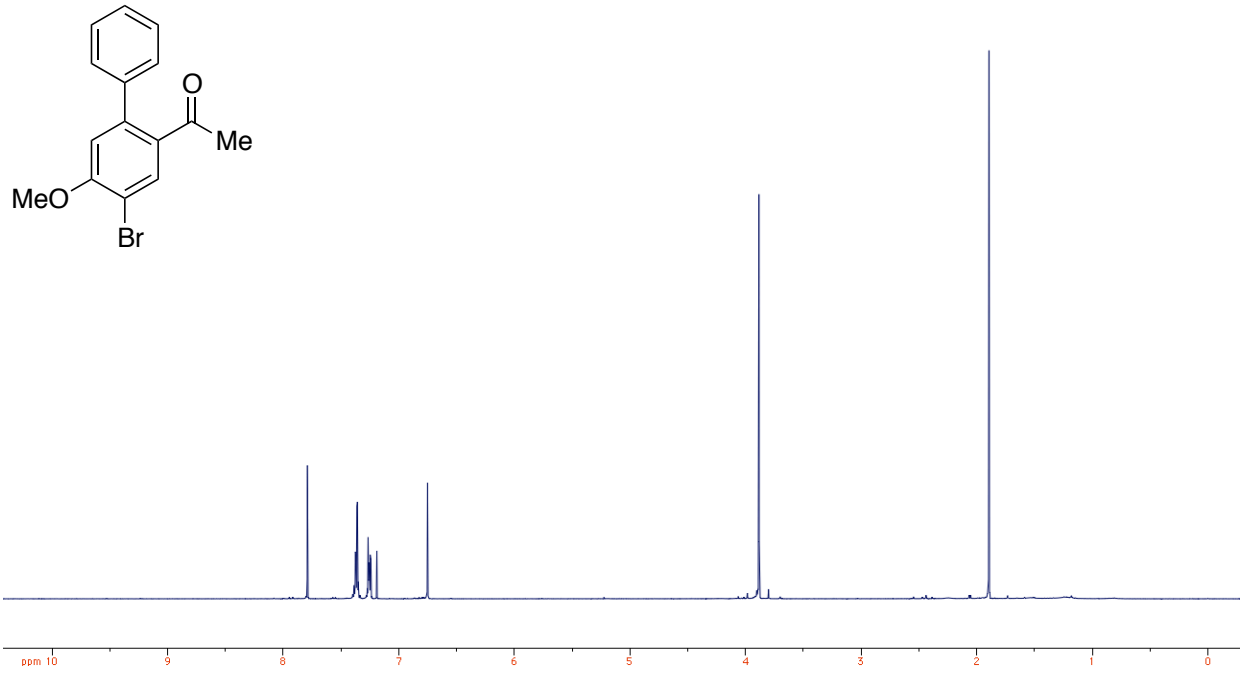
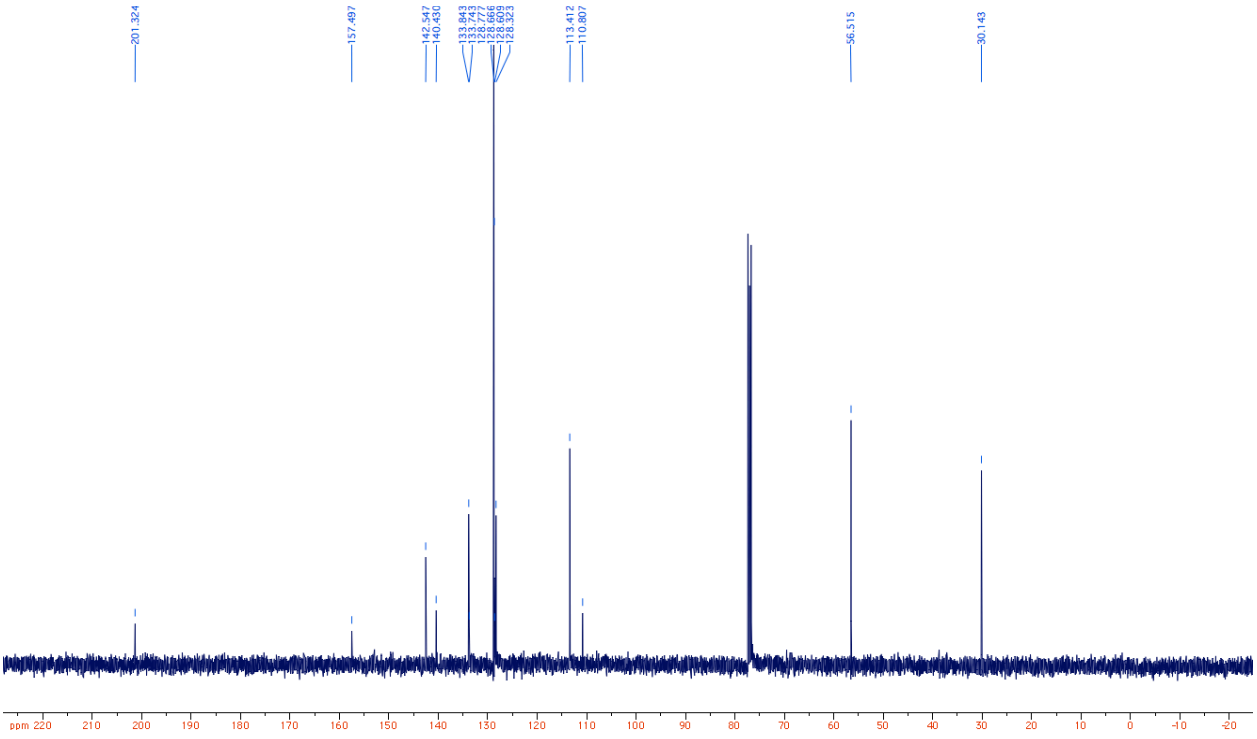


18 (^{13}C NMR, 100 MHz, $CDCl_3$)



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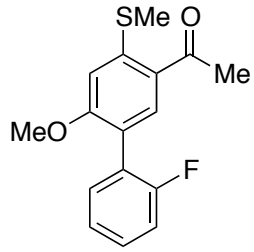
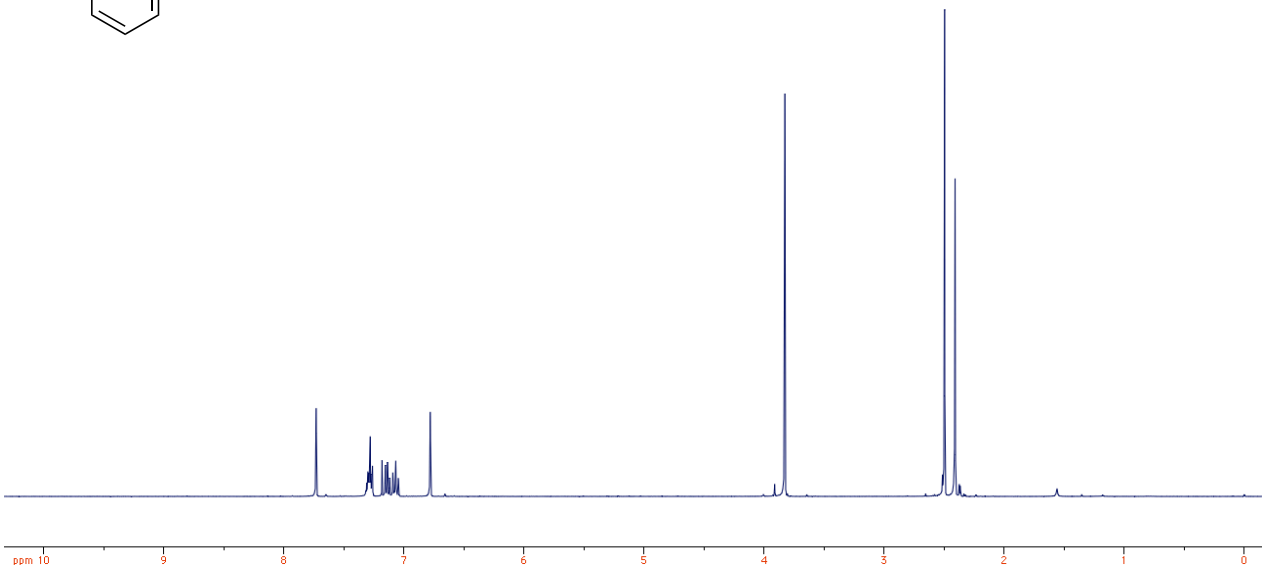
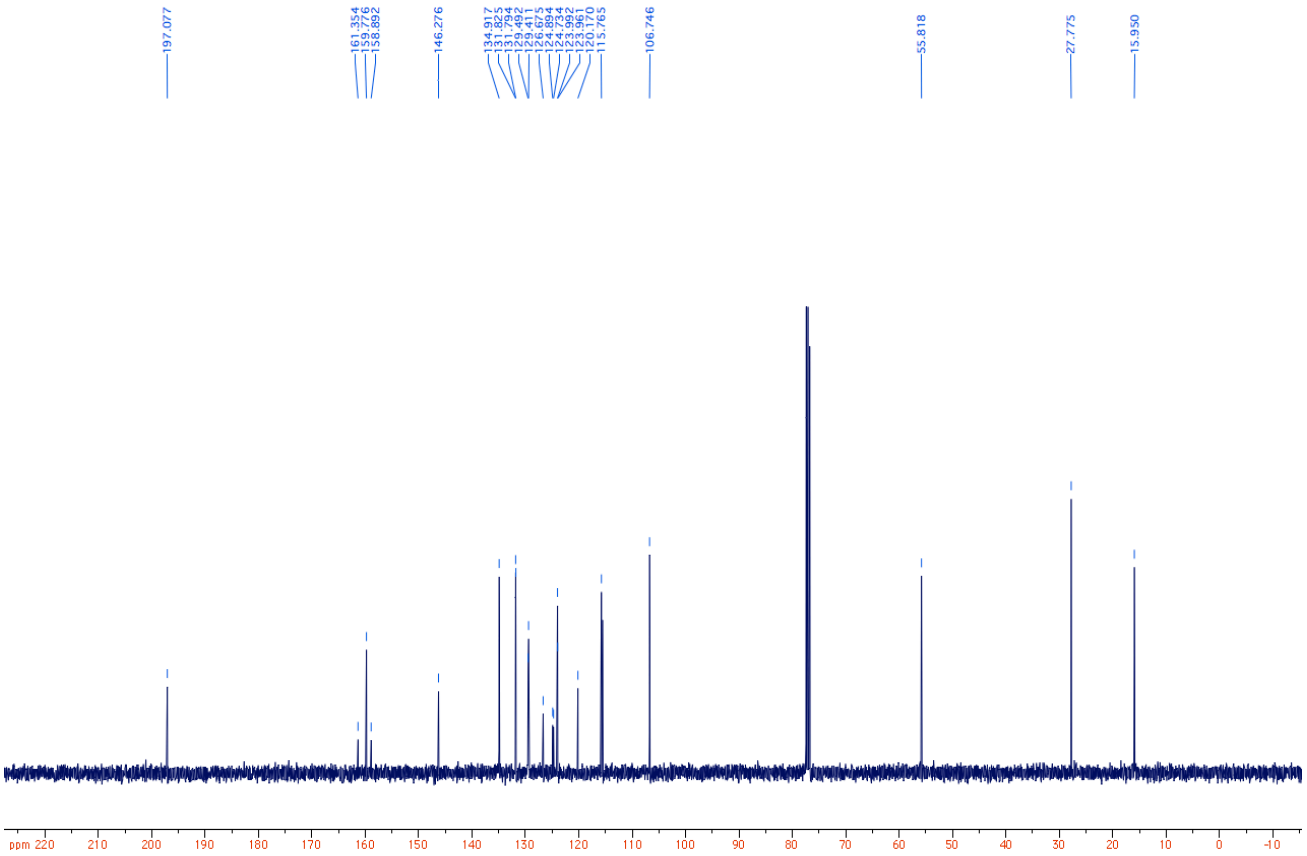




19 (^{13}C NMR, 100 MHz, $CDCl_3$)



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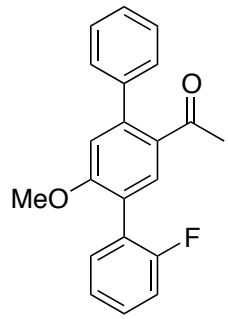
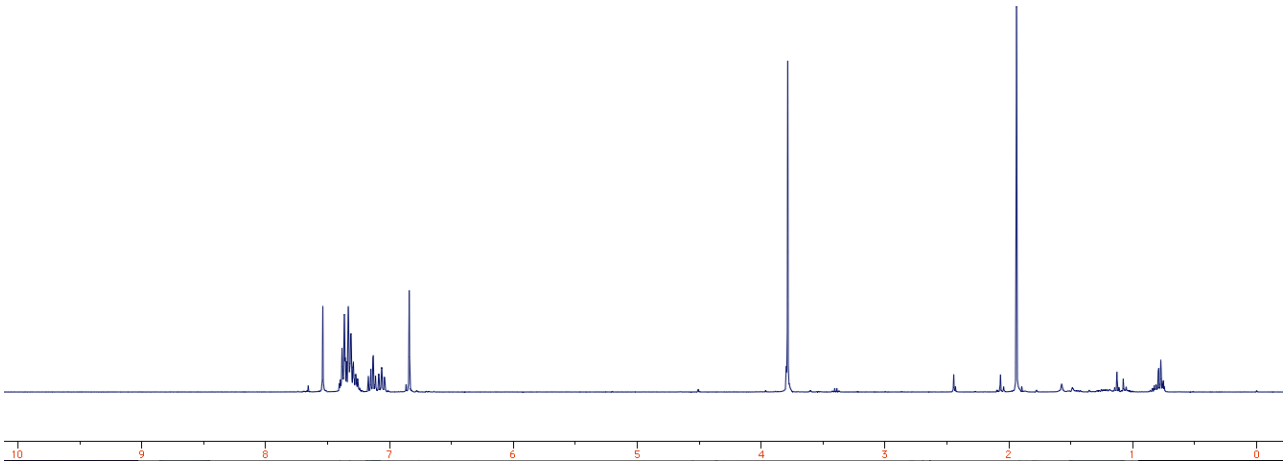
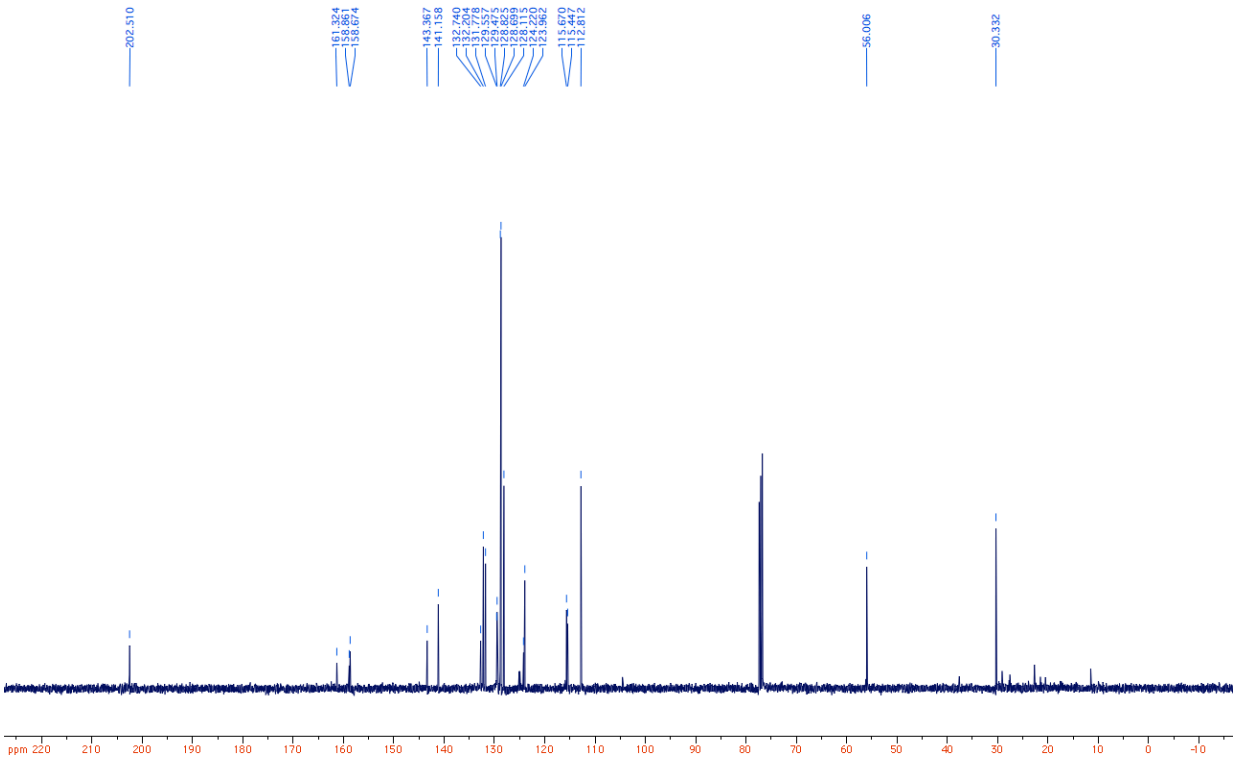
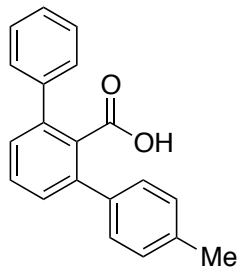


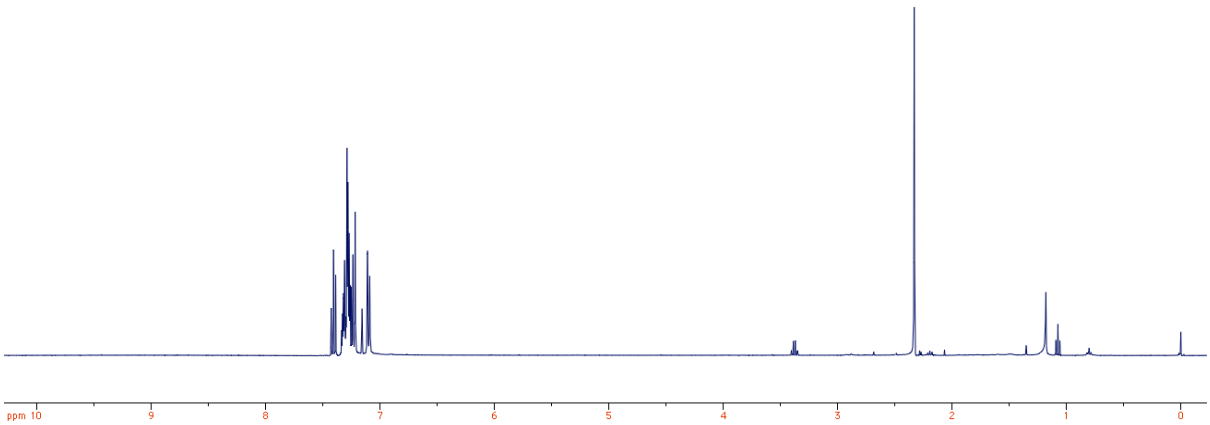


20 (^{13}C NMR, 100 MHz, $CDCl_3$)



21 (^{1}H NMR, 400 MHz, $CDCl_3$)





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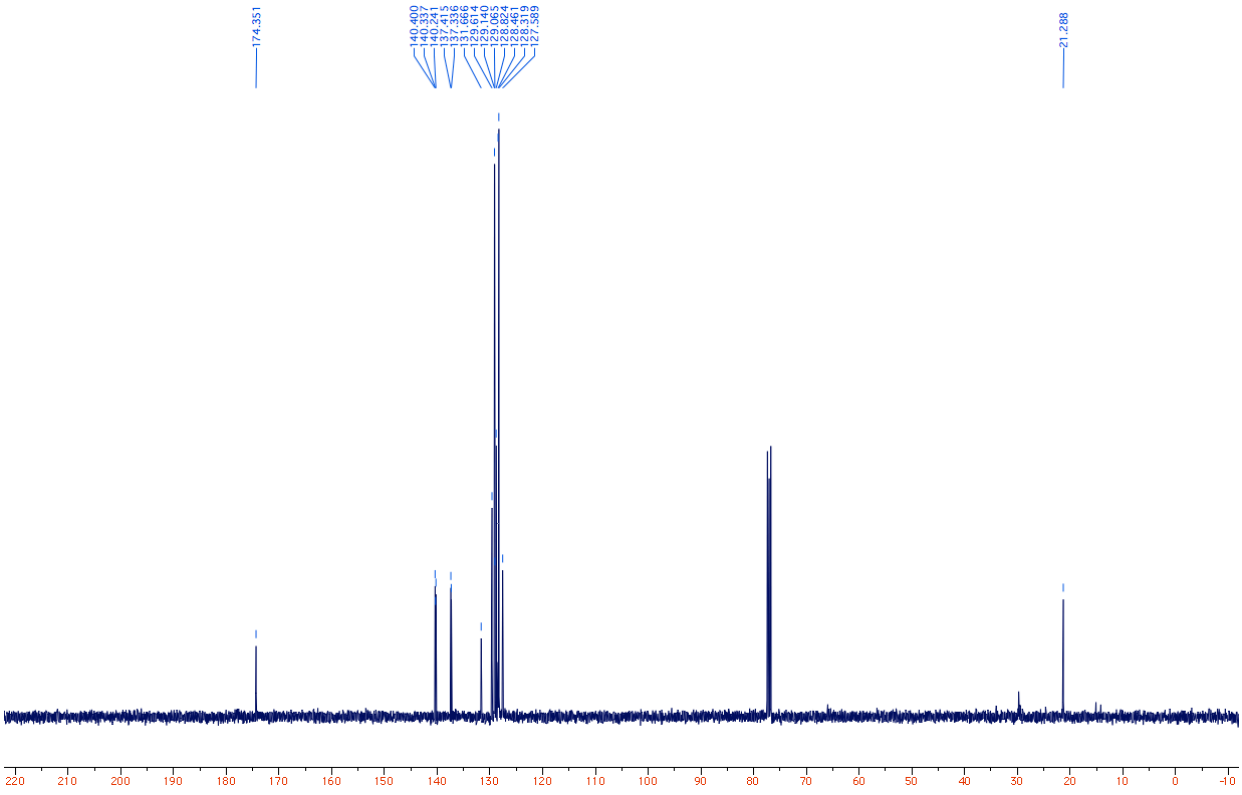
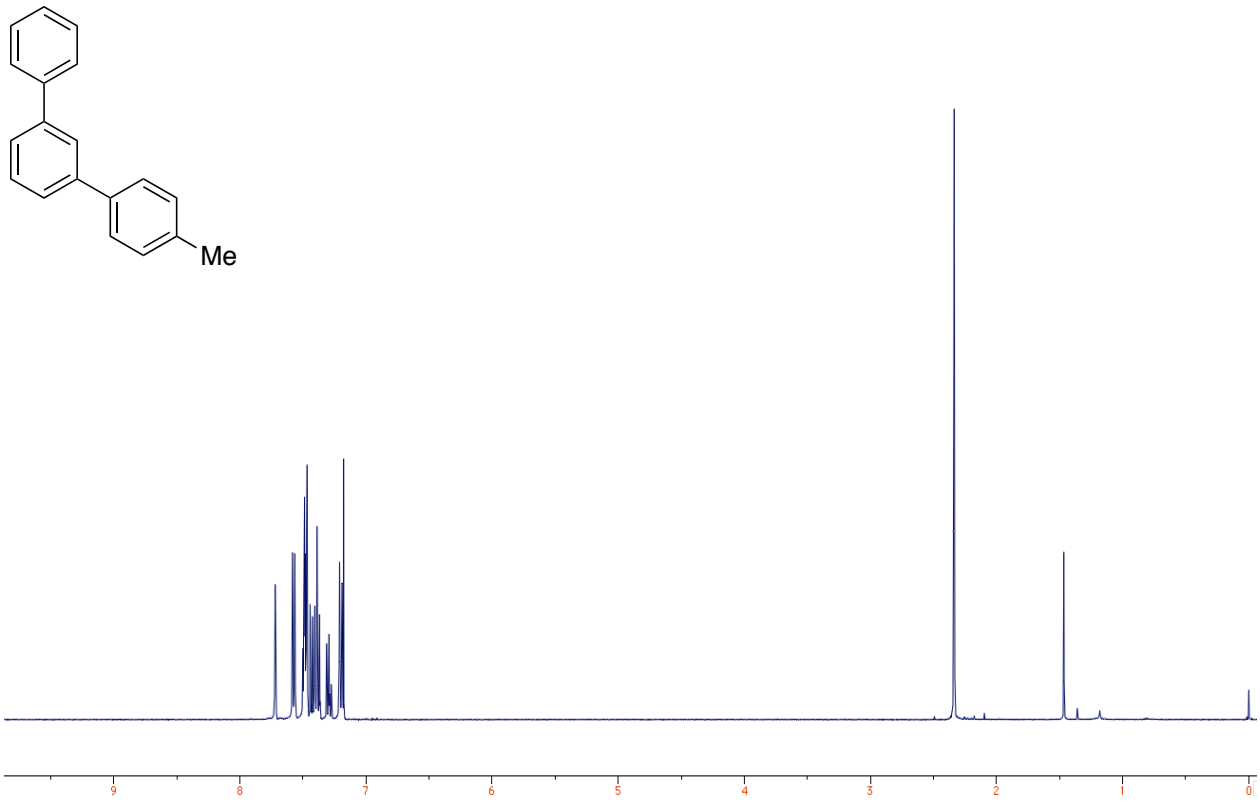


21 (^{1}H NMR, 400 MHz, $CDCl_3$)



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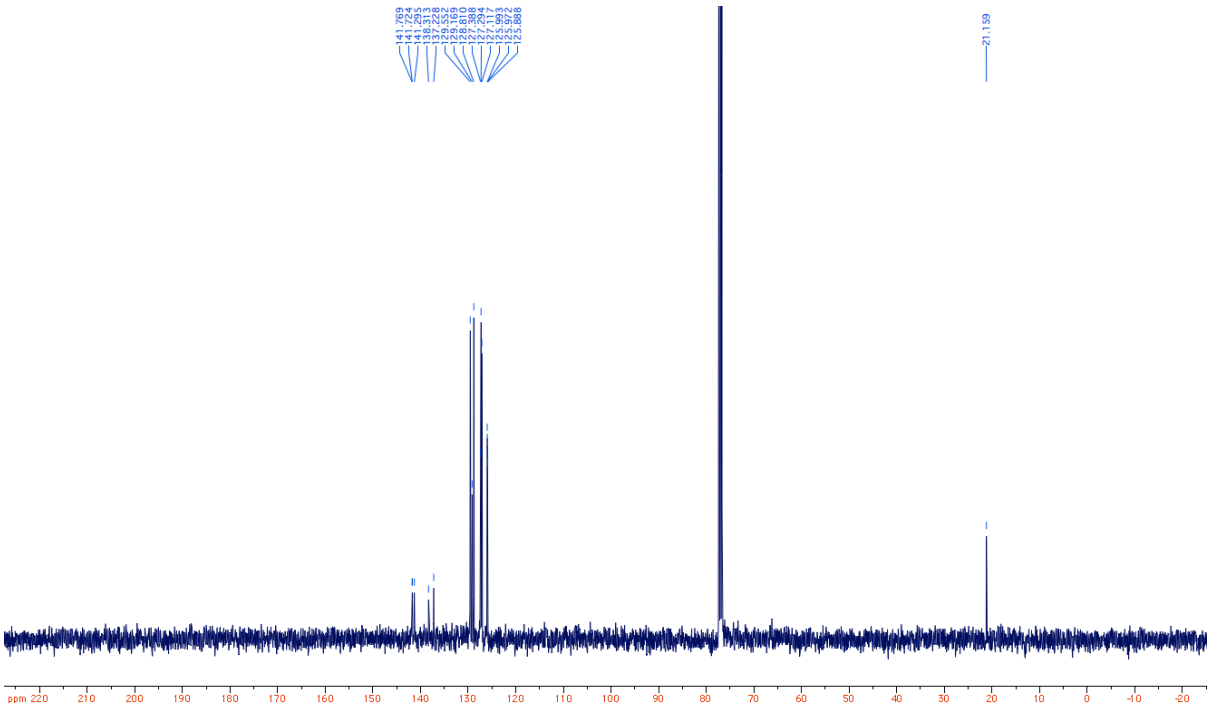

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