Electronic Supplementary Material (ESI) for ChemComm.

A rhodium-catalysed Sonogashira-type coupling exploiting C-S functionalisation: Orthogonality with palladium-catalysed variants

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Electronic Supporting Information

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1 General Experimental Considerations

Reactions were performed under an inert atmosphere of nitrogen, using 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 aluminum backed silica plates. Plates were visualized 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. Ortho-xylene (<0.003% H_2O) was purchased from Sigma-Aldrich Chemical Co. Ltd. Anhydrous acetonitrile, diethylether, 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®. Petrol refers to the fractions obtained between 30 °C 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) spectrometer using the residual solvent as an internal standard. ^{13}C NMR spectra were obtained on a Bruker DQX-400 (101 MHz) spectrometer using the 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 Bruker 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.

2 General Procedures

Formation of ethynyl compounds via rhodium-catalysis

General procedure A

$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and dcpe (3.2 mg, 0.0075 mmol) were dissolved in DCE (2 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This was transferred via cannula to a mixture of aryl sulfide (0.15 mmol), alkyne (0.30 mmol), copper bromide (42 mg, 0.3 mmol) and silver carbonate (41 mg, 0.15 mmol). The reaction mixture was heated to 80 °C until completion, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography to yield the product. (nbd = norbornadiene; dcpe = *bis*(dicyclohexylphosphino)ethane)

General procedure B

$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and dcpe (3.2 mg, 0.0075 mmol) were dissolved in DCE (2 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This was transferred via cannula to a mixture of aryl sulfide (0.15 mmol), alkyne (0.30 mmol), copper bromide (84 mg, 0.60 mmol) and potassium carbonate (40 mg, 0.30 mmol). The reaction mixture was heated to 80 °C until completion, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography to yield the product. (nbd = norbornadiene; dcpe = *bis*(dicyclohexylphosphino)ethane)

Hydroacylation-Sonogashira cascade

General procedure C

$[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol) and dcpe (6.3 mg, 0.015 mmol) were dissolved in DCE (2 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This was transferred via cannula to a

mixture of aldehyde (0.30 mmol), alkyne (0.45 mmol) and stirred at room temperature until starting material was consumed. This was then transferred to a mixture containing copper bromide (86 mg, 0.60 mmol), silver carbonate (83 mg, 0.30 mmol) and the appropriate alkyne (0.60 mmol). The reaction mixture was stirred and heated to 80 °C until completion, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography to yield the product. (nbd = norbornadiene; dcpe = *bis*(dicyclohexylphosphino)ethane)

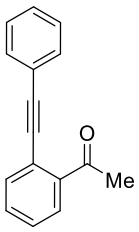
General procedure D

$[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol) and dcpe (6.3 mg, 0.015 mmol) were dissolved in DCE (2 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This was transferred via cannula to a mixture of aldehyde (0.30 mmol), alkyne (0.45 mmol) and stirred at room temperature until starting material was consumed. This was then transferred to a mixture containing copper bromide (172 mg, 1.2 mmol), potassium carbonate (80 mg, 0.60 mmol) and the appropriate alkyne (0.60 mmol). The reaction mixture was stirred and heated to 80 °C until completion, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography to yield the product. (nbd = norbornadiene; dcpe = *bis*(dicyclohexylphosphino)ethane)

3 Characterisation of Compounds

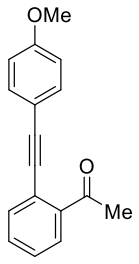
3.1 Sonogashira-type coupling products

1-(2-(Phenylethynyl)phenyl)ethanone, 3a



Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and phenylacetylene (33 µL, 0.30 mmol). After 16 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a dark yellow oil (31 mg, 95%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.79 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44-7.39 (m, 4H), 2.83 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.4, 140.8, 133.9, 131.6, 131.4, 128.82, 128.75, 128.5, 128.3, 122.9, 121.7, 95.1, 88.6, 30.0; ν_{max} (film)/cm^{-1} 1681, 755;
Data consistent with the literature.[i]

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)ethanone, 3b

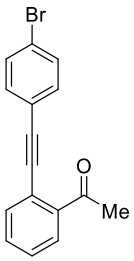


Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 4-ethynylanisole (39 µL, 0.30 mmol). After 16 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a bright yellow oil (34 mg, 92%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.54 (dd, *J* = 8.0,

1.0 Hz, 1H), 7.43-7.37 (m, 3H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 6.84-6.81 (m, 2H), 3.76 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.6, 160.1, 140.6, 133.7, 133.1, 131.3, 128.7, 127.9, 122.1, 115.0, 114.2, 95.3, 87.4, 55.4, 30.1; ν_{max} (film)/cm^{-1} 2212, 1979, 1510, 1247; MS (ESI$^+$) *m/z* (rel intensity) 273 [100, (M+Na)$^+$].

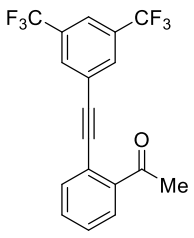
Data consistent with the literature.[ii]

1-(2-((4-Bromophenyl)ethynyl)phenyl)ethanone, 3c



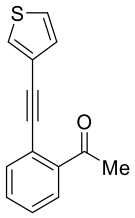
Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 1-bromo-ethynyl-benzene (54 mg, 0.30 mmol). After 16 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (70% toluene in petrol), to yield the product as a yellow oil, (39 mg, 89%); preparation following general procedure **B** gave yellow oil, (33 mg, 75%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.56-7.54 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.44-7.39 (m, 3H), 7.36-7.32 (m, 3H), 2.69 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.0, 140.6, 134.0, 133.0, 131.8, 131.4, 128.9, 128.5, 123.1, 121.9, 121.4, 93.7, 89.6, 29.8; ν_{max} (film)/cm^{-1} 2360, 1686, 1491, 823, 761; MS (ESI$^+$) *m/z* (rel intensity) 321 [100, (M+Na)$^+$], 323 [97, (M+Na)$^+$], 299 [40, (M+H)$^+$];; *HRMS* (ESI$^+$) 299.0070 ((M+H)$^+$, $C_{16}H_{12}OBr^{79}$ requires 299.0065).

1-(2-((3,5-Bis(trifluoromethyl)phenyl)ethynyl)phenyl)ethanone, 3d



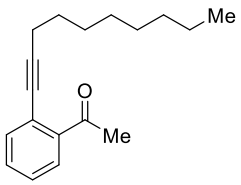
Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and (3-5-trifuloro)-1-ethynyl-benzene (53 µL, 0.30 mmol). After 8 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a white solid, (50 mg, 96%); M.p: 72 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.91 (s, 2H), 7.76 (s, 1H), 7.74 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 199.1, 140.5, 134.5, 132.1 (q, *J* = 33.5 Hz), 131.6, 131.4 (q, *J* = 3.5 Hz), 129.20, 129.1, 125.4, 122.9 (q, *J* = 272.0 Hz), 122.0 (heptet, *J* = 3.5 Hz), 20.4, 91.8, 90.9, 29.3; ν_{max} (film)/cm^{-1} 1691,1377, 1131; HRMS (FI^{+}) 358.0630 ((M)$^{+}$, $C_{18}H_{10}OF_6$ requires 358.063).

1-(2-(Thiophen-3-ylethynyl)phenyl)ethanone, 3e



Prepared following general procedure **B** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 3-ethynylthiophene (30 µL, 0.30 mmol). After 16 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (50% toluene in petrol), to yield the product as a dark yellow oil, (23 mg, 70%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.50 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.0 Hz, 1H), 7.26 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.15 (dd, *J* = 5.0, 1.0 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.3, 140.7, 133.8, 131.3, 129.6, 129.2, 128.8, 128.2, 125.7, 122.0, 121.7, 90.3, 88.1, 30.0; ν_{max} (film)/cm^{-1} 1672, 1283, 700; MS (ESI^{+}) *m/z* (rel intensity) 249 [100, (M+Na)$^{+}$]; *HRMS* (ESI^{+}) 226.0460 ((M+H)$^{+}$, $C_{14}H_{10}OS$ requires 226.0452).

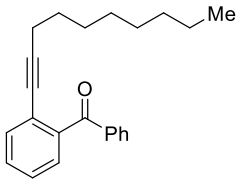
1-(2-(Dec-1-yn-1-yl)phenyl)ethanone, 3f



Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 1-octyne (44 µL, 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (50% toluene in petrol), to yield the product as a pail yellow oil, (17 mg, 45%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.59 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.0 Hz, 1H), 7.25 (td, *J* = 7.5, 1.0 Hz, 1H), 2.65 (s, 3H), 2.39 (t, *J* = 7.0 Hz, 2H), 1.55 (dt, *J* = 15.0, 7.5 Hz, 3H), 1.42-1.35 (m, 3H), 1.26-1.23 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 201.2, 141.1, 134.0, 131.1, 128.3, 127.6, 122.5, 97.0, 79.7, 31.4, 30.2, 28.7, 28.5, 22.6, 19.8, 14.1; ν_{max} (film)/cm^{-1} 2926, 1711, 756; MS (ESI^{+}) *m/z* (rel intensity) 229 [70, (M+Na)$^{+}$].

Data consistent with the literature.[iii]

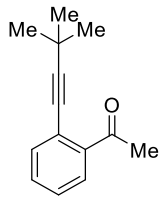
(2-(Oct-1-yn-1-yl)phenyl)(phenyl)methanone, 3g



Prepared following general procedure **B** using (2-(methylthio)phenyl)(phenyl)methanone (44 mg, 0.15 mmol) and 1-octyne (44 µL , 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (1% EtOAc in petrol), to yield the product as a yellow oil, (39 mg, 90%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.74 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.48 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.41-7.27 (m, 6H), 2.02 (t, *J* = 6.5 Hz, 2H), 1.18-1.05 (m, 8H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 197.4, 141.8, 137.4, 133.0, 132.6, 130.2, 130.1, 130.0, 128.3, 128.1, 127.4, 122.5, 96.7, 78.6, 31.3, 28.4, 28.2, 22.5, 19.3, 14.1; ν_{max} (film)/cm^{-1} 2929, 1666, 1287, 755, 703; MS

(ESI$^+$) *m/z* (rel intensity) 313 [100, (M+Na)$^+$], 291 [65, (M+H)$^+$]; *HRMS* (ESI$^+$) 291.17439 ((M+Na)$^+$, $C_{21}H_{22}O$ requires 291.17434).

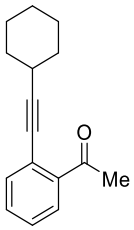
1-(2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)ethanone, 3h



Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 3,3-dimethyl-1-butyne (25 mg, 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (50% toluene in petrol), to yield the product as a pail yellow oil, (22 mg, 73%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 2.74 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 201.3, 141.1, 133.8, 131.1, 128.3, 127.6, 122.4, 104.7, 78.5, 30.7, 30.3, 28.3; ν_{max} (film)/cm^{-1} 2967, 1684, 1278, 759; MS (ESI$^+$) *m/z* (rel intensity) 223 [90, (M+Na)$^+$].

Data consistent with the literature.[iv]

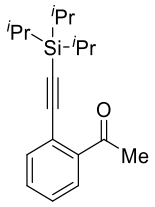
1-(2-(Cyclohexylethynyl)phenyl)ethanone, 3i



Prepared following general procedure **B** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and cyclohexylacetylene (30 µL, 0.30 mmol). After 16 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (50% toluene in petrol), to yield the product as a dark yellow oil, (16 mg, 50%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.59 (dd, *J* = 7.5, 1.0 Hz, 1H),

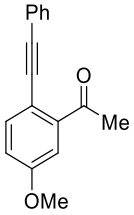
7.41 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25 (td, *J* = 7.5, 1.5 Hz, 1H), 2.64 (s, 3H), 2.60-2.53 (m, 1H), 1.85-1.82 (m, 2H), 1.72-1.65 (m, 2H), 1.54-1.44 (m, 4H), 1.29-1.26 (m, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 201.3, 141.1, 134.0, 131.1, 128.3, 127.5, 122.5, 100.9, 79.7, 32.4, 30.3, 30.0, 29.7, 25.9, 25.0; ν_{max} (film)/cm^{-1} 2927, 2362, 1703, 1647, 1448, 756; *m/z* (rel intensity) 267 [100, $(M+H)^+$].

1-(2-((Triisopropylsilyl)ethynyl)phenyl)ethanone, 3j



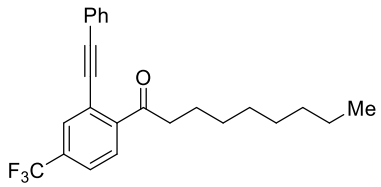
Prepared following general procedure **B** using 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and (triisopropylsilyl)-acetylene (67 µL , 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a pail yellow oil, (43 mg, 96%); using procedure **A** also gave colourless oil, (42 mg, 94%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.68 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 2.78 (s, 3H), 1.12-1.15 (m, 21H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.8, 141.4, 134.8, 131.0, 128.44, 128.26, 121.8, 105.6, 98.2, 30.3, 18.7, 11.4; ν_{max} (film)/cm^{-1} 2942, 2864, 2153, 1685; MS (ESI$^+$) *m/z* (rel intensity) 323 [100, $(M+Na)^+$], 301 [45, $(M+H)^+$]; *HRMS* (ESI$^+$) 323.17988 ($(M+Na)^+$, $C_{19}H_{28}NaOSi$ requires 323.18016).

1-(5-Methoxy-2-(phenylethynyl)phenyl)ethanone, 3k



Prepared following general procedure **B** using 1-(5-methoxy-2-(methylthio)phenyl)ethanone (29 mg, 0.15 mmol) and phenylacetylene (33 µL , 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (0.5% ether in toluene), to yield the product as a yellow oil, (28.9 mg, 77%), using general procedure **A** also gave desired product (mg, 76%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 1H), 7.46-7.43 (m, 2H), 7.27-7.20 (m, 3H), 7.20 (d, *J* = 3.0 Hz, 1H), 6.94 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.79 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.4, 159.5, 142.3, 135.4, 131.3, 128.5, 124.6, 123.2, 118.0, 114.0, 113.1, 93.8, 88.5, 55.6, 30.3; ν_{max} (film)/cm^{-1} 1679, 1223, 822, 756; *m/z* (rel intensity) 273 [100, $(M+Na)^+$], 351 [45, $(M+H)^+$]; *HRMS* (ESI^+) 251.10654 ($(M+H)^+$, $C_{17}H_{15}O_2$ requires 251.10666).

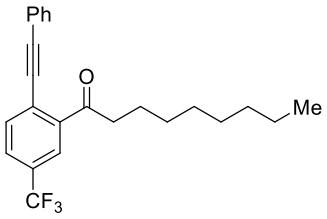
1-(2-(Phenylethynyl)-4-(trifluoromethyl)phenyl)nonan-1-one, 3l



Prepared following general procedure **A** using $[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol), dcpe (6.4 mg, 0.015 mmol), 1-(2-(methylthio)-4-(trifluoromethyl)phenyl)nonan-1-one (40 mg, 0.12 mmol) and phenylacetylene (30 µL , 0.24 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5-30% CH_2Cl_2 in petrol), to yield the product as a yellow oil, (46 mg, 91%); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.79 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.33-7.29 (m, 3H), 3.07 (t, *J* = 7.5 Hz, 2H), 1.67 (quintet, *J* = 7.5 Hz, 2H), 1.30-1.12 (m, 10H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 203.2, 144.5, 132.7 (q, *J* = 33 Hz), 131.7, 130.4 (q, *J* = 3.5 Hz), 129.3, 128.6, 128.50, 124.8 (q, *J* = 3.5 Hz), 123.3 (q, *J* = 273 Hz), 122.2, 121.9, 96.0, 86.7, 42.4, 31.8, 29.42, 29.34, 29.17, 24.3, 22.7, 14.1; ν_{max} (film)/cm^{-1} 2926,

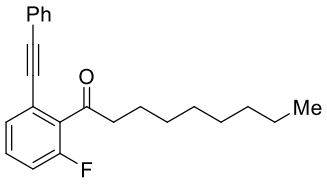
1689, 1336, 1130, 755; *m/z* (rel intensity) 409 [100, $(M+Na)^+$], 387 [40, $(M+H)^+$]; *HRMS* (ESI^+) 387.19268 ($(M+H)^+$, $C_{24}H_{26}O_2F_3$ requires 387.19303).

1-(2-(Phenylethynyl)-5-(trifluoromethyl)phenyl)nonan-1-one, 3m



Prepared following general procedure **A** using $[Rh(nbd)_2].BF_4$ (2.1 mg, 0.0055 mmol), dcpe (2.3 mg, 0.0055 mmol), 1-(2-(methylthio)-5-(trifluoromethyl)phenyl)nonan-1-one (35 mg, 0.11 mmol) and phenylacetylene (25 µL , 0.22 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% CH_2Cl_2 in petrol), to yield the product as a yellow oil, (37 mg, 89%), using general procedure **B** also gave desired product (32 mg, 76%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.83 (s, 1H), 7.66-7.60 (m, 2H), 7.49-7.46 (m, 2H), 7.34-7.30 (m, 3H), 3.09 (t, *J* = 7.5 Hz, 2H), 1.68 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.32-1.15 (m, 10H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 202.4, 141.8, 134.2, 131.7, 130.2 (q, *J* = 33 Hz), 129.3, 128.6, 127.2 (q, *J* = 3.5 Hz), 125.2 (q, *J* = 3.5 Hz), 124.8, 122.2, 120.8 (q, *J* = 273 Hz), 97.1, 87.1, 42.3, 31.8, 29.42, 29.34, 29.17, 24.3, 22.7, 14.1; ν_{max} (film)/cm^{-1} 2926, 1688, 1127; *m/z* (rel intensity) 409 [100, $(M+Na)^+$], 387 [50, $(M+H)^+$]; *HRMS* (ESI^+) 387.19280 ($(M+H)^+$, $C_{24}H_{26}O_2F_3$ requires 387.19303).

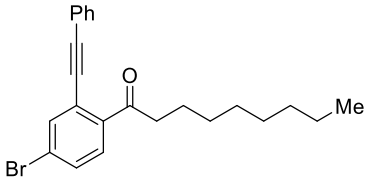
1-(2-Fluoro-6-(phenylethynyl)phenyl)nonan-1-one, 3n



Prepared following general procedure **B** using 1-(2-fluoro-6-(methylthio)phenyl)nonan-1-one (42 mg, 0.15 mmol) and phenylacetylene (33 µL ,

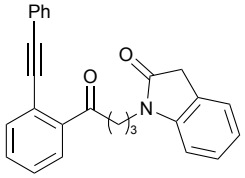
0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (45% ether in petrol), to yield the product as a yellow oil, (45 mg, 91%); ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.29-7.26 (m, 5H), 7.00 (ddd, *J* = 9.5, 7.5, 2.0 Hz, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H), 1.32-1.27 (m, 2H), 1.22-1.13 (m, 8H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 202.2, 158.7 (d, *J* = 273.0 Hz), 131.89 (d, *J* = 20.0 Hz), 131.71, 130.7 (d, *J* = 8.5 Hz), 128.9, 128.5 (d, *J* = 3.0 Hz), 128.43, 122.4, 122.14 (d, *J* = 6.0 Hz), 116.0 (d, *J* = 22.0 Hz), 94.2, 85.86 (d, *J* = 3.0 Hz), 44.49, 31.8, 29.43, 29.23, 29.16, 23.8, 22.7, 14.1; ν_{max} (film)/cm^{-1} 2925, 1705, 755; *m/z* (rel intensity) 359 [100, $(M+Na)^+$], 337 [75, $(M+H)^+$]; *HRMS* (ESI$^+$) 337.19589 ($(M+H)^+$, $C_{23}H_{26}OF$ requires 337.19622).

1-(4-Bromo-2-(phenylethynyl)phenyl)nonan-1-one, 3o



Prepared following general procedure **B** using $[Rh(nbd)_2].BF_4$ (1.9 mg, 0.005 mmol), dcpe (2.1 mg, 0.005 mmol), 1-(4-bromo-2-(methylthio)phenyl)nonan-1-one (35 mg, 0.10 mmol) and phenylacetylene (22 µL , 0.20 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (20% toluene in petrol), to yield the product as a yellow oil, (38 mg, 97%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.77 (d, *J* = 1.5 Hz, 1H), 7.54-7.52 (m, 4H), 7.39-7.36 (m, 3H), 3.12 (t, *J* = 7.5 Hz, 2H), 1.73 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.34-1.22 (m, 10H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 202.6, 139.9, 136.2, 131.6, 131.5, 129.8, 129.1, 128.5, 125.3, 123.2, 122.4, 95.8, 87.0, 42.2, 31.8, 29.44, 29.37, 29.19, 24.5, 22.7, 14.1; ν_{max} (film)/cm^{-1} 2924, 1685, 755, 689; *HRMS* (ESI$^+$) 397.11600 ($(M+H)^+$, $C_{23}H_{26}O^{79}Br$ requires 397.11615).

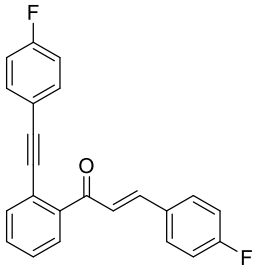
1-(4-Oxo-4-(2-(phenylethynyl)phenyl)butyl)indolin-2-one, 3p



Prepared following general procedure **B** using 1-(4-(2-(methylthio)phenyl)-4-oxobutyl)indolin-2-one (49 mg, 0.15 mmol) and phenylacetylene (33 µL , 0.30 mmol). After 24 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (45% ether in petrol), to yield the product as a yellow oil, (50 mg, 89%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.60 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.45-7.43 (m, 2H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29-7.26 (m, 3H), 7.18-7.12 (m, 2H), 6.95-6.90 (m, 2H), 3.73 (t, *J* = 7.5 Hz, 2H), 3.39 (s, 2H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.07 (quintet, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 202.1, 175.1, 144.5, 140.8, 133.9, 131.6, 131.2, 128.8, 128.6, 128.4, 128.3, 128.0, 124.6, 124.4, 122.8, 122.2, 121.3, 108.6, 94.7, 88.2, 39.3, 38.9, 35.8, 22.1; ν_{max} (film)/cm^{-1} 1708, 1614, 753; *m/z* (rel intensity) 402 [100, $(M+Na)^+$], 380 [80, $(M+H)^+$]; *HRMS* (ESI^+) 380.16440 ($(M+H)^+$, $C_{26}H_{22}O_2N$ requires 380.16451).

3.2 Tandem hydroacylation/sonogashira coupling products

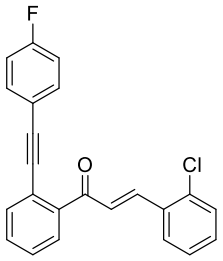
(*E*)-3-(4-Fluorophenyl)-1-(2-((4-fluorophenyl)ethynyl)phenyl)prop-2-en-1-one, 9a



Prepared following general procedure **C** using 2-(methylthio)benzaldehyde (38 mg, 0.30 mmol) and 1-ethynyl-4-fluorobenzene (52 µL , 0.45 mmol) for 30 mins, followed by 1-ethynyl-4-fluorobenzene (69 µL, 0.60 mmol) for 6 h. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a pale yellow solid, (78 mg, 76%); M.p: 102 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.70-7.62 (m, 3H), 7.59-7.56 (m, 2H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.47-7.43 (m, 2H), 7.35-7.31 (m, 2H), 7.07-7.03 (m, 2H), 6.94-6.89 (m, 2H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.4, 164.1 (d, *J* = 250.0 Hz), 162.7 (d, *J* = 250.0 Hz), 143.0, 141.8, 133.4 (d, *J* = 8.5 Hz), 133.1, 131.1 (d, *J* = 3.0 Hz), 130.96, 130.4 (d, *J* = 8.5 Hz), 128.8, 128.5, 125.5 (d, *J* = 3.0 Hz), 121.4, 118.8 (d, *J* = 3.0 Hz), 116.1 (d, *J* = 22.0 Hz), 115.7(d, *J* = 22.0 Hz), 94.3, 87.7; ν_{max} (film)/cm^{-1} 1665, 1597, 1507, 1231, 832; *m/z* (rel intensity) 345 [100, $(M+H)^+$]; *HRMS* (ESI^+) 345.10854 ($(M+H)^+$, $C_{23}H_{15}OF_2$ requires 345.10855).

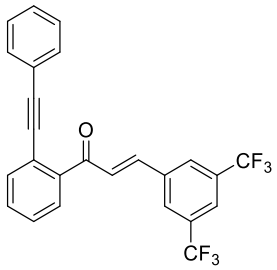
Data consistent with the literature.[v]

(*E*)-3-(2-Chlorophenyl)-1-(2-((4-fluorophenyl)ethynyl)phenyl)prop-2-en-1-one, 9b



Prepared following general procedure **D** using 2-(methylthio)benzaldehyde (38 mg, 0.30 mmol) and 1-chloro-2-ethynylbenzene (55 µL , 0.45 mmol) for 30 mins, followed by 1-ethynyl-4-fluorobenzene (69 µL, 0.60 mmol) for 6 h . The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% ether in petrol), to yield the product as a yellow oil, (95 mg, 88%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.02 (d, *J* = 16.0 Hz, 1H), 7.64-7.53 (m, 3H), 7.46-7.31 (m, 4H), 7.31-7.23 (m, 2H), 7.21 (td, *J* = 7.5, 1.5 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.88-6.81 (m, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 193.3, 162.7 (d, *J* = 250.0 Hz), 141.6, 140.0, 135.5, 133.50 (d, *J* = 8.5 Hz), 133.19, 133.15, 131.26, 131.08, 130.3, 128.9, 128.5, 128.2, 127.8, 127.1, 121.5, 118.83 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.0 Hz), 94.5, 87.8; ν_{max} (film)/cm^{-1} 1662, 1597, 1506, 754; *m/z* (rel intensity) 383 [100, $(M+Na)^+$]; *HRMS* (ESI^+) 361.07917 ($(M+H)^+$, $C_{23}H_{15}O^{35}ClF$ requires 361.07900).

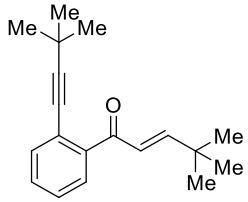
(*E*)-3-(3,5-Bis(trifluoromethyl)phenyl)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one, 9c



Prepared following general procedure **D** using 2-(methylthio)benzaldehyde (38 mg, 0.30 mmol) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (80 µL , 0.45 mmol) for 10 mins, followed by phenylacetylene (66 µL, 0.60 mmol) for 6 h. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (20% CH_2Cl_2 in petrol), to yield the product as a pale yellow solid, (97 mg, 73%); M.p: 85 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.88 (s, 2H), 7.74 (s, 1H), 7.70-7.65 (m, 3H), 7.61-7.57 (m, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40-7.36 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28-7.25 (m, 2H), 7.21-7.17 (m, 1H), 7.14-7.10 (m, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 192.4, 141.1, 139.6, 137.2, 133.4, 132.4 (q, *J* = 33.0 Hz), 131.6, 131.3,

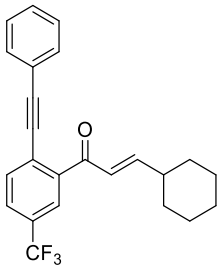
129.06, 129.00, 128.95, 128.6, 128.37, 127.8 (br), 123.3 (quintet, *J* = 3.5 Hz), 123.0 (q, *J* = 273 Hz), 122.2, 121.8, 96.3, 87.9; ν_{max} (film)/cm^{-1} 1665, 1129; HRMS (FI^{+}) 444.0952 ((M)$^{+}$, $C_{25}H_{14}F_6O$ requires 444.0949).

(*E*)-1-(2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)-4,4-dimethylpent-2-en-1-one, 9d



Prepared following general procedure **C** using 2-(methylthio)benzaldehyde (38 mg, 0.30 mmol) and 3,3-dimethylbut-1-yne (55 µL , 0.45 mmol) for 4 h, followed by 3,3-dimethylbut-1-yne (74 µL , 0.60 mmol) for 24 h. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (45% ether in petrol), to yield the product as a yellow oil, (55 mg, 64%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.42 (d, *J* = 0.5 Hz, 1H), 7.40-7.28 (m, *J* = 1.5 Hz, 3H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 1.27 (s, 3H), 1.11(s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 196.3, 159.7, 142.6, 133.0, 129.9, 127.7, 127.4, 125.1, 121.8, 104.0, 77.5, 34.1, 30.8, 28.7, 28.2; ν_{max} (film)/cm^{-1} 2963, 1658, 1615, 1300, 753; *m/z* (rel intensity) 269 [100, (M+H)$^{+}$]; *HRMS* (ESI^{+}) 269.18998 ((M+H)$^{+}$, $C_{19}H_{25}O$ requires 269.18999).

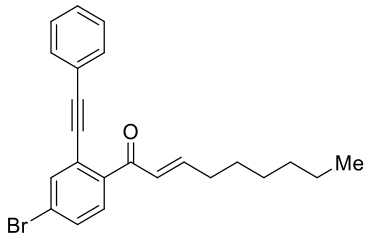
(*E*)-3-Cyclohexyl-1-(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)prop-2-en-1-one, 9e



Prepared following general procedure **D** using 2-(methylthio)-5-(trifluoromethyl)benzaldehyde (66 mg, 0.30 mmol) and ethynylcyclohexane (59 µL , 0.45 mmol) for 1h, followed by phenylacetylene (66 µL , 0.60 mmol) for 24 h. The

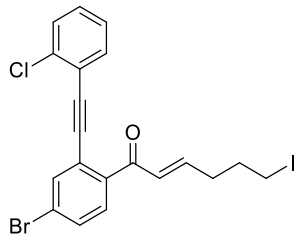
mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (20% toluene in petrol), to yield the product as a yellow oil, (92 mg, 87%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.72 (s, 1H), 7.64-7.61 (m, 2H), 7.43-7.39 (m, 2H), 7.32-7.26 (m, 3H), 6.80 (dd, *J* = 16.0, 6.5 Hz, 1H), 6.65 (dd, *J* = 16.0, 1.5 Hz, 1H), 2.16-2.08 (m, 1H), 1.70-1.57 (m, 5H), 1.21-1.04 (m, 5H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 193.5, 156.6, 142.5, 133.4, 131.7, 130.1 (q, *J* = 33.0 Hz), 129.2, 128.4, 126.8 (q, *J* = 3.0 Hz), 126.7, 125.5 (q, *J* = 3 Hz), 125.0, 123.6 (q, *J* = 272.0 Hz), 122.3, 97.3, 86.7, 41.0, 31.6, 25.9, 25.7; ν_{max} (film)/cm^{-1} 2926, 1663, 1617,1334, 1126; HRMS (FI^{+}) 382.1553 ((M)$^{+}$, $C_{24}H_{21}OF_3$ requires 382.1544).

(*E*)-1-(4-Bromo-2-(phenylethynyl)phenyl)non-2-en-1-one, 9f



Prepared following general procedure **D** using 4-bromo-2-(methylthio)benzaldehyde (69 mg, 0.30 mmol) and 1-octyne (66 µL , 0.45 mmol) for 30 mins, followed by Phenylacetylene (66 µL , 0.60 mmol) for 24 h. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (30% toluene in petrol), to yield the product as a yellow oil, (65 mg, 55%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.75 (d, *J* = 12.0 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48-7.41 (m, 3H), 7.37-7.33 (m, 3H), 6.91 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.75 (dt, *J* = 15.5, 1.5 Hz, 1H), 2.29-2.24 (m, 2H), 1.43 (quintet, *J* = 7.0 Hz, 2H), 1.31-1.18 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 193.5, 151.4, 140.6, 135.5, 131.6, 131.4, 130.0, 129.3, 129.0, 128.4, 124.7, 123.4, 122.5, 96.1, 86.5, 32.9, 31.6, 29.0, 28.0, 22.5, 14.1; ν_{max} (film)/cm^{-1} 2926, 16662, 1616; HRMS (FI^{+}) 394.0928 ((M)$^{+}$, $C_{23}H_{23}{}^{79}BrO$ requires 394.0932).

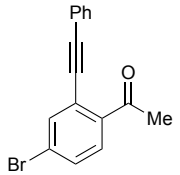
(*E*)-1-(4-Bromo-2-((2-chlorophenyl)ethynyl)phenyl)-7-iodohept-2-en-1-one, 9g



$[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol) and dcpe (6.3 mg, 0.015 mmol) were dissolved in DCE (2 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This was transferred via cannula to a mixture of 4-bromo-2-(methylthio)benzaldehyde (69 mg, 0.30 mmol), 6-iodohex-1-yne (52 µL, 0.45 mmol) and stirred at room temperature for 1 h. This was then transferred to a mixture containing copper iodide (86 mg, 0.60 mmol), silver carbonate (83 mg, 0.30 mmol) and 1-chloro-2-ethynylbenzene (73 µL, 0.60 mmol). The reaction mixture was stirred and heated to 80 °C for 24 h, and then allowed to cool to room temperature and the crude product was purified by column chromatography (50% toluene in petrol), to yield the product as a colourless oil, (97 mg, 63%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.72 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.43 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.37-7.34 (m, 2H), 7.25-7.16 (m, 2H), 6.79 (dt, *J* = 15.5, 6.5 Hz, 1H), 6.70 (d, *J* = 15.5 Hz, 1H), 3.01 (t, *J* = 7.0 Hz, 2H), 2.22 (q, *J* = 7.0 Hz, 2H), 1.71 (quintet, *J* = 7.5 Hz, 2H), 1.48 (quintet, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 193.1, 150.2, 140.4, 136.0, 135.8, 133.4, 131.9, 130.0, 129.94, 129.86, 129.5, 126.6, 124.8, 122.9, 122.4, 92.7, 91.2, 32.8, 31.7, 28.9, 6.1; ν_{max} (film)/cm^{-1} 1659, 1616, 1577, 755; HRMS (FI$^+$) 527.9152 ((M)$^+$, $C_{21}H_{17}{}^{79}Br^{35}ClIO$ requires 527.9175).

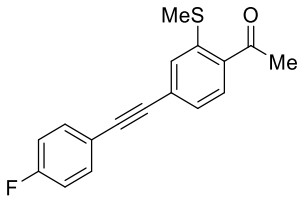
3.3 Miscellaneous further reactions

1-(4-Bromo-2-(phenylethynyl)phenyl)ethan-1-one, 3q



Prepared following general procedure **B** using 1-(4-bromo-2-(methylthio)phenyl)ethan-1-one (74 mg, 0.30 mmol) and phenylacetylene (66 µL, 0.45 mmol) for 24 h. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (5% Et_2O in petrol), to yield the product as a colourless oil (72 mg, 80%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.57-7.52 (m, 3H), 7.40-7.37 (m, 3H), 2.78 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 199.2, 139.3, 136.5, 131.8, 131.6, 130.4, 129.3, 128.7, 126.1, 123.8, 122.5, 96.6, 87.4, 30.1; ν_{max} (film)/cm^{-1} 3060, 2925, 2853, 2215, 1683, 1578, 1492, 1268, 1090, 881; *m/z* (rel intensity) 299 [100, $(M+H)^+$], 300 [97, $(M+H)^+$]; HRMS (ESI$^+$) 320.9886 ($(M+Na)^+$, $C_{16}H_{11}Br^{79}O^{23}Na^{32}$ requires 320.9886).

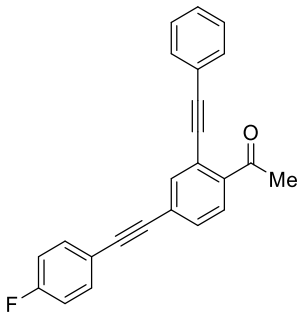
1-(4-((4-Fluorophenyl)ethynyl)-2-(methylthio)phenyl)ethenone, 6



Diisopropylamine (4.0 mL) was added to a mixture of 1-(4-bromo-2-(methylthio)phenyl)ethanone (100 mg, 0.41 mmol), 1-ethynyl-4-fluorobenzene (57 µL, 0.50 mmol), palladium acetate (1.9 mg, 0.0082 mmol), triphenylphosphine (4.3 mg, 0.0164 mmol) and copper iodide (3.2 mg, 0.0164 mmol) in an inert atmosphere. This was heated to 75 °C and stirred for 2 h. The mixture was allowed to cool to room temperature, dried under *vacuo* and the crude product was purified by column chromatography (1% EtOAc in petrol), to yield the product as white needles (34 mg, 92%); M.p: 125 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.57-7.52 (m,

2H), 7.41 (d, *J* = 1.0 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.10-7.04 (m, 2H), 2.62 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 198.2, 162.9 (d, *J* = 250.0 Hz), 143.3, 133.8 (d, *J* = 8.0 Hz), 133.2, 131.1, 127.45, 127.39, 126.3, 118.6 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 22.0 Hz), 91.4, 88.2, 28.1, 15.9; ν_{max} (film)/cm^{-1} 1668, 1584, 835; *m/z* (rel intensity) 307 [100, $(M+Na)^+$], 285[30, $(M+H)^+$]; HRMS (ESI^+) 307.05601 ($(M+Na)^+$, $C_{17}H_{13}O^{23}Na^{32}S$ requires 307.05634).

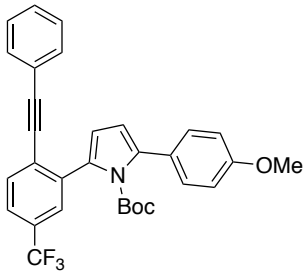
1-(4-((4-Fluorophenyl)ethynyl)-2-(phenylethynyl)phenyl)ethanone, 7



Prepared following general procedure **B** using 1-(4-((4-fluorophenyl)ethynyl)-2-(methylthio)phenyl)ethanone (30 mg, 0.11 mmol) and phenylacetylene (24 µL, 0.22 mmol). After 4 h the mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (40% CH_2Cl_2 in petrol), to yield the product as a white solid, (31 mg, 83%); Alternatively, diisopropylamine (4.0 mL) was added to a mixture of 1-(4-((4-fluorophenyl)ethynyl)-2-(methylthio)phenyl)ethanone (50 mg, 0.17 mmol), 1-ethynyl-4-fluorobenzene (24 µL, 0.204 mmol), palladium acetate (1.0 mg, 0.0034 mmol), triphenylphosphine (1.7 mg, 0.0068 mmol) and copper iodide (1.7 mg, 0.0068 mmol) in an inert atmosphere. This was heated to 75 °C and stirred for 2 h. The mixture was allowed to cool to room temperature, dried under *vacuo* and the crude product was purified by column chromatography (1% EtOAc in petrol), to yield the product as white solid (47 mg, 81%); M.p: 65 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.79 (d, *J* = 1.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.58-7.50 (m, 5H), 7.40-7.37 (m, *J* = 2.0 Hz, 3H), 7.10-7.05 (m, 2H), 2.81 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 199.4, 162.6 (d, *J* = 250.0 Hz), 139.5, 136.8, 133.8

(d, *J* = 8.0 Hz), 131.6, 131.0, 129.09, 129.02, 128.6, 126.7, 122.7, 122.3, 118.7 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.0 Hz), 95.7, 91.6, 87.9, 87.5, 30.0; ν_{max} (film)/cm^{-1} 1680, 753; HRMS (FI^+) 338.1112 ($(M)^+$, $C_{24}H_{15}OF$ requires 338.1107).

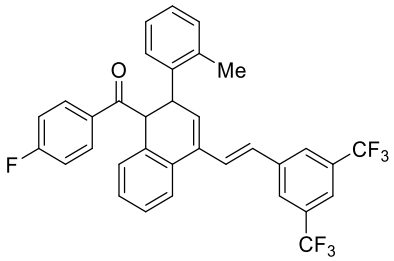
tert-Butyl 2-(4-methoxyphenyl)-5-[2-(phenylethynyl)-5-(trifluoromethyl)phenyl]-1*H*- pyrrole-1-carboxylate, 11



An oven-dried microwave vial was charged with $[Rh(nbd)_2]BF_4$ (7.5 mg, 0.02 mmol), and dcpe (8.5 mg, 0.02 mmol). Once under an inert atmosphere, they were dissolved in 1,2-DCE (1.0 mL). Hydrogen gas was bubbled through the solution at room temperature for 1-2 mins in order to generate the active catalyst species. The hydrogen gas was purged using nitrogen gas, and this was bubbled through the catalyst to dryness. The dry catalyst was dissolved in acetone (88 µL, 1.0 M with respect to aldehyde minus the volume or mass of both aldehyde and alkyne) and this was transferred to a nitrogen-filled microwave vial containing 2-(methylthio)-5-(trifluoromethyl)benzaldehyde (44 mg, 0.20 mmol) and *tert*-butyl [1-(4-methoxyphenyl)prop-2-yn-1-yl]carbamate (67.9 mg, 0.26 mmol). After 2 mins at room temperature the reaction mixture was transferred to silver carbonate (55.0 mg, 0.20 mmol), copper bromide (114.8 mg, 0.8 mmol) and phenylacetylene (44 µL, 0.40 mmol) using 1,2-DCE (0.5 mL). After stirring for 16 h at 80 °C the reaction was filtered through a plug of siliva and stirred with CH_2Cl_2 (3 mL) and *p*-TSA (57 mg, 0.30 mmol) at room temperature for a further 3 h. The crude product was purified by column chromatography (5-10% Et_2O in petrol) to afford *pyrrole* **9** as an off white solid (56 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74-7.72 (m, 1H), 7.67 (app dt, *J* 8.0, 1.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.44-7.41 (m, 2H), 7.36-7.32 (m, 5H), 6.96-6.94 (m,

2H), 6.34 (d, *J* 3.5 Hz, 1H), 6.26 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 149.2, 138.7, 136.5, 132.4 (q, *J* = 36.0 Hz), 131.9, 131.5, 130.5, 130.0, 128.7, 128.6, 127.6 (q, *J* = 200.5 Hz), 127.3, 126.1 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 3.5 Hz), 122.6, 114.6, 113.7, 113.2, 112.5, 94.9, 87.3, 83.7, 55.3, 27.0; ^{19}F NMR (377 MHz, $CDCl_3$, ^{1}H decoupled): δ -62.1; IR: ν_{max} (neat)/cm^{-1} 2980, 2838, 1745, 1581, 1325, 1248, 1172, 1097, 991; LRMS (ESI^+): *m/z* 540 ($[M+Na]^+$, 100%), 518 ($[M+H]^+$, 40%); HRMS (ESI^+) found 540.17474 $[M+Na]^+$, $C_{31}H_{26}O_3F_3NNa^+$ requires 540.17570; mp: 136-137 °C (Et_2O/petrol).

(*E*)-(4-(3,5-Bis(trifluoromethyl)styryl)-2-(*o*-tolyl)-1,2-dihydronaphthalen-1-yl)(4-fluorophenyl)methanone, 13

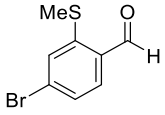


Prepared following general procedure **D** using 2-(methylthio)benzaldehyde (38 mg, 0.30 mmol) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (80 µL, 0.45 mmol) for 10 mins, followed by 4-fluorophenylacetylene (66 µL, 0.60 mmol) for 6 h. The mixture was allowed to cool to room temperature and the crude product was filtered through a plug of silica then dried *in vacuo*. To this was added copper triflate (12 mg, 0.030 mmol), 1-methyl-2-vinylbenzene (58 µL, 0.45 mmol), DCE (2 mL) and stirred under nitrogen at 80 °C for 5 mins. The mixture was allowed to cool to room temperature and the crude product was purified by column chromatography (20% toluene in petrol), to yield the product as an amorphous solid, (106 mg, 61%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.92 (dd, J = 9.0, 5.5 Hz, 2H), 7.87 (s, 2H), 7.75 (1H, s), 7.51 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.24-6.98 (m, 9H), 6.93 (d, J = 7.5 Hz, 1H), 6.26 (d, J = 4.0 Hz, 1H), 5.14 (d, J = 10.0 Hz, 1H), 4.56 (dd, J = 10.0, 4.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.1, 165.9 (d, J_{CF} = 250 Hz), 140.3, 139.6, 135.9, 134.9, 134.2 (d, J_{CF} = 3 Hz), 134.0, 133.4, 132.2 (q, J_{CF} = 33 Hz), 131.8, 131.2 (d, J_{CF} = 9 Hz), 131.0, 130.5, 128.5, 128.0 (2C), 127.8, 127.4, 127.1, 126.5, 126.3, 124.7, 123.5

(q, J_{CF} = 273 Hz), 121.0 (sept. J_{CF} = 4 Hz), 116.0 (d, J_{CF} = 21 Hz), 52.3, 39.8, 20.1; ν_{max} (film)/cm^{-1} 1681, 1277, 1130, 751; HRMS (ESI^+) found 581.1710 $[M+H]^+$, $C_{34}H_{24}F_7O^+$ requires 581.1710.

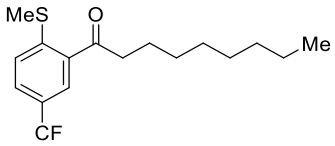
3.4 Starting material synthesis

4-Bromo-2-(methylthio)benzaldehyde, 8a



To a stirred suspension of sodium thiomethoxide (345.2 g, 4.9 mmol) in DMF (25 mL) was added 4-bromo-2-fluorobenzaldehyde (1.0 g, 4.9 mmol) over 30 mins at -45 °C. After the addition was complete, the solution was stirred for a further 3 h at -45 °C, then stirred at room temperature overnight. The reaction was then quenched with water and the precipitate was filtered off to yield the product as white needles (747 mg, 66%); M.p: 78 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 10.13 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38-7.35 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 190.3, 145.5, 134.6, 131.3, 129.7, 127.8, 127.5, 15.4; ν_{max} (film)/cm^{-1} 2920, 2825, 2776, 2733, 1680, 1570, 1534, 1455, 1255, 1194, 1083, 847, 799; HRMS (FI^{+}) 229.9398 ((M)$^{+}$, $C_8H_7OBr^{79}S$ requires 229.9401).

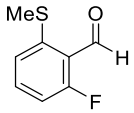
1-(2-(Methylthio)-5-(trifluoromethyl)phenyl)nonan-1-one, 1m



To a solution of 2-(methylthio)-5-(trifluoromethyl)benzaldehyde (45 mg, 0.35 mmol) and [Rh(Bn-(*p*-F))(dtmp)].Bar$^{f}_{4}$ (2.7 mg, 0.002) in acetone (0.25 mL) was added 1-octene (47 µL, 0.30 mmol). This was stirred at 55 °C for 4 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether in petrol) to yield the ketone as a yellow oil (116 mg, 97%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.93 (d, *J* = 1.0 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.5, 147.5, 134.3, 128.1 (q, *J*

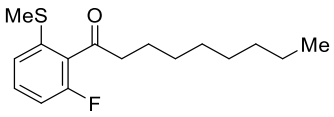
= 3.5 Hz), 126.6 (q, *J* = 3.5 Hz), 126.5 (q, *J* = 33.0 Hz), 125.18, 123.8 (q, *J* = 271.5 Hz), 39.9, 31.8, 29.43, 29.24, 29.15, 24.2, 22.7, 15.9, 14.1; ν_{max} (film)/cm^{-1} 1674, 1116,

2-Fluoro-6-(methylthio)benzaldehyde



To a stirred suspension of sodium thiomethoxide (494 mg, 7.0 mmol) in DMF (25 mL) was added 2,6-difluorobenzaldehyde (1.0 g, 7.0 mmol) over 30 mins at -45 °C. After the addition was complete, the solution was stirred for a further 3 h at -45 °C. The reaction was then quenched with water and the precipitate was filtered off to yield the product as pale yellow needles (786 mg, 66%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 10.48 (d, *J* = 5.0 Hz, 1H), 7.52-7.45 (m, 1H), 6.91-6.86 (m, 1H), 2.46-2.45 (m, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 187.2 (d, *J* = 11.0 Hz), 166.6 (d, *J* = 259.0 Hz), 146.1, 135.05 (d, *J* = 11.0 Hz), 120.6 (d, *J* = 8.0 Hz), 119.8 (d, *J* = 3.5 Hz), 110.9 (d, *J* = 22.0 Hz), 15.4; ν_{max} (film)/cm^{-1} 1672, 773; *m/z* (rel intensity) 193 [100, (M+Na)$^+$], *HRMS* (ESI$^+$) 171.02744 ((M+H)$^+$, C_8H_8OFS requires 171.02744).

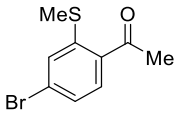
1-(2-Fluoro-6-(methylthio)phenyl)nonan-1-one, 1n



To a solution of 2-fluoro-6-(methylthio)benzaldehyde (85 mg, 0.50 mmol) and [Rh(Bn-(*p*-F))(dtmp)].BAr$^f_4$ (70 mg, 0.025 mmol) in acetone (0.25 mL) was added 1-octene (118 µL, 0.75 mmol). This was stirred at 55 °C for 4 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether in petrol) to yield the ketone as a colourless oil (64 mg, 46%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.31 (td, *J* = 8.0, 6.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.88 (ddd, *J* = 9.5, 8.5, 1.0 Hz, 1H), 2.84 (td, *J* = 7.5, 2.0 Hz, 2H), 2.43 (s, 3H), 1.70 (quintet, *J* = 7.5 Hz, 2H), 1.36-1.25 (m, 10H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 202.3, 156.8 (d, *J* = 249.0 Hz), 139.7 (d, *J* = 4.0 Hz), 131.2 (d, *J* = 9.0

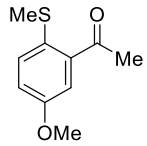
Hz),, 128.2 (d, *J* = 18.0 Hz), 122.4 (d, *J* = 3.0 Hz), 112.4 (d, *J* = 22.0 Hz), 44.61, 44.57, 31.9, 29.4, 29.2, 23.8, 22.7, 16.9, 14.1; ν_{max} (film)/cm^{-1} 1687, 1447,894,777;

1-(4-Bromo-2-(methylthio)phenyl)ethanone, 5



To a stirred suspension of sodium thiomethoxide (323 mg, 4.6 mmol) in DMF (25 mL) was added 1-(4-bromo-2-fluorophenyl)ethanone (1.0 g, 4.6 mmol) over 30 mins at -45 °C. After the addition was complete, the solution was stirred for a further 3 h at -45 °C. The reaction was then quenched with water and the precipitate was filtered off to yield the product as a white solid (913 mg, 81%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.59 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 197.9, 145.4, 132.5, 132.4, 127.8, 127.5, 126.4, 28.1, 16.0 ν_{max} (film)/cm^{-1} 1739, 1663, 788; *m/z* (rel intensity) 267 [50, $(M+Na)^+$]; *HRMS* (ESI^+) 244.96303 ($(M+H)^+$, $C_9H_{10}O^{79}BrS$ requires 244.96303).

1-(5-Methoxy-2-(methylthio)phenyl)ethanone, 1k



To a stirred suspension of sodium thiomethoxide (282 mg, 4.0 mmol) in DMF (25 mL) was added 1-(2-bromo-5-methoxyphenyl)ethanone (1.0 g, 3.36 mmol) over 30 mins at 0 °C. After the addition was complete, the solution was stirred for a further 3 h at r.t. The reaction was then quenched with water and the precipitate was filtered off to yield the product as pale yellow needles (481 mg, 73%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.07 (dd, *J* = 8.5, 2.5 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 199.5, 156.6, 137.1, 131.8, 127.7, 118.0, 116.0, 55.6, 28.7, 16.9; ν_{max} (film)/cm^{-1} 1659; *m/z* (rel intensity) 219 [100, $(M+Na)^+$], *HRMS* (ESI^+) 197.0636 ($(M+H)^+$, $C_{10}H_{13}O_2S$ requires 197.0639).

4 References

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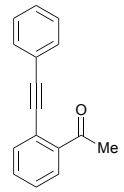
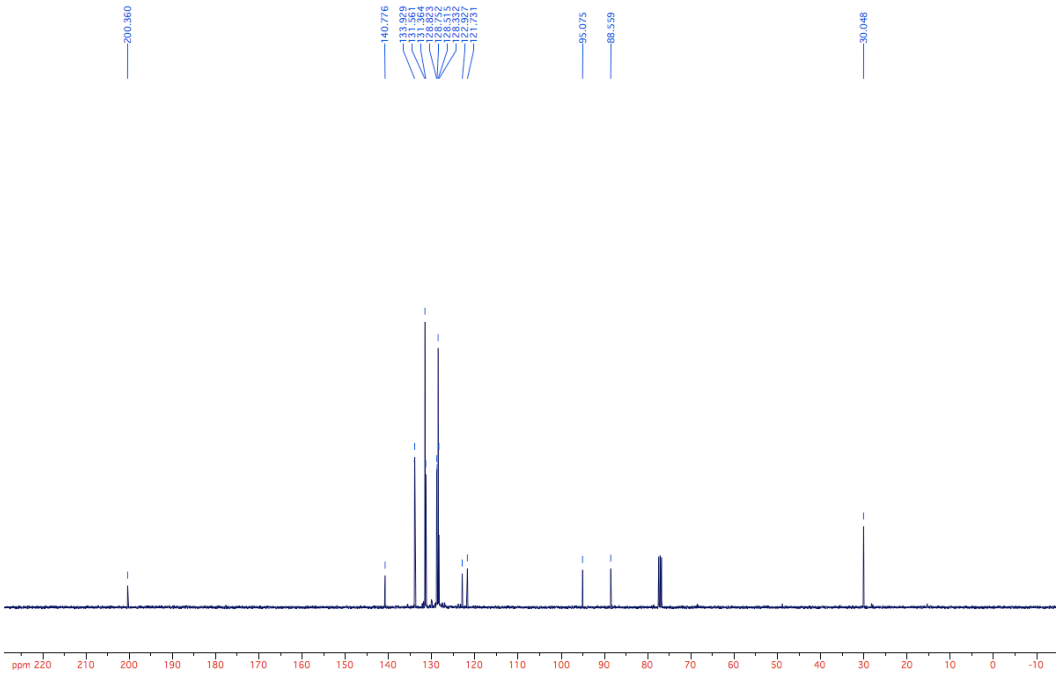
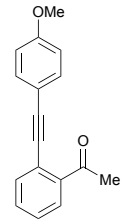
ii. N. Chernyak, S. Gorelsky and V. Gevorgyan, *Angew. Chem. Int. Ed.*, 2011, **50**, 2342.
iii. M. Feuerstein, F. Berthiol, H. Doucet and M. Santelli, *Synthesis*, 2004, **8**, 1281.
iv. X. Chen, J. Jin, N. Wang, P. Lu and Y. Wang, *Eur. J. Org. Chem.*, 2012, **4**, 824.
v. Q. Zhao, Q. Hu, L. Wen, M. Wu and Y Hu, *Adv. Synth. Catal.*, 2012, **11**, 2113.

5 NMR Spectra



3a

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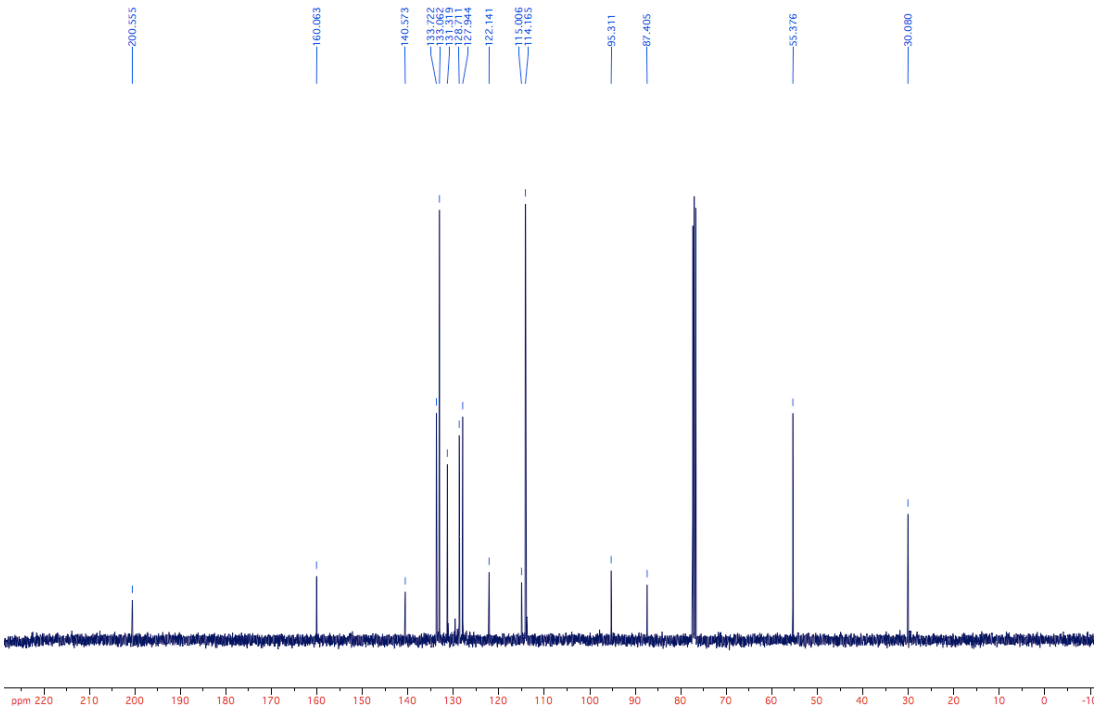
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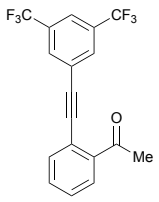
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1
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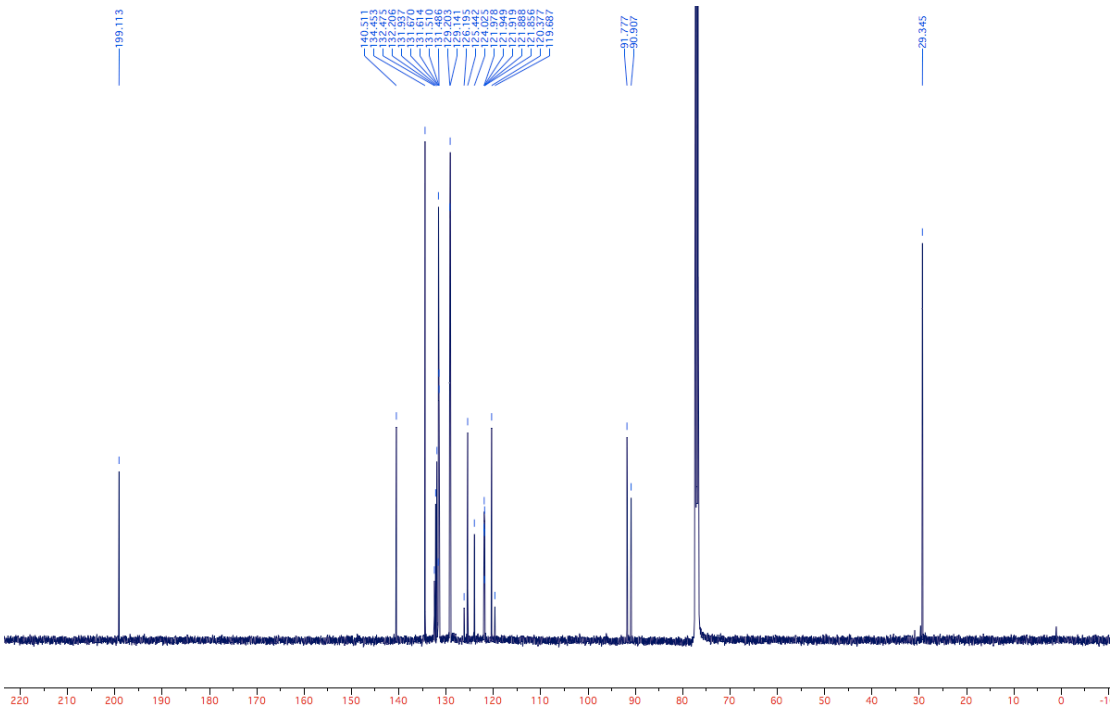
199.113
140.511
134.453
132.475
132.206
131.597
131.670
131.614
131.510
131.486
131.405
129.141
126.195
126.155
124.025
122.444
121.948
121.919
121.888
121.859
120.377
119.887
91.777
90.907
29.345
220
210
200
190
180
170
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150
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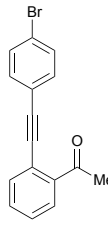
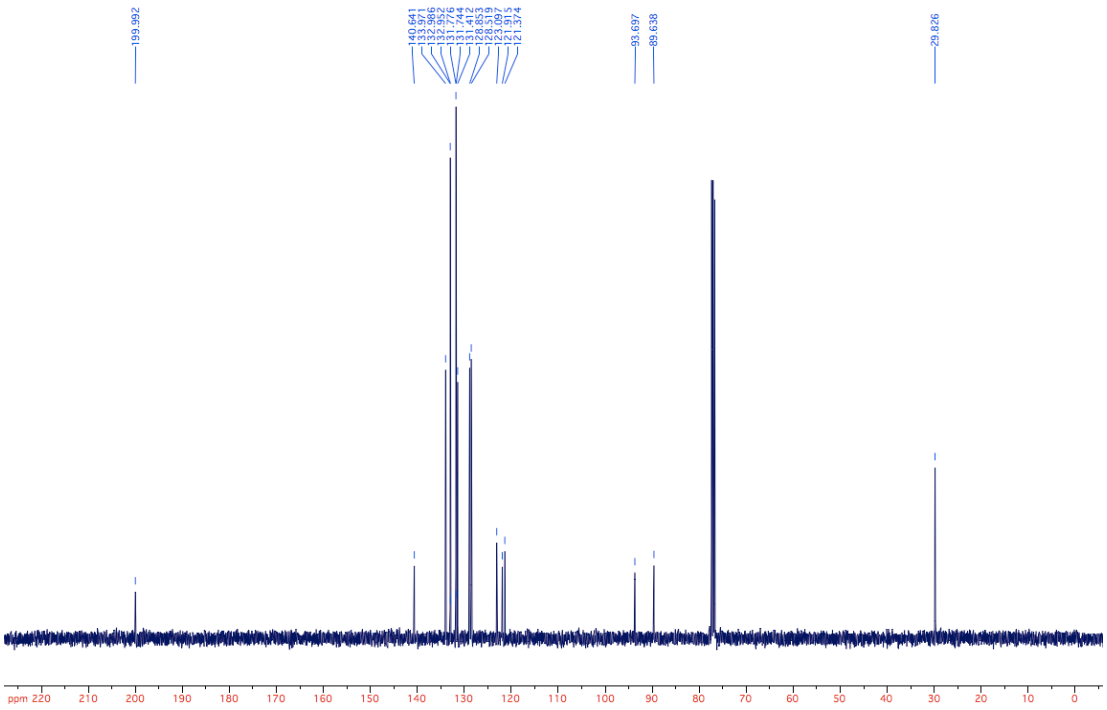
30
20
10
0


Br
O
Me

3c

0.958
1
3.05
3.01
3.02
ppm 10
9
8
7
6
5
4
3
2
1
0


199.992
140.641
133.971
132.966
132.952
131.776
131.744
131.412
128.853
128.659
123.097
121.971
121.915
121.314
93.697
89.638
29.826
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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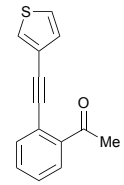
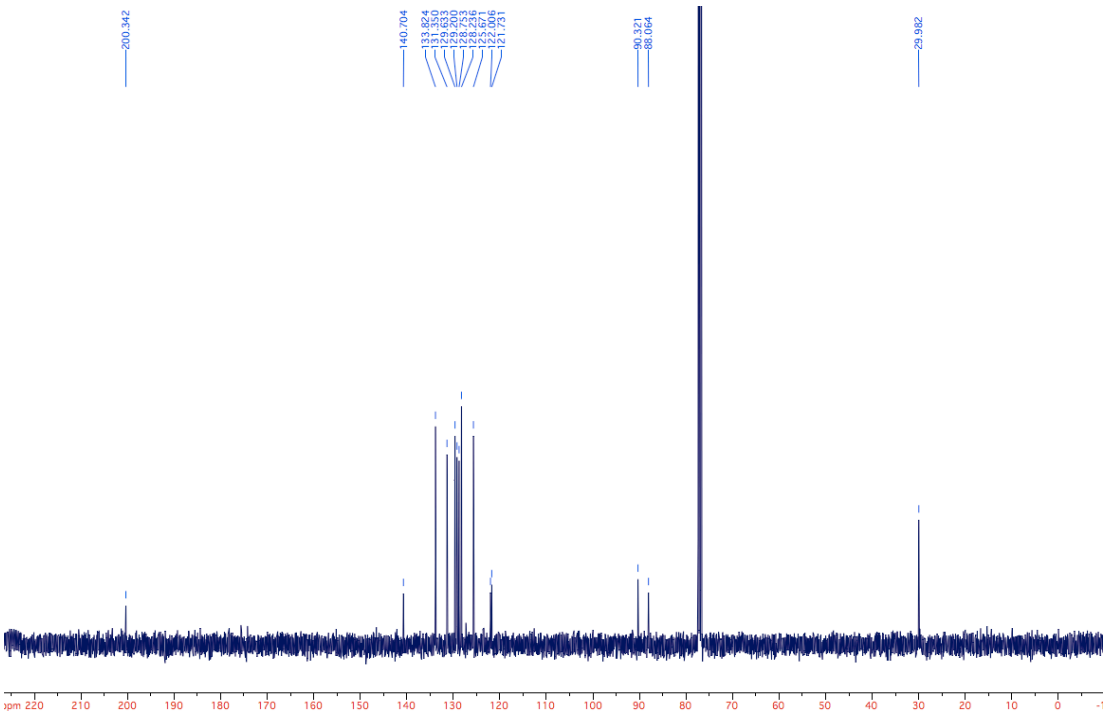
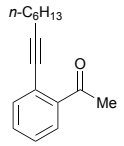

S
O
Me

3e

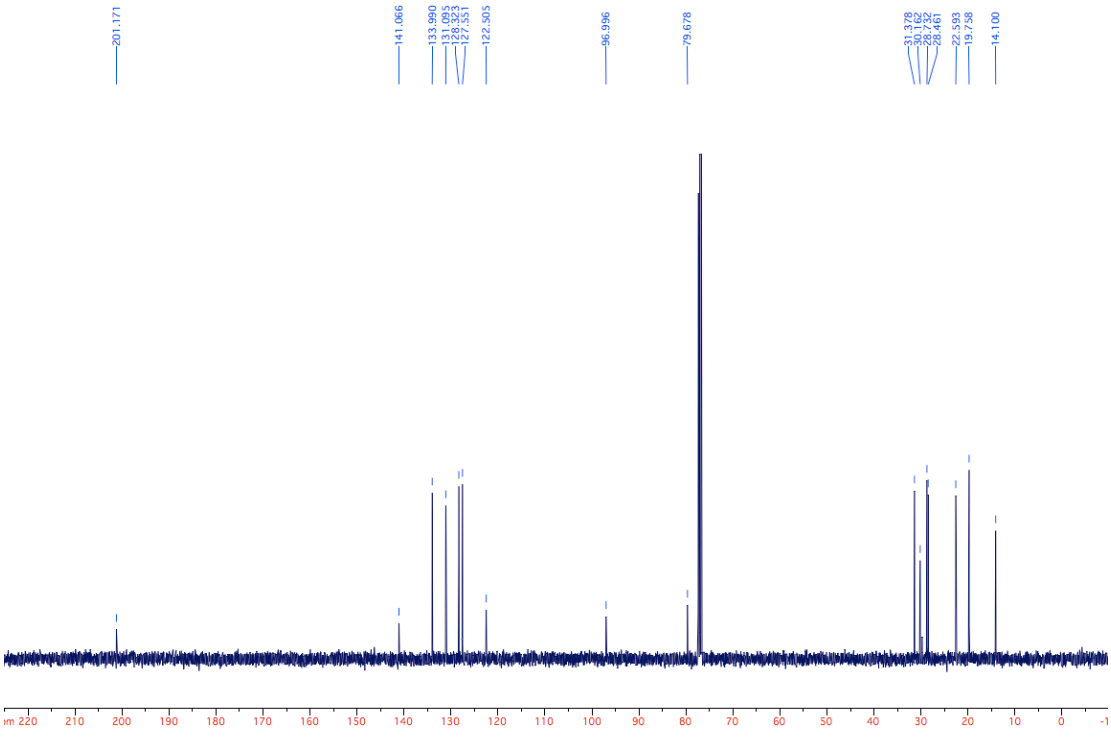
1.03
1.19
0.984
0.801
1.16
0.992
3.12
ppm 10
9
8
7
6
5
4
3
2
1
0


200.342
140.704
133.864
131.550
129.633
129.200
128.753
128.236
125.671
125.006
121.731
90.321
88.064
29.982
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


n-C6H13
O
Me

3f

1.05
1.13
1.15
3.12
1.96
2.19
1.92
4.52
3.65
ppm 10
9
8
7
6
5
4
3
2
1
0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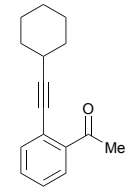
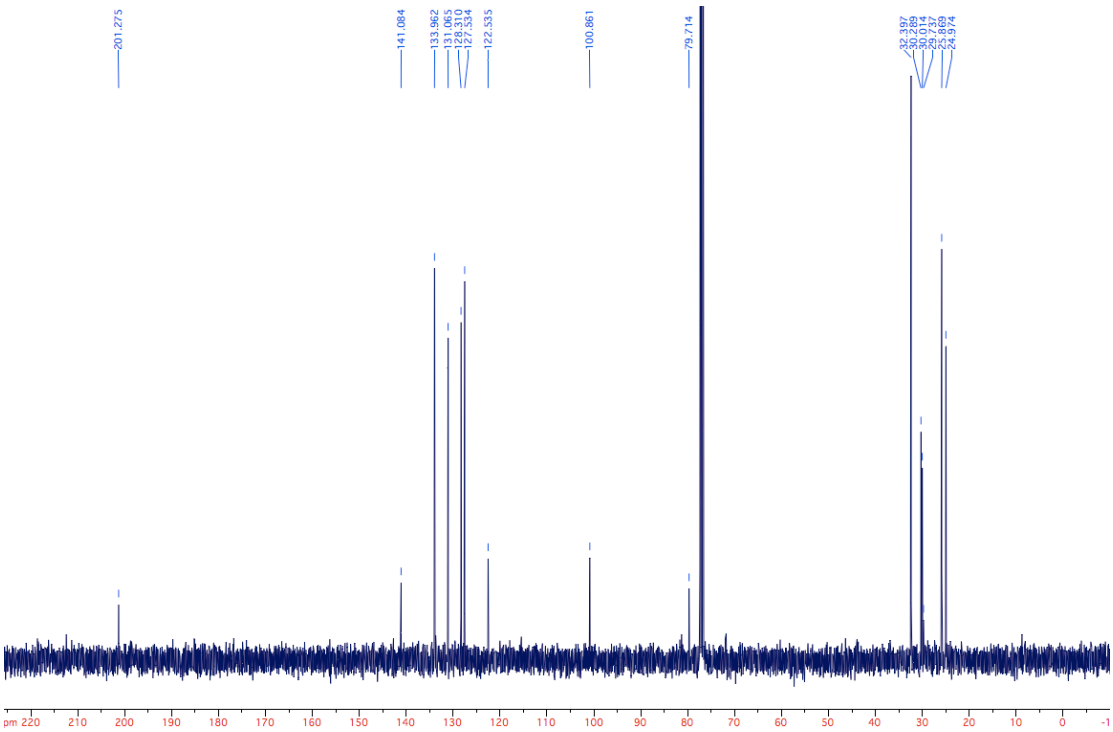
141.066
133.990
131.095
128.323
127.551
122.505
96.996
79.678
31.378
30.162
28.727
28.446
22.593
19.758
14.100
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


O
Me

3i

0.959
1.04
0.875
1.08
1
2.33
3.18
2.65
2.92
ppm 10
9
8
7
6
5
4
3
2
1
0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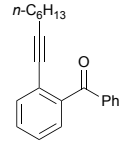
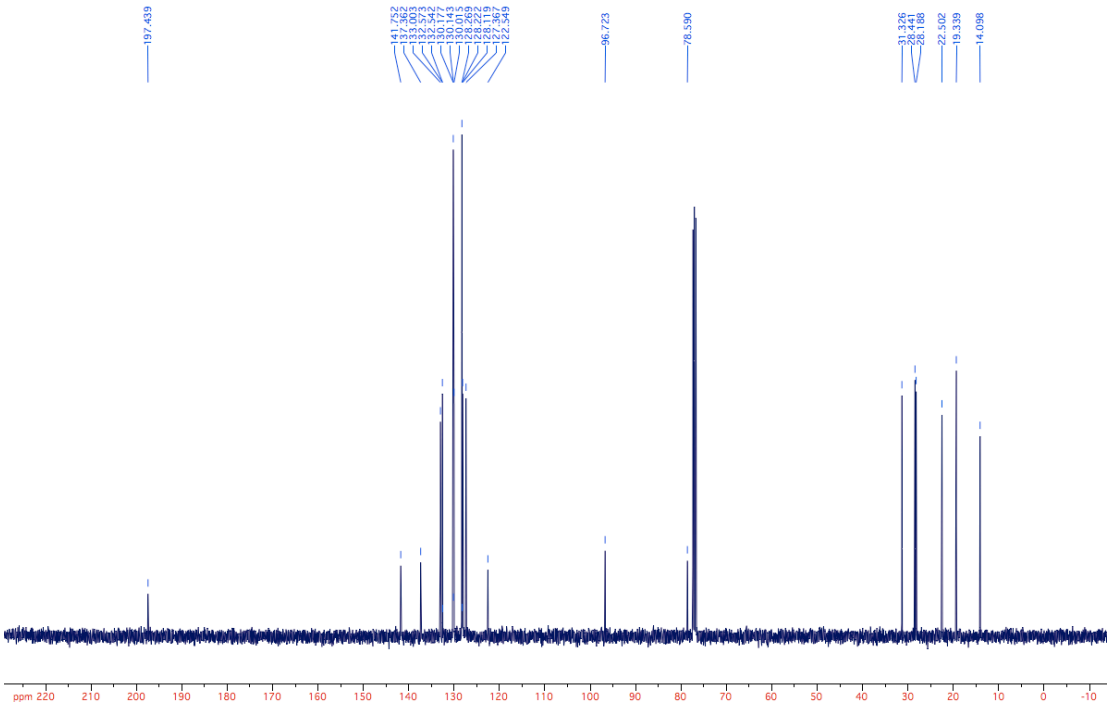
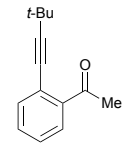
141.084
133.962
131.065
128.310
127.534
122.535
100.861
79.714
32.397
30.069
30.014
29.737
25.869
24.374
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


n-C6H13
O
Ph

3g

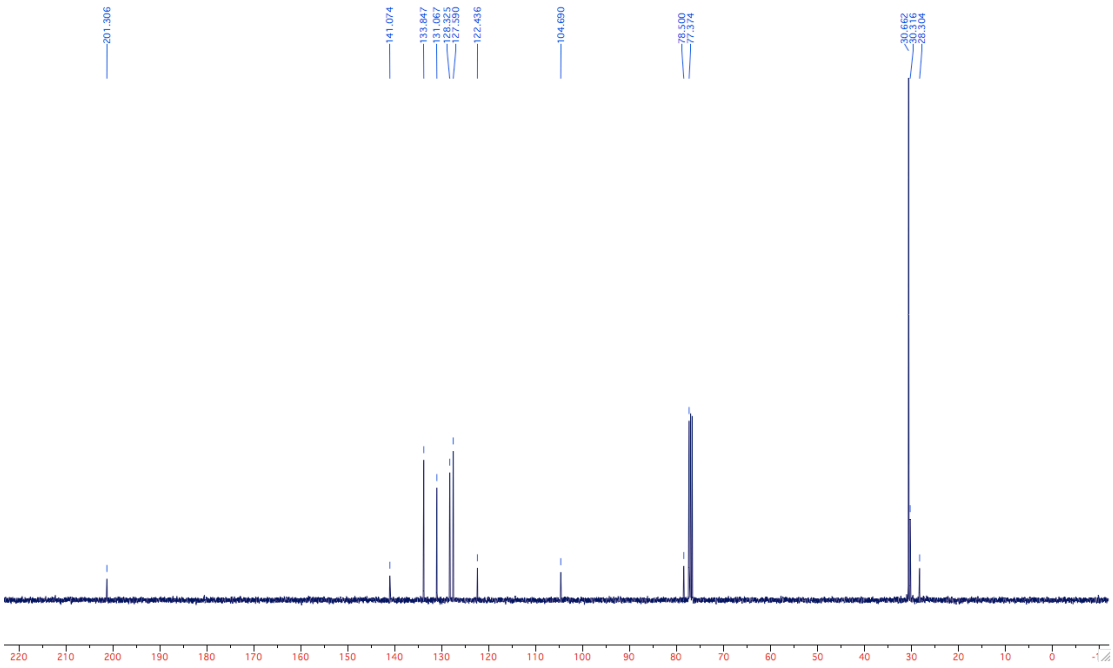
1.79
1
5.93
2.08
8.57
3.11
10
9
8
7
6
5
4
3
2
1
0


197.439
141.752
137.362
133.003
132.542
130.177
130.013
130.011
128.269
128.227
128.119
127.367
122.349
96.723
78.590
31.326
24.441
28.188
22.502
19.339
14.098
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


t-Bu
O
Me

3h

1.07
1.11
1.12
3.26
9.74
ppm 10
9
8
7
6
5
4
3
2
1
0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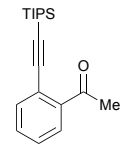
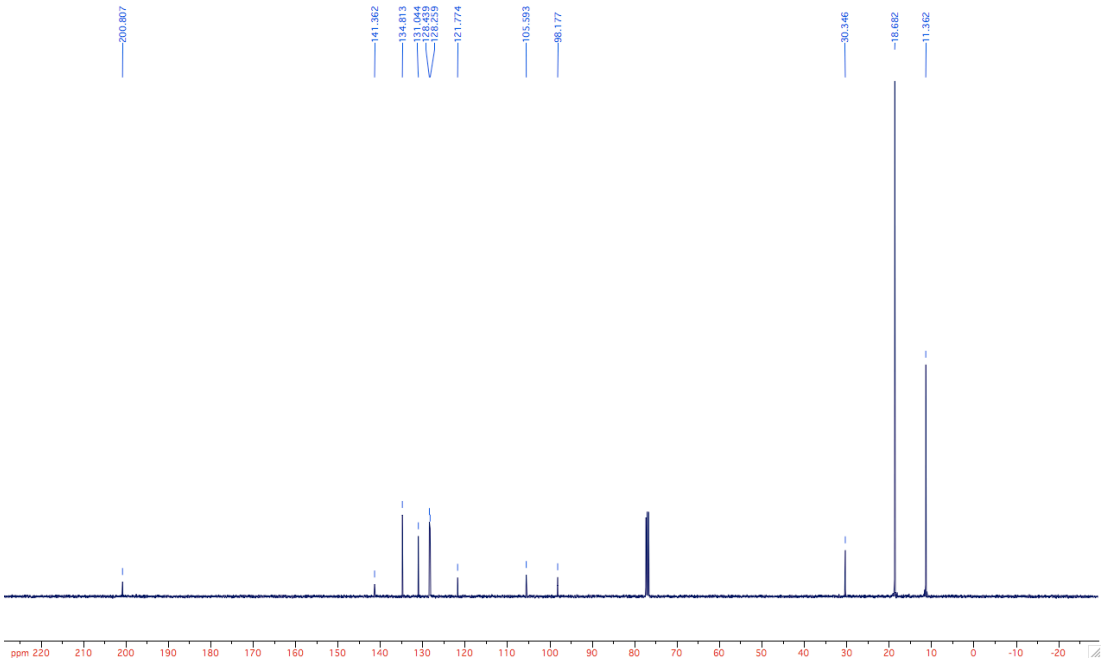
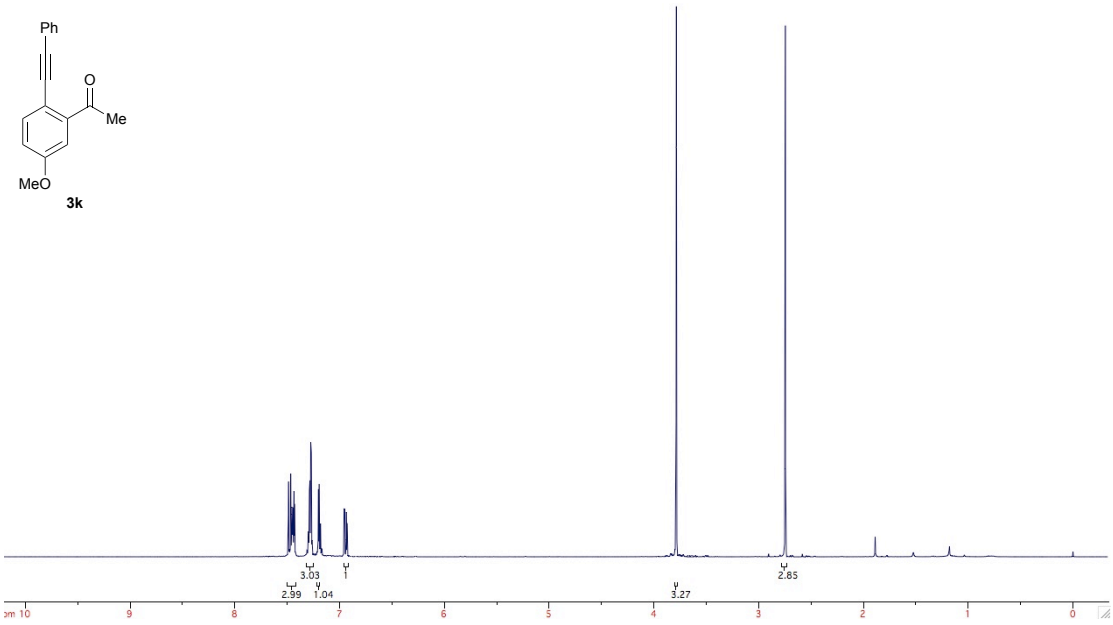
141.074
133.847
131.057
128.325
127.390
122.436
104.690
78.500
77.374
30.662
30.114
28.304
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

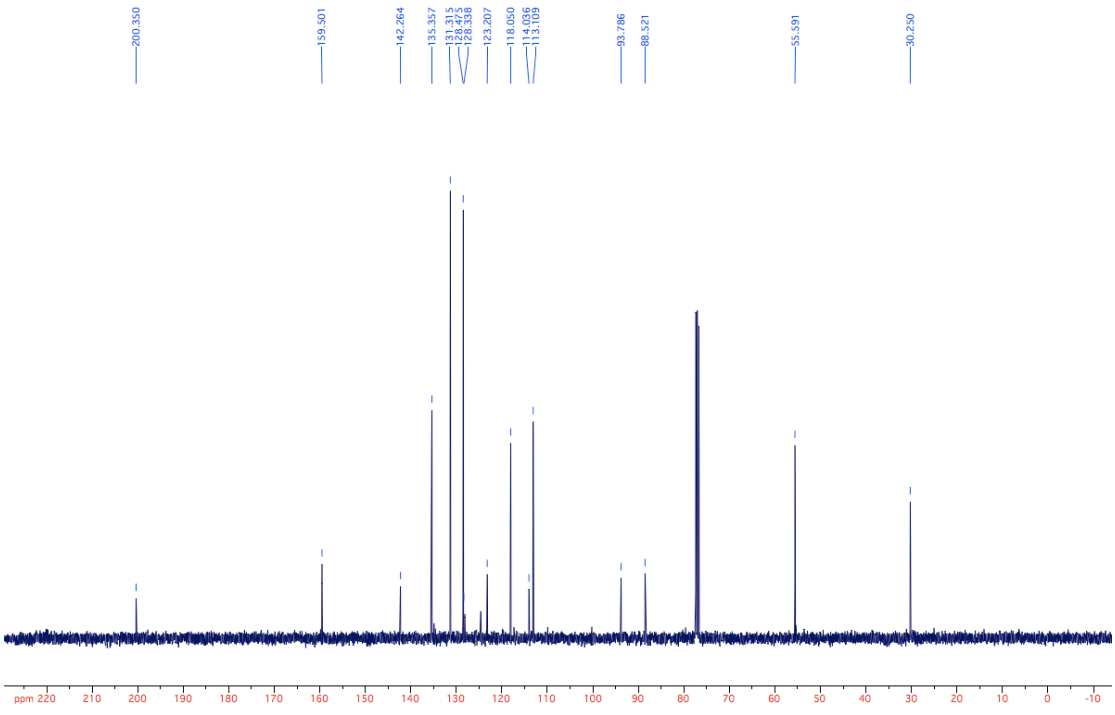

TIPS
O
Me

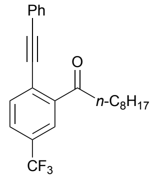
3j

1.09
1.11
1.17
3.04
21.5
ppm 10
9
8
7
6
5
4
3
2
1
0

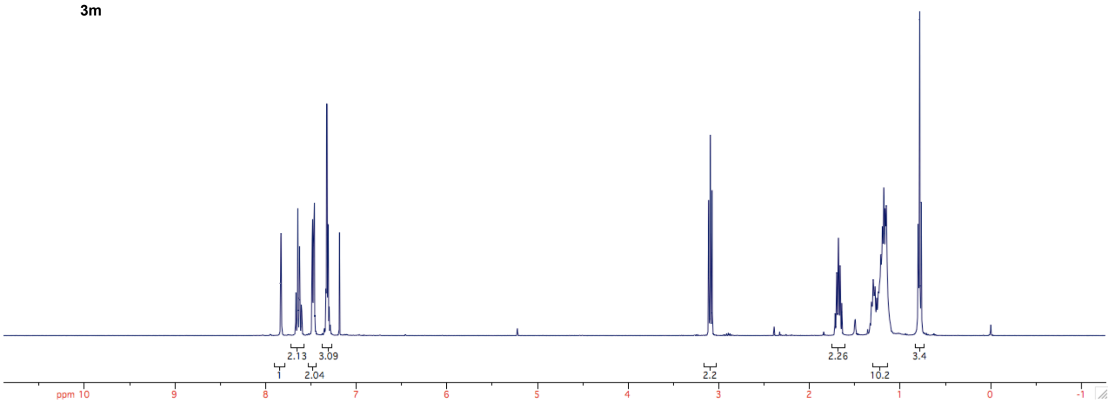

200.807
141.362
134.813
131.044
128.439
128.259
121.774
105.593
88.177
30.346
18.682
11.362
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

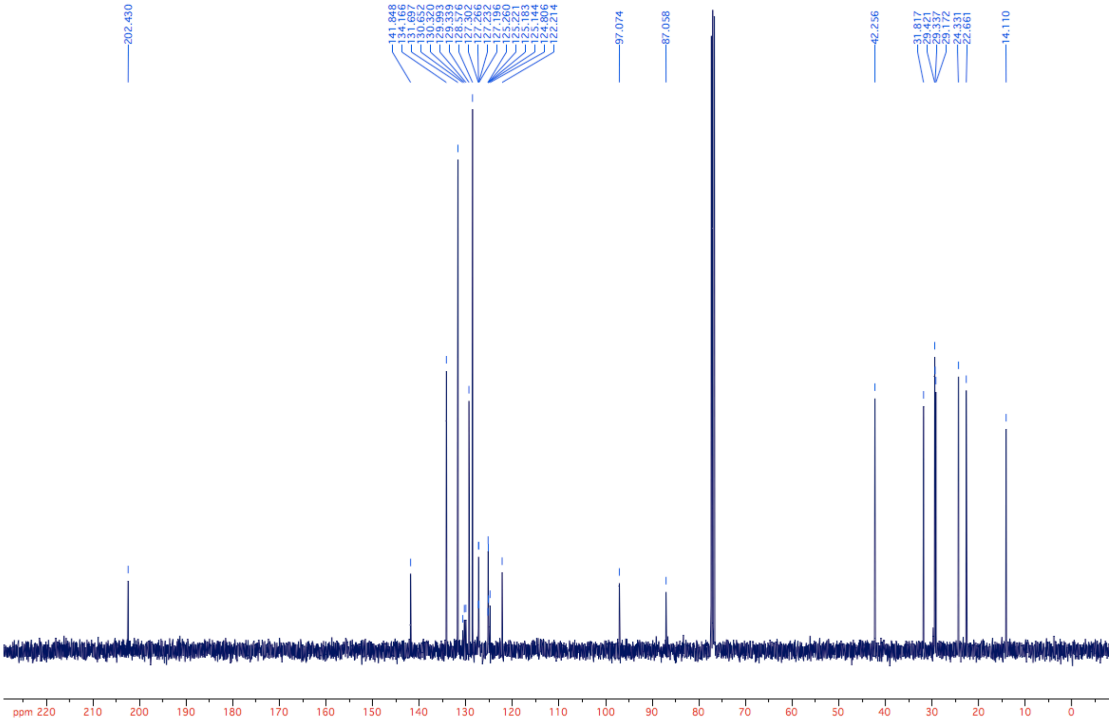

Ph
O
Me
MeO
3k
3.03
1.04
2.99
3.27
2.85

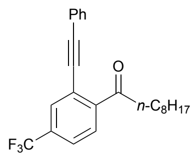

200.350
159.501
142.264
135.357
131.315
128.475
128.338
123.207
118.050
114.036
113.109
93.786
88.521
55.591
30.250


Ph
O
n-C8H17
CF3

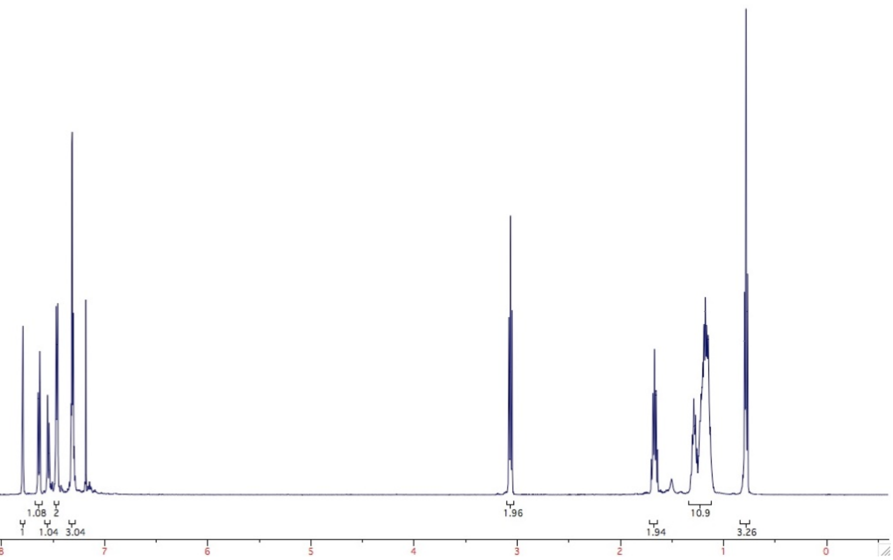
3m

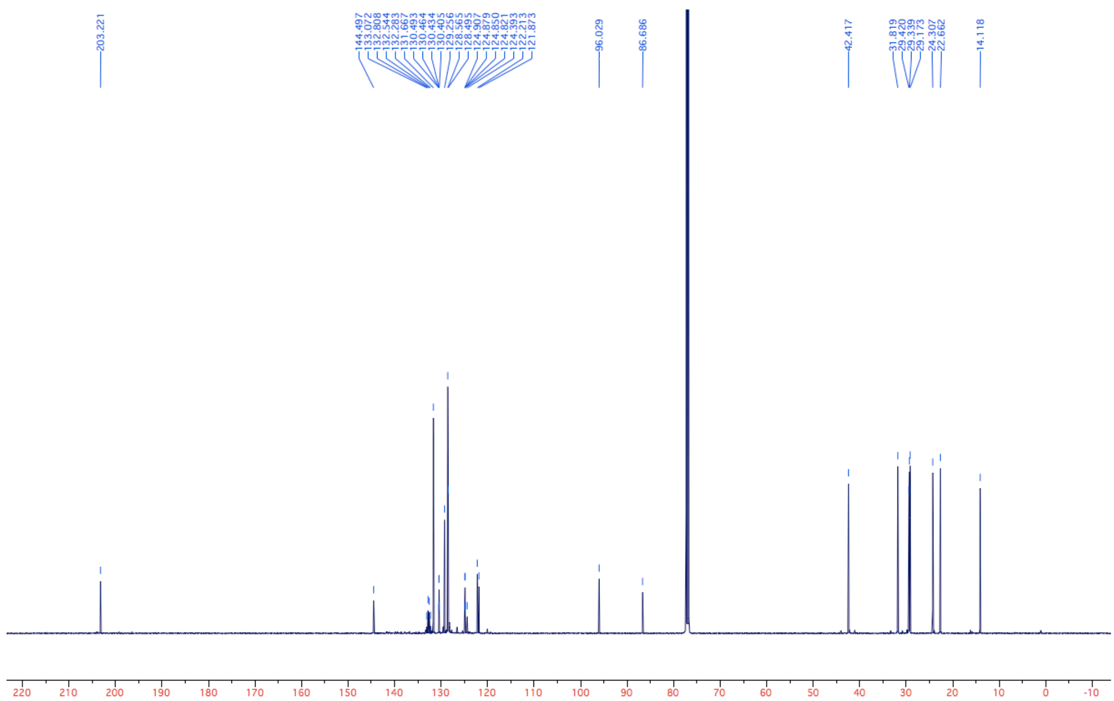

2.13
3.09
1
2.04
2.2
2.26
10.2
3.4
ppm 10
9
8
7
6
5
4
3
2
1
0
-1


202.430
141.848
134.166
131.697
130.652
130.320
129.993
129.339
128.576
127.302
127.266
127.232
127.196
125.260
125.221
125.183
125.144
124.806
122.214
97.074
87.058
42.256
31.817
29.421
29.337
29.172
24.331
22.861
14.110
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
O
n-C_8H_{17}
F_3C

3l


1.08
2
1
1.04
3.04
1.96
1.94
10.9
3.26
10
9
8
7
6
5
4
3
2
1
0


203.221
144.497
133.072
132.808
132.544
132.283
131.667
130.493
130.464
130.434
130.405
129.256
128.565
128.495
124.907
124.879
124.850
124.821
124.393
122.213
121.873
96.029
86.686
42.417
31.819
29.420
29.339
29.173
24.307
22.662
14.118
220
210
200
190
180
170
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130
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100
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80
70
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20
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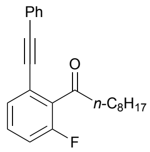
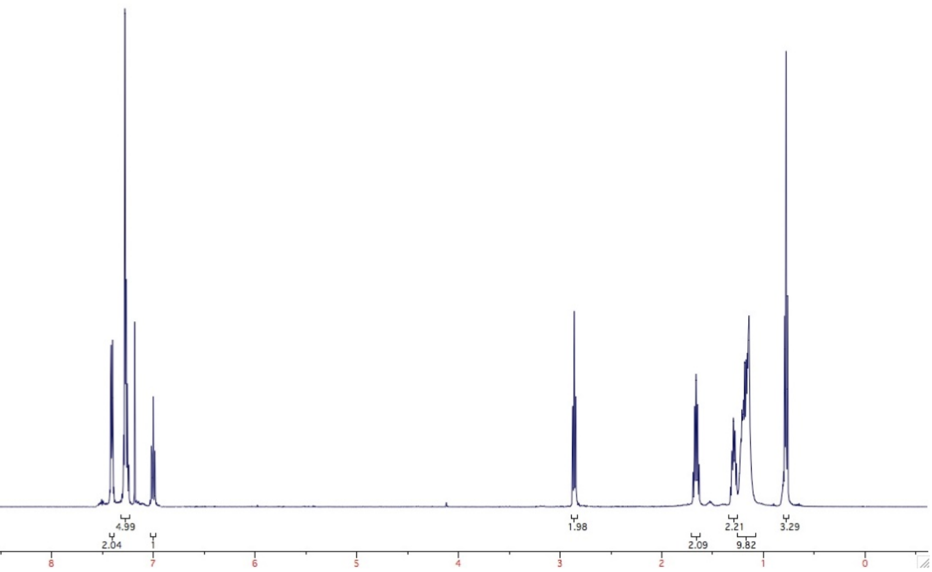
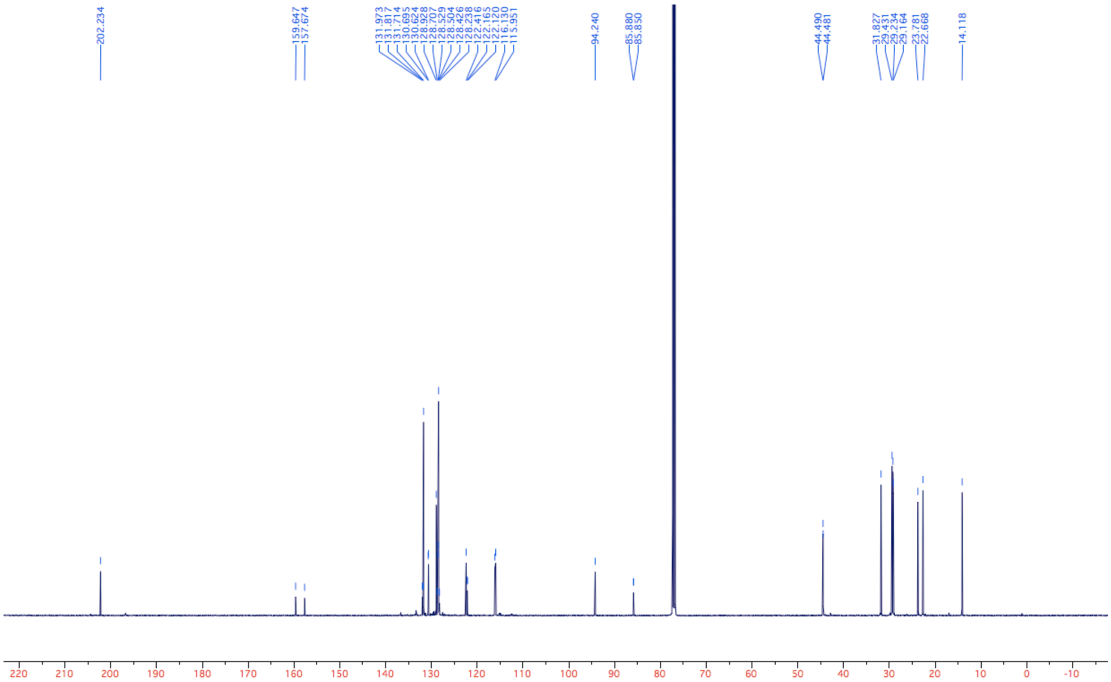
-10


Ph
O
n-C8H17
F

3n


4.99
2.04
1
1.98
2.09
2.21
9.82
3.29
ppm 10
9
8
7
6
5
4
3
2
1
0


202.234
159.647
157.674
131.973
131.817
131.714
130.685
130.624
128.928
128.707
128.529
128.504
128.426
128.238
122.416
122.165
122.120
116.130
115.951
94.240
85.880
85.850
44.490
44.481
31.827
29.431
29.234
29.164
23.781
22.668
14.118
220
210
200
190
180
170
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140
130
120
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100
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80
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50
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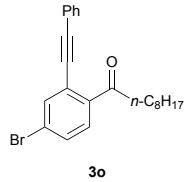
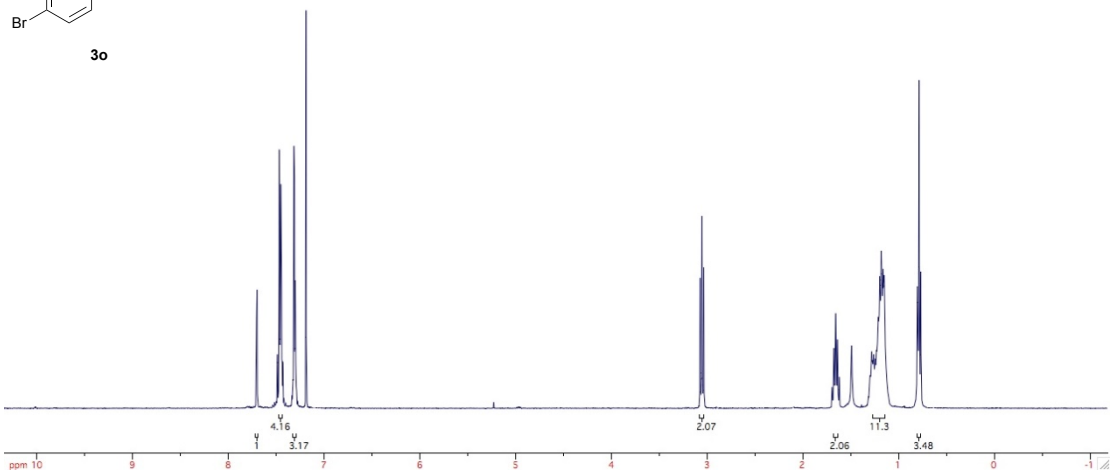
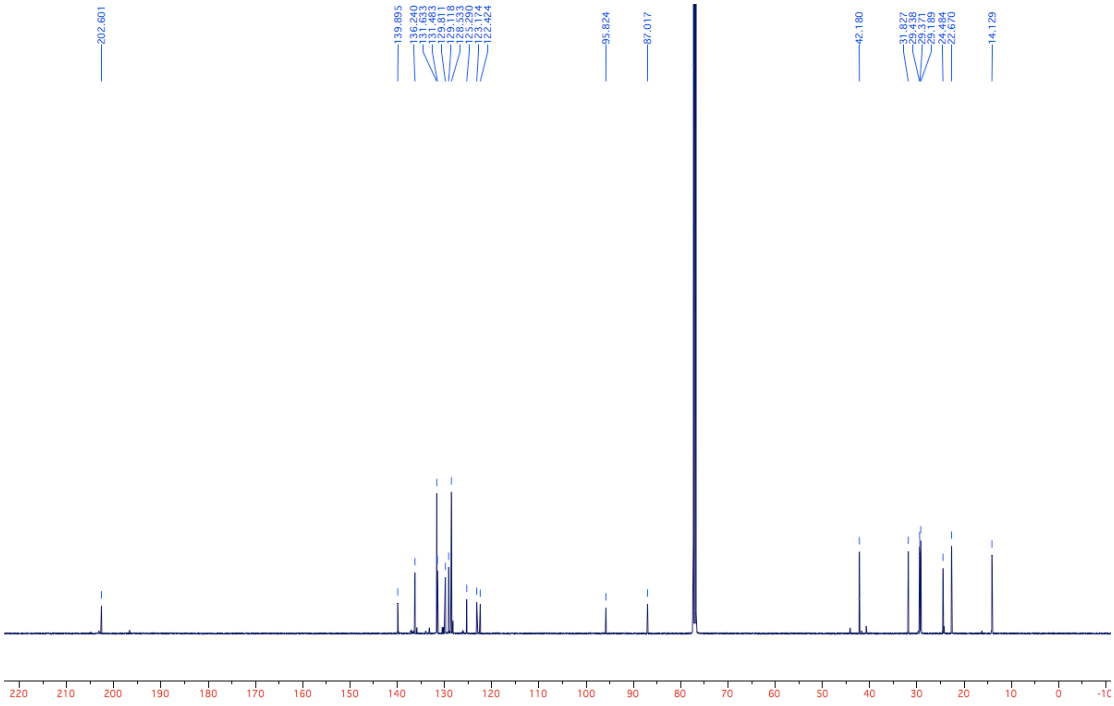
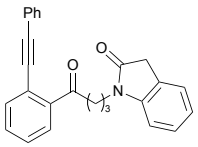
10
0
-10


Ph
O
n-C8H17
Br

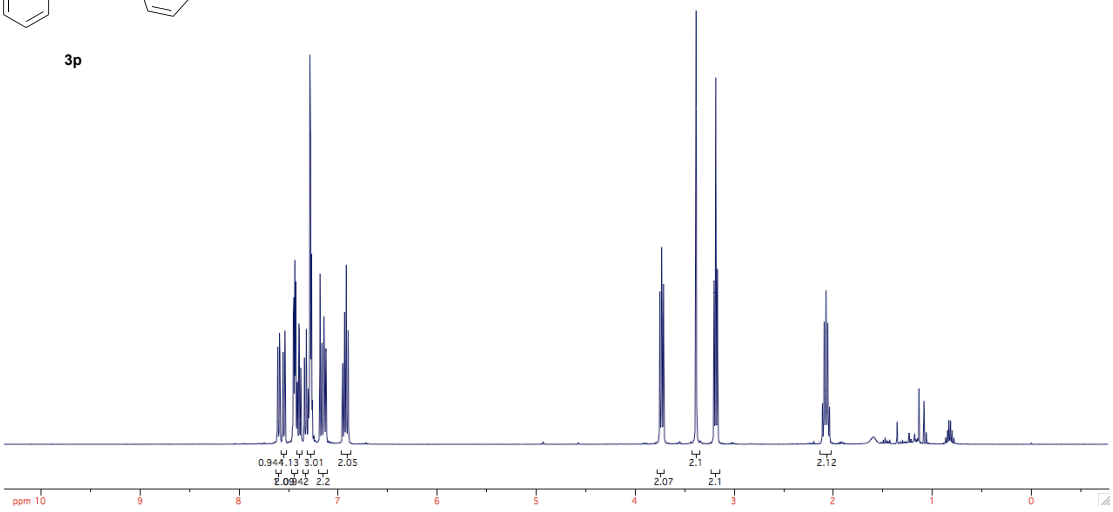
3o

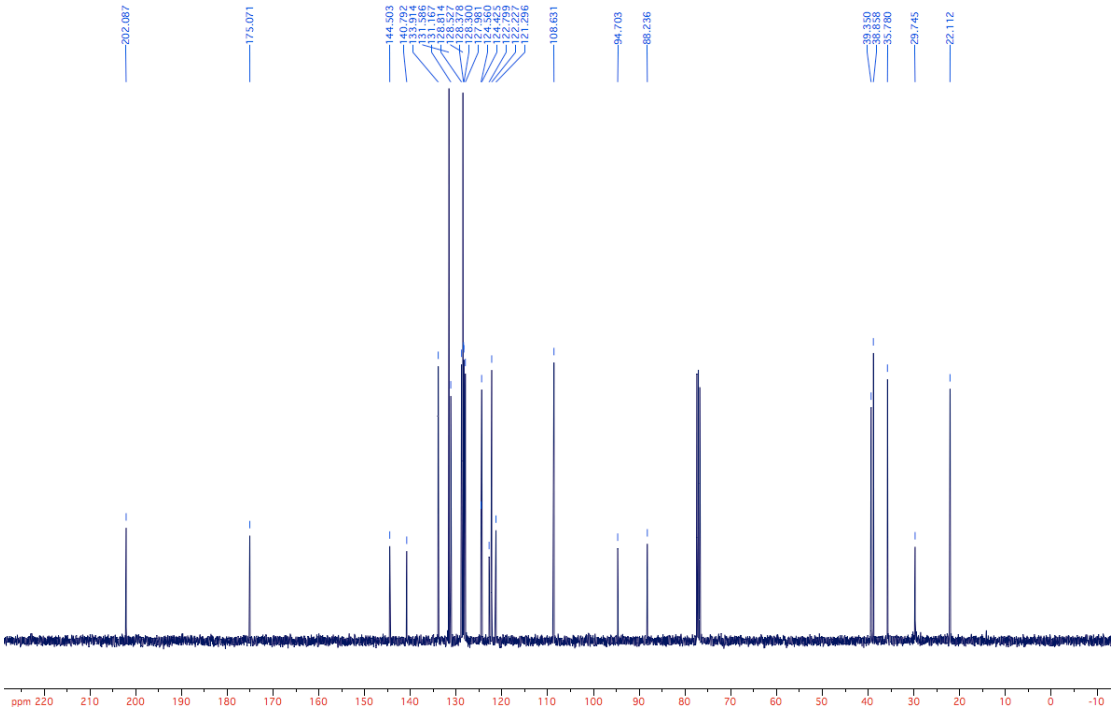

4.16
3.17
2.07
2.06
11.3
3.48
ppm 10
9
8
7
6
5
4
3
2
1
0


202.601
139.895
136.240
131.483
131.483
129.811
128.533
128.533
125.290
123.424
123.424
95.824
87.017
42.180
31.827
29.418
29.371
29.189
24.484
22.670
14.129
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
O
O
N
3

3p


0.94
4.13
3.01
2.05
2.03
2.42
2.2
2.07
2.1
2.1
2.12
ppm 10
9
8
7
6
5
4
3
2
1
0


202.087
175.071
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140.792
133.914
133.566
131.167
128.814
128.577
128.378
128.300
128.081
124.560
124.425
123.709
122.227
121.296
108.631
94.703
88.236
39.350
38.858
35.780
29.745
22.112
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
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70
60
50
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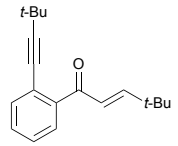
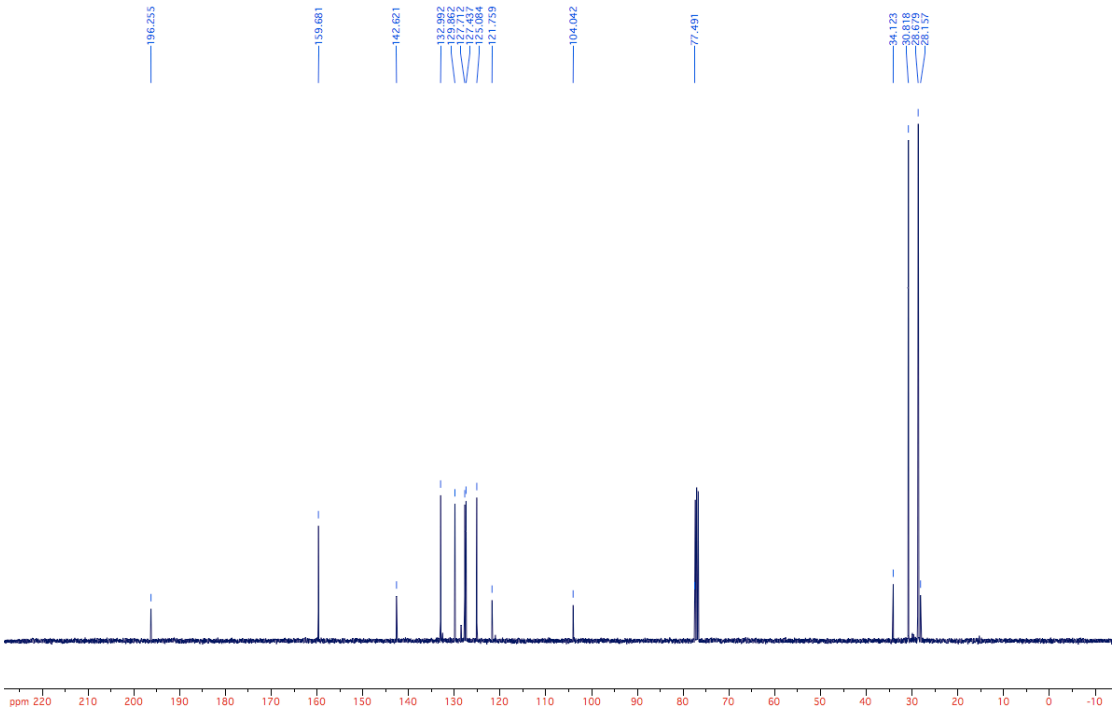
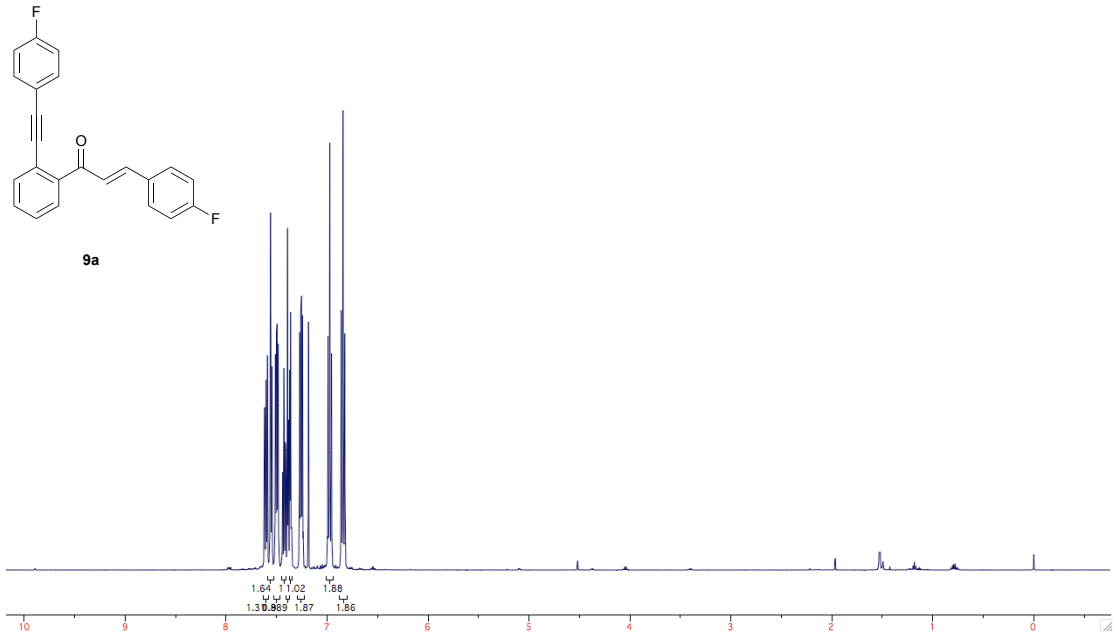
20
10
0
-10


t-Bu
O
t-Bu

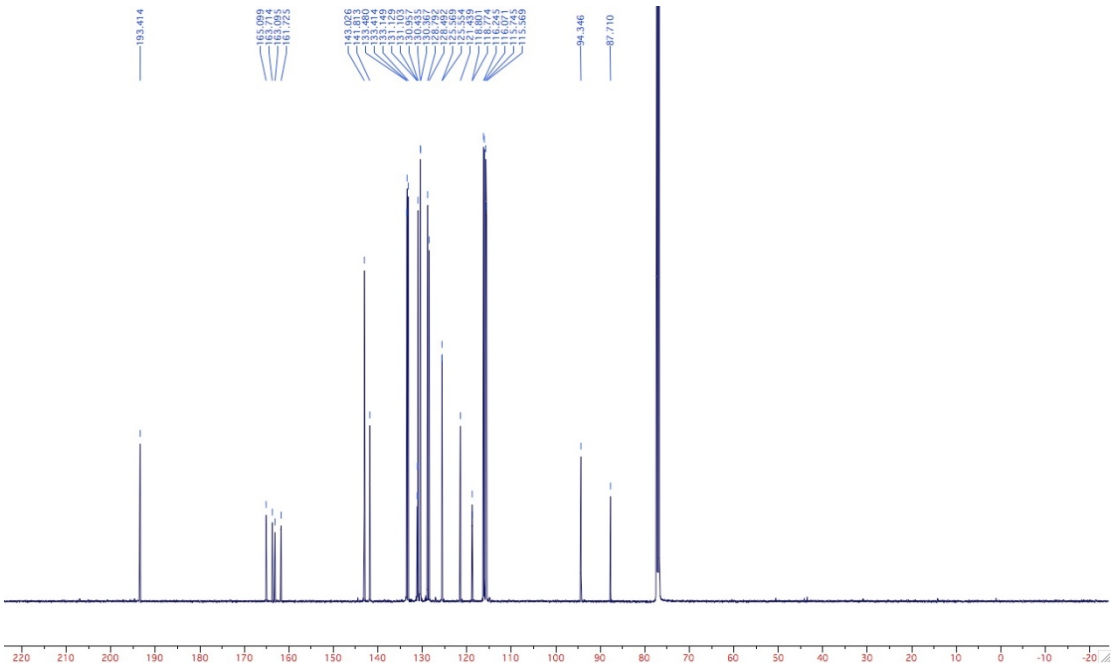
9d

3.22
1.02
1
1.01
9.64
9.69
ppm 10
9
8
7
6
5
4
3
2
1
0


196.253
159.681
142.621
132.992
129.862
127.712
127.437
125.084
121.759
104.042
77.491
34.123
30.818
28.679
28.137
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


F
O
F
1.64
1.02
1.88
1.87
1.86

9a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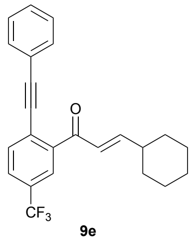
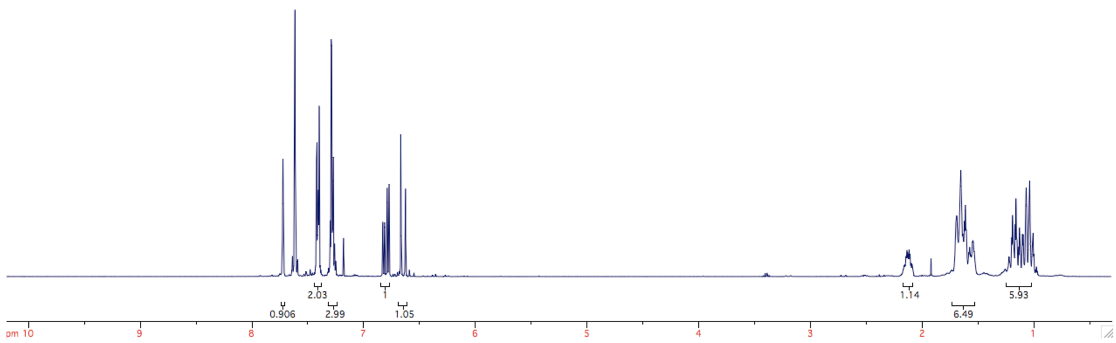
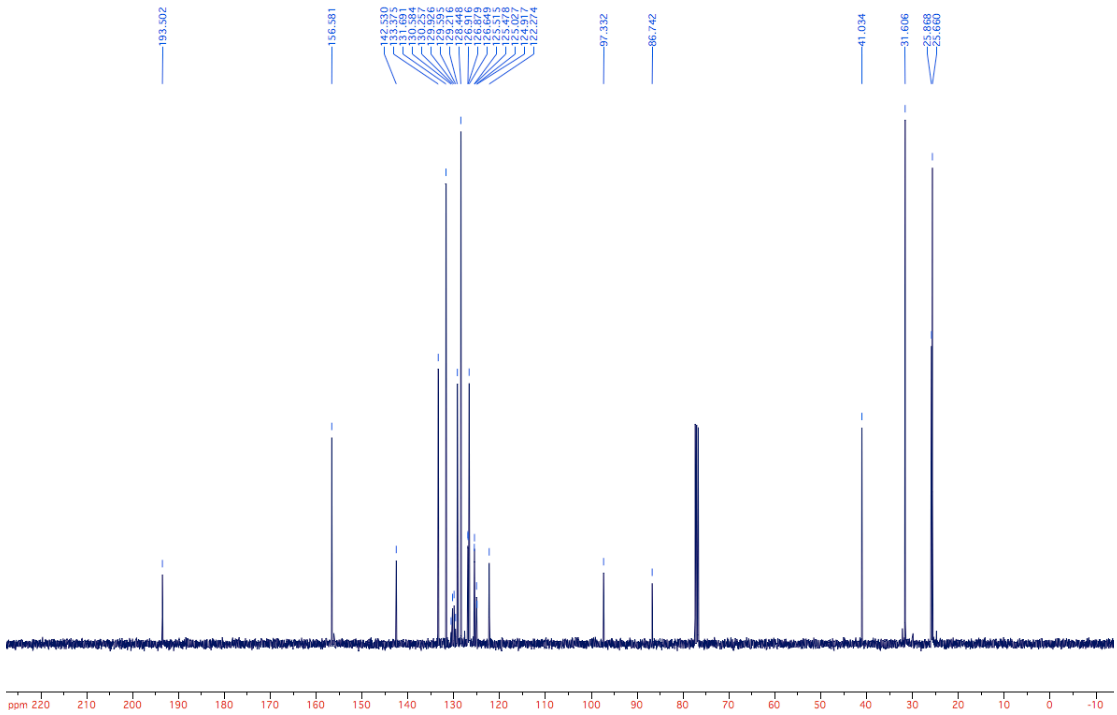
165.089
163.144
163.095
161.725
143.026
141.813
141.400
133.414
133.149
131.124
131.103
130.437
130.335
130.267
128.422
128.462
125.569
125.544
121.439
121.391
118.774
116.245
116.071
115.745
115.569
94.346
87.710


O
CF3

9e


2.03
1
1.14
5.93
0.906
2.99
1.05
6.49
ppm 10
9
8
7
6
5
4
3
2
1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156.581
142.530
133.375
131.691
130.584
130.257
129.926
129.595
129.216
128.448
126.916
126.879
126.649
125.515
125.478
125.027
124.917
122.274
97.332
86.742
41.034
31.606
25.868
25.660
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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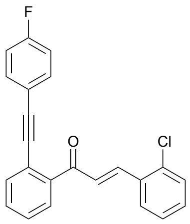
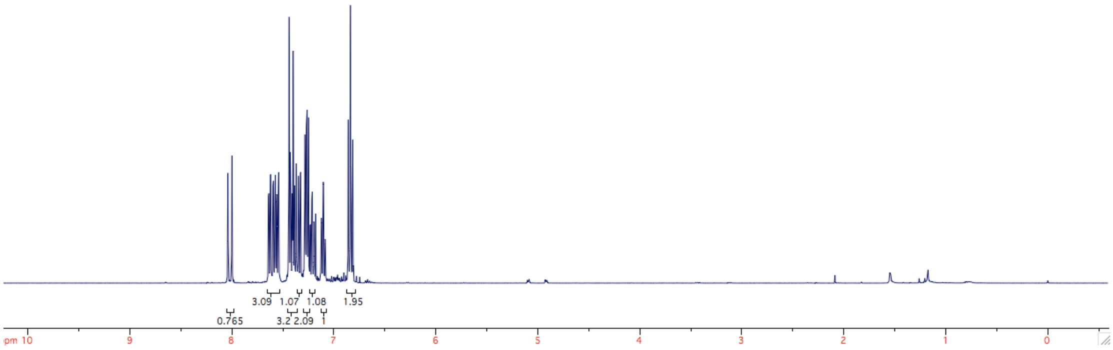
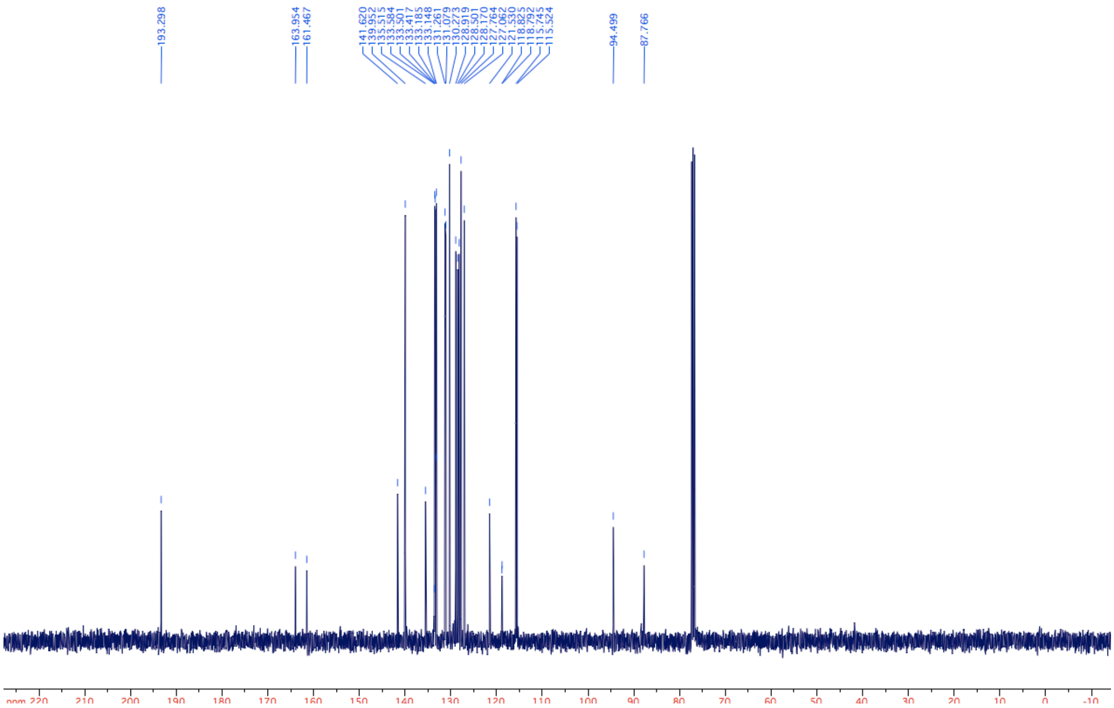
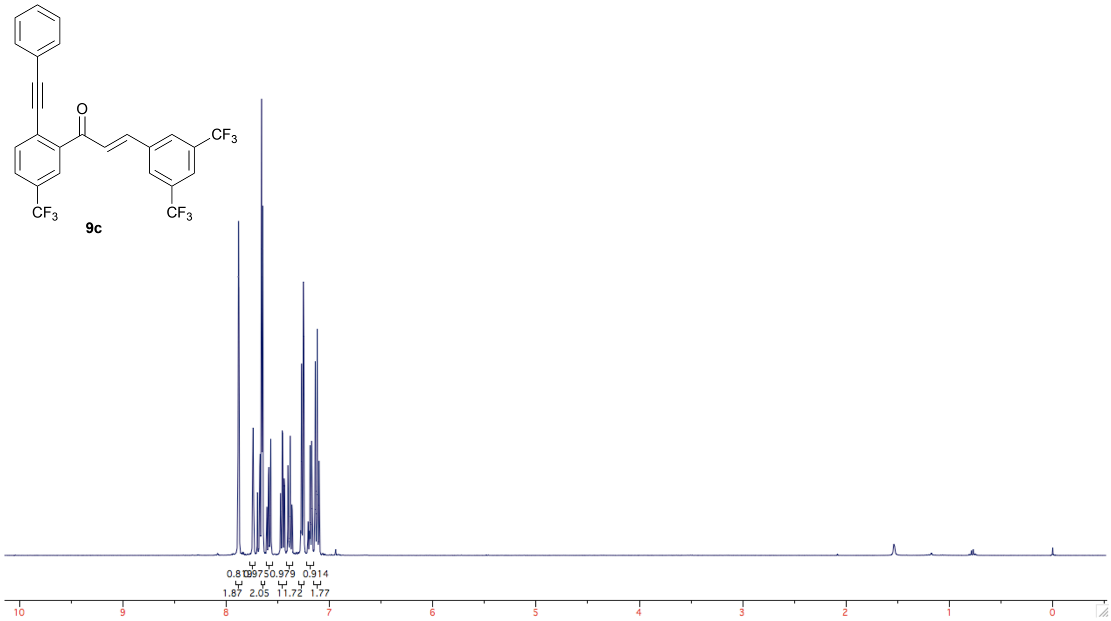
0
-10

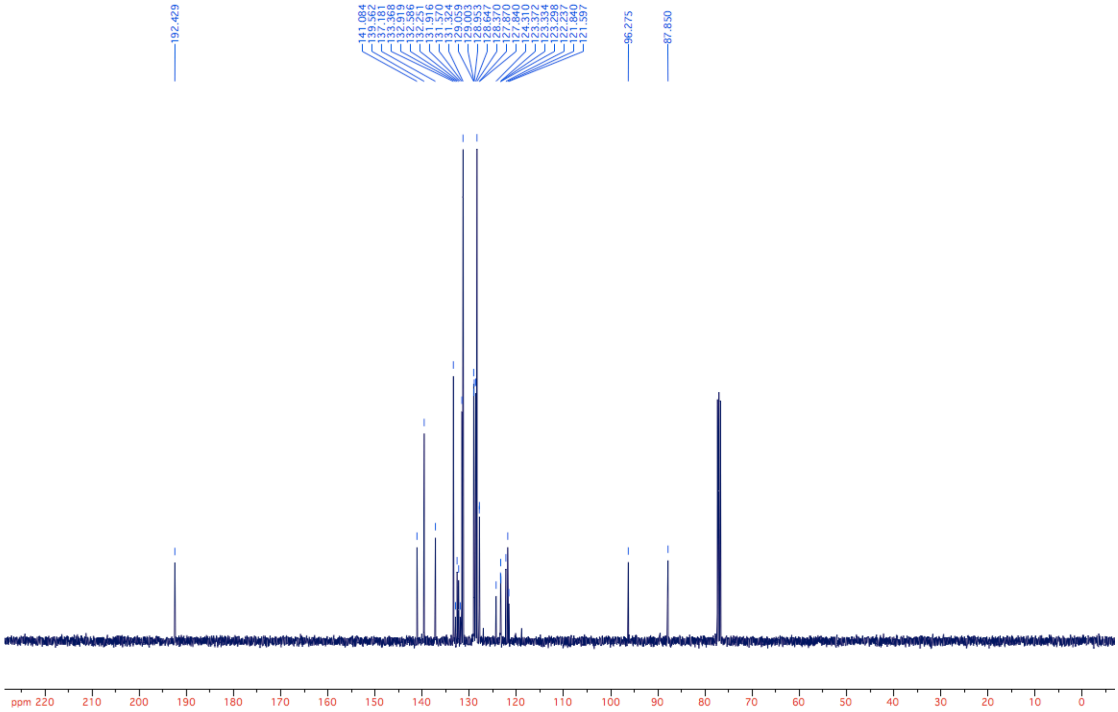

F
O
Cl

9b


3.09
1.07
1.08
1.95
0.765
3.2
2.09
1
pm 10
9
8
7
6
5
4
3
2
1
0


193.298
163.954
161.467
141.620
139.952
135.515
133.584
133.501
133.417
133.185
133.148
131.261
131.079
130.273
128.919
128.501
128.170
127.764
127.062
121.530
118.825
118.792
115.745
115.524
94.499
87.766
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


O
CF3
CF3
CF3
9c
0.810
0.975
0.979
0.914
1.87
2.05
11.72
1.77
10
9
8
7
6
5
4
3
2
1
0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141.084
139.562
137.181
133.368
132.919
132.586
132.251
131.916
131.570
131.324
129.059
129.003
128.953
128.647
128.370
127.870
127.840
124.310
123.372
123.334
123.298
122.237
121.840
121.597
96.275
87.850
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
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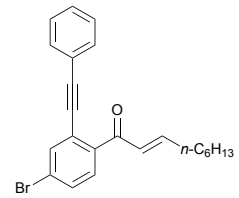
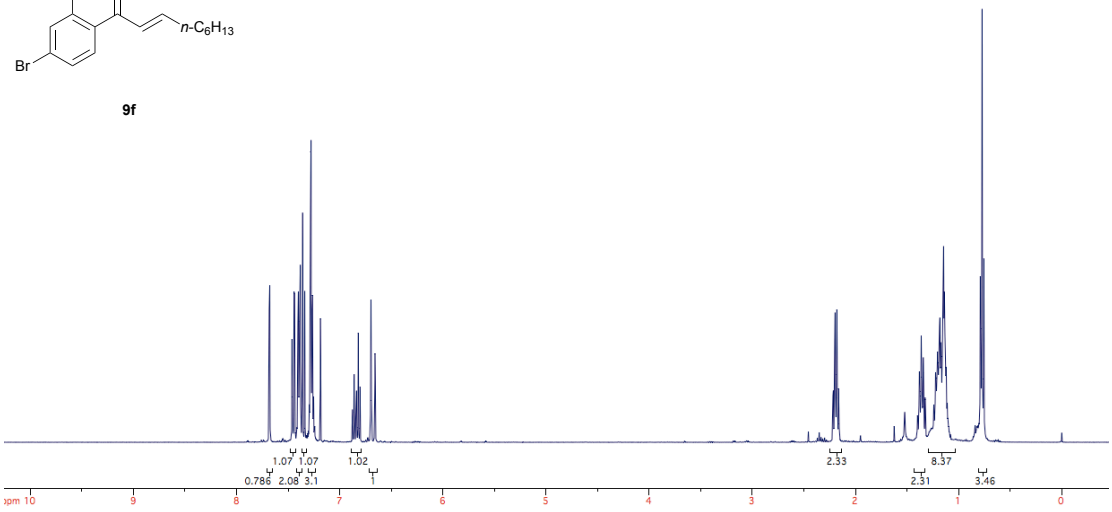
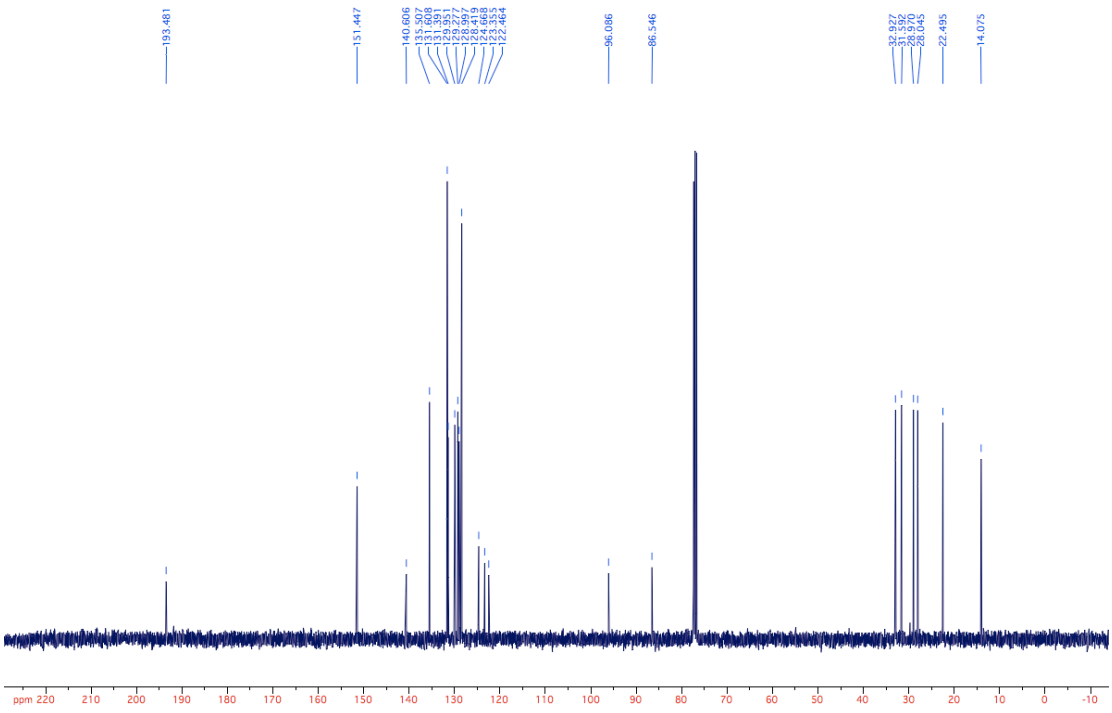
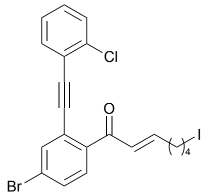
80
70
60
50
40
30
20
10
0


O
n-C6H13
Br

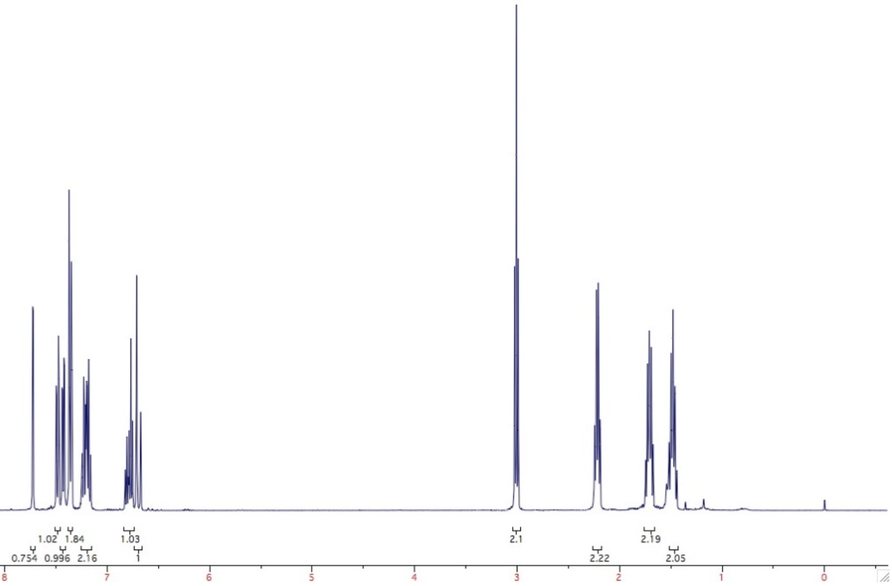
9f


1.07
1.07
1.02
0.786
2.08
3.1
1
2.33
8.37
2.31
3.46
ppm 10
9
8
7
6
5
4
3
2
1
0

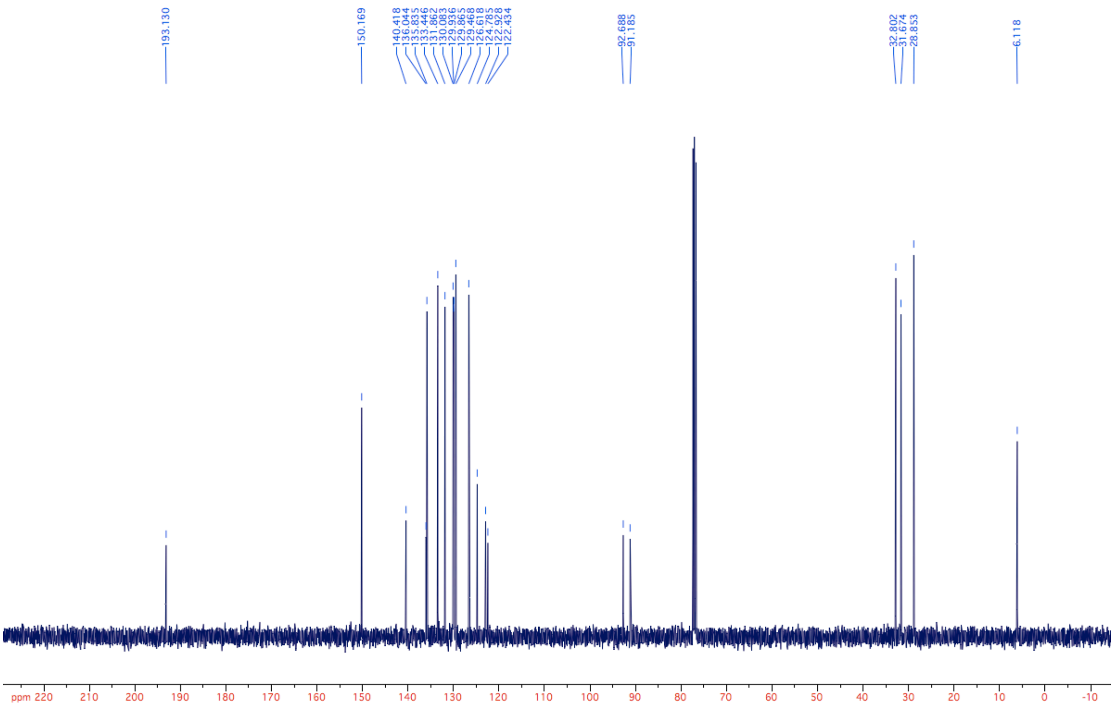

193.481
151.447
140.606
135.507
131.608
131.351
129.277
128.697
128.419
124.668
123.155
122.464
96.086
86.546
32.927
31.592
31.330
28.045
22.495
14.075
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



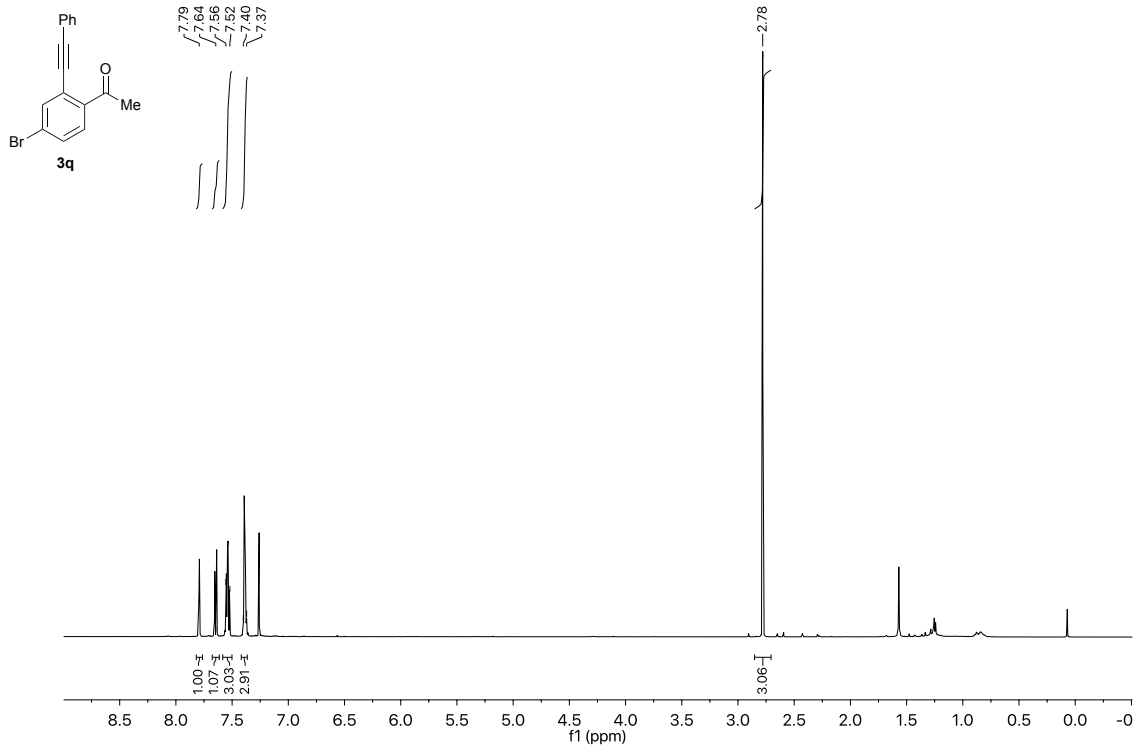
9g

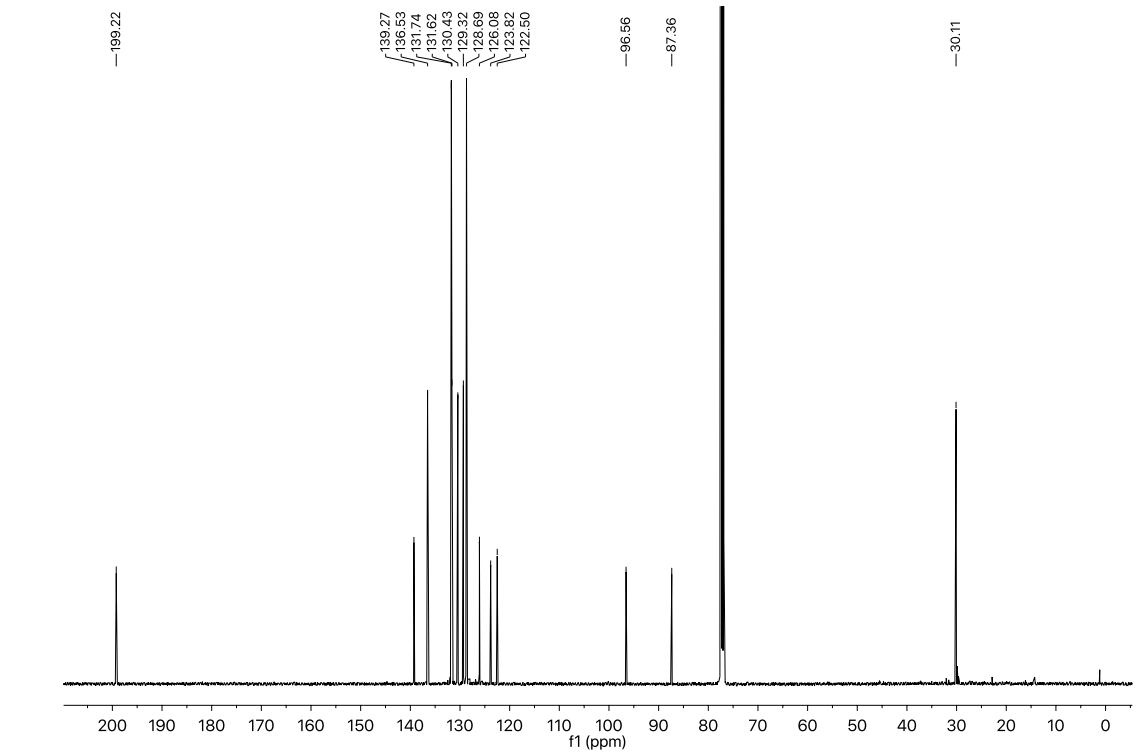


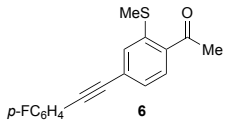
1.02
1.84
1.03
0.754
0.996
2.16
1
2.1
2.22
2.19
2.05



193.130
150.169
140.418
136.044
135.835
133.446
131.862
130.083
129.936
129.865
129.468
126.618
124.785
122.928
122.434
92.688
91.185
32.802
31.674
28.853
6.118

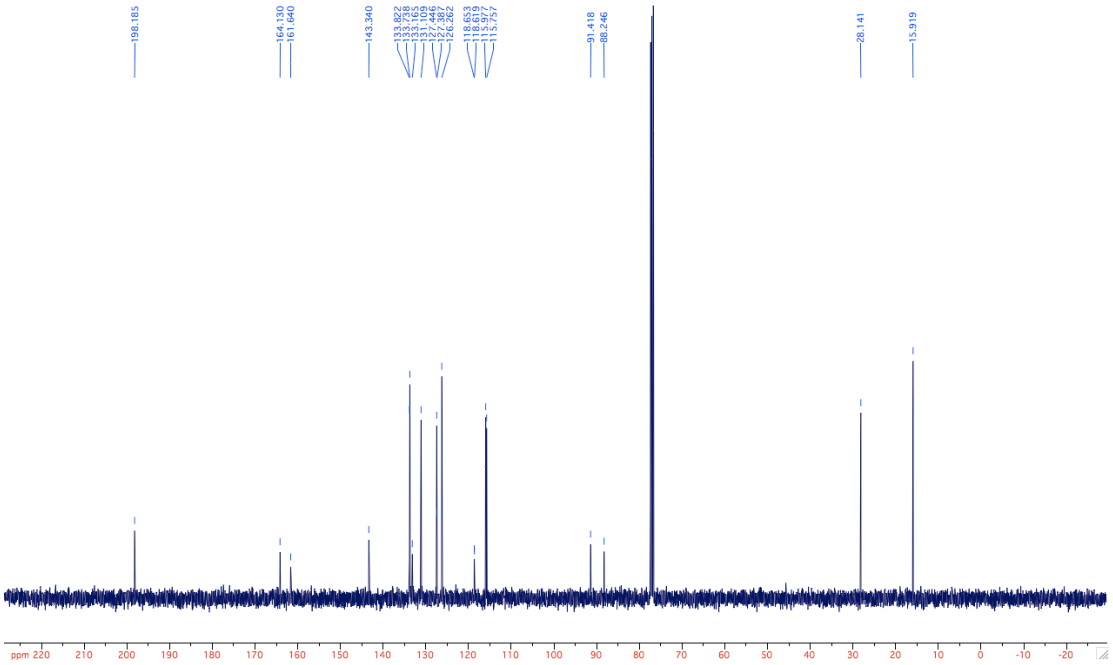

Ph
O
Me
Br
3q
7.79
7.64
7.56
7.52
7.40
7.37
2.78
1.00
1.07
3.03
2.91
3.06
f1 (ppm)

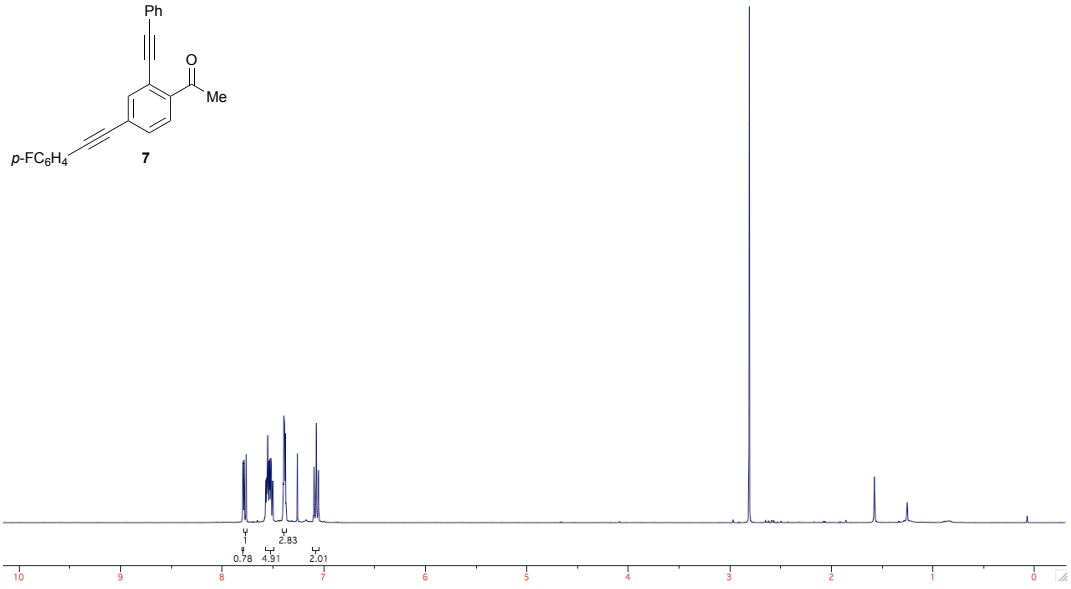

199.22
139.27
136.53
131.74
131.62
130.43
129.32
128.69
126.08
123.82
122.50
96.56
87.36
30.11
f1 (ppm)

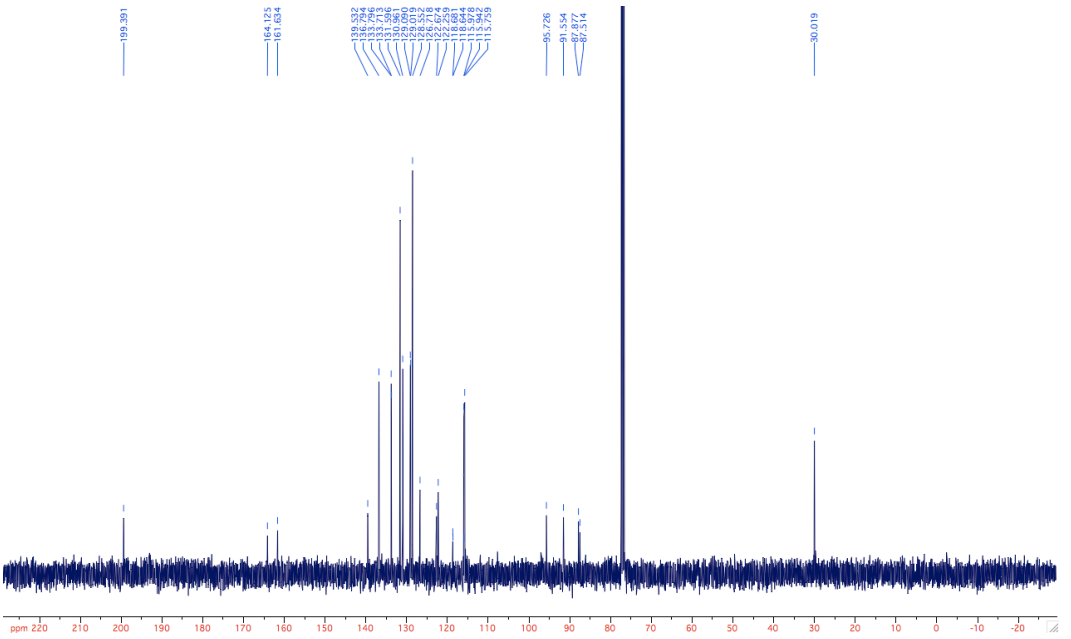

MeS
O
Me
p-FC6H4

6

1.93
0.964
0.901
1.95
3.01
3.08
ppm 10
9
8
7
6
5
4
3
2
1


198.185
164.130
161.640
143.340
133.822
133.788
133.165
132.448
132.419
127.387
126.282
116.653
116.619
115.977
115.757
91.418
88.246
28.141
15.919
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20


Ph
O
Me
p-FC6H4
7
0.78
4.91
2.83
2.01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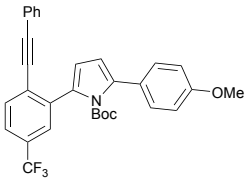
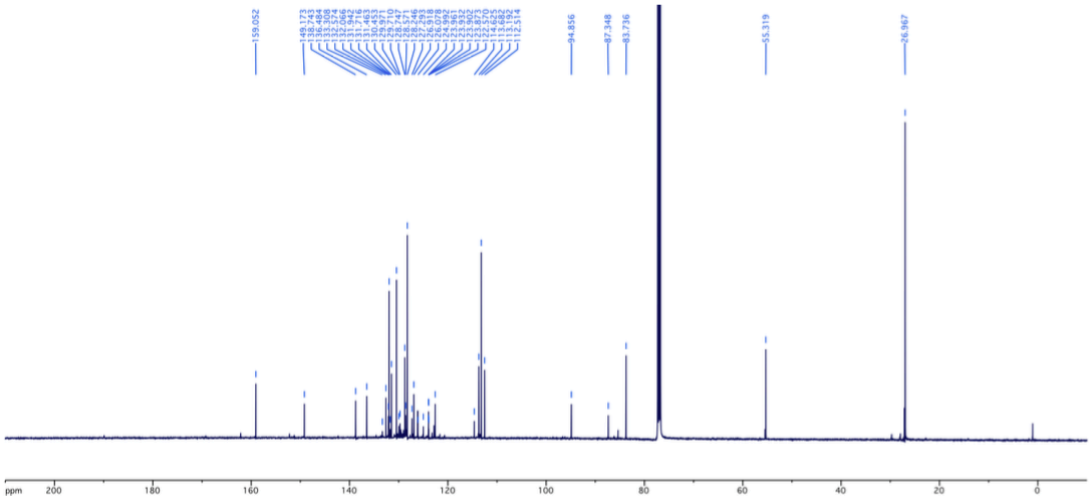
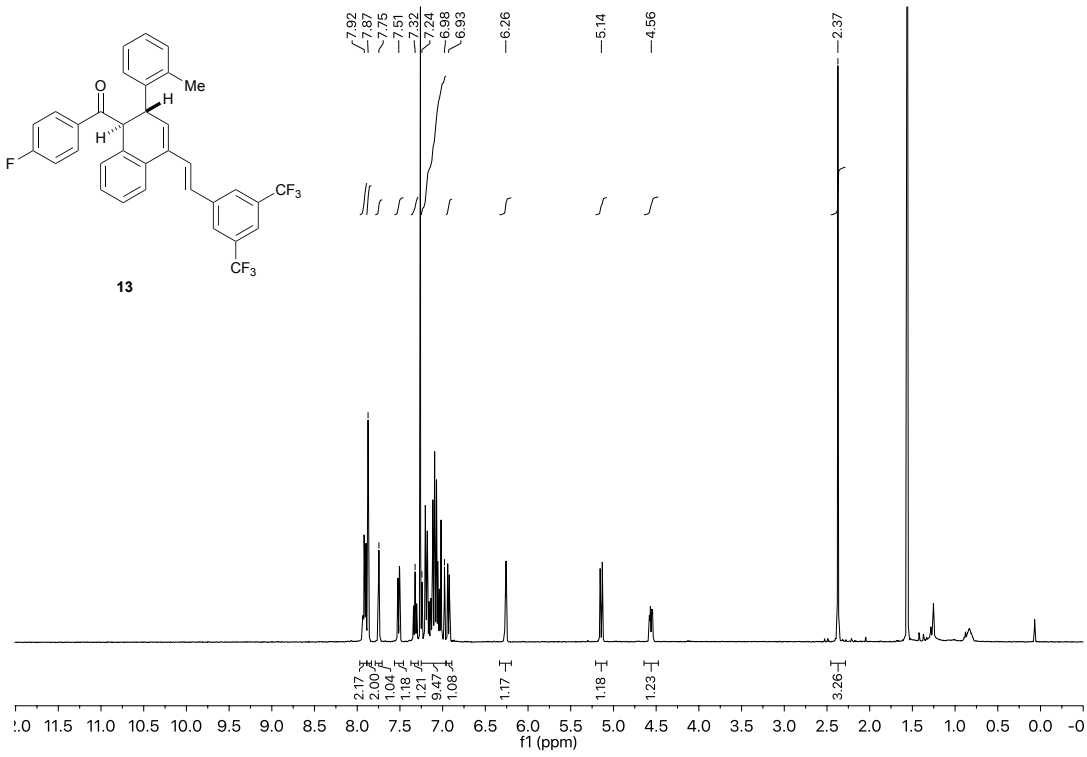
164.125
161.634
95.726
91.534
87.877
87.514
30.019

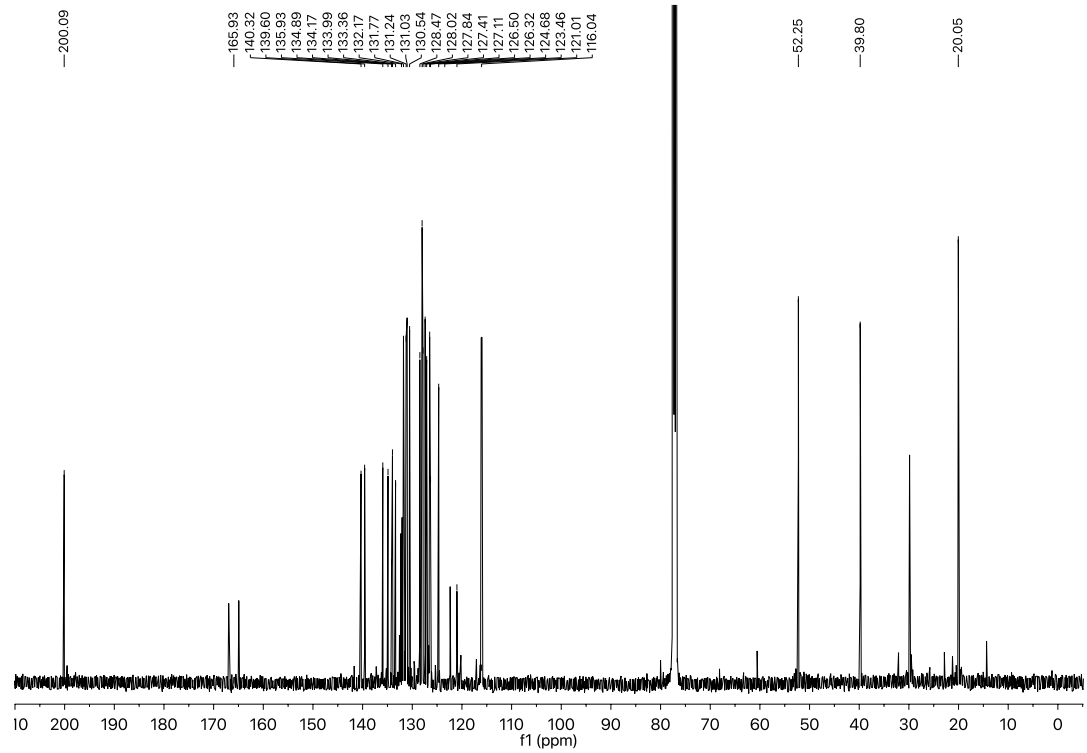

Ph
N
Boc
OMe
CF3

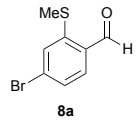
11

1.07
0.967
1.15
2.21
5.1
2.09
0.929
0.902
3
9.09
ppm


159.052
149.173
94.856
87.348
83.736
55.319
26.967
ppm

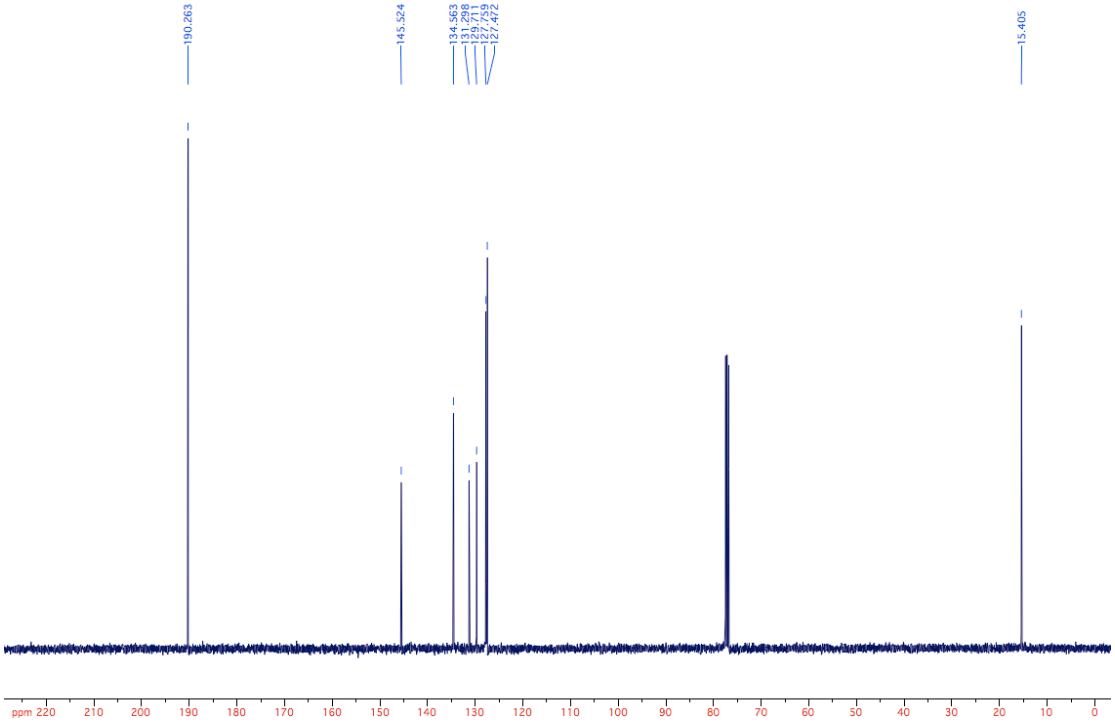

7.92
7.87
7.75
7.51
7.32
7.24
6.98
6.93
6.26
5.14
4.56
2.37
Me
H
O
H
F
CF3
CF3
13
2.17
2.00
1.04
1.18
1.21
9.47
1.08
1.17
1.18
1.23
3.26
f1 (ppm)

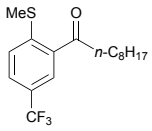

200.09
165.93
140.32
139.60
135.93
134.89
134.17
133.99
133.36
132.17
131.77
131.24
131.03
130.54
128.47
128.02
127.84
127.41
127.11
126.50
126.32
124.68
123.46
121.01
116.04
52.25
39.80
20.05
f1 (ppm)


MeS
O
H
Br

8a

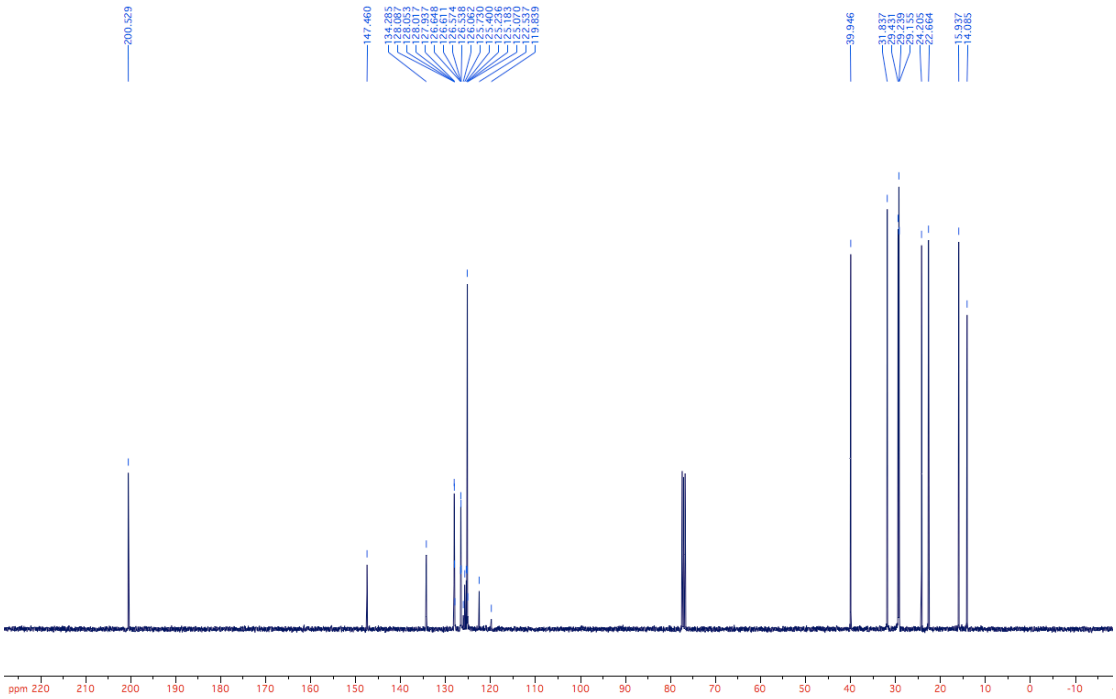
1.06
2.01
3.41
12
11
10
9
8
7
6
5
4
3
2
1
0


190.263
145.524
134.563
131.298
130.711
127.759
127.472
15.405
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeS
O
n-C8H17
CF3

1m

0.979
0.951
1
2.02
3
2.04
10.1
2.93
ppm 10
9
8
7
6
5
4
3
2
1
0


200.529
147.460
134.285
128.087
128.053
128.017
127.937
127.848
126.611
126.574
126.538
126.062
125.450
125.449
125.236
125.103
125.070
122.537
119.839
39.946
31.837
29.431
29.239
29.155
24.205
22.664
15.937
14.085
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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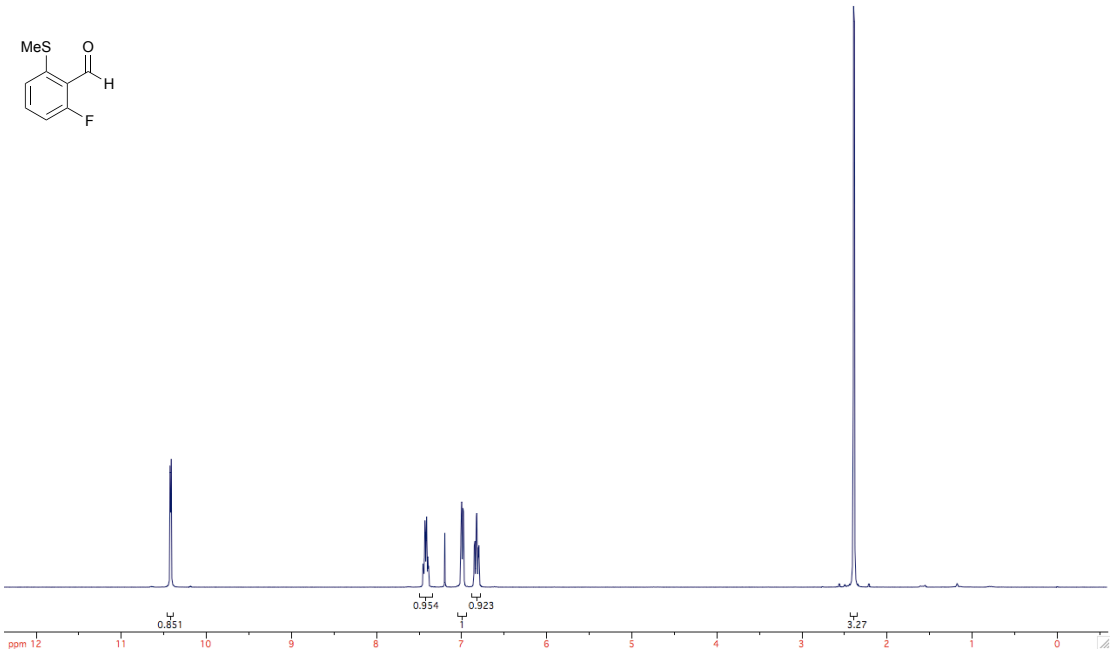
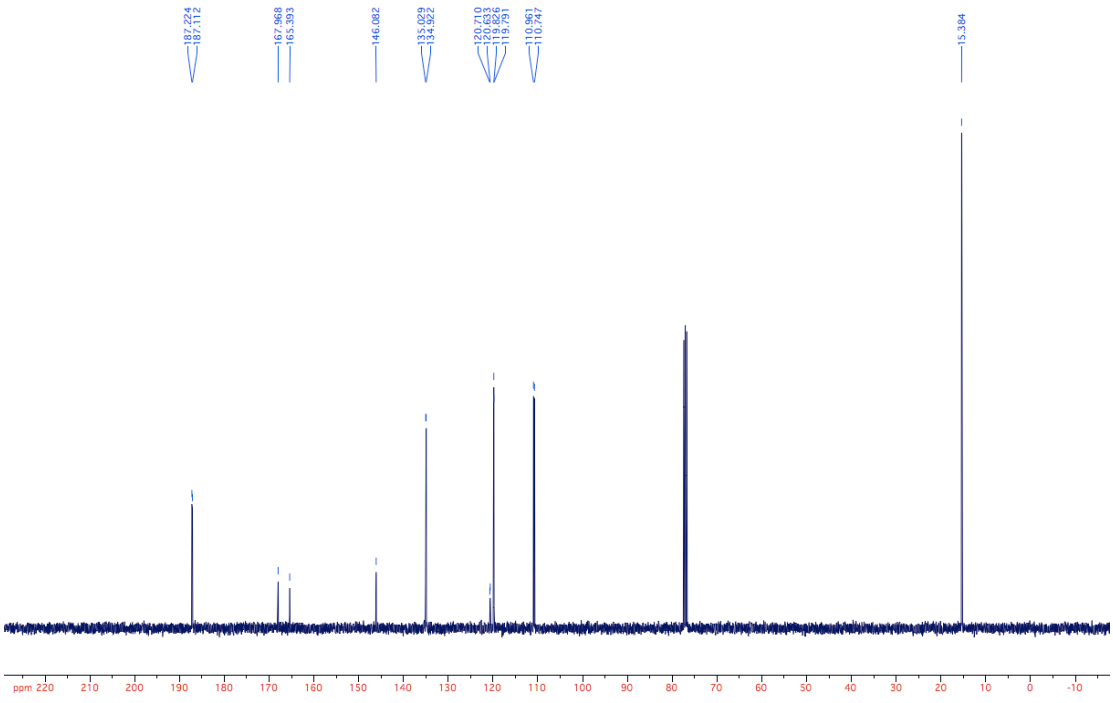
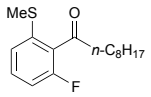
50
40
30
20
10
0
-10

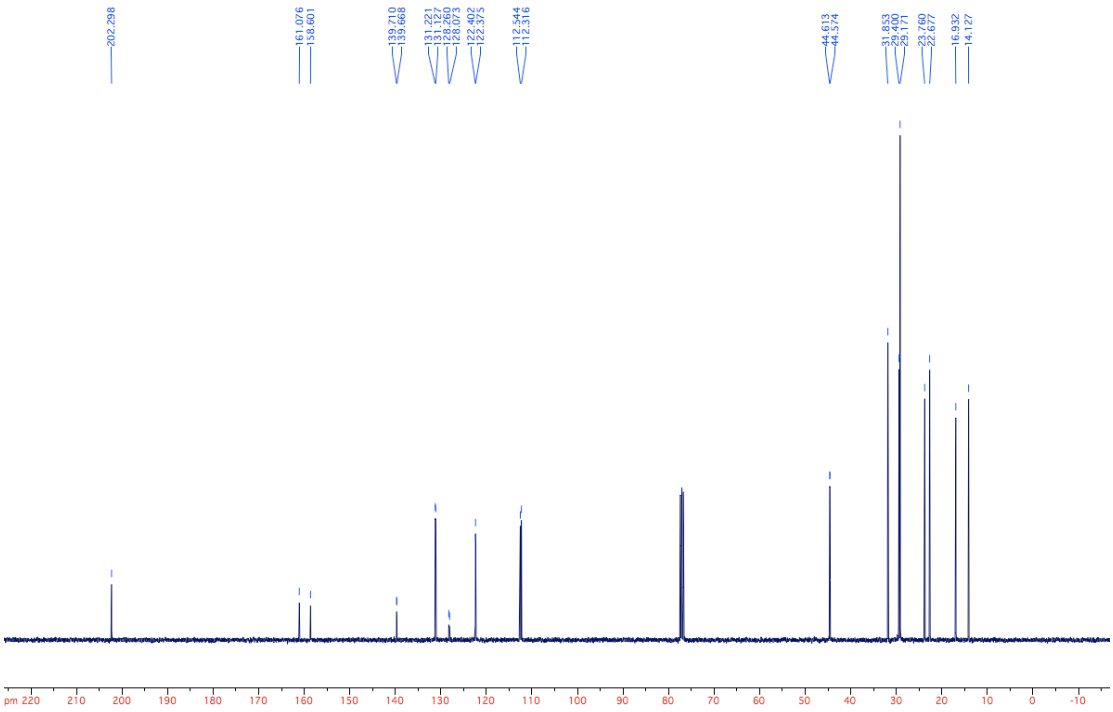

MeS
O
H
F
0.851
0.954
0.923
3.27
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0

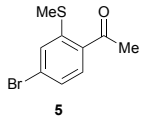

187.224
187.112
167.968
165.393
146.082
135.029
134.922
120.710
120.633
118.826
118.791
110.961
110.747
15.384
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


MeS
O
n-C8H17
F

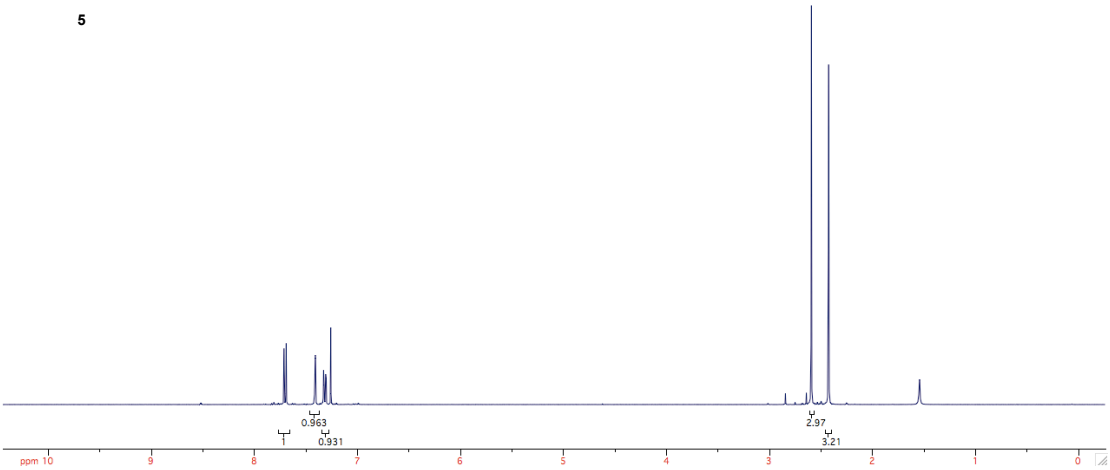
1n

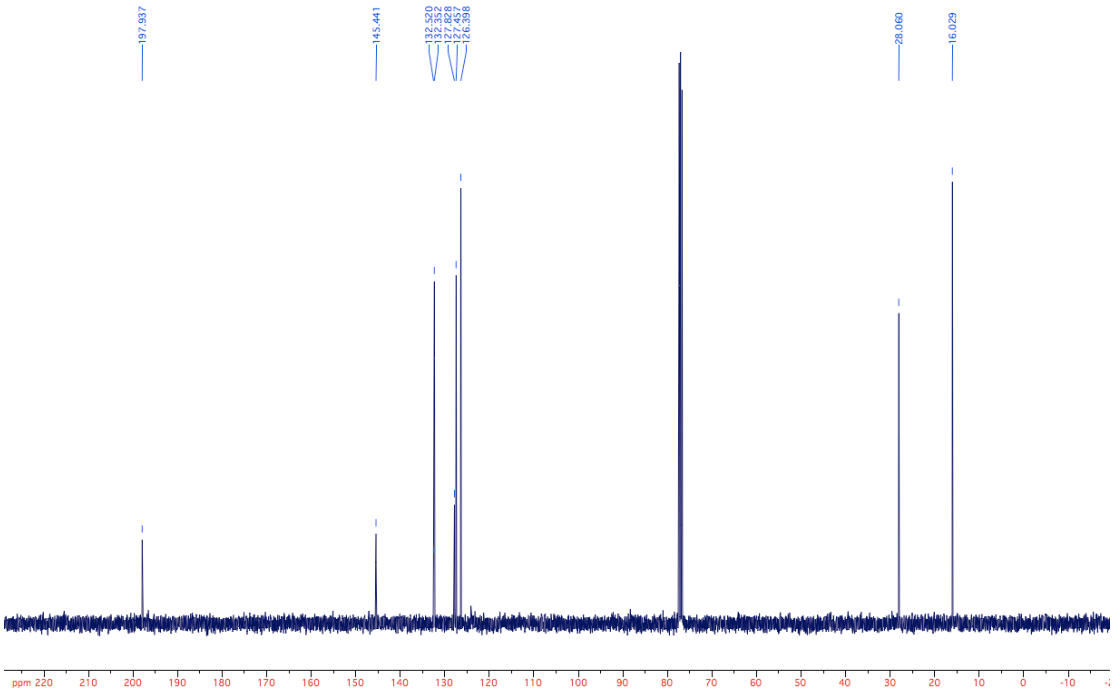
1.01
1.03
2.24
3.26
2.21
10.9
2.91
ppm 10
9
8
7
6
5
4
3
2
1
0

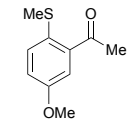

202.298
161.076
158.601
139.710
139.668
131.221
131.157
131.060
128.073
122.402
122.375
112.544
112.316
44.613
44.574
31.853
29.400
29.260
29.171
23.760
22.677
16.932
14.127
pm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


MeS
O
Me
Br

5

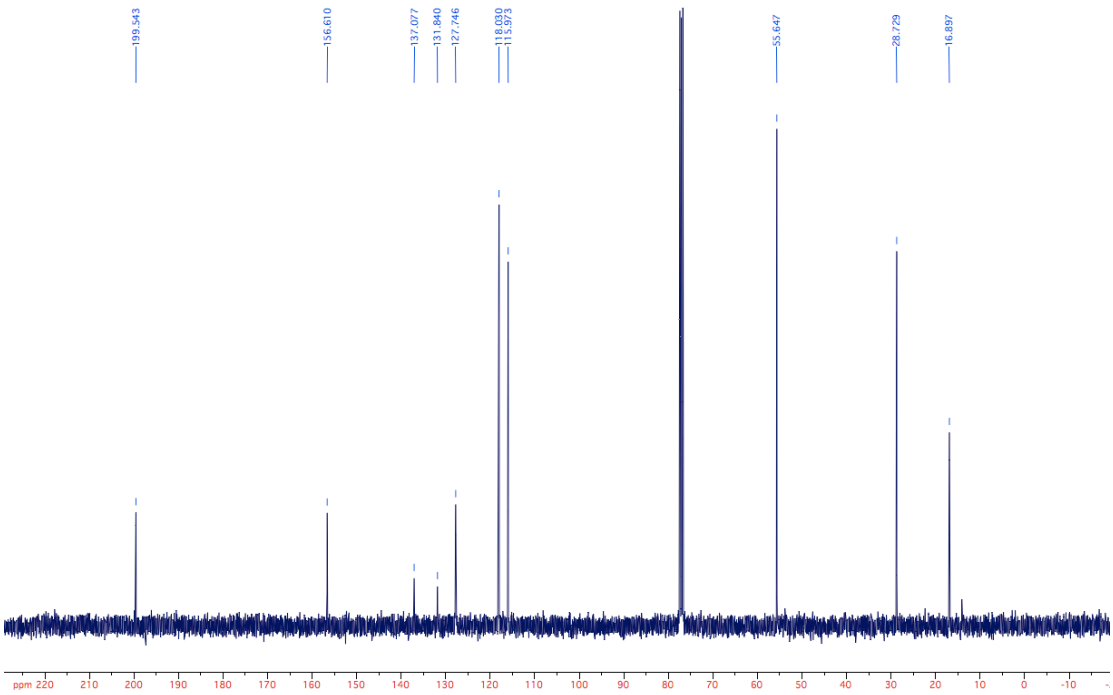

0.963
0.931
2.97
3.21
ppm 10
9
8
7
6
5
4
3
2
1
0


197.937
145.441
132.520
132.352
132.268
127.457
126.398
28.060
16.029
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


MeS
O
Me
OMe

1k

2.1
1
3.17
3.06
3.2
ppm 10
9
8
7
6
5
4
3
2
1
0


199.543
156.610
137.077
131.840
127.746
118.030
115.973
55.647
28.729
16.897
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10