Activating Group Recycling in Action: A Rhodium-Catalysed Carbothiolation Route to Substituted Isoquinolines**

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Contents

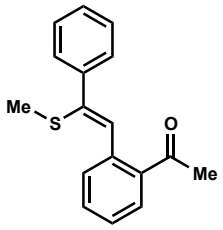
General Considerations

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 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 microTO (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.

Preparation of carbothiolated products

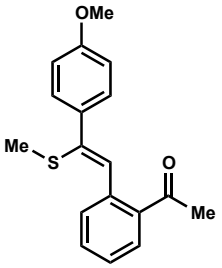
(*Z*)-1-(2-(2-(Methylthio)-2-phenylvinyl)phenyl)ethanone, 6: Entry **5**



$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xanpthos (4.3 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. To this solution was added 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and phenylacetylene (33 µL, 0.30 mmol). The reaction mixture was heated to 80 °C for 24 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the product (39 mg, 99%) as a yellow oil; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.70-7.68 (m, 2H), 7.55-7.45 (m, 2H), 7.43-7.41 (m, 4H), 7.18 (s, 1H), 2.65 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.1, 139.5, 138.6, 137.2, 136.9, 131.5, 131.2, 131.0, 129.1, 128.46 (2C), 128.40, 127.8, 29.0, 16.1; ν_{max} (film)/cm^{-1} 1726, 1656, 1420, 1361, 1245, 780, 700; MS (ESI$^+$) *m/z* (rel intensity) 291 [100, $(M+Na)^+$].

Data consistent with the literature.[1]

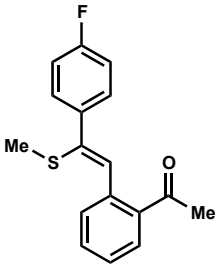
(*Z*)-1-(2-(2-(4-Methoxyphenyl)-2-(methylthio)vinyl)phenyl)ethanone, 6: Entry **6**



$[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol) and Xanpthos (8.8 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. To this solution was added 1-(2-(methylthio)phenyl)ethanone (50 mg, 0.30 mmol) and 1-ethynyl-4-methoxybenzene (78 µL, 0.60 mmol). The reaction mixture was heated to 80 °C for 24 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the product (89 mg, 99%) as a yellow oil; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.65-7.58 (m, 2H), 7.55-7.50 (m, 2H), 7.39 (ddd, *J* = 9.0, 6.5, 2.0 Hz, 2H), 7.2 (s, 1H), 6.98 (ddd, *J* = 9.5, 5.0, 3.0 Hz, 1H), 3.90 (s, 3H), 2.60 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 201.0, 158.9, 139.7, 137.6, 137.2, 132.4, 131.5, 131.2, 131.0, 129.4, 129.0, 127.4, 113.8, 55.3, 29.5, 16.9; ν_{max} (film)/cm^{-1} 1725, 1613, 1509, 1311, 1099, 1032, 790, 763; MS (ESI$^+$) *m/z* (rel intensity) 321 [100, $(M+Na)^+$].

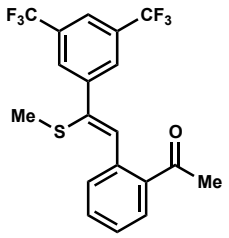
Data consistent with the literature.[1]

(*Z*)-1-(2-(2-(4-Fluorophenyl)-2-(methylthio)vinyl)phenyl)ethanone, 6: Entry **7**



$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xanpthos (4.3 mg, 0.0075 mmol) were dissolved in chlorobenzene (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. To this solution was added 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 1-ethynyl-4-fluorobenzene (59 µL, 0.30 mmol). The reaction mixture was heated to 80 °C for 24 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the product (41 mg, 99%) as a yellow oil; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 2H), 7.54 (d, *J* = 5.0 Hz, 2H), 7.42-7.37 (m, 1H), 7.15 (s, 1H), 7.10 (tt, *J* = 9.0 Hz, 2H), 2.61 (s, 3H,), 1.88 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 200.9, 162.7(d, *J* = 247.5 Hz, CF), 137.4, 137.1, 136.1, 131.6, 131.5, 131.4, 130.2, 130.1, 129.4, 127.4, 115.5 (d, *J* = 21 Hz), 29.3, 16.4; ν_{max} (film)/cm^{-1} 2923, 1763, 1681, 1597, 1503, 1503, 1434, 1355, 1245, 1157, 955, 832, 759; MS (ESI$^+$) *m/z* (rel intensity) 309 [100, $(M+Na)^+$]; HRMS (ESI$^+$) 309.0725 ($(M+Na)^+$, $C_{17}H_{15}FOSNa$ requires 309.0720).

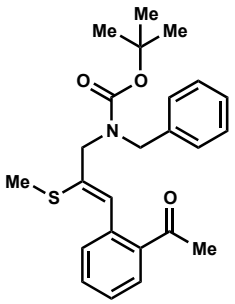
(*Z*)-1-(2-(2-(3,5-Bis(trifluoromethyl)phenyl)-2-(methylthio)vinyl)phenyl)ethanone, 6: Entry **8**



$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xanpthos (4.3 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. To this solution was added 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (35 µL, 0.30 mmol). The reaction mixture was heated to 80 °C for 24 h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the product (48 mg, 80%) as a yellow oil; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15 (s, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.65-7.55 (m, 2H), 7.48-7.44 (m, 1H), 7.40 (m, 1H), 2.67 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): 200.1, 142.7, 136.8, 135.5, 135.0, 134.5, 133.2 (q, *J* = 35.5 Hz), 131.7, 128.9, 128.2, 125.1 (q, *J* = 269.0 Hz, CF_3), 122.9 (q, *J* = 4.0 Hz), 28.9, 16.4; ν_{max} (film)/cm^{-1} 1691, 1281, 1264, 1156, 1098, 889; MS (ESI$^+$) *m/z* (rel intensity) 427 [70, $(M+Na)^+$], 684 [100].

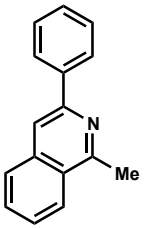
Data consistent with the literature.[1]

(*Z*)-*Tert*-butyl (3-(2-acetylphenyl)-2-(methylthio)allyl)(benzyl)carbamate, 6: Entry **9**



$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xanpthos (4.3 mg, 0.0075 mmol) were dissolved inDCE (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. To this solution was added 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and *tert*-butyl benzyl(prop-2-yn-1-yl)carbamate (74 mg, 0.30 mmol). The reaction mixture was heated to 80 °C for 24h, and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by flash chromatography (25% ether/petrol) to yield the product as a colourless oil (49 mg, 81%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.75 (d, *J* = 7.0 Hz, 1H), 7.51-7.28 (m, 8H), 6.89 (s, 1H), 4.63-4.54 (m, 2H), 4.22-4.07 (m, 2H), 2.75 (s, 3H), 2.20-2.05 (m, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 199.8, 155.7, 138.3, 137.4, 136.5, 133.6, 131.3, 130.8, 129.1, 128.6, 128.2, 127.7, 127.4, 127.2, 80.3, 50.1, 48.8, 29.3, 28.5, 14.9; ν_{max} (film)/cm^{-1} 2976, 2925, 1745, 1686, 1454, 1413, 1365, 1244, 1163, 1117, 955, 879, 757, 701; MS (ESI$^+$) *m/z* (rel intensity) 295 [100], 434 [30, $(M+Na)^+$]; HRMS (ESI$^+$) 434.1745 ($(M+Na)^+$, $C_{24}H_{29}NNaO_3S$ requires 434.1760).

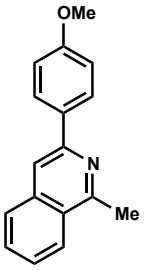
General Procedure A exemplified by the preparation of 1-Methyl-3-phenylisoquinoline, 7a



$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xantphos (4.3 mg, 0.0075 mmol) were dissolved in chlorobenzene (0.5 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 solution was then transferred to mixture of 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and phenylacetylene (33 µL, 0.30 mmol) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C, stirred for 1.5 h and then allowed to cool to room temperature. To the reaction mixture was added acetic acid (4 mL) and ammonium acetate (115 mg, 1.5 mmol). This was heated to 110 °C, stirred for 16 h and allowed to cool to room temperature. The solvent was removed *in vacuo* and the crude product purified by column chromatography (5% ether/petrol), to yield the product as a pale yellow oil (30 mg, 90%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15-8.12 (m, 3H), 7.93 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.67 (ap. td, *J* = 8.0, 1.0 Hz, 1H), 7.57 (ap.td, *J* = 8.5, 1.0 Hz, 1H), 7.51 (ap.t, *J* = 8.0, Hz, 2H), 7.40 (ap.t, *J* = 8.0, Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 158.8, 150.3, 140.1, 137.0, 130.3, 129.0, 128.6, 127.9, 127.2, 127.0, 126.8, 125.9, 115.5, 23.0; ν_{max} (film)/cm^{-1}158.7, 150.1, 140.0, 136.9, 130.1, 128.8, 128.4, 127.7, 127.1, 126.9, 126.7, 125.8, 115.4, 22.8; MS (ESI$^+$) *m/z* (rel intensity) 242 [100, $(M+H)^+$].

Data consistent with the literature.[2]

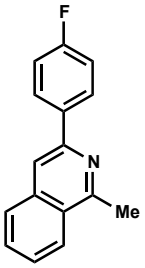
3-(4-Methoxyphenyl)-1-methylisoquinoline, 7b



Prepared following general procedure **A** using 1-ethynyl-4-methoxybenzene (39 µL, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a pale yellow solid (32 mg, 85%); M.p: 41-43 °C; ^{1}H NMR (200 MHz; $CDCl_3$): δ 8.15-8.06 (m, 3H), 7.87-7.78 (m, 2H), 7.65 (ap.ddd, *J* = 8.0, 7.0, 1.5 Hz, 1H), 7.53 (ap.ddd, *J* = 8.0, 7.0, 1.5 Hz, 1H), 7.10-6.99 (m, 2H), 3.88 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 160.1, 158.5, 149.9, 137.0, 132.6, 130.1, 128.3, 127.6, 126.52, 126.38, 125.8, 114.2 (2C), 55.5, 22.8; ν_{max} (film)/cm^{-1} 2970, 2360, 2341, 1739, 1670, 1568, 1514, 1439, 1365, 1248, 1174, 1033, 833, 731; MS (ESI$^+$) *m/z* (rel intensity) 250 [100, (M+H)$^+$], 251 [40]; HRMS (ESI$^+$) 250.1226 ((M+H)$^+$, $C_{17}H_{15}NO$ requires 250.1226).

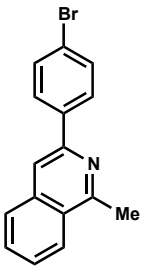
Data consistent with the literature.[3]

3-(4-Fluorophenyl)-1-methylisoquinoline, 7c



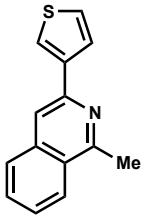
Prepared following general procedure **A** using 1-ethynyl-4-fluorobenzene (59 µL, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a pale pink solid (35 mg, 88%); M.p: 60-63 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.18-8.08 (m, 3H), 7.88-7.81 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 9.0 Hz), 3.03 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 163.3 (d, *J* = 247.5 Hz) 158.8, 149.1, 136.8, 130.3, 128.84, 128.76, 127.7, 127.0, 126.6, 125.8, 115.7 (d, *J* = 22.5 Hz), 115.0, 22.8; ν_{max} (film)/cm^{-1} 3016, 2970, 1739, 1569, 1510, 1441, 1366, 1217, 1156, 807; MS (ESI$^+$) *m/z* (rel intensity) 238 [100, (M+H)$^+$], 291 [45], 423 [50], 643 [40]; HRMS (ESI$^+$) 238.1031 ((M+H)$^+$, $C_{16}H_{12}FN$ requires 238.1027).

3-(4-Bromophenyl)-1-methylisoquinoline, 7d



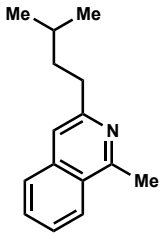
Prepared following general procedure **A** using 1-bromo-4-ethynylbenzene (54 mg, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a red solid (35 mg, 80%); M.p: 46-48 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (m, 3H), 3.03 (s, 1H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 158.9, 148.8, 138.8, 136.8, 131.9, 130.3, 128.6, 127.8, 127.2, 126.8, 125.8, 122.8, 115.2, 22.8; ν_{max} (film)/cm^{-1} 2361, 1621, 1592, 1568, 1498, 1444, 1390, 1331, 1070, 1009, 829, 749, 717; HRMS (FI^{+}) 297.0146 ((M)$^{+}$, $C_{16}H_{12}Br^{79}$ requires 297.0153).

1-Methyl-3-(thiophen-3-yl)isoquinoline, 7e



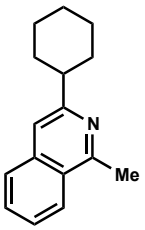
Prepared following general procedure **A** using 3-ethynylthiophene (53 µL, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a yellow oil (25 mg, 76%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.11 (dd, *J* = 8.5, 0.5 Hz, 1H), 8.08 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.73 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.66 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.42 (dd, *J* = 5.0, 3.0 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 158.4, 145.7, 141.8, 136.5, 130.0, 127.1, 126.4, 126.1, 125.9, 125.8, 125.4, 123.0, 114.4, 22.1; ν_{max} (film)/cm^{-1} 3016, 2360, 1760, 1716, 1368, 1229, 1216; MS (ESI$^+$) *m/z* (rel intensity) 144 [50], 226 [100, (M+H)$^+$], 513 [55]; *HRMS* (ESI$^+$) 226.0687 ((M+H)$^+$, $C_{14}H_{12}NS$ requires 226.0685).

3-Isopentyl-1-methylisoquinoline, 7f



Prepared following general procedure **A** using 5-methylhex-1-yne (37 µL, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a colorless oil (39 mg, 84%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.33 (s, 1H), 2.96 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 1.74-1.65 (m, 3H), 0.98 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 158.1, 155.0, 136.8, 129.9, 126.9, 126.1, 125.9, 125.7, 116.4, 39.2, 36.3, 28.1, 22.8, 22.6; ν_{max} (film)/cm^{-1} 3067, 2953, 2869, 2360, 2341, 1626, 1591, 1497, 1467, 1446, 1366, 1333, 747; MS (ESI$^+$) *m/z* (rel intensity) 214 [100, (M+H)$^+$]; HRMS (ESI$^+$) 214.1593 ((M+H)$^+$, $C_{15}H_{20}N$ requires 214.1590).

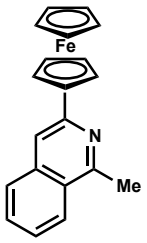
3-Cyclohexyl-1-methylisoquinoline, 7g



Prepared following general procedure **A** using ethynylcyclohexane (39 μL, 0.30 mmol). The crude product was purified by column chromatography (30% ether/petrol), to yield the product as an orange oil (28 mg, 82%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.32 (s, 1H), 2.95 (s, 3H), 2.82 (tt, *J* = 12.0, 4.0 Hz, 1H), 2.10 (d, *J* = 12.0 Hz, 2H), 1.89 (d, *J* = 12.0 Hz, 2H), 1.81-1.76 (m, 1H), 1.60-1.43 (m, 4H), 1.37-1.26 (m, 1H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 159.4, 158.0, 137.1, 129.9, 127.3, 126.4, 126.3, 125.8, 114.7, 46.4, 33.6, 27.1, 26.6, 22.7; ν_{max} (film)/cm^{-1} 2924, 2853, 2360, 2341, 1733, 1624, 1571, 1277, 748; MS (ESI$^+$) *m/z* (rel intensity) 226 [100, $(M+H)^+$]; HRMS (ESI$^+$) 226.1595 ($(M+H)^+$, $C_{16}H_{20}N$ requires 226.1590).

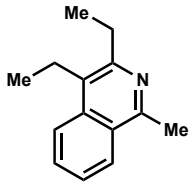
Data consistent with the literature.[4]

3-Ferrocenyl-1-methylisoquinoline, 7h



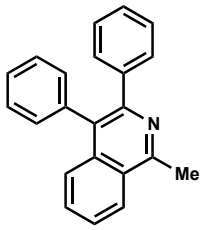
Prepared following general procedure **A** using ethynylferrocene (63 mg, 0.30 mmol). The crude product was purified by column chromatography (5% ether/petrol), to yield the product as a red solid (45 mg, 91%); M.p: 158-160 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (m, 2H), 7.51 (t, *J* = 8.5 Hz, 1H), 5.05 (s, 2H), 4.41 (s, 2H), 4.06 (s, 5H), 3.00 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 157.9, 136.6, 129.8, 126.9, 126.0, 125.8, 113.7, 69.6, 69.5, 67.3, 65.9, 22.7, 15.3; ν_{max} (film)/cm^{-1} 2970, 1744, 1567, 1367, 1229, 1216, 818; MS (ESI^{+}) *m/z* (rel intensity) 144 [40], 328 [100, $(M+H)^{+}$]; HRMS (ESI^{+}) 328.0775 ($(M+H)^{+}$, $C_{20}H_{18}FeN$ requires 328.0783).

3,4-Diethyl-1-methylisoquinoline, 7i



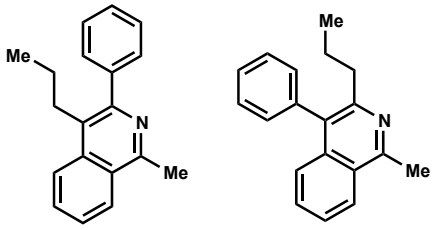
Prepared following general procedure **A** using $[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol), Xantphos (8.6 mg, 0.015 mmol) and hex-3-yne (34 µL, 0.30 mmol). The crude product was purified by column chromatography (15% ether/DCM), to yield the product as yellow oil (14 mg, 45%); ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.67 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H), 3.05 (q, *J* = 7.5 Hz, 2H), 2.97 (q, *J* = 7.5 Hz, 2H), 2.92 (s, 3H), 1.34 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 155.8, 152.5, 135.2, 129.5, 127.2, 126.2, 126.1, 125.3, 123.4, 28.5, 22.3, 20.7, 15.2, 14.9; ν_{max} (film)/cm^{-1} 2950, 1739, 1558, 1366, 1216, 770; HRMS (FI$^+$) 199.1358 ((M)$^+$, $C_{14}H_{17}N$ requires 199.1361).

1-Methyl-3,4-diphenylisoquinoline, 7j



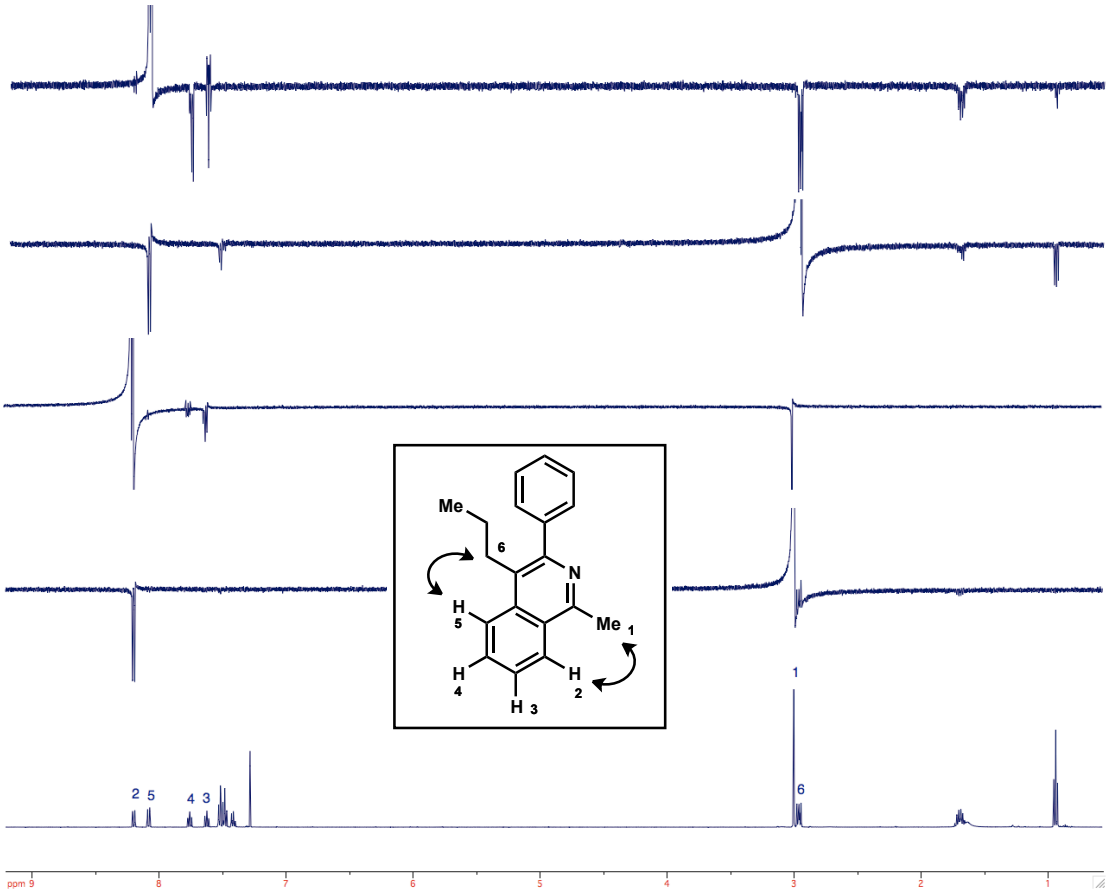
Prepared following general procedure **A** using $[Rh(nbd)_2].BF_4$ (5.6 mg, 0.015 mmol), Xantphos (8.6 mg, 0.015 mmol) and 1,2-diphenylethyne (53 mg, 0.30 mmol). The cyclisation was stirred for 72 h. The crude product was purified by column chromatography (5% ether/petrol), to yield the product as yellow oil (19 mg, 39%); ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.24-8.20 (m, 1H), 7.69-7.66 (m, 1H), 7.62-7.59 (m, 2H), 7.39-7.33 (m, 5H), 7.25-7.17 (m, 5H), 3.10 (s, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 157.7, 149.4, 140.9, 137.6, 136.0, 131.4, 130.3, 129.9, 129.2, 128.2, 127.6, 127.1, 126.9, 126.5, 126.2, 126.1, 125.5, 22.7; ν_{max} (film)/cm^{-1} 2971, 2362, 1739, 1366, 1216, 779; HRMS (FI$^+$) 295.1364 ((M)$^+$, $C_{14}H_{17}N$ requires 295.1361).

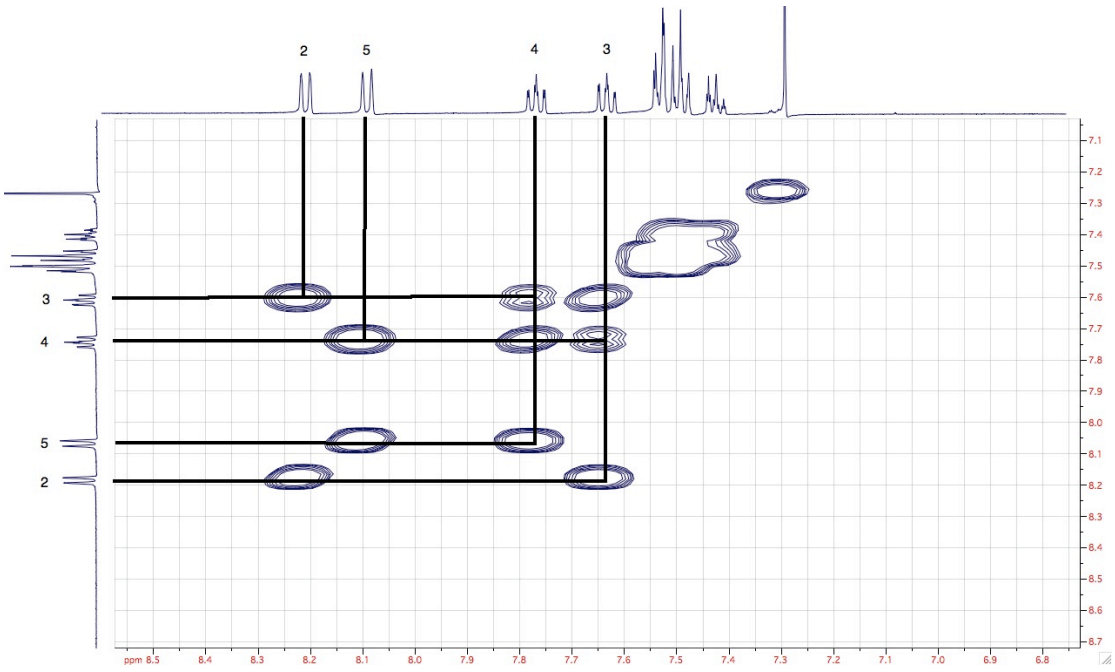
1-Methyl-3-phenyl-4-propylisoquinoline, 7k and 1-Methyl-4-phenyl-3-propylisoquinoline, 7k'



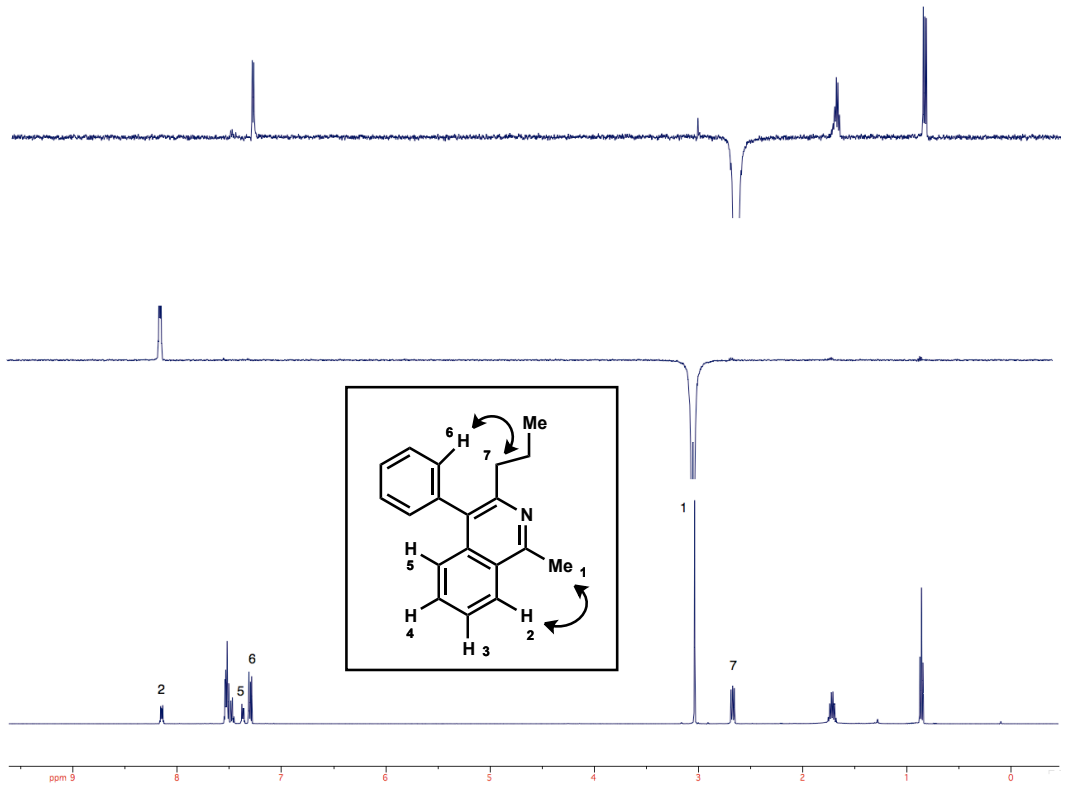
Prepared following general procedure **A** using 1-(2-(methylthio)phenyl)ethanone (50 mg, 0.30 mmol) $[Rh(nbd)_2].BF_4$ (11.2 mg, 0.030 mmol), Xantphos (17.2 mg, 0.030 mmol) and 1-Phenyl-1-pentyne (96 µL, 0.60 mmol). The cyclisation prepared using ammonium acetate (220 mg, 3.0 mmol) and acetic acid (4 mL), which was stirred for 72 h. The crude product was purified by column chromatography (1% acetone/petrol), to elute product **7k'** (12 mg, 15%) and regioisomer **7k** (35 mg, 45%). **7k**: M.p: 102-105 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.74 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H), 7.52-7.45 (m, 4H), 7.42-7.39 (m, 1H), 2.99 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.72-1.64 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl^3$): δ 155.8, 150.9, 141.8, 135.4, 129.8, 129.3, 128.1, 127.4, 127.3, 126.6, 126.3, 126.2, 124.3, 30.7, 24.6, 22.5, 14.4. ν_{max} (film)/cm^{-1}2961, 2160, 2013, 1561, 775, 699. *HRMS* (ESI$^+$) 262.1600 ((M+H)$^+$, $C_{19}H_{19}N$ requires 262.1590). **7k'**: ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.14-8.12 (m, 1H), 7.53-7.47 (m, 4H), 7.47-7.44 (m, 1H), 7.37-7.33 (m, 1H), 7.30-7.28 (m, 2H), 3.02 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.74-1.66 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 157.4, 151.4, 137.9, 136.1, 130.5, 129.6, 129.1, 128.3, 127.3, 125.9, 125.7, 125.4, 125.4, 37.6, 23.7, 22.5, 14.2. ν_{max} (film)/cm^{-1} 2959, 1562, 758, 701. *HRMS* (ESI$^+$) 262.1593 ((M+H)$^+$, $C_{19}H_{19}N$ requires 262.1587).

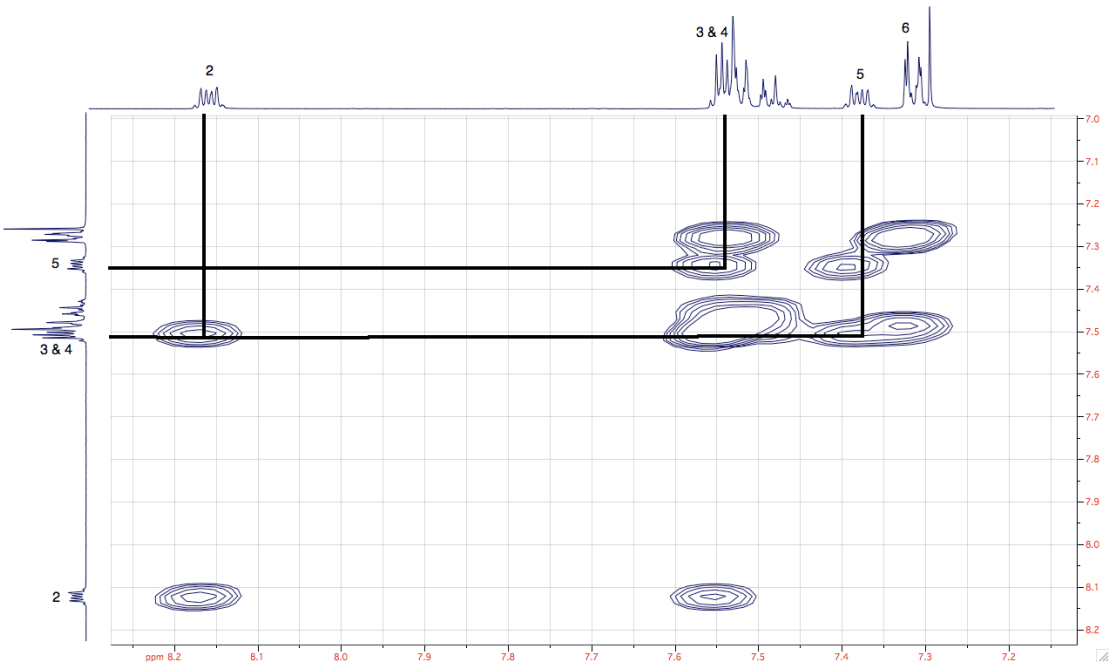
nOe and COSY of **7k**



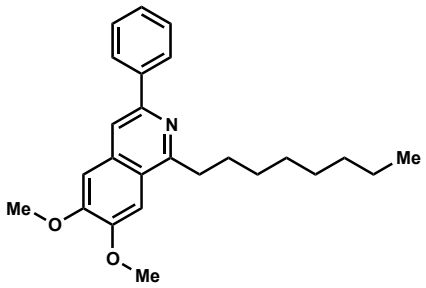


nOe and COSY of **7k'**



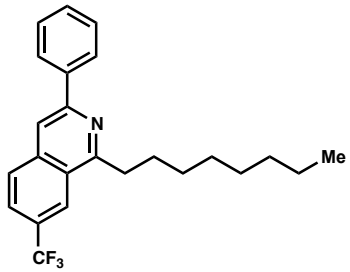


6,7-Dimethoxy-1-octyl-3-phenylisoquinoline, 7l



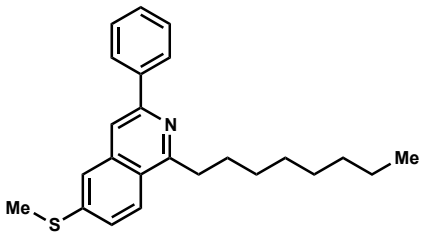
Prepared following general procedure **A** using 1-(4,5-dimethoxy-2-(methylthio)phenyl)nonan-1-one[5] (48 mg, 0.15 mmol). The crude product was purified by column chromatography (20-30% DCM/petrol), to yield the product as a pale yellow solid (45 mg, 79%); M.p: 67-70 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.14-8.11 (m, 2H), 7.79 (s, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.37 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.35 (s, 1H), 7.11 (s, 1H), 4.05 (s, 3H), 4.04 (s, 3H), 3.27 (t, *J* = 8.0 Hz, 2H), 1.97 (ap. quin, *J* = 7.5, 2H) 1.54-1.48 (m, 2H), 1.47-1.39 (m, 2H), 1.38-1.26 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 159.6, 152.5, 149.8, 149.1, 140.4, 133.9, 128.7, 128.1, 126.9, 121.8, 114.2, 105.9, 103.8, 56.1, 56.1, 35.5, 32.1, 30.0, 29.7, 29.5, 29.1, 22.8, 14.3; ν_{max} (film)/cm^{-1} 3004, 2953, 2926, 2853, 1738, 1728, 1573, 1507, 1467, 1425, 1368, 1245, 1217, 1162; MS (ESI$^+$) *m/z* (rel intensity) 378 [55, $(M+H)^+$], 817 [100]; HRMS (ESI$^+$) 378.2418 ($(M+H)^+$, $C_{25}H_{32}NO_2$ requires 378.2428).

1-Octyl-3-phenyl-7-(trifluoromethyl)isoquinoline, 7m



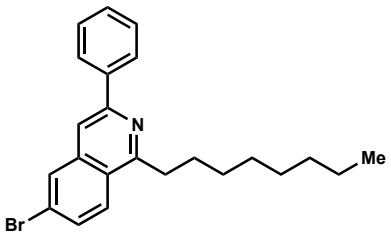
Prepared following general procedure **A** using 1-(2-(methylthio)-5-(trifluoromethyl)phenyl)nonan-1-one[1] (50 mg, 0.15 mmol). The crude product was purified by column chromatography (20-30% DCM/petrol), to yield the product as a pale yellow oil (29 mg, 50%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.45 (s, 1H), 8.20-8.18 (m, 2H), 8.00-7.90 (m, 2H), 7.84-7.82 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.50-7.40 (m, 1H), 3.42 (t, *J* = 7.4 Hz, 2H), 1.98 (ap. quin, *J* = 7.5 Hz, 2H), 1.55-1.51 (m, 2H), 1.44-1.30 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 163.1, 151.8, 139.2, 138.6, 129.0, 128.9, 128.8, 128.3 (q, *J* = 32.4), 127.1, 126,0 (q, *J* = 222.1), 125.4 (q, *J* = 2.9), 123.3 (q, *J* = 4.5), 114.4, 35.2, 31.9, 29.7, 29.5, 29.3, 29.2, 22.7 14.1; ν_{max} (film)/cm^{-1} 2926, 2855, 1633, 1573, 1326, 1290, 1126, 885, 691.4; *m/z* (rel intensity) 386 [55, $(M+H)^+$]; HRMS (ESI^+) 386.2082 ($(M+H)^+$, $C_{24}H_{27}F_3N$ requires 386.2090).

6-(Methylthio)-1-octyl-3-phenylisoquinoline, 7n



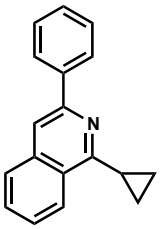
Prepared following general procedure **A** using 1-(2,4-bis(methylthio)phenyl)nonan-1-one[5] (57 mg, 0.18 mmol). The crude product was purified by column chromatography (20-30% DCM/petrol), to yield the product as a yellow oil (57 mg, 88%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.17-8.15 (m, 2H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.80 (s, 1H), 7.52-7.49 (m, 3H), 7.43-7.38 (m, 2H), 3.31 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 1.95 (ap. quin, *J* = 8.0 Hz, 2H) 1.54-1.47 (m, 2H), 1.44-1.25 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 162.0, 150.7, 141.7, 140.0, 137.8, 128.8, 128.4, 127.1, 125.8, 125.6, 123.8, 114.0, 35.5, 32.0, 30.0, 29.7, 29.6, 29.5, 22.8, 15.1, 14.3; ν_{max} (film)/cm^{-1} 3016, 1739, 1367, 1229, 1216, 1207; HRMS (FI^{+}) 363.2021 ((M)$^{+}$, $C_{24}H_{29}SN$ requires 363.2018).

6-Bromo-1-octyl-3-phenylisoquinoline, 7o



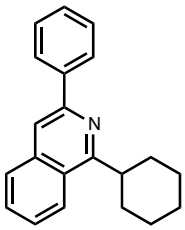
Prepared following general procedure **A** using 1-(4-bromo-2-(methylthio)phenyl)nonan-1-one (50 mg, 0.15 mmol). The crude product was purified by column chromatography (20% DCM/petrol), to yield the product as a pale yellow solid (45 mg, 76%); M.p: 39-40 °C; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.16-8.13 (m, 2H), 8.02-7.99 (m, 2H), 7.80 (s, 1H), 7.61 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.42 (tt, *J* = 7.5, 1.5 Hz, 1H), 3.32 (t, *J* = 8.0 Hz, 2H), 1.93 (ap. quin, *J* = 8.0 Hz, 2H), 1.53-1.26 (m, 10H), 0.89 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 162.4, 151.0, 139.6, 138.5, 130.2, 129.9, 128.9, 128.8, 127.2, 127.2, 124.6, 113.9, 35.5, 32.1, 29.9, 29.7, 29.5, 29.5, 22.8, 14.3; ν_{max} (film)/cm^{-1} 3063, 2924, 2853, 1610, 1563, 1452, 1402, 1380, 1261, 1071, 1029, 887, 821, 803, 766, 691, 678; MS (ESI$^+$) *m/z* (rel intensity) 144 [90], 237 [100] 396 [55, $(M+H)^+$]; HRMS (ESI$^+$) 396.1308 ($(M+H)^+$, $C_{23}H_{27}Br^{79}N$ requires 396.1321).

1-Cyclopropyl-3-phenylisoquinoline, 7p



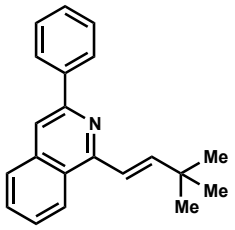
Prepared following general procedure **A** using cyclopropyl(2-(methylthio)phenyl)methanone (26 mg, 0.14 mmol). The crude product was purified by column chromatography (2.5% DCM/petrol), to yield the product as a pale yellow solid (16 mg, 47%); M.p: 35-37 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.41 (d, *J* = 8.5 Hz, 1H), 8.18-8.16 (m, 2H), 7.89 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.58 (ddd, *J* = 8.5, 7.0, 2.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 1H), 2.85-2.77 (m, 1H), 1.43 (ap. dq, *J* = 3.0, 4.5, 2H), 1.14 (ap. dq, *J* = 8.0, 3.0, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 153.5, 149.3, 139.9, 137.1, 129.9, 128.7, 128.4, 127.9, 126.92, 126.88, 126.76, 125.1, 114.0, 13.6, 10.0; ν_{max} (film)/cm^{-1} 3058, 3005, 2924, 2852, 1620, 1565, 1499, 1412, 1359, 1029, 693; HRMS (FI^{+}) 245.1199 ((M)$^{+}$, $C_{18}H_{15}N$ requires 245.1205).

1-Cyclohexyl-3-phenylisoquinoline, 7q



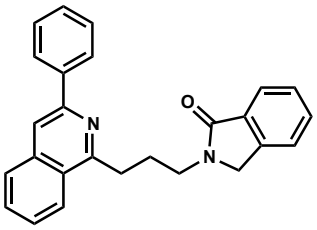
Prepared following general procedure **A** using cyclohexyl(2-(methylthio)phenyl)methanone (20 mg, 0.09 mmol). The crude product was purified by column chromatography (2.5% DCM/petrol), to yield the product as a pale yellow oil (16 mg, 60%); ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.25-8.20 (m, 3H), 7.92 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.63 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.39 (tt, *J* = 7.5, 1.5 Hz, 1H), 3.62-3.56 (m, 1H), 2.07-1.93 (m, 6H), 1.59-1.41 (m, 4H); ^{13}C NMR (126 MHz; $CDCl_3$): δ 165.2, 149.3, 140.0, 137.3, 129.5, 128.6, 128.2, 128.0, 126.8, 126.5, 125.3, 124.7, 114.3, 41.9, 32.6, 26.9, 26.3; ν_{max} (film)/cm^{-1} 3057, 2928, 2851, 2360, 1620, 1567, 1450, 770; HRMS (FI^{+}) 287.1675 ((M+H)$^{+}$, $C_{21}H_{21}N$ requires 287.1674).

(*E*)-1-(3,3-Dimethylbut-1-en-1-yl)-3-phenylisoquinoline, 7r



Prepared following general procedure **A** using *E*)-4,4-dimethyl-1-(2-(methylthio)phenyl)pent-2-en-1-one (52 mg, 0.22 mmol). The crude product was purified by column chromatography (5% DCM/petrol), to yield the product as a pale yellow solid (35 mg, 55%); M.p: 84-86 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.30 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.97 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.60-7.50 (m, 3H), 7.45-7.41 (m, 1H), 7.36 (d, *J* = 15.5 Hz, 1H), 7.28 (d, *J* = 15.5 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 155.1, 150.11, 150.00, 140.0, 137.8, 130.0, 128.8, 128.5, 127.8, 127.2, 126.8, 125.6, 124.9, 120.1, 115.4, 34.2, 29.7; ν_{max} (film)/cm^{-1} 2958, 2360, 1640, 1558, 1359, 1260, 972, 787, 692; HRMS (FI^{+}) 287.1674 ((M)$^{+}$, $C_{21}H_{21}N$ requires 287.1663).

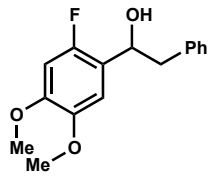
2-(3-(3-Phenylisoquinolin-1-yl)propyl)isoindolin-1-one, 7s



Prepared following general procedure **A** using 2-(4-(2-(methylthio)phenyl)-4-oxobutyl)isoindolin-1-one[1] (48 mg, 0.15 mmol). The crude product was purified by column chromatography (2.5-5% ether/DCM), to yield the product as white needles (40 mg, 71%); M.p: 116- 119 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.19-8.16 (m, 2H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.58-7.49 (m, 3H), 7.45-7.40 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.99 (td, *J* = 7.5, 1.5 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.95 (t, *J* = 7.5 Hz, 2H), 3.51-3.45 (m, 4H), 2.49 (quin, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 175.3, 160.0, 149.7, 144.8, 139.7, 137.1, 130.2, 128.8, 128.6, 128.0, 127.20, 127.16, 126.3, 125.0, 124.6, 124.4, 122.2, 115.5, 108.9, 40.1, 36.0, 31.7, 25.6; ν_{max} (film)/cm^{-1} 3057, 1706, 1615, 1490, 1357, 749, 696; MS (ESI$^+$) *m/z* (rel intensity) 379 [100, $(M+H)^+$], HRMS (ESI$^+$) 379.1794 ($(M+H)^+$, $C_{26}H_{23}N_2O$ requires 379.1805).

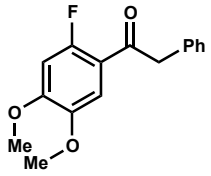
3-Pr-Moxaverine synthesis

1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanol



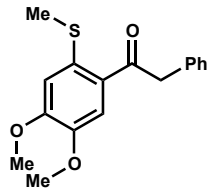
To a stirred solution of 6-Fluoroveratraldehyde (200 mg, 1.09 mmol) in THF (2 mL) was added benzyl magnesium chloride (1.2 mL, 2.1 mmol, 1.83M) dropwise at -78 °C. The mixture was stirred for 6 h and was allowed to warm room temperature. The reaction was quenched with sat. NH_4Cl solution (7 mL) and extracted with ether. The ethereal extract was dried ($MgSO_4$), filtered, solvent removed in *vacuo* and purified by flash chromatography (15% ether/petrol) to yield the alcohol as a pale yellow solid (210 mg, 70%); M.p: 98-100 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35-7.23 (m, 5H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 11.5 Hz, 1H), 5.21 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.10 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.96 (dd, *J* = 13.5, 8.5 Hz, 1H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 153.5 (d, J = 239.0 Hz, CF), 148.9 (d, *J* = 10.0 Hz, C-C-CF), 145.4, 137.8, 129.59, 128.52, 126.7, 121.3 (d, *J* = 15.0 Hz, C-CF), 109.2 (d, *J* = 6.0 Hz, C-C-CF), 99.8 (d, *J* = 28.5 Hz, C-CF), 68.7, 56.4, 56.2, 45.0; ν_{max} (film)/cm^{-1} 3503, 2937, 1625, 1509, 1452, 1406, 1212, 1191, 700; MS (ESI$^+$) *m/z* (rel intensity) 259 [100], 299 [100, $(M+Na)^+$]; HRMS (ESI$^+$) 299.1062 ($(M+Na)^+$, $C_{16}H_{17}FNaO_3$ requires 299.1054).

1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanone



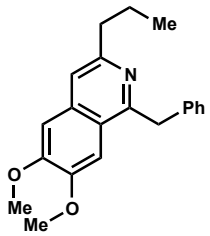
To a stirred solution of 1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanol (200 mg, 0.72 mmol) in DCM (10 mL) was added DMP (610 mg, 1.44 mmol) in one portion. The mixture was stirred for 25 mins at room temperature. The reaction was washed with sat. $Na_2S_2O_3$ and extracted with DCM. The DCM extract was washed once more with $NaHCO_3$ and the aqueous extracts were further washed with DCM. The combined organic layers were dried ($MgSO_4$), filtered, solvent removed *in vacuo* and purified by flash chromatography (25% ether/petrol) to yield the ketone as a white solid (193 mg, 98%); M.p: 109-111 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.29-7.28 (m, 3H), 6.64 (d, *J* = 12.5 Hz, 1H), 4.29 (d, *J* = 3.0 Hz, 2H), 3.95 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 194.5, 157.8 (d, J = 250.0 Hz, CF), 154.3 (d, *J* = 10.0 Hz, C-C-CF), 145.6, 134.5, 129.6, 128.5, 126.8, 116.4 (d, *J* = 14.4 Hz, C-CF), 111.1 (d, *J* = 3.7 Hz, C-C-CF), 100.0 (d, *J* = 30.0 Hz, C-CF), 56.47, 56.28, 49.6; ν_{max} (film)/cm^{-1} 1702, 1669, 1609, 1519, 1325, 1133, 1024, 843, 711; MS (ESI$^+$) *m/z* (rel intensity) 275 $(M+H)^+$ [100], 297 [50, $(M+Na)^+$]; HRMS (ESI$^+$) 297.0899 ($(M+Na)^+$, $C_{16}H_{15}FNaO_3$ requires 297.0897).

1-(4,5-Dimethoxy-2-(methylthio)phenyl)-2-phenylethanone, 9



To a stirred suspension of sodium thiomethoxide (48 g, 0.69 mmol) in DMF (5 mL) was added 1-(2-fluoro-4,5-dimethoxyphenyl)-2-phenylethanone (184 mg, 64 mmol) over 5 mins at -45 °C. After the addition was complete, the solution was stirred for a further 3 h at room temperature. The reaction was then quenched with water and extracted with DCM. The combined organic layers were dried ($MgSO_4$), filtered, solvent removed *in vacuo* and purified by flash chromatography (45% ether/petrol) to yield the sulfide as a thick yellow oil (180 mg, 95%); ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.26-7.12 (m, 6H), 6.69 (s, 1H), 4.16 (s, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 197.1, 152.4, 145.3, 136.7, 135.2, 129.3, 128.7, 126.8, 114.0, 108.5, 56.2, 56.0, 47.4, 16.6; ν_{max} (film)/cm^{-1} 1739, 1655, 1552, 1501, 1340, 1257, 1205, 1166; MS (ESI$^+$) *m/z* (rel intensity) 303 $(M+H)^+$ [100], 225 [30, $(M+Na)^+$]; HRMS (ESI$^+$) 325.0866 ($(M+Na)^+$, $C_{17}H_{18}NaO_3S$ requires 325.0869).

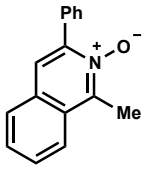
1-Benzyl-6,7-dimethoxy-3-propylisoquinoline – Moxaverine derivative, 10



Prepared following general procedure **A** using 1-(4,5-dimethoxy-2-(methylthio)phenyl)-2-phenylethanone(50 mg, 0.165 mmol) and 1-pentyne (162 µL, 1.65 mmol) at 80 °C. The crude product was purified by column chromatography (20-30% ether/petrol) to give a yellow oil (40 mg, 75%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.77 (s, 1H), 7.21-7.14 (m, 5H), 7.09-7.06 (m, 1H), 6.90 (s, 1H), 4.55 (s, 2H), 3.90 (s, 3H), 3.75 (s, 3H), 2.85 (t, *J* = 8.0 Hz, 2H), 1.76 (qt, *J* = 7.5, 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 175.6, 156.9, 152.78, 152.73, 149.4, 139.6, 134.5, 128.5, 126.2, 121.2, 116.9, 104.9, 104.4, 56.00, 55.83, 41.8, 39.3, 23.4, 13.9; ν_{max} (film)/cm^{-1} 2958, 2359, 1598, 1251, 1160; MS (ESI$^+$) *m/z* (rel intensity) 322 (M+H)$^+$ [100]; HRMS (ESI$^+$) 322.1804 ((M+H)$^+$, $C_{21}H_{24}NO_2$ requires 322.1802).

Use of alternative *N*-nucleophiles

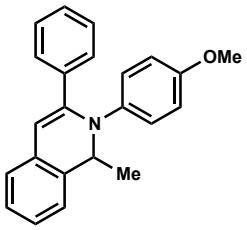
1-Methyl-3-phenylisoquinoline 2-oxide, 11



To a solution of (*Z*)-1-(2-(2-(methylthio)-2-phenylvinyl)phenyl)ethanone (29 mg, 0.26 mmol) in AcOH (2mL) was added hydroxylamine hydrochloride (118 mg, 1.7 mmol). The resulting mixture was heated to 110 °C for 16 h and allowed to cool to room temperature. The solvent was removed *in vacuo* and the crude product purified by column chromatography (5-30% ether/petrol) - (20-80% ethyl acetate/petrol), to yield the product as a pale colourless solid (15 mg, 41%); M.p: 142-145 °C, (lit m.p 143-144 °C); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.79-7.76 (m, 3H), 7.69 (s, 1H), 7.63 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.58 (t, *J* = 8.5, 1.5 Hz, 1H), 7.50-7.44 (m, 3H), 2.96 (s, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 146.9, 146.5, 133.8, 130.0, 129.2, 129.0, 128.8, 128.47, 128.41, 128.2, 127.5, 124.1, 122.8, 13.8; ν_{max} (film)/cm^{-1} 3382, 3057, 2925, 2360, 2341, 1500, 1353, 1333, 1290, 1203, 1153, 1153, 1137, 770, 696; MS (ESI$^+$) *m/z* (rel intensity) 236 [100, $(M+H)^+$], 258 [35], 274 [10]; HRMS (ESI$^+$) 236.1065 ($(M+H)^+$, $C_{16}H_{14}NO$ requires 236.1070).

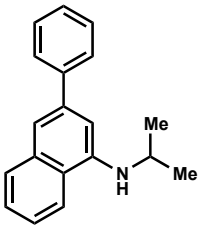
Data consistent with the literature.[6]

2-(4-Methoxyphenyl)-1-methyl-3-phenyl-1,2-dihydroisoquinoline, 12



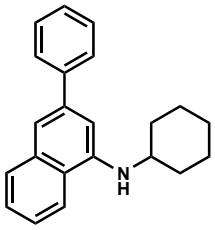
$[Rh(nbd)_2].BF_4$ (2.8 mg, 0.0075 mmol) and Xantphos (4.3 mg, 0.0075 mmol) were dissolved in chlorobenzene (0.5 mL). H_2 gas was bubbled through the solution for 2 mins, and the solution was purged with N_2 gas for a further 30 secs. This solution was then transferred to mixture of 1-(2-(methylthio)phenyl)ethanone (25 mg, 0.15 mmol) and phenylacetylene (33 µL, 0.30 mmol) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C, stirred for 1.5 h and then allowed to cool to room temperature. To the reaction mixture was added acetic acid (4 mL) and *p*-anisidine (185 µL, 1.5 mmol). This was heated to 110 °C, stirred for 16 h and allowed to cool to room temperature. The solvent was removed *in vacuo* and the reaction mixture was then re-dissolved in MeOH (5 mL). To this sodium borohydride (85 mg, 2.25 mmol) was added in portions at 0 °C while stirring vigorously. The solution was allowed to warm to room temperature and then stirred for a further 24 h. The reaction was quenched with water (20 mL), extracted with ether (3 x 10 mL), dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified by column chromatography (5-30% DCM/petrol), to yield the product as a yellow oil (28 mg, 58%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.54-7.52 (m, 2H), 7.27-7.20 (m, 5H), 7.16-7.12 (m, 1H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.46 (s, 1H), 5.00 (q, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 138.4, 135.8, 134.1, 131.7, 129.6, 128.3, 127.82, 127.72, 127.1, 126.3, 125.1, 124.2, 123.5, 114.0, 111.2, 110.0, 61.2, 55.5, 22.0; ν_{max} (film)/cm^{-1} 3016, 2970, 1739, 1601, 1508, 1442, 1366, 1229, 1217, 829; HRMS (FI$^+$) 327.1623 ((M)$^+$, $C_{23}H_{21}NO$ requires 327.1623).

***N*-Isopropyl-3-phenylnaphthalen-1-amine, 13**



Prepared following general procedure **A** using isopropyl amine (128 µL, 1.5 mmol). The crude product was purified by column chromatography (10% DCM/petrol), to yield the product as a green solid (30 mg, 77%); M.p: 71-73 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76-7.74 (m, 2H), 7.52-7.37 (m, 6H), 6.90 (s, 1H), 3.95 (hep, *J* = 6.5 Hz, 1H), 1.40 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz; $CDCl_3$): 142.0, 139.3, 134.7, 132.9, 129.0, 128.7, 127.4, 127.2, 126.2,124.9, 124.5, 123.0, 120.0, 115.8, 105.1, 44.7, 22.6; ν_{max} (film)/cm^{-1} 3434, 2970, 1739, 1592, 1525, 1416, 1366, 1228, 761, 698; HRMS (FI^{+}) 261.1520 ((M)$^{+}$, $C_{19}H_{19}N$ requires 261.1518).

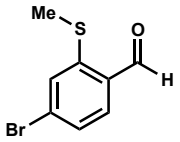
***N*-Cyclohexyl-3-phenylnaphthalen-1-amine, 14**



Prepared following general procedure **A** using cyclohexyl amine (172 µL, 1.5 mmol). The crude product was purified by column chromatography (10-30% DCM/petrol), to yield the product as a white solid (37 mg, 82%); M.p: 92 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.72-7.70 (m, 2H), 7.50-7.40 (m, *J* = 7.5 Hz, 5H), 7.38 (tt, *J* = 7.5, 1.5 Hz, 1H), 6.92 (bs, 1H), 3.59-3.55 (m, 1H), 2.23-2.21 (m, 2H), 1.84-1.81 (m, 2H), 1.61-1.29 (m, 6H); ^{13}C NMR (101 MHz; $CDCl_3$): 142.2, 139.4, 134.8, 129.0, 128.7, 127.2, 126.1, 124.7, 122.8, 119.9, 115.3, 104.3, 51.8, 33.1, 25.9, 25.0; ν_{max} (film)/cm^{-1} 2928, 2853, 1581, 1525, 1414, 761; HRMS (FI^{+}) 301.1837 ((M)$^{+}$, $C_{30}H_{35}NO$ requires 301.1830).

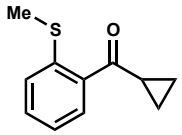
Preparation of starting materials

4-Bromo-2-(methylthio)benzaldehyde



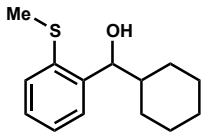
To a stirred suspension of sodium thiomethoxide (345.2 g, 4.9 mmol) in DMF (25 mL) was added 4-bromo-2-fluorobenzaldehyde (1.0 g, 4.9 mmol) over 30 mins at -45 °C. After the addition was complete, the solution was stirred for a further 3 h at -45 °C, then stirred at room temperature overnight. The reaction 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).

Cyclopropyl(2-(methylthio)phenyl)methanone



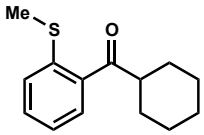
To a stirred solution of 2-Bromothioanisole (200 mg, 0.98 mmol) in anhydrous THF (2 mL) at -78 °C was added nBuLi (1.6 M, 0.675 mL, 1.08 mmol) dropwise over 10 mins under nitrogen. After stirring for 20 mins, a solution of cyclopropanecarboxaldehyde (81 µL, 1.1 mol) in anhydrous THF (1 mL) was added dropwise over 20 mins at -78 °C. The mixture was stirred for a further 1 h at -78 °C before being allowed to warm to room temperature. The reaction was quenched with sat. NH_4Cl solution (10 mL) and extracted with ether. The ethereal extract was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave the crude alcohol. This was dissolved in DCM (7 mL) and at 0 °C was added TEA (550 µL, 3.90 mmol) and the mixture stirred for 10 mins. To this was added a solution of SO_3.pyridine (467 mg, 2.94 mmol) in DMSO (3 mL) dropwise. The resulting mixture was stirred at 0 °C for 2 h. The reaction was quenched with sat. $NaHCO_3$ (20 mL) and extracted with ether. The ethereal extract was dried ($MgSO_4$), filtered, solvent removed *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the ketone as a colorless oil (112 mg, 60%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 2.55 (tt, *J* = 8.0, 4.5 Hz, 1H), 2.43 (s, 3H), 1.29-1.25 (m, 2H), 1.05-1.00 (m, 2H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 201.9, 141.1, 136.4, 131.8, 130.0, 125.4, 123.8, 19.3, 16.2, 12.0; ν_{max} (film)/cm^{-1} 3007, 2920, 2362, 2342, 1658, 1434, 1380, 1215, 988; MS (ESI$^+$) *m/z* (rel intensity) 215 [100, $(M+Na)^+$]; HRMS (ESI$^+$) 215.0500 ($(M+Na)^+$, $C_{11}H_{12}NaOS$ requires 215.0501).

Cyclohexyl(2-(methylthio)phenyl)methanol



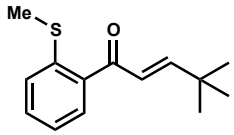
To a stirred solution of 2-Bromothioanisole (200 mg, 0.98 mmol) in THF (2 mL) was added ^{n}BuLi (0.675 mL, 1.08 mmol, 1.60M) dropwise at -78 °C. After stirring for 20 mins a solution of cyclohexyl carboxaldehyde (131µL, 1.08 mmol) in THF (1 mL) was added dropwise at -78 °C. This was stirred for 1 h allowing it to warm up to room temperature. The reaction was quenched with sat. NH_4Cl solution (10 mL) and extracted with ether. The ethereal extract was dried ($MgSO_4$), filtered, solvent removed *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the alcohol as colourless oil. (151 mg, 65%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.24-7.17 (m, 3H), 4.87 (d, *J* = 6.5 Hz, 1H), 2.46 (s, 3H), 2.30 (s, 1H), 1.92 (d, *J* = 11.0 Hz, 1H), 1.75-1.65 (m, 3H), 1.41 (d, *J* = 10.0 Hz, 1H), 1.21-1.11 (m, 5H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 142.2, 136.0, 127.6, 126.9, 126.3, 125.2, 75.2, 44.1, 29.6, 28.0, 26.46, 26.35, 26.1, 16.7; ν_{max} (film)/cm^{-1} 3414, 2921, 2850, 1588, 1437, 1011, 751; MS (ESI^{+}) *m/z* (rel intensity) 219 [70], 259 [100, (M+Na)$^{+}$]; HRMS (ESI^{+}) 259.1119 ((M+Na)$^{+}$, $C_{14}H_{20}NaOS$ requires 259.1127).

Cyclohexyl(2-(methylthio)phenyl)methanone



To a stirred solution of cyclohexyl(2-(methylthio)phenyl)methanol (105 mg, 0.45 mmol) in DCM (4.5 mL) was added DMP (382 mg, 0.90 mmol) in one portion. The mixture was stirred for 30 mins at room temperature. The reaction was washed with sat. $Na_2S_2O_3$ and extracted with DCM. The DCM extract was washed once more with $NaHCO_3$ and the aqueous extracts were further washed with DCM. The combined organic layers were dried ($MgSO_4$), filtered, solvent removed *in vacuo* and purified by flash chromatography (5% ether/petrol) to yield the ketone as a colourless oil. (103 mg, 99%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.46-7.42 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 3.18 (tt, *J* = 11.5, 3.5 Hz, 1H), 2.43 (s, 3H), 1.90-1.71 (m, 5H), 1.56-1.50 (m, 2H), 1.35-1.26 (m, 3H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 205.7, 141.3, 135.5, 131.5, 129.2, 125.8, 123.7, 47.5, 29.2, 25.94, 25.84, 16.3; ν_{max} (film)/cm^{-1}2929, 2854, 1666, 1433, 974, 739; MS (ESI$^+$) *m/z* (rel intensity) 235 [50, $(M+H)^+$], 257 [100, $(M+Na)^+$]; HRMS (ESI$^+$) 257.0971 ($(M+Na)^+$, $C_{14}H_{18}NaOS$ requires 257.0971).

(*E*)-4,4-Dimethyl-1-(2-(methylthio)phenyl)pent-2-en-1-one



$[Rh(nbd)_2]BF_4$ (12 mg, 0.033 mmol) and bis(dicyclohexylphosphino)methane (13 mg, 0.033 mmol) were dissolved in +acetone (0.25 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. To this solution was added 2-(methylthio)benzaldehyde (46 mg, 0.30 mmol) and 3,3-dimethylbut-1-yne (55 µL, 0.45 mmol). The reaction mixture was heated to 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/petrol) to yield the product (52 mg, 74%) as a yellow oil; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.58 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45-7.41 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22-7.18 (m, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 2.44 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (101 MHz; $CDCl_3$): δ 194.1, 160.5, 140.4, 137.4, 131.4, 129.5, 126.3, 124.1, 123.9, 34.3, 28.8, 16.6; ν_{max} (film)/cm^{-1} 3002, 2969, 2959, 2573, 1738, 1614, 1366, 1217; MS (ESI$^+$) ***m/z*** (rel intensity) 257 [100, $(M+Na)^+$]. HRMS (ESI$^+$) 257.0968 ($(M+Na)^+$, $C_{14}H_{18}NaOS$ requires 257.0971).

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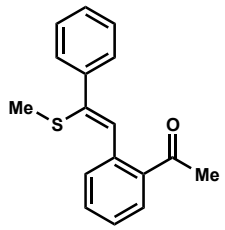
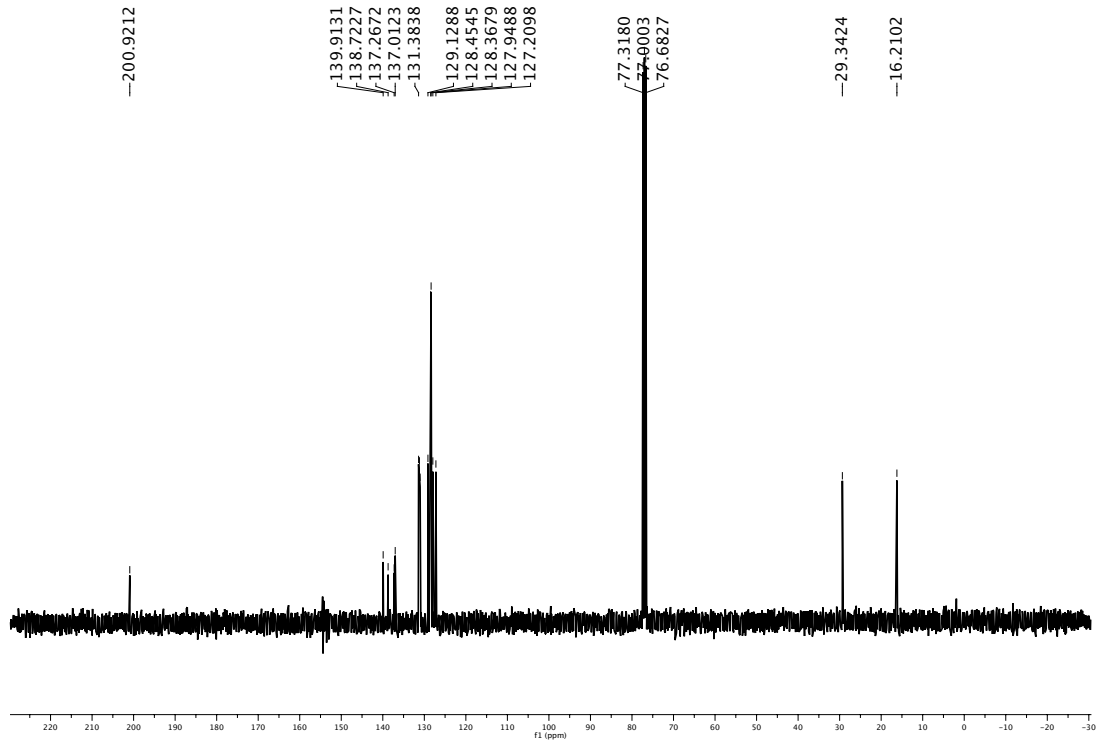
[6] Hyun-Suk, Y.; Youngun, L.; Seunghoon, S.; Ji-Eun, L. *Org. Biomol. Chem.*, **7**, 4744 – 4752 (2009)

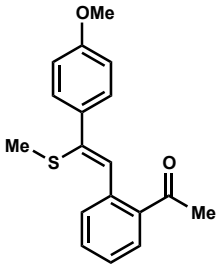
Spectral Data:



6: Entry **5** (^{1}H, 400 MHz, $CDCl_3$)

6: Entry **5** (^{13}C, 100 MHz, $CDCl_3$)





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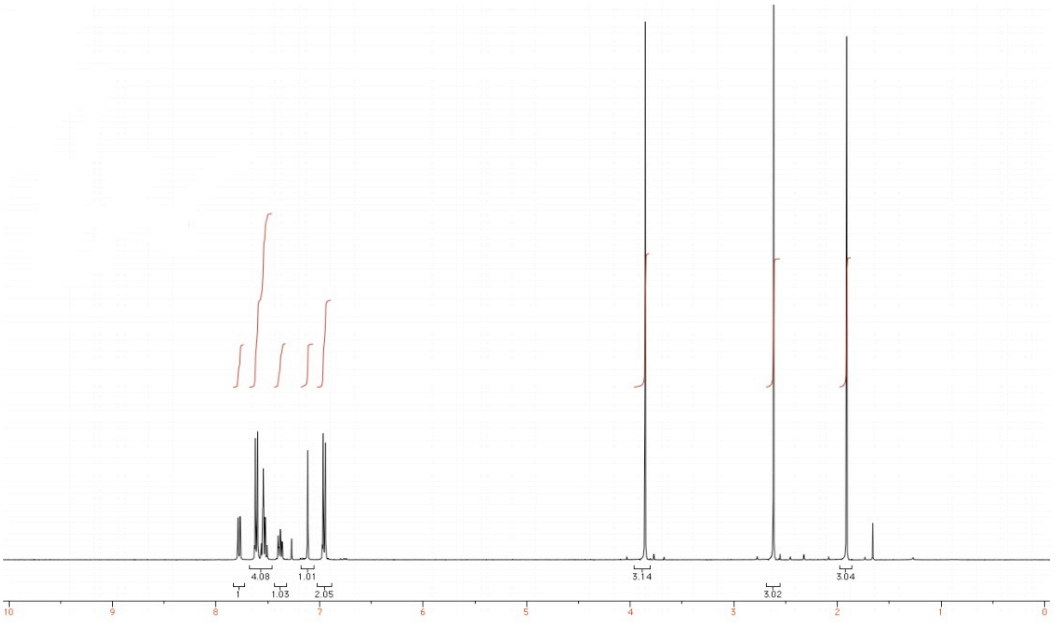
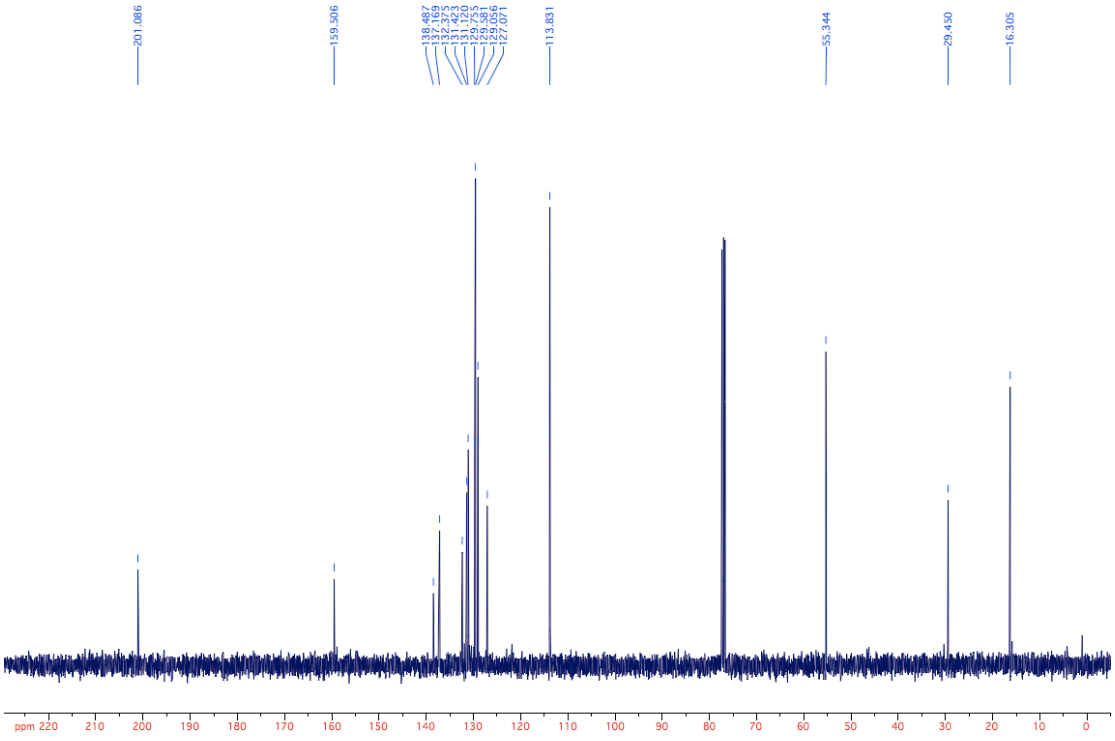
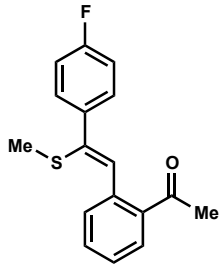
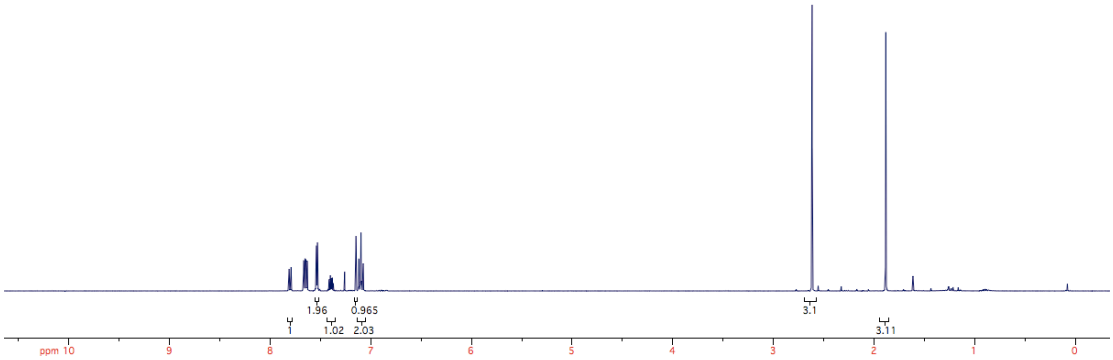


6: Entry **6** (^{13}C, 100 MHz, $CDCl_3$)

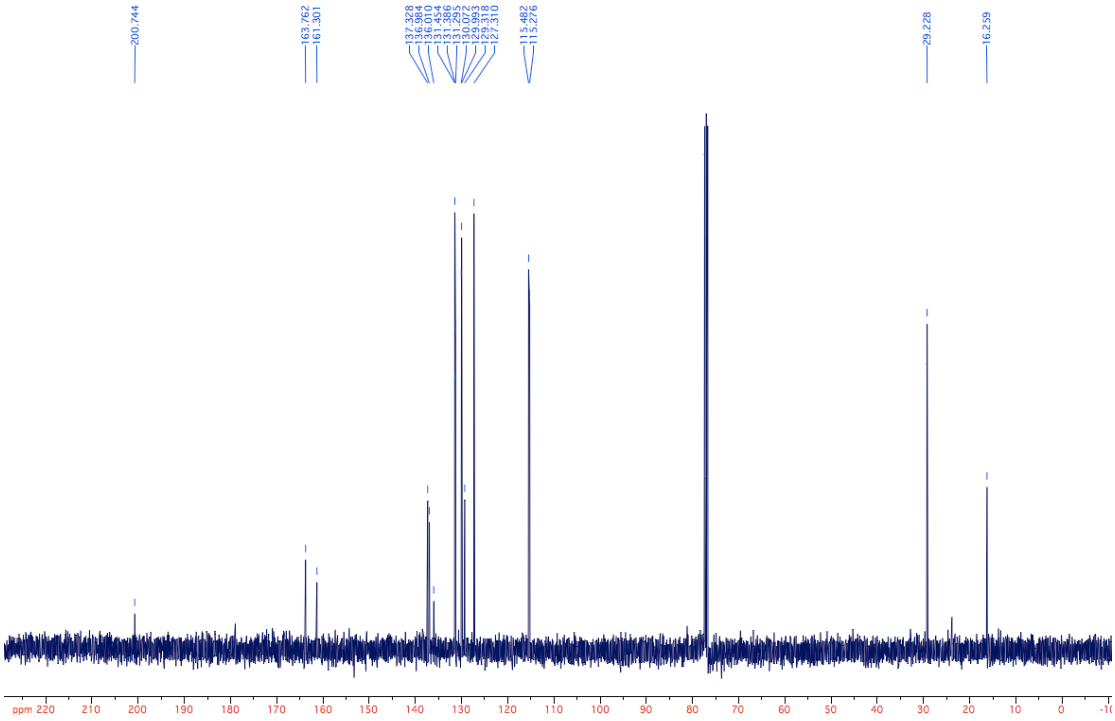


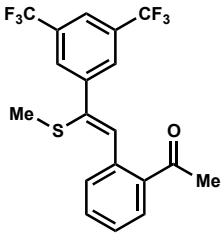


6: Entry **7** (^{1}H, 400 MHz, $CDCl_3$)



c6: Entry **7** (^{13}C, 100 MHz, $CDCl_3$)





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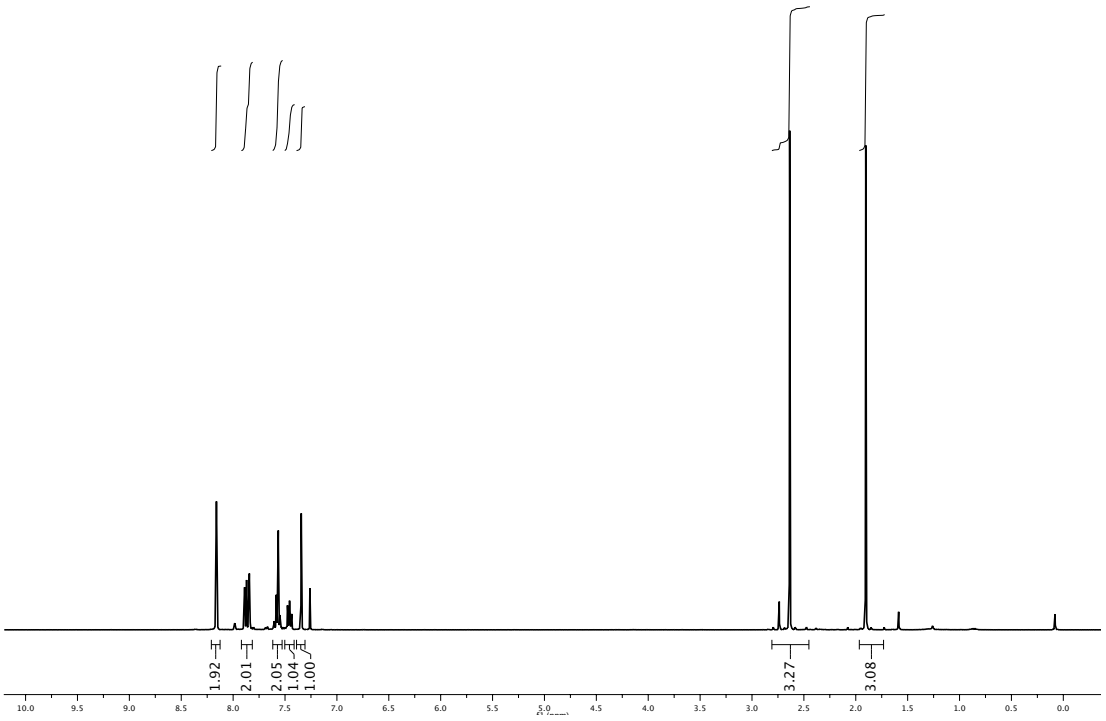

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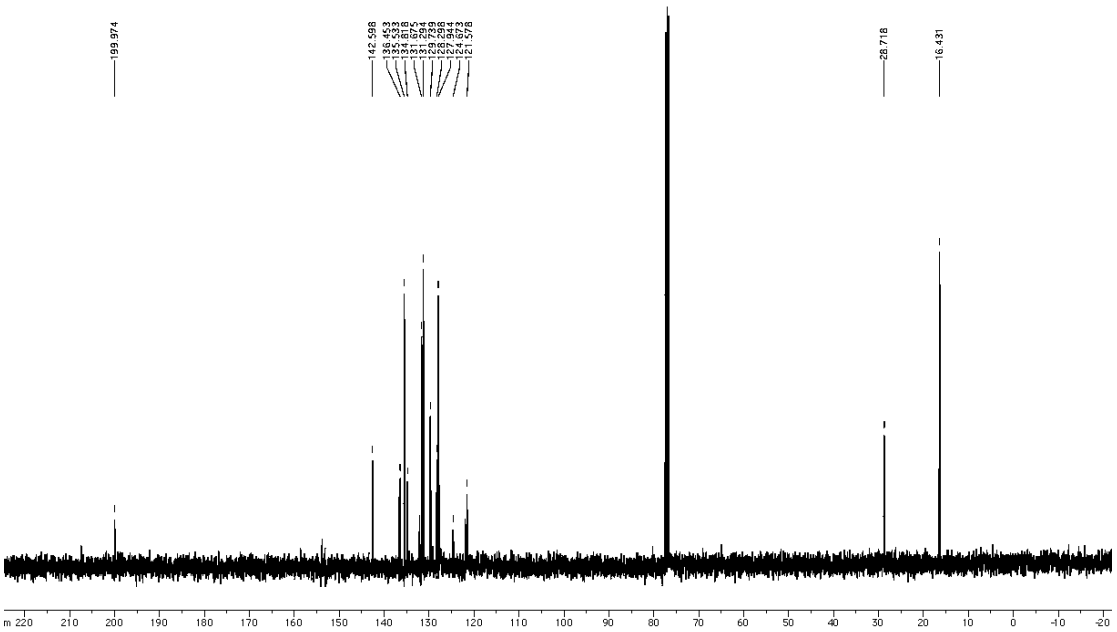
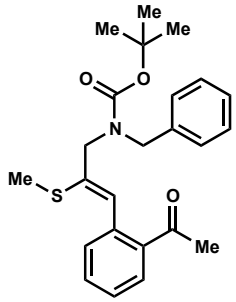
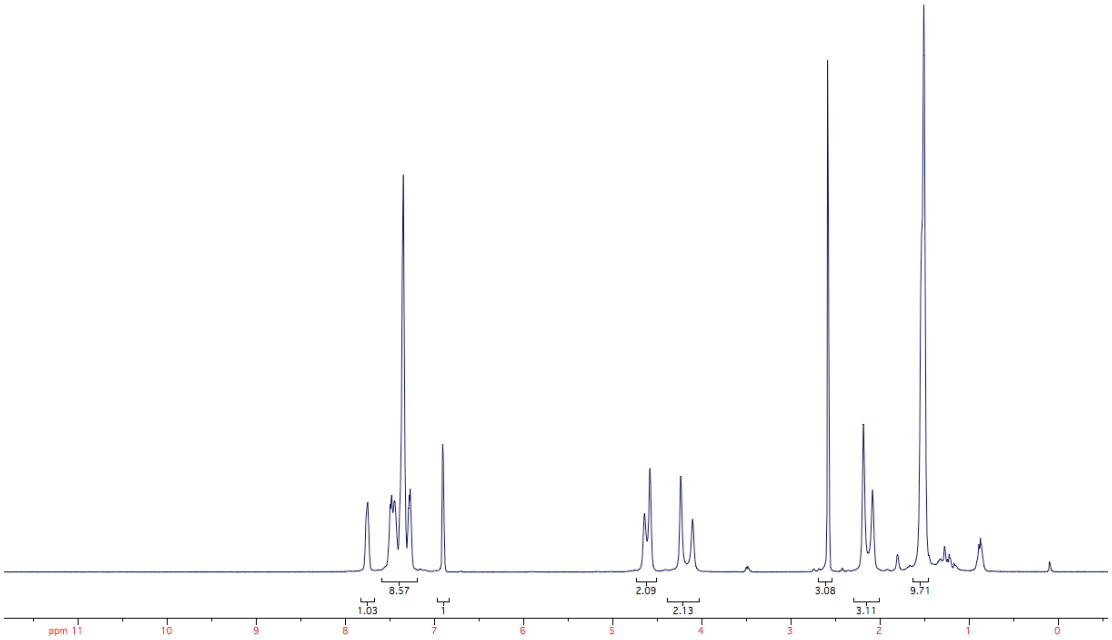




6: Entry **9** (^{1}H, 400 MHz, $CDCl_3$)



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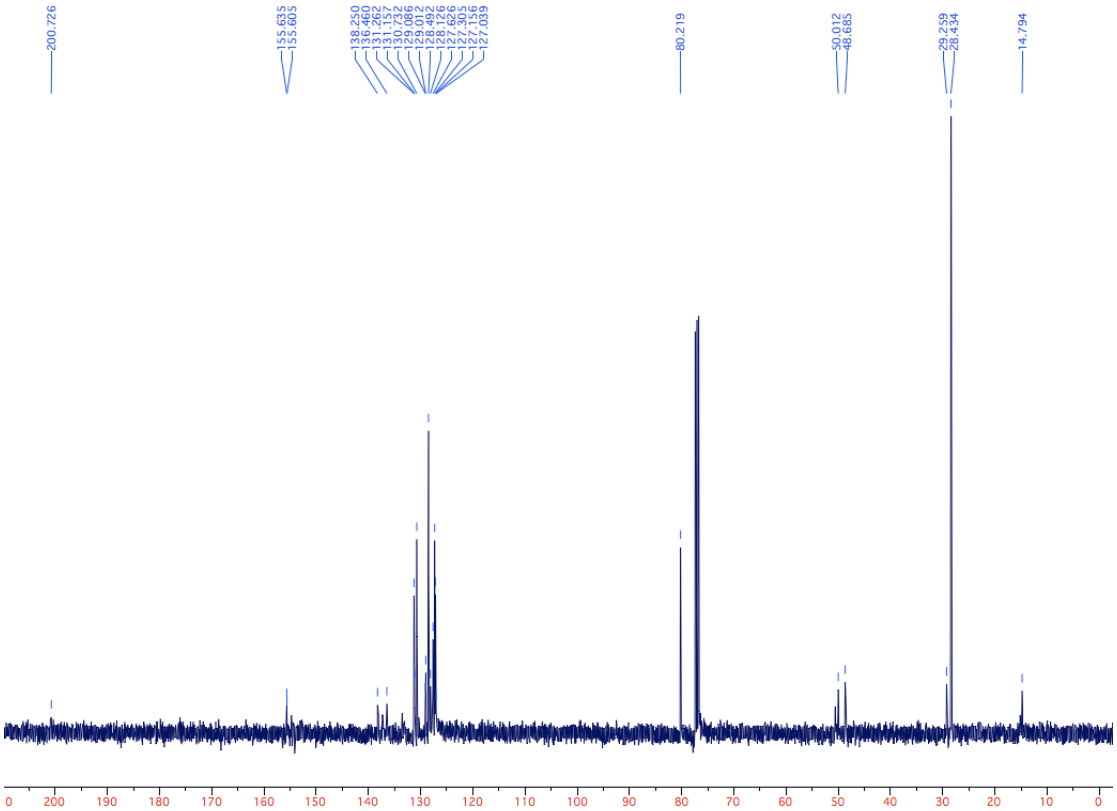
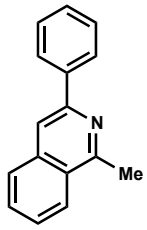
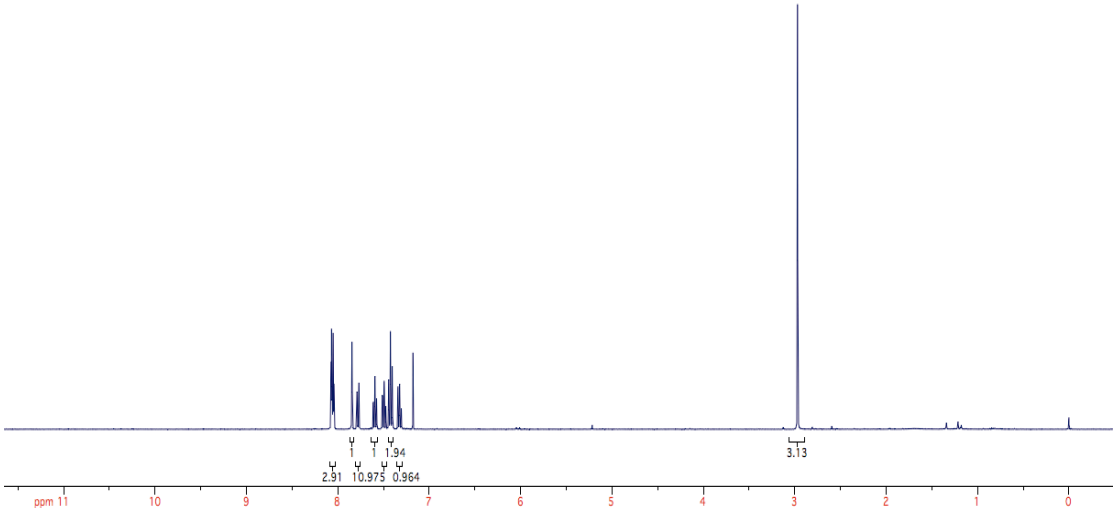
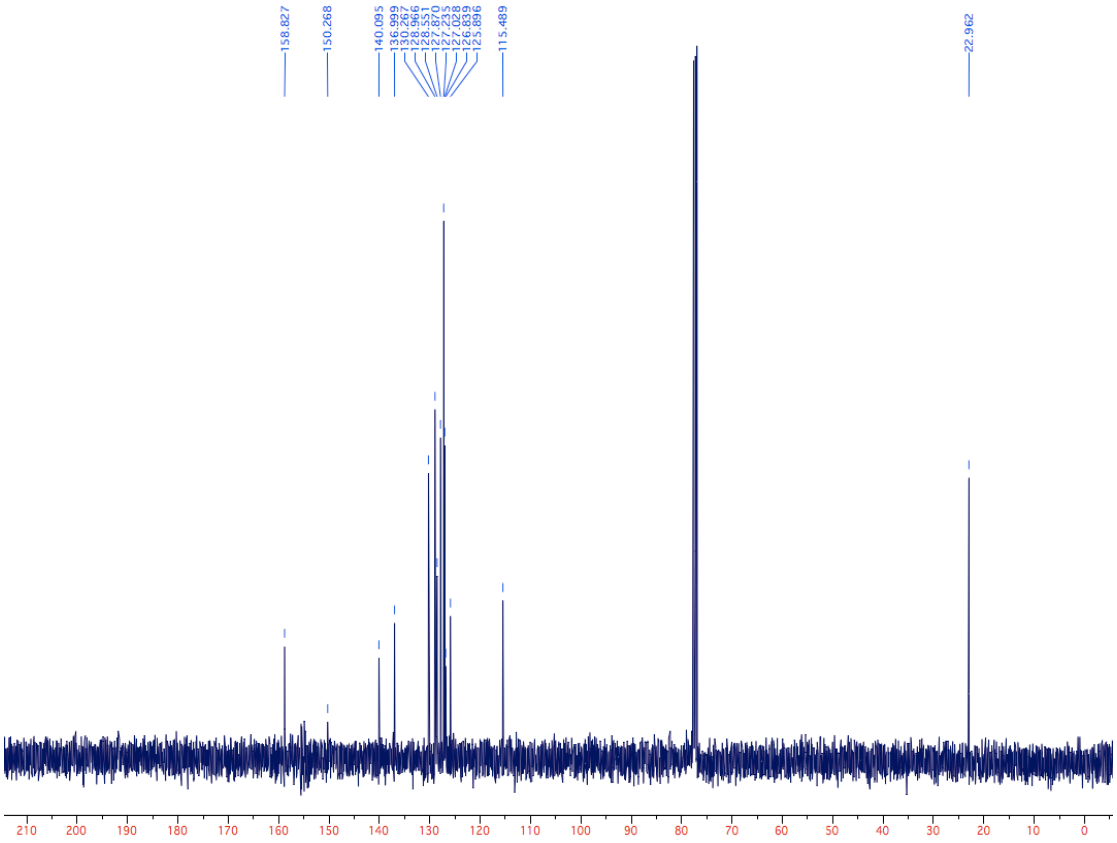


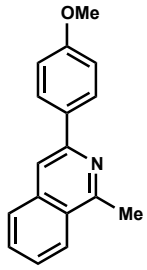


7a (^{1}H, 400 MHz, $CDCl_3$)



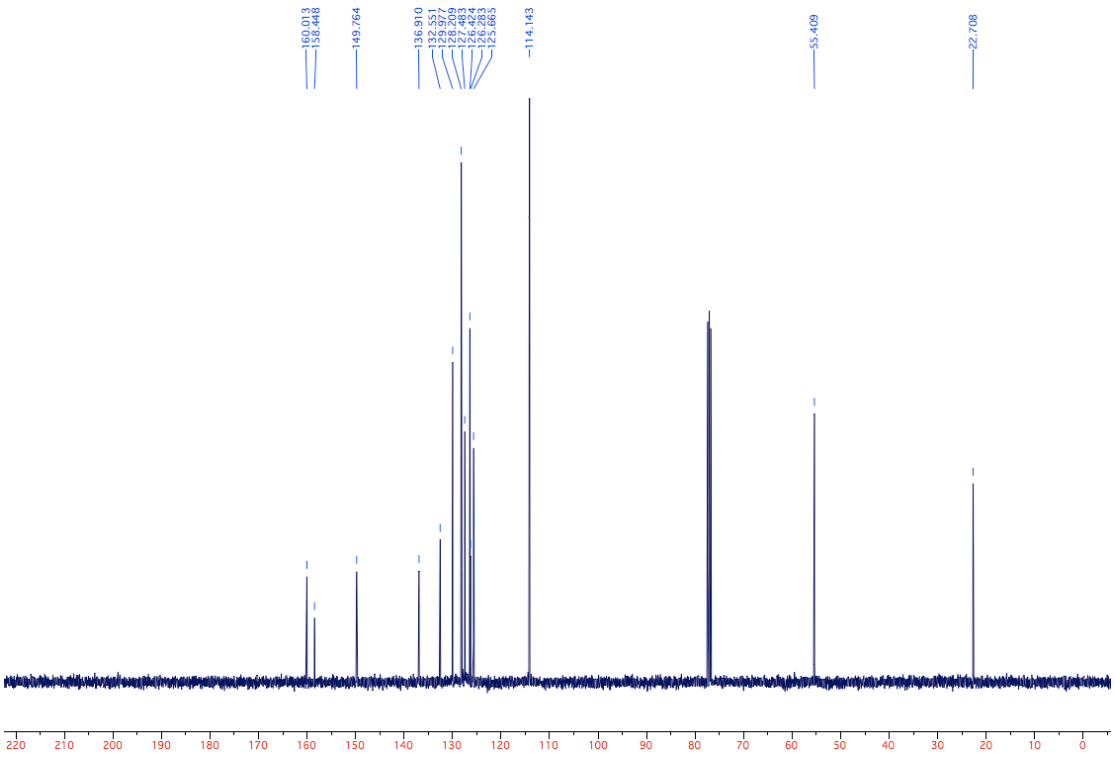
7a (^{13}C, 100 MHz, $CDCl_3$)

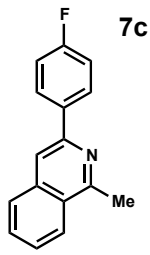




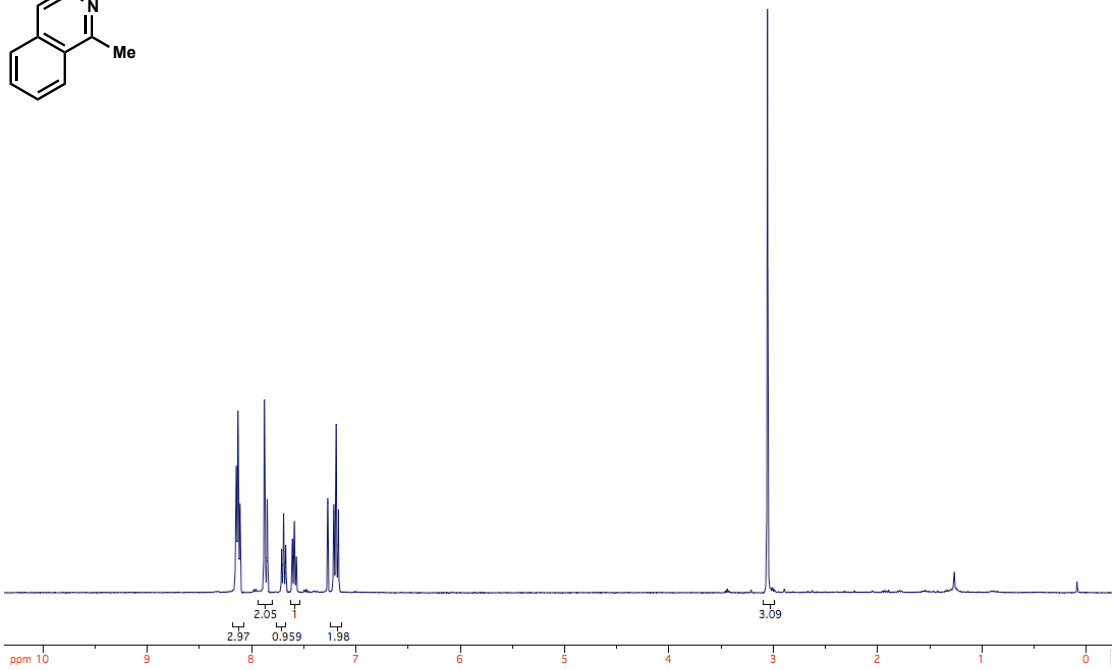
7b (^{1}H, 400 MHz, $CDCl_3$)

7b (^{13}C, 100 MHz, $CDCl_3$)





7c (^{1}H, 400 MHz, $CDCl_3$)



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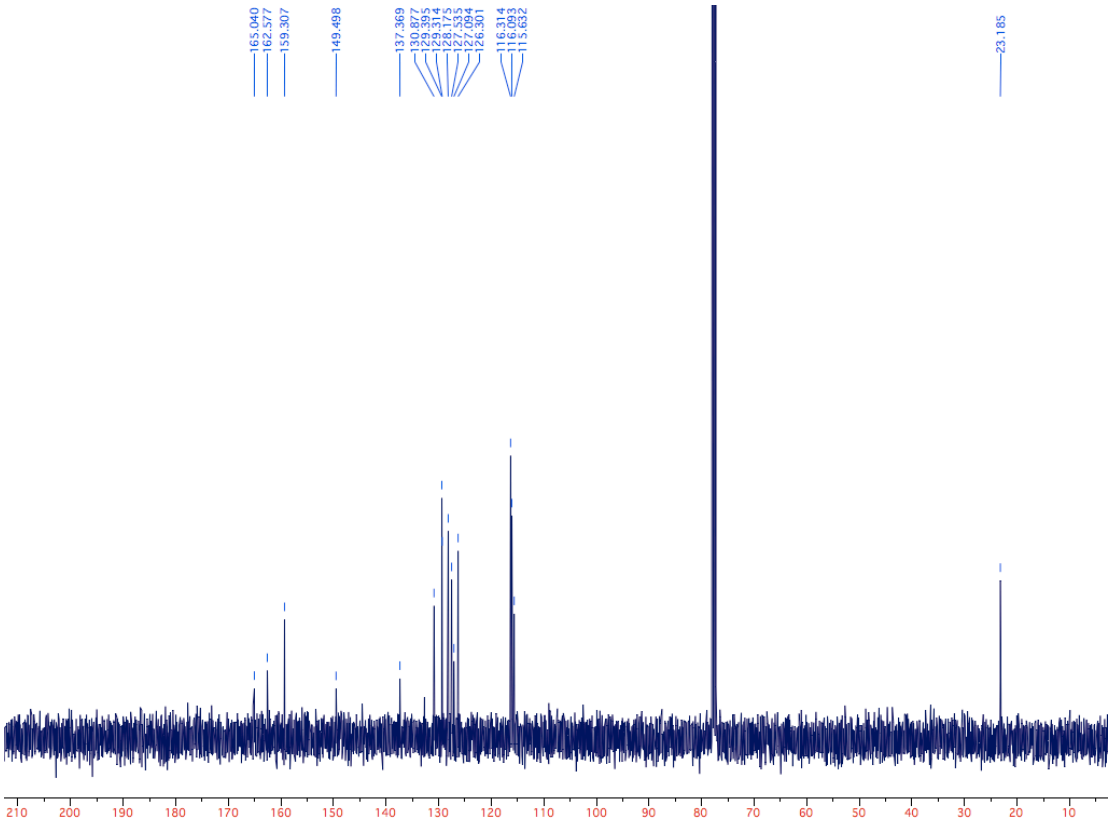

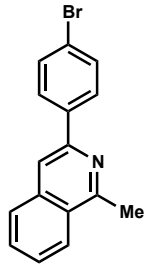

7d (^{1}H, 400 MHz, $CDCl_3$)

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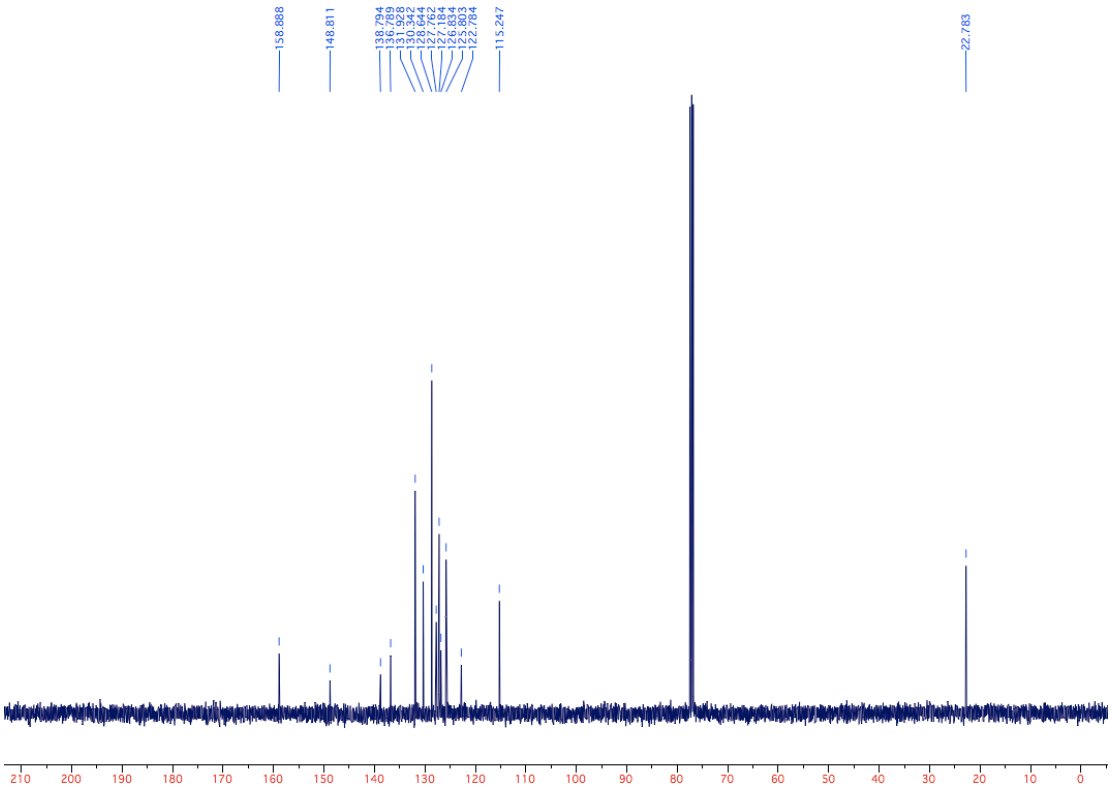

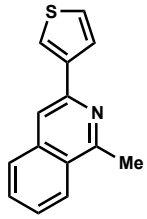

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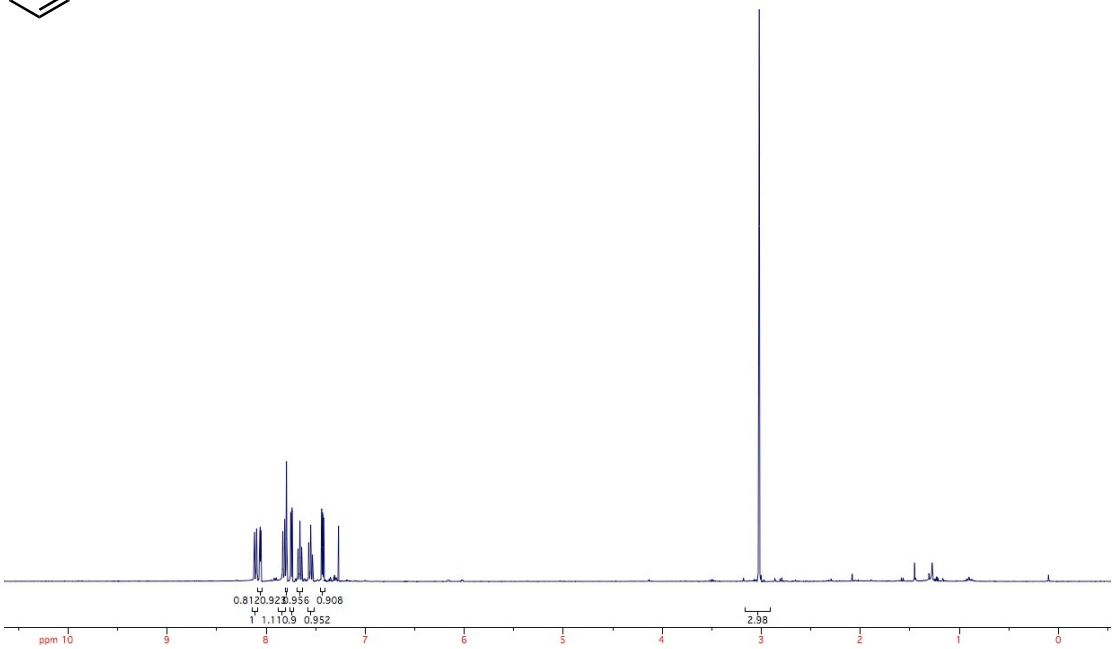
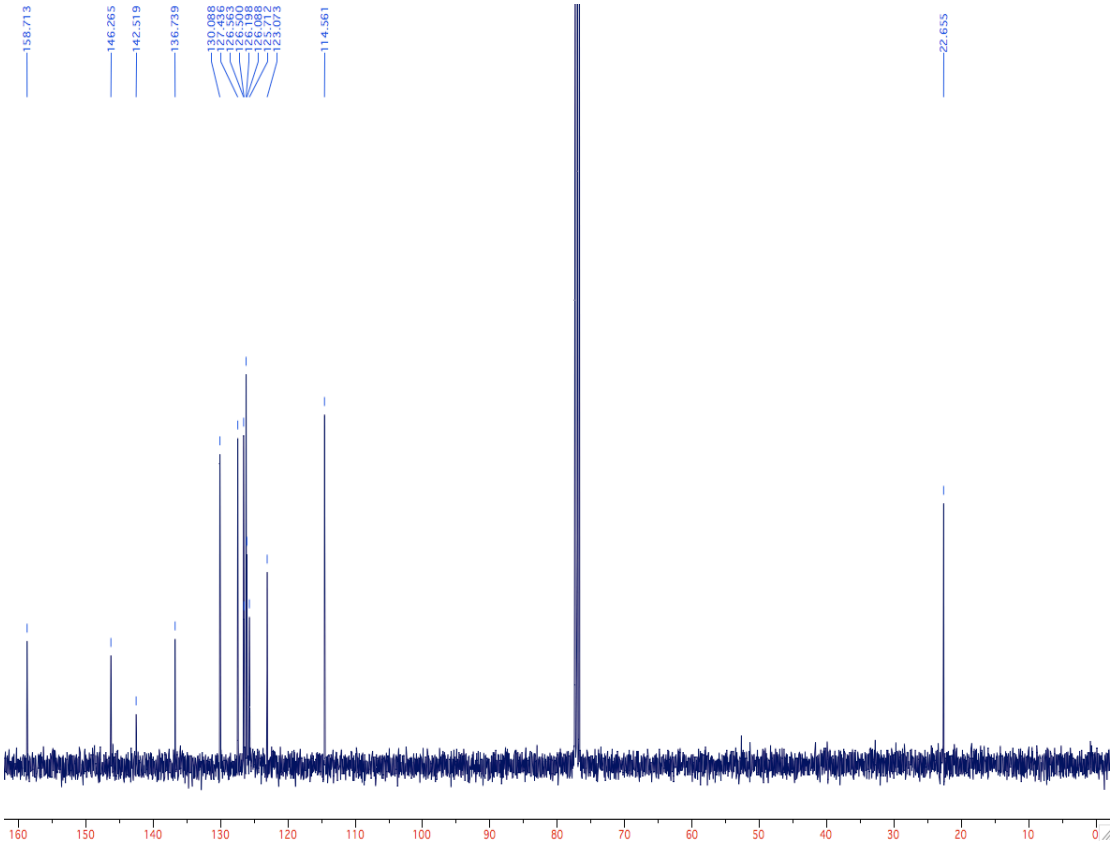
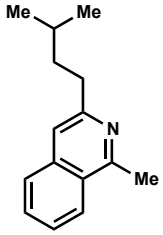


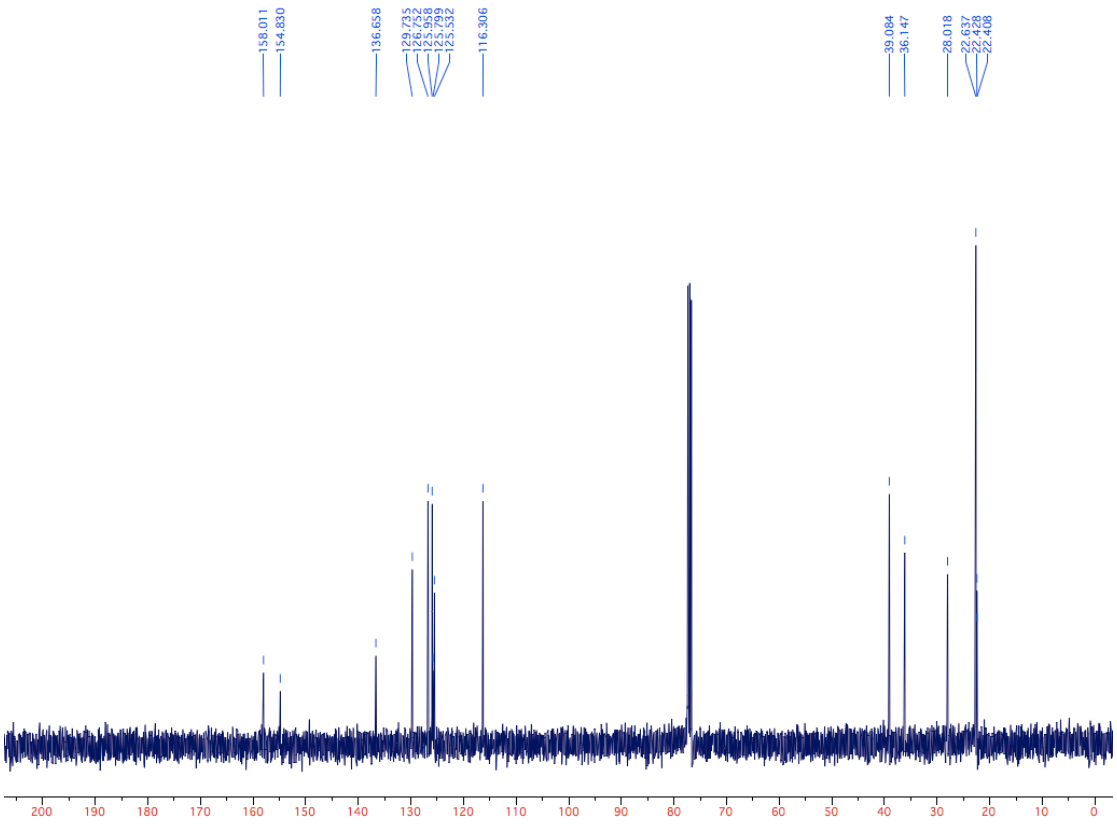
7e (^{13}C, 100 MHz, $CDCl_3$)

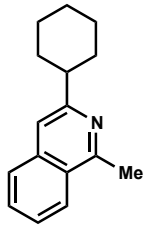




7f (^{1}H, 400 MHz, $CDCl_3$)

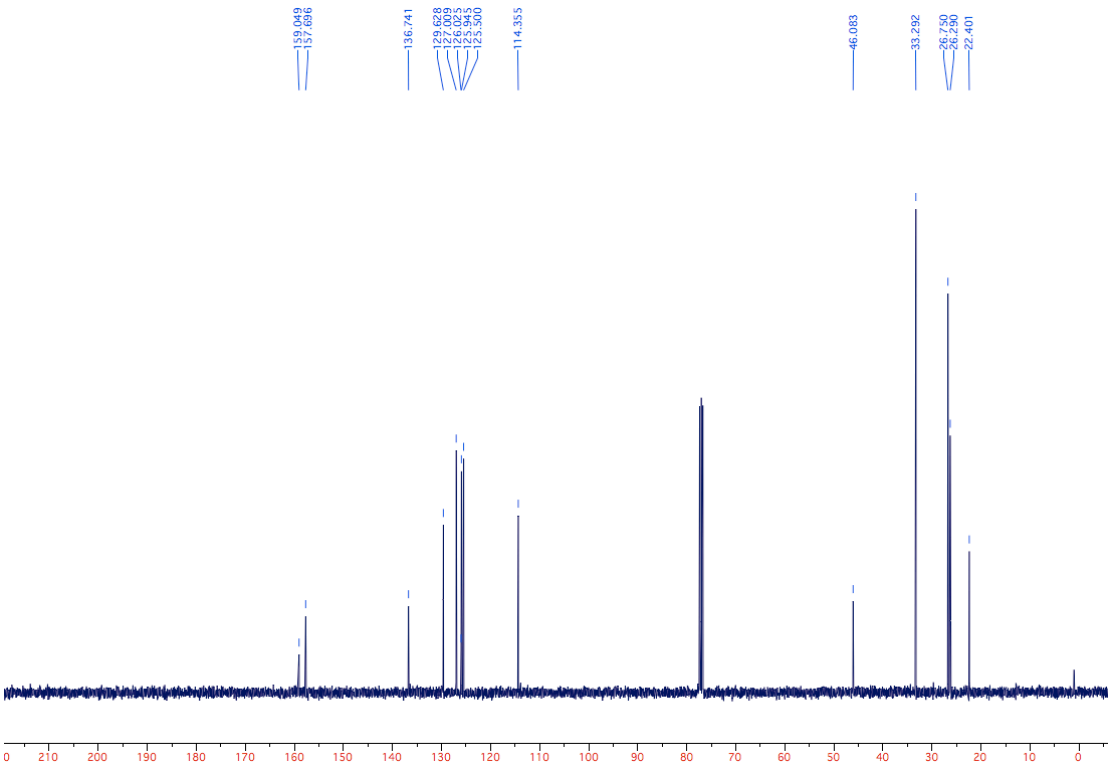
7f (^{13}C, 100 MHz, $CDCl_3$)

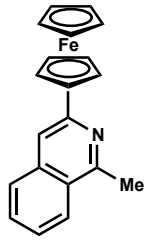




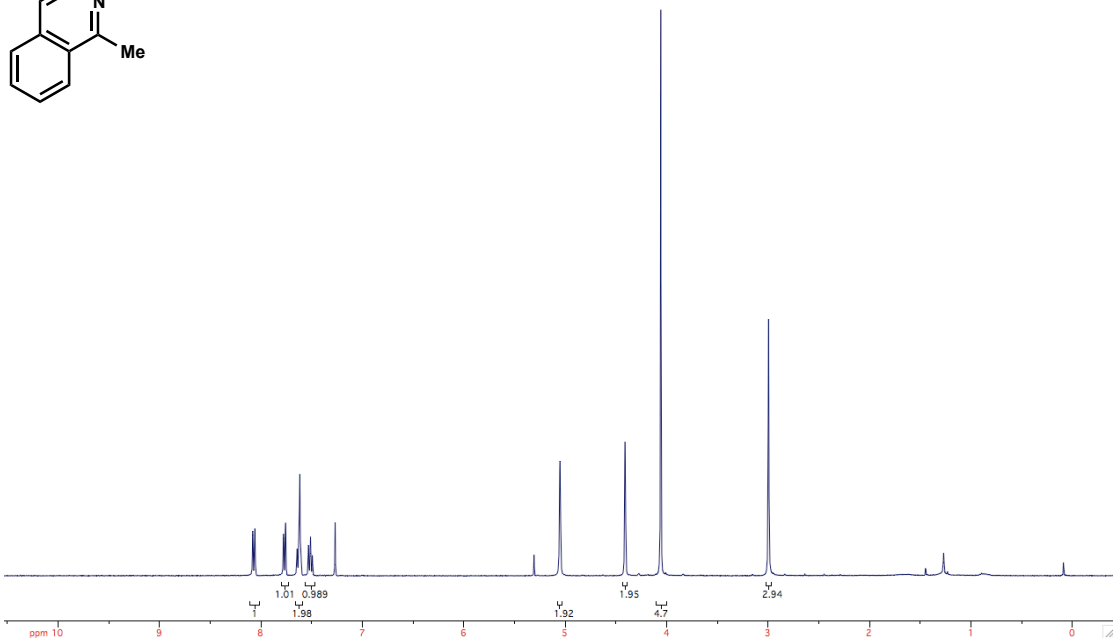
7g (^{1}H, 400 MHz, $CDCl_3$)

7g (^{13}C, 100 MHz, $CDCl_3$)

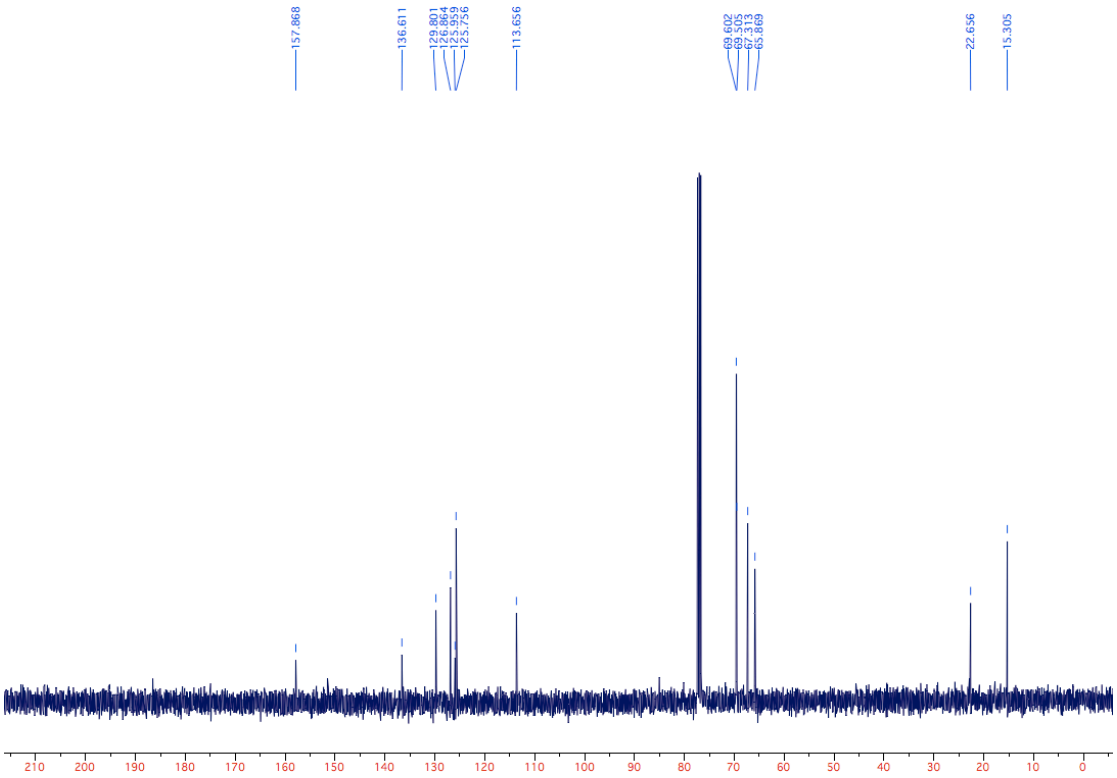


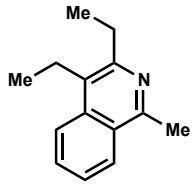


7h (^{1}H, 400 MHz, $CDCl_3$)

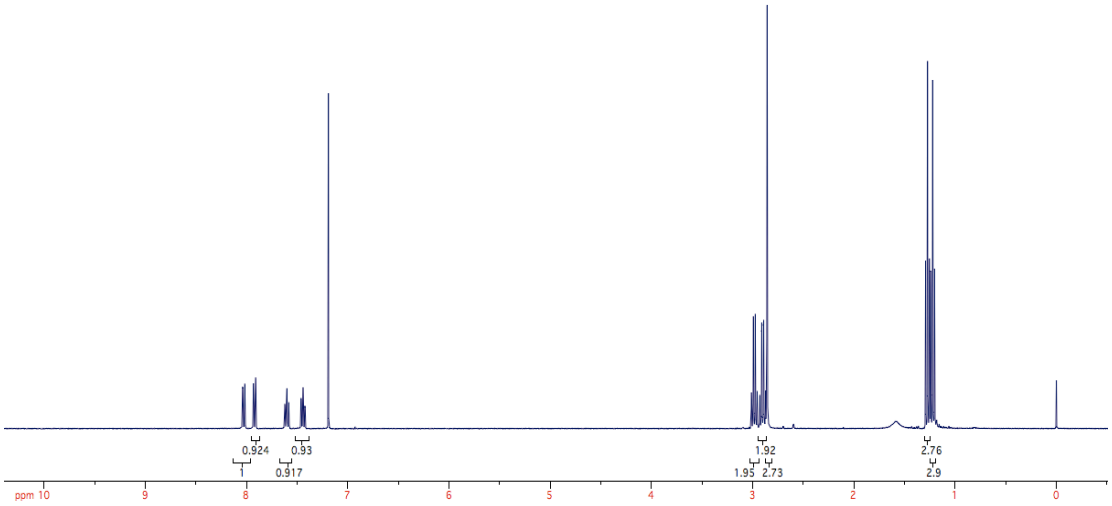


7h (^{13}C, 100 MHz, $CDCl_3$)

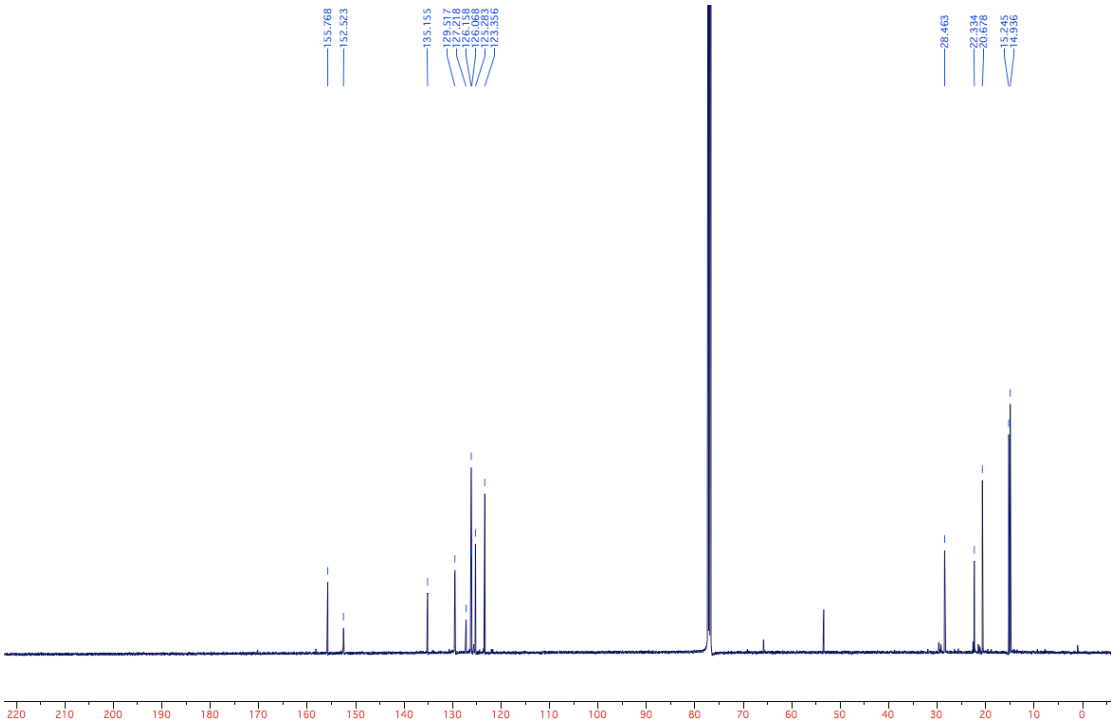


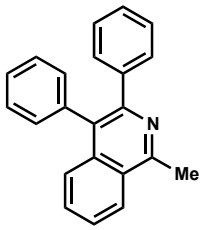


7i (^{1}H, 400 MHz, $CDCl_3$)

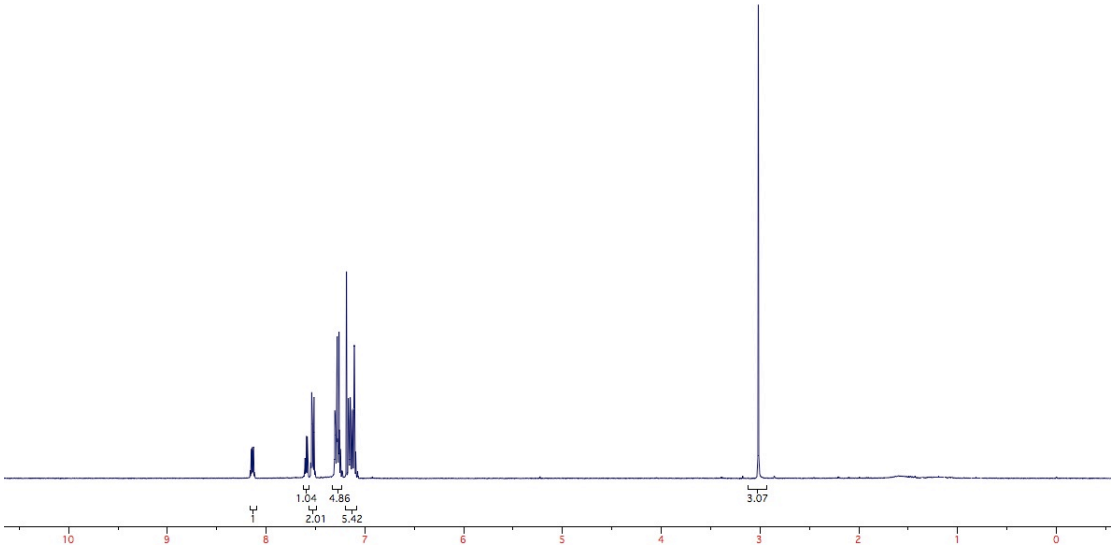


7i (^{13}C, 100 MHz, $CDCl_3$)

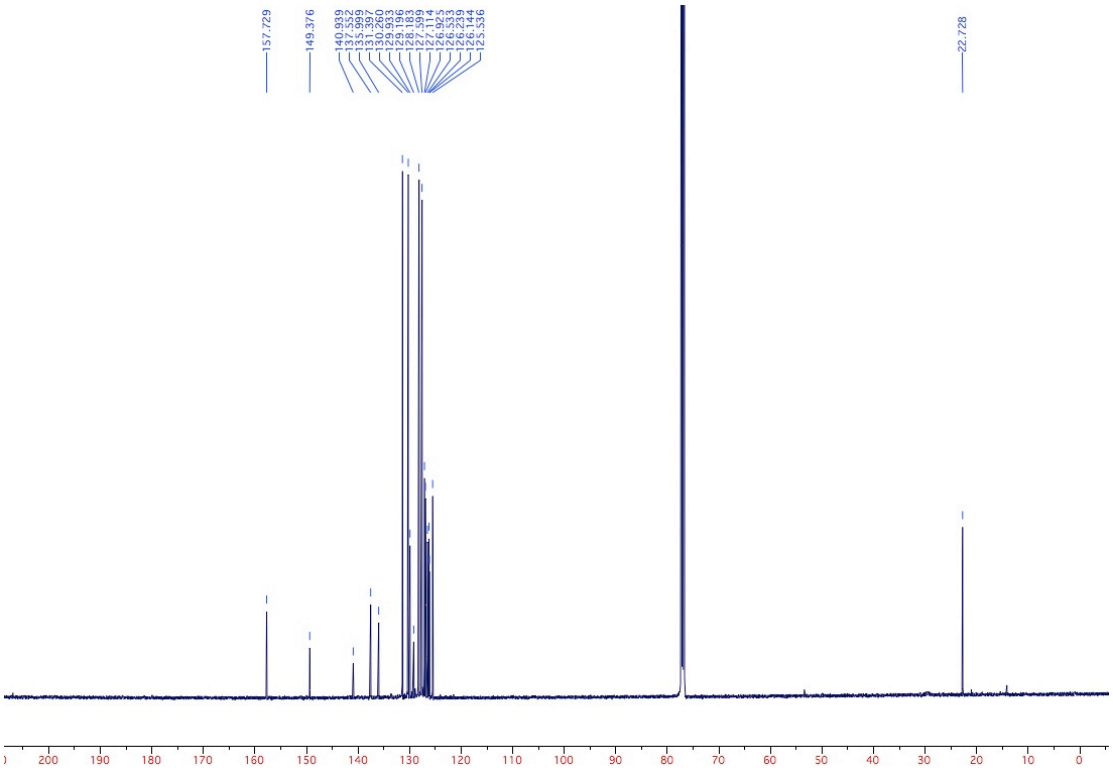


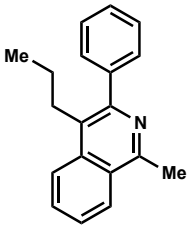


7j (^{1}H, 400 MHz, $CDCl_3$)

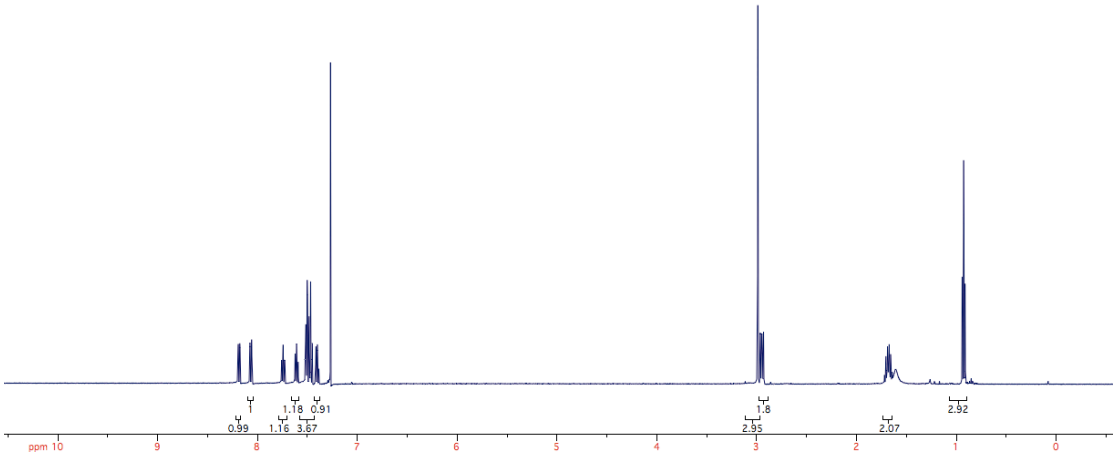


7j (^{13}C, 100 MHz, $CDCl_3$)

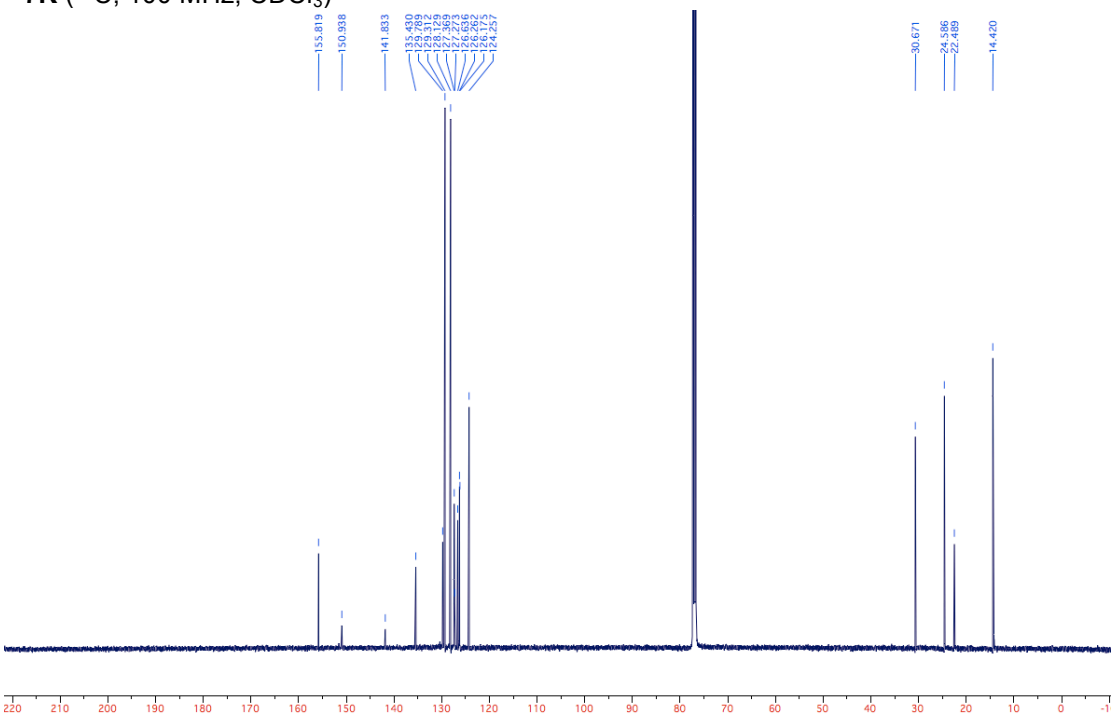


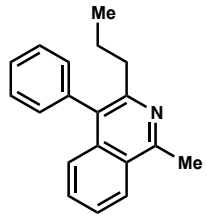


7K (^{1}H, 400 MHz, $CDCl_3$)

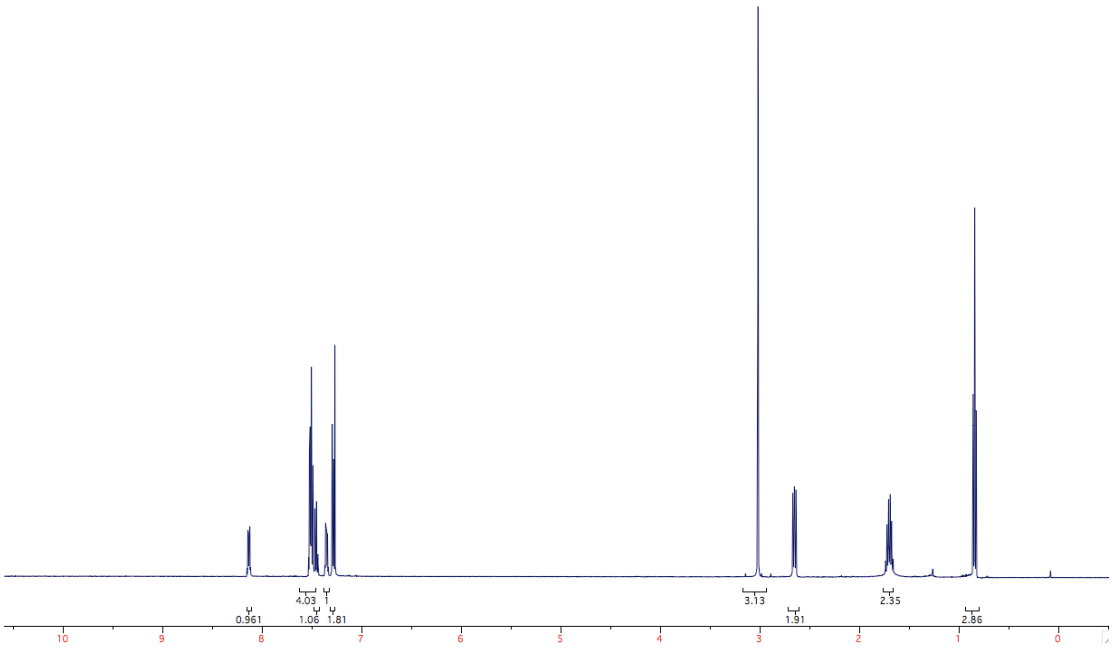


7K (^{13}C, 100 MHz, $CDCl_3$)

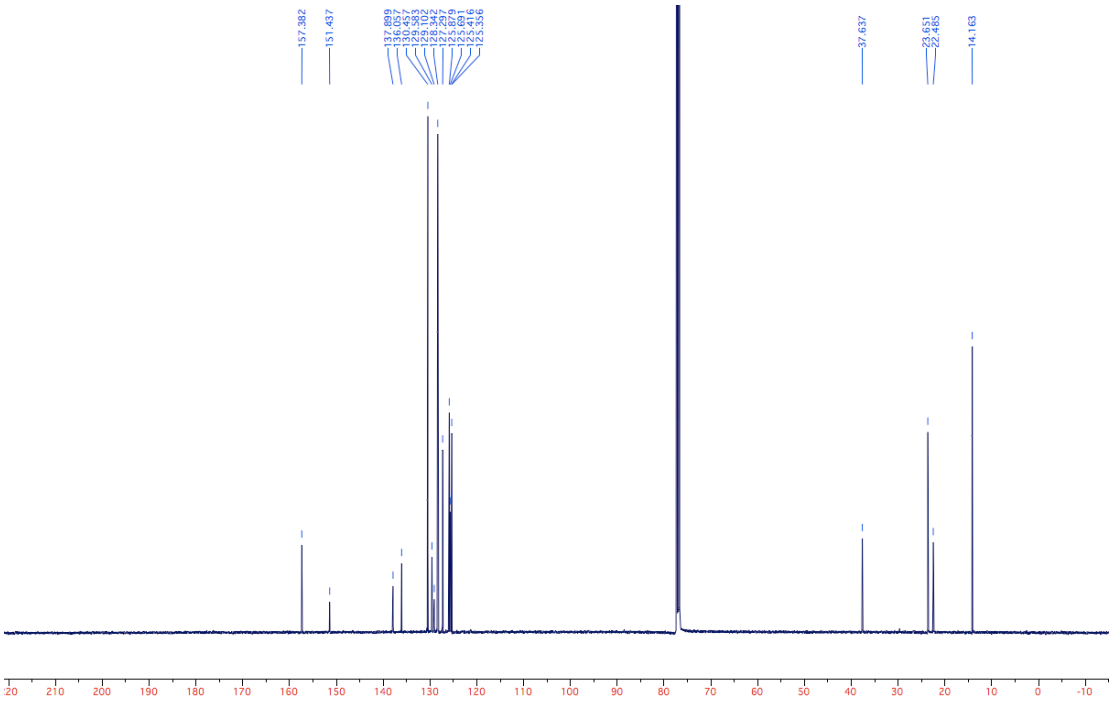




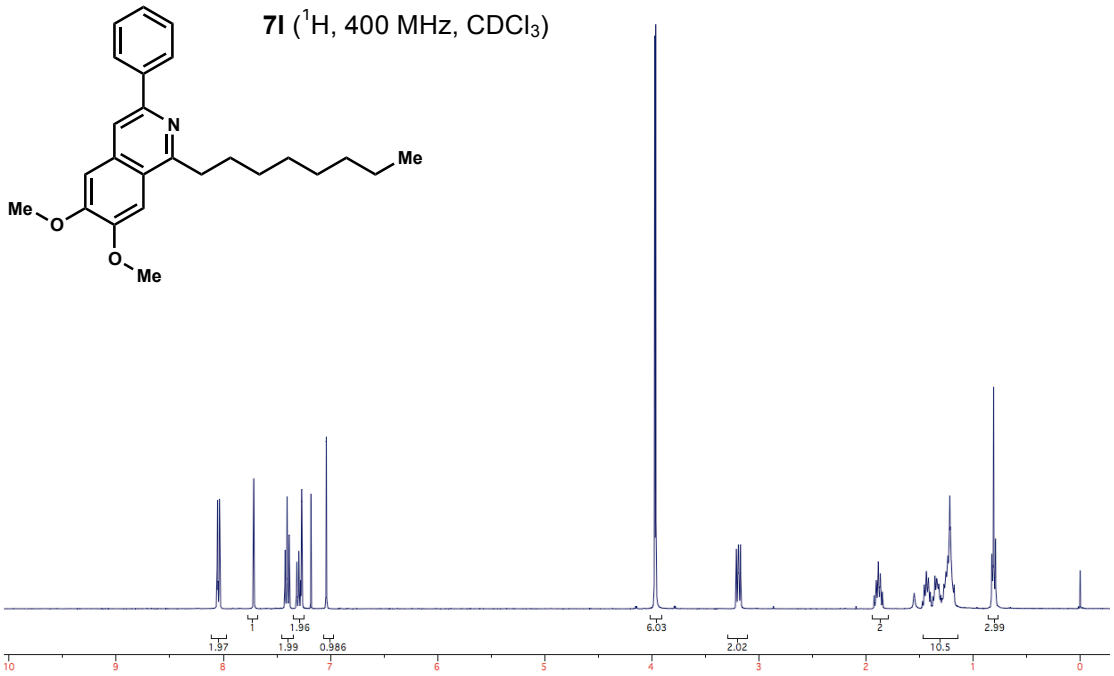
7K' (^{1}H, 400 MHz, $CDCl_3$)



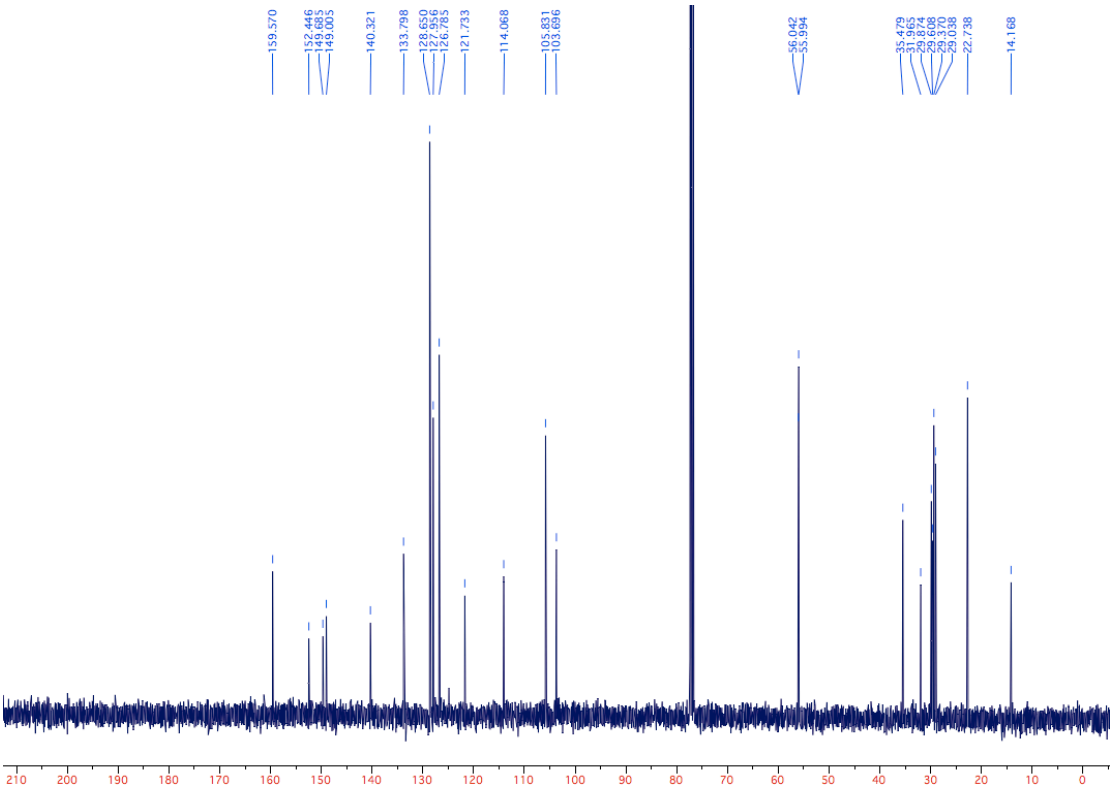
7K' (^{13}C, 100 MHz, $CDCl_3$)

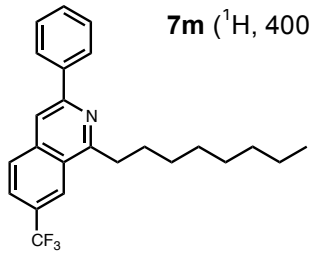


7l (^{1}H, 400 MHz, $CDCl_3$)

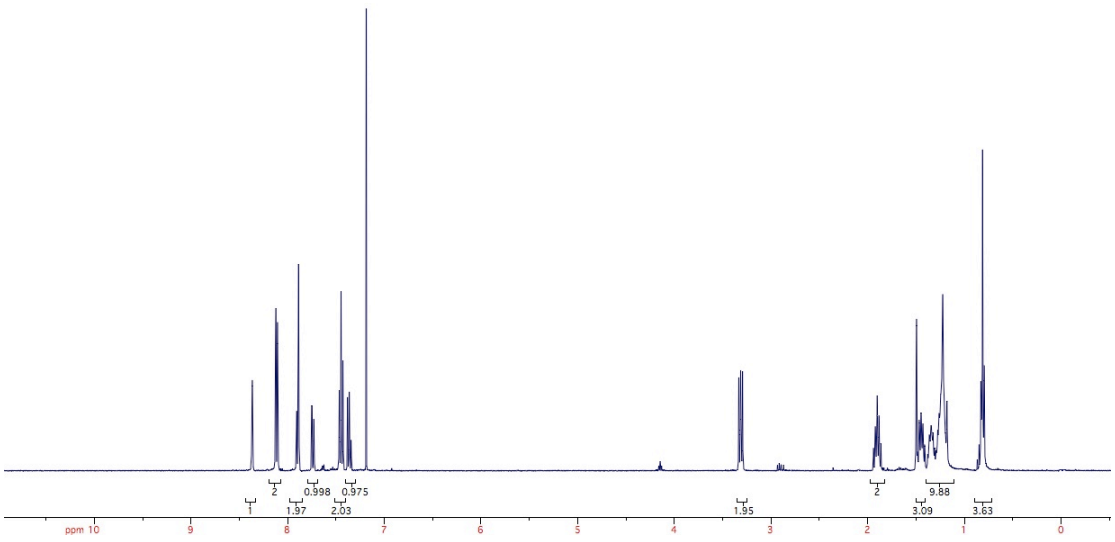


7l (^{13}C, 100 MHz, $CDCl_3$)

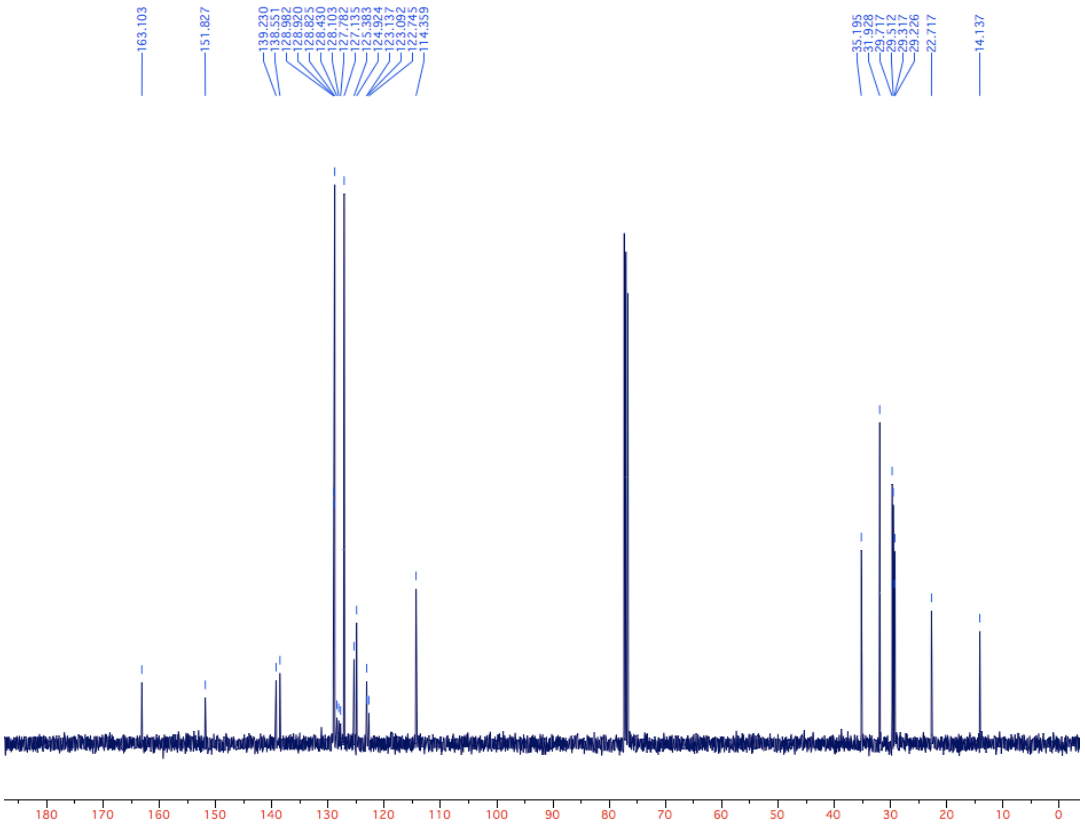




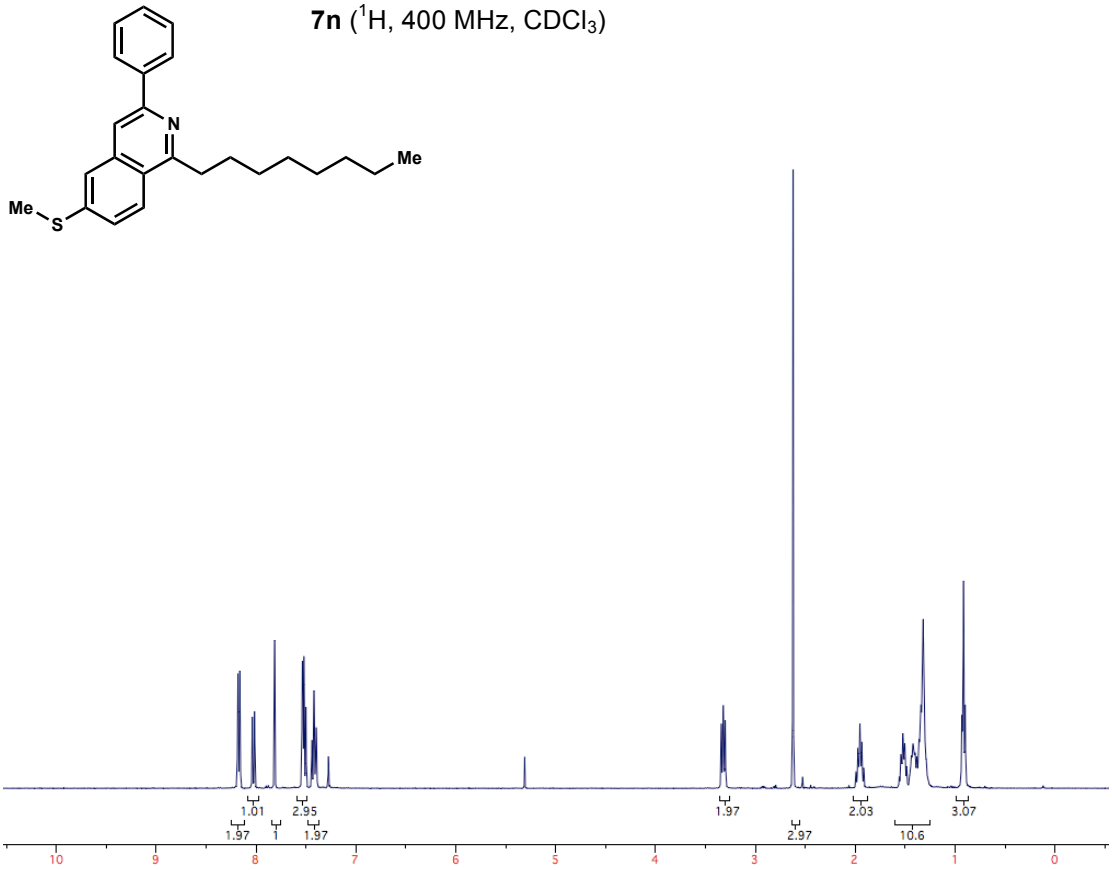
7m (^{1}H, 400 MHz, $CDCl_3$)



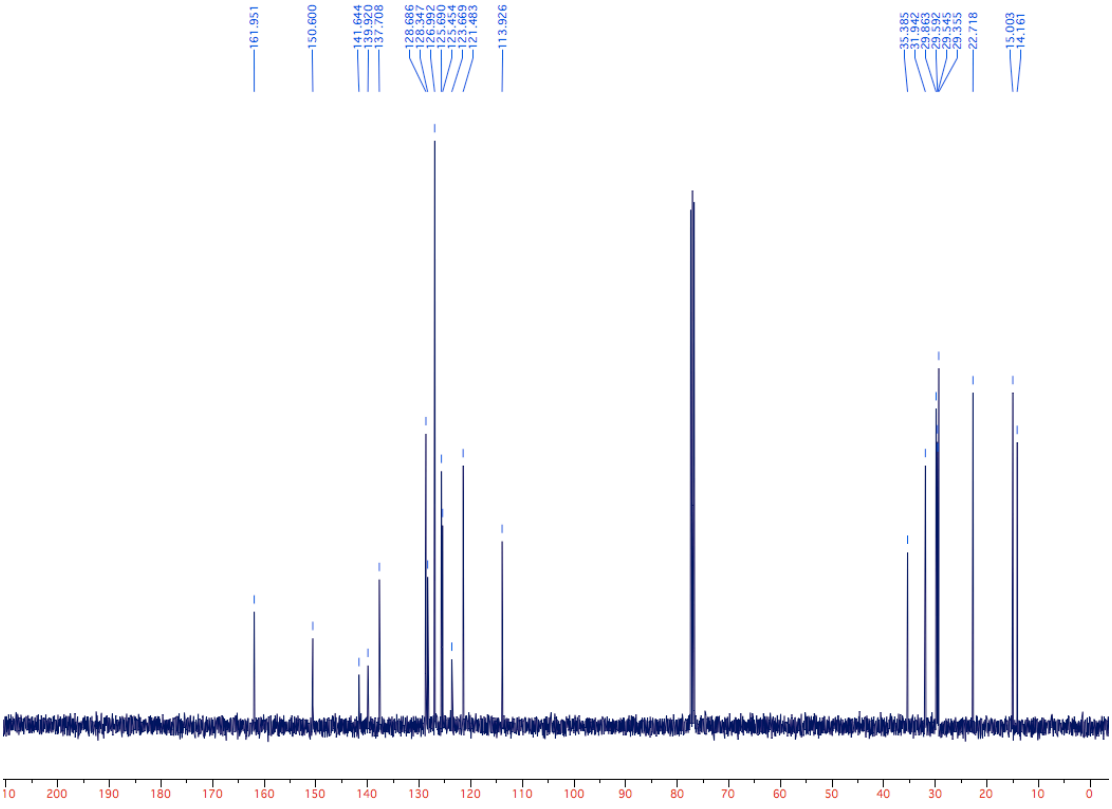
7m (^{13}C, 100 MHz, $CDCl_3$)

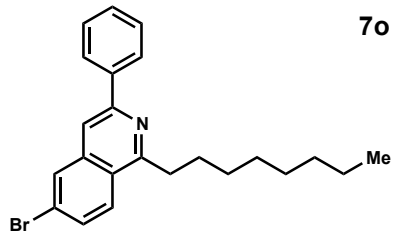


7n (^{1}H, 400 MHz, $CDCl_3$)

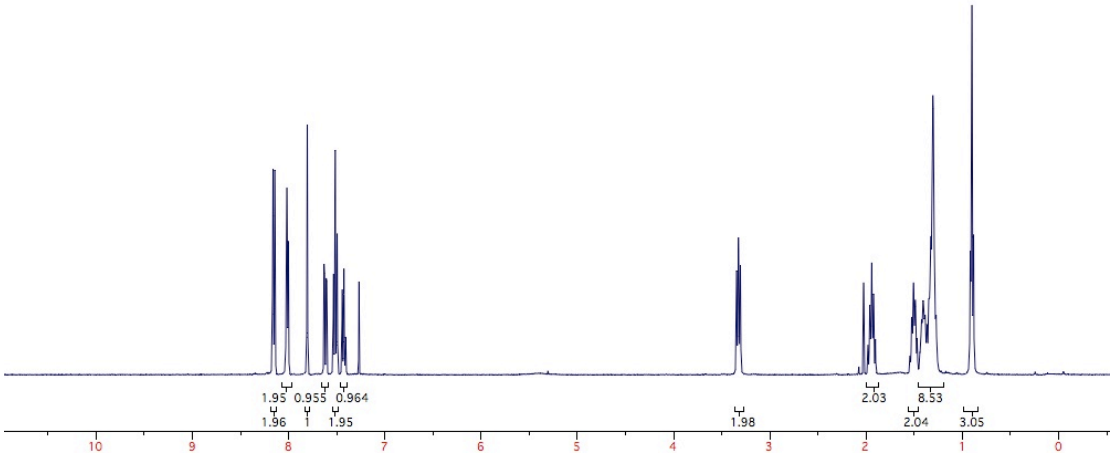


7n (^{13}C, 100 MHz, $CDCl_3$)

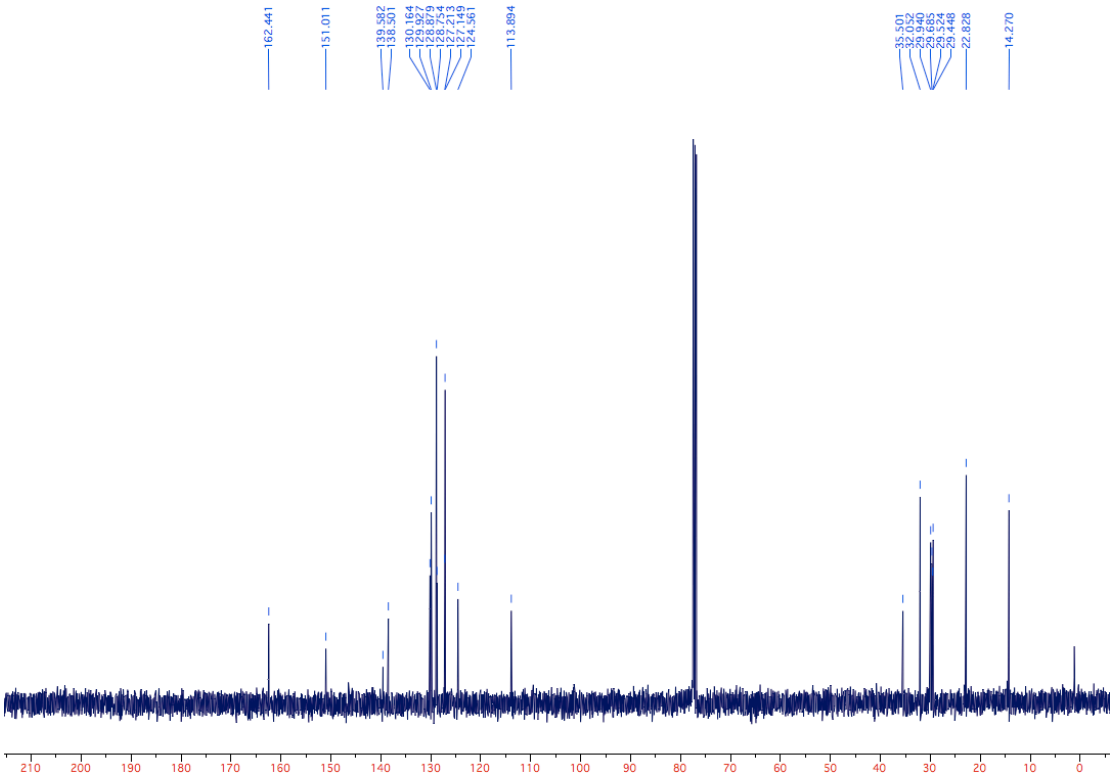


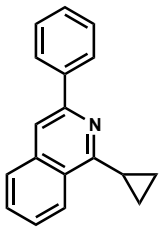


7o (^{1}H, 400 MHz, $CDCl_3$)

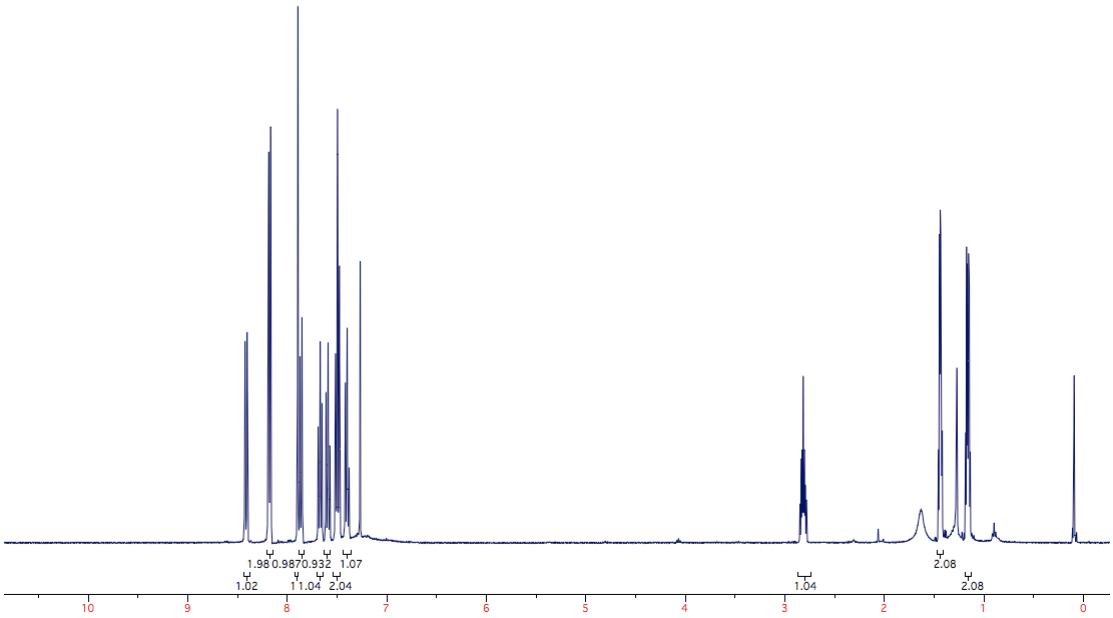


7o (^{13}C, 100 MHz, $CDCl_3$)

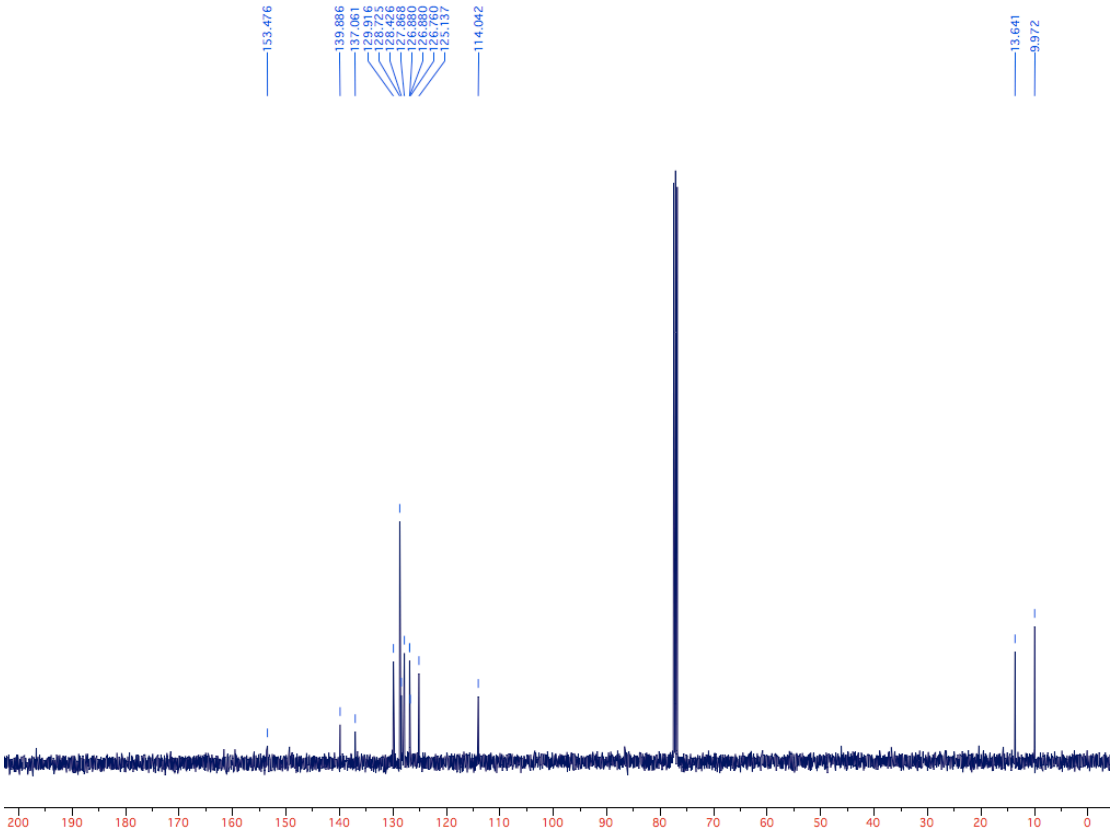


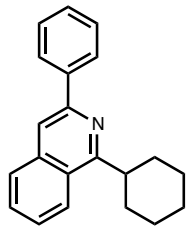


7p (^{1}H, 400 MHz, $CDCl_3$)



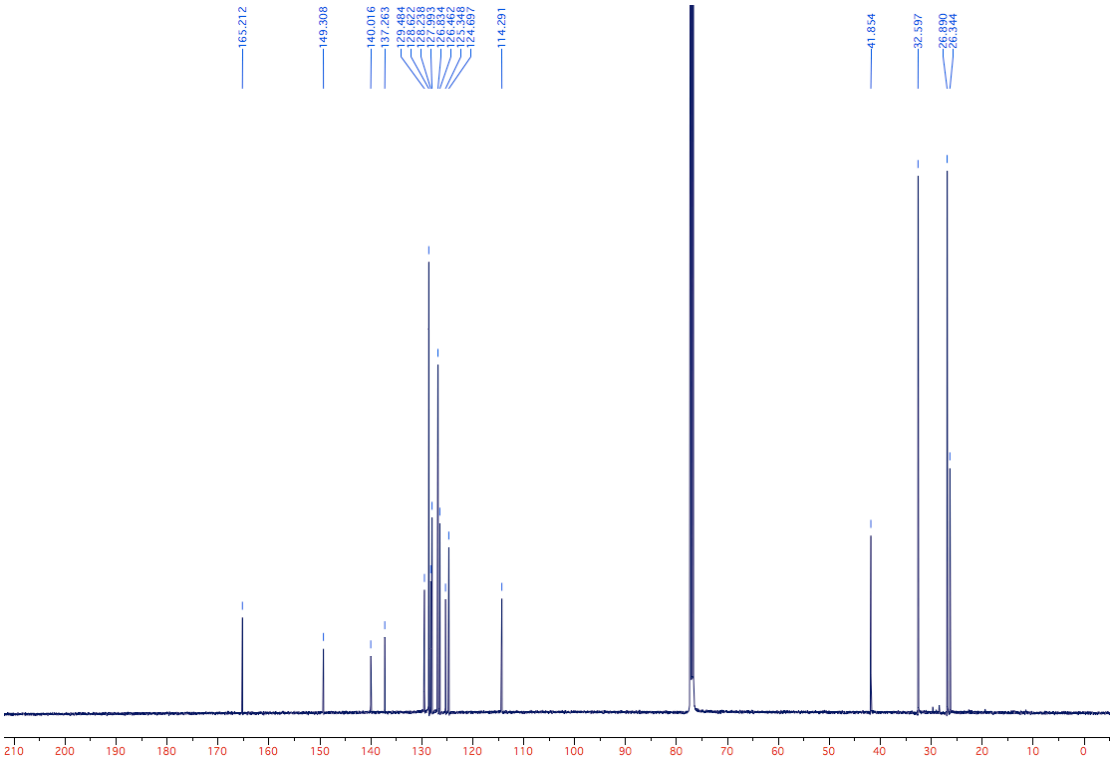
7p (^{13}C, 100 MHz, $CDCl_3$)

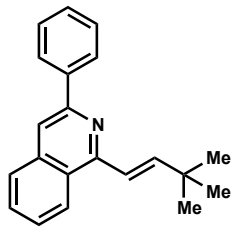




7q (^{1}H, 400 MHz, $CDCl_3$)

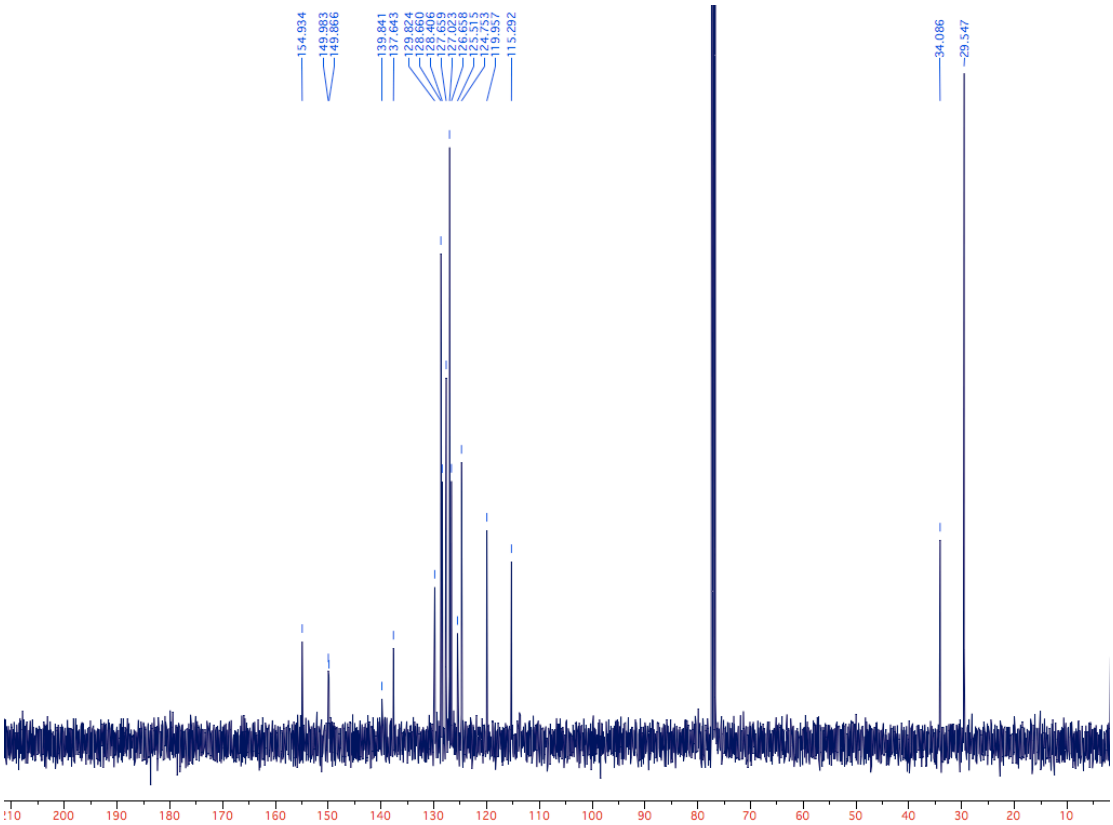
7q (^{13}C, 100 MHz, $CDCl_3$)

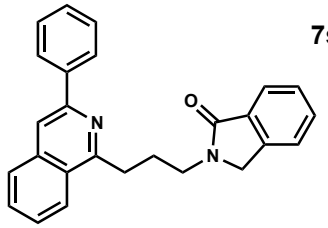




7r (^{1}H, 400 MHz, $CDCl_3$)

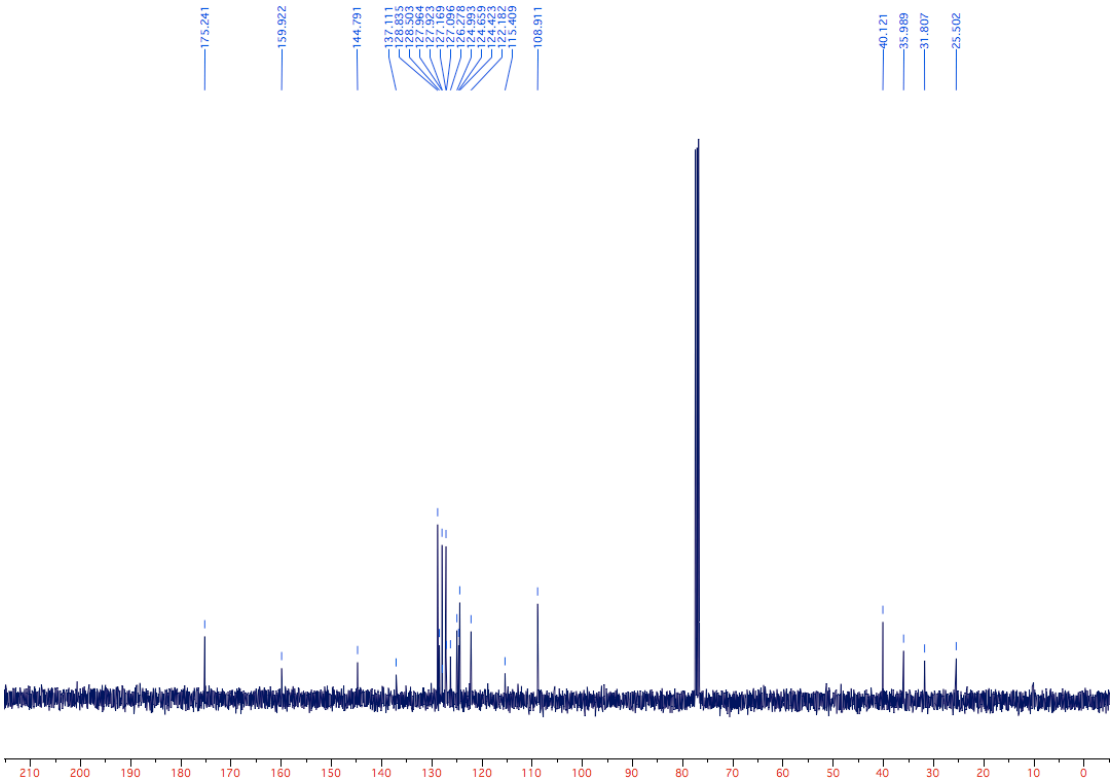
7r (^{13}C, 100 MHz, $CDCl_3$)

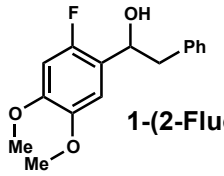




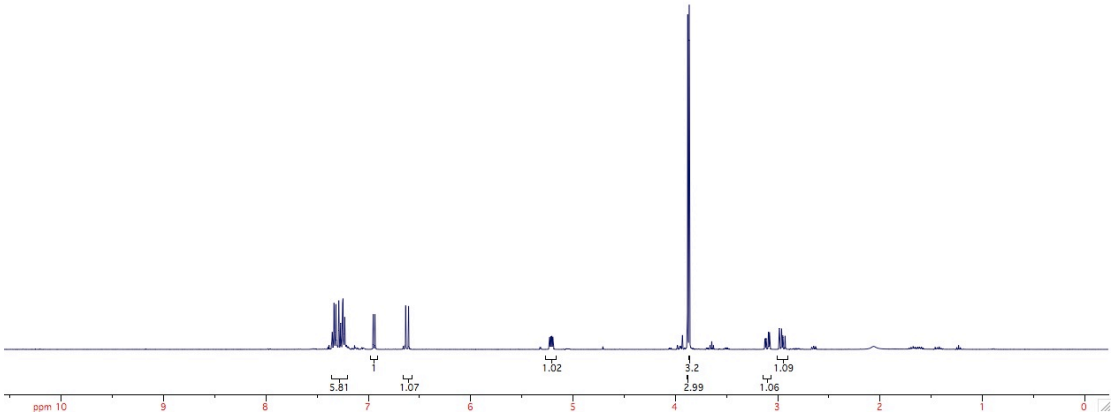
7s (^{1}H, 400 MHz, $CDCl_3$)

7s (^{13}C, 100 MHz, $CDCl_3$)

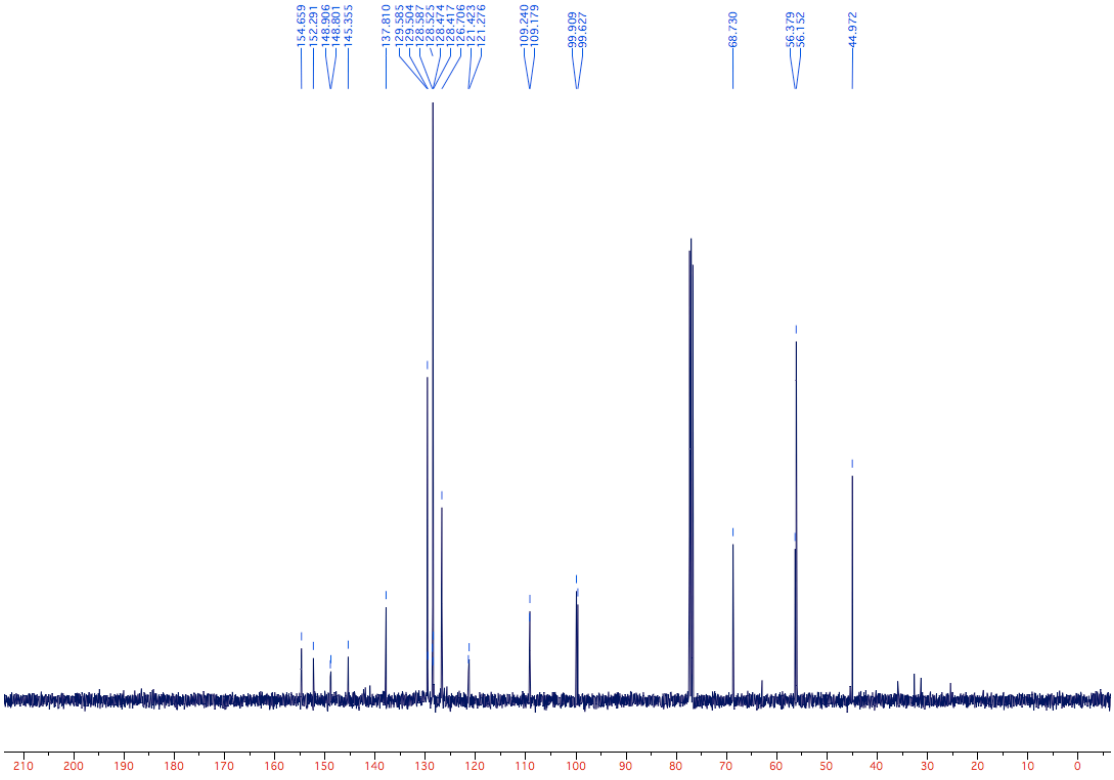


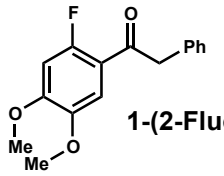


1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanol (^{1}H, 400 MHz, $CDCl_3$)

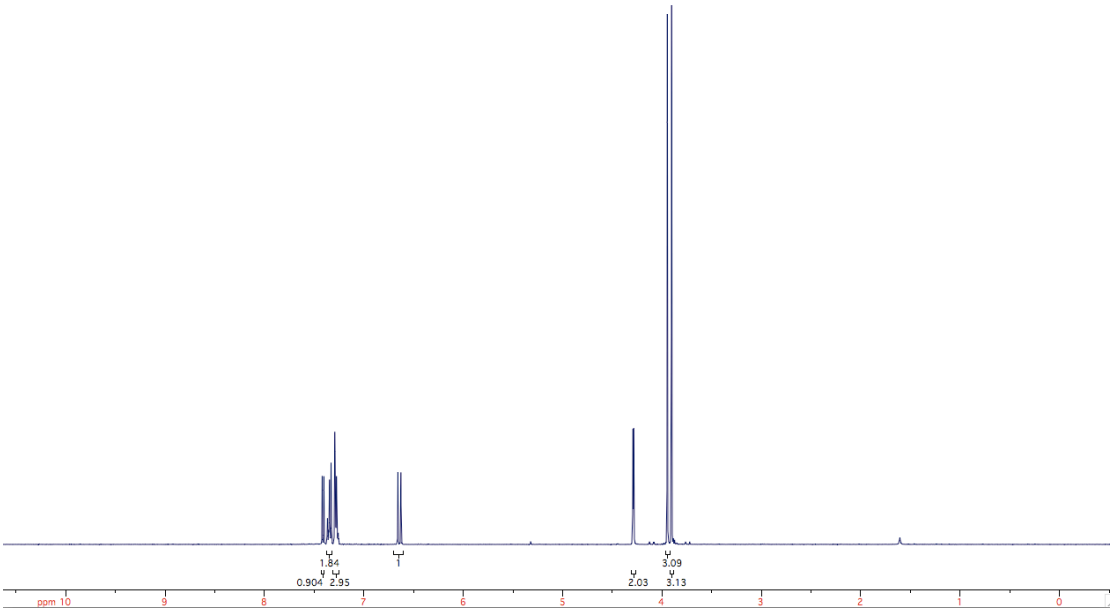


1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanol (^{13}C, 101 MHz, $CDCl_3$)

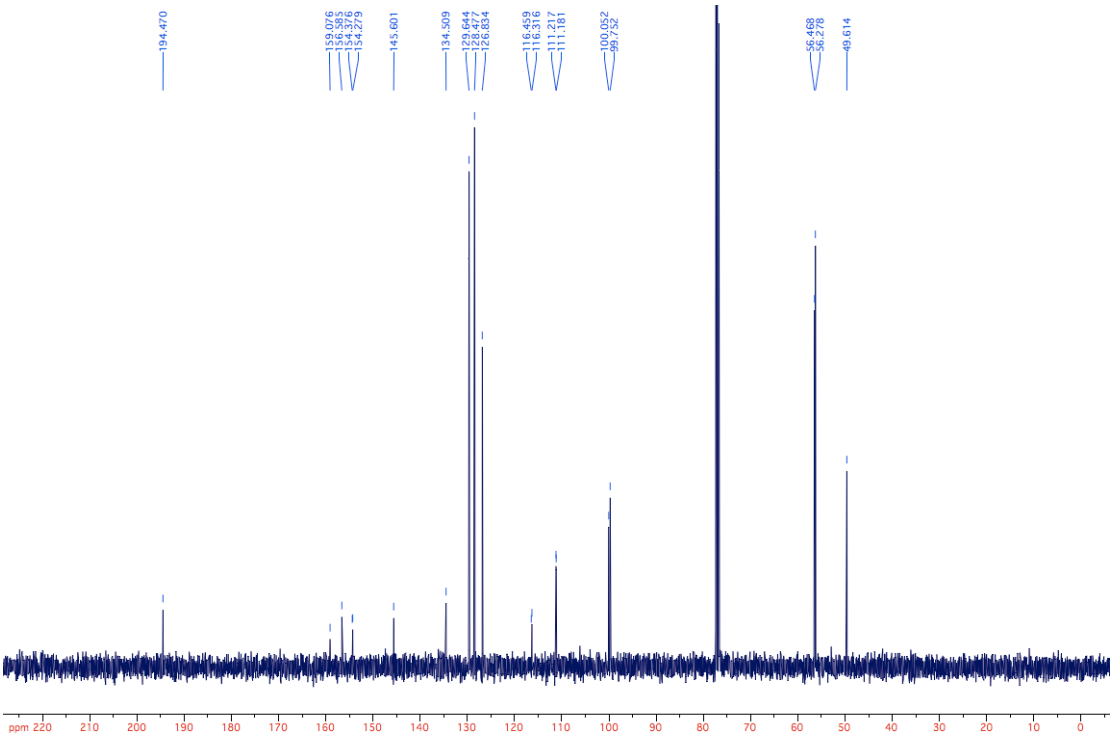


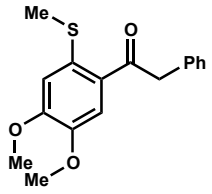


1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanone (^{1}H, 400 MHz, $CDCl_3$)

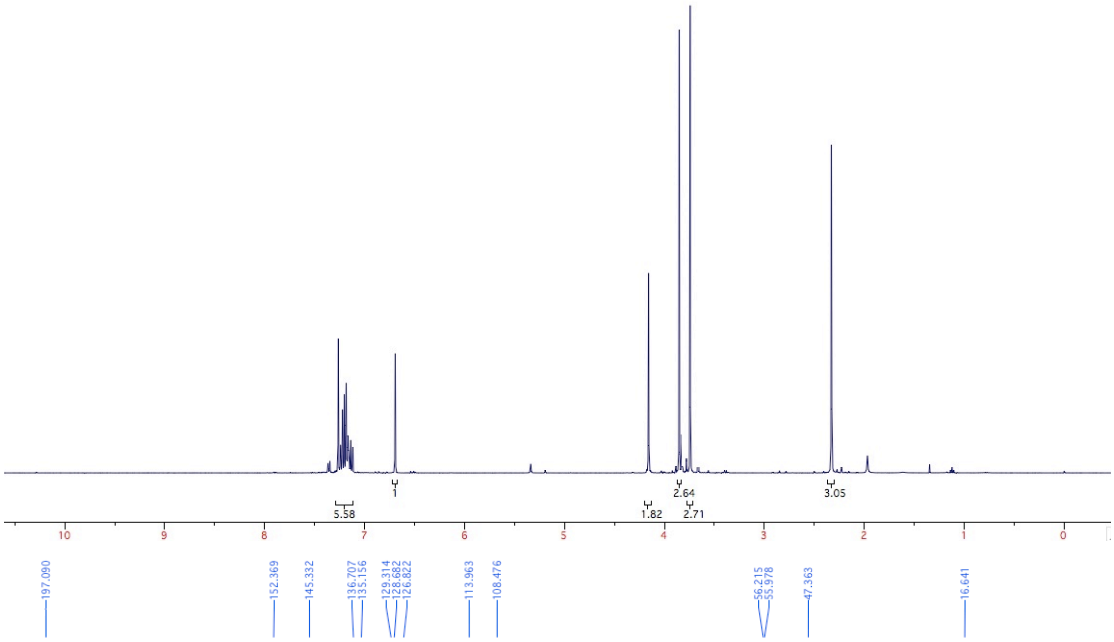


1-(2-Fluoro-4,5-dimethoxyphenyl)-2-phenylethanone (^{13}C, 101 MHz, $CDCl_3$)

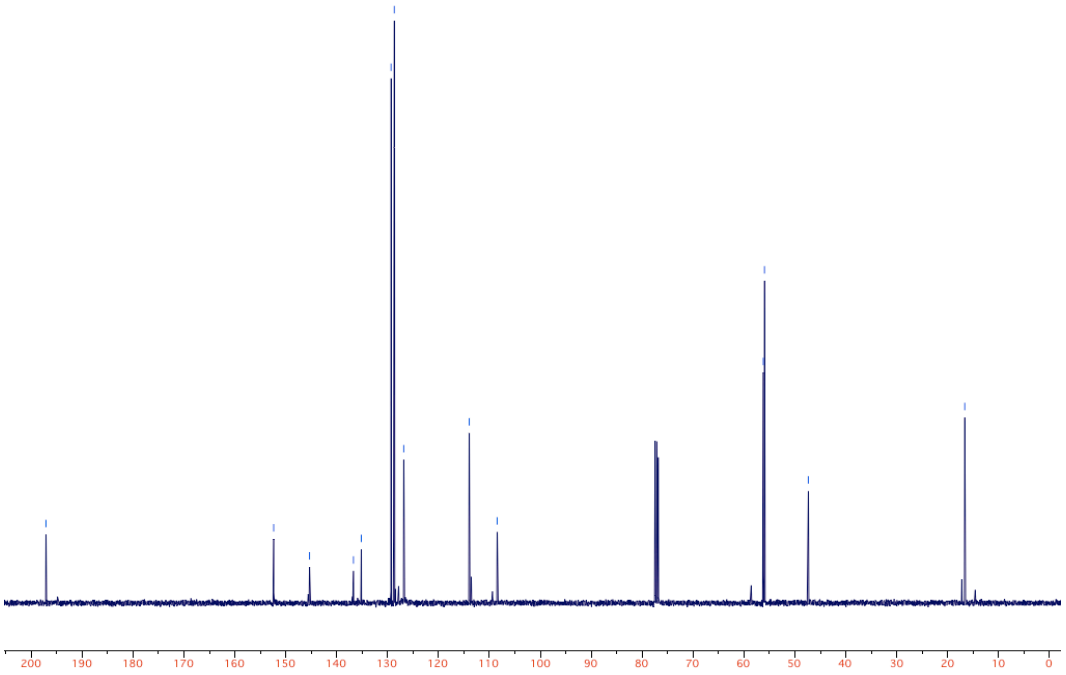


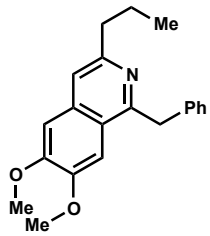


9 (^{1}H, 400 MHz, $CDCl_3$)

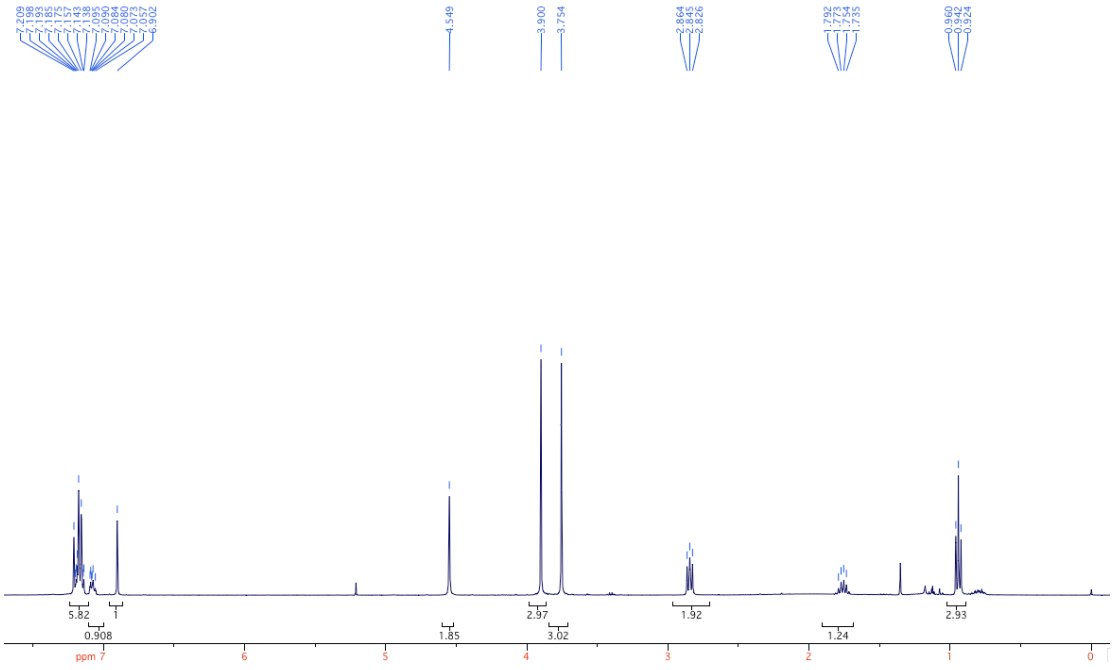


9 (^{13}C, 100 MHz, $CDCl_3$)

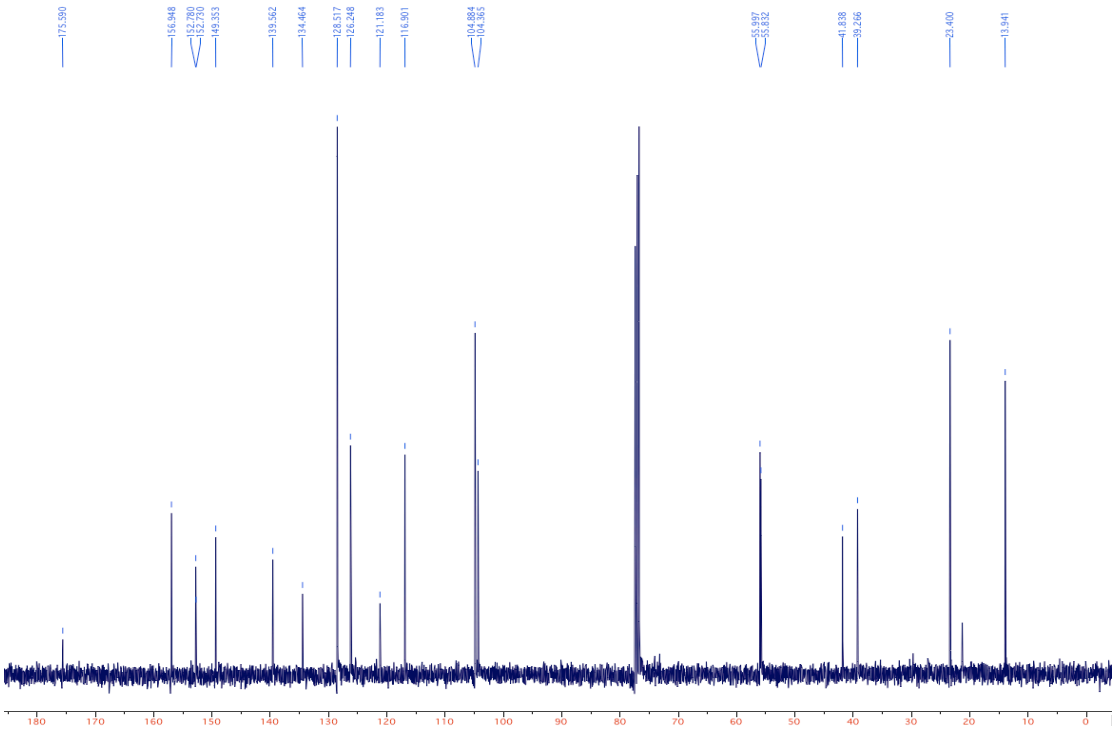


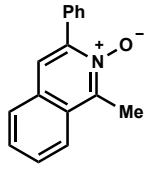


10 (^{1}H, 400 MHz, $CDCl_3$)

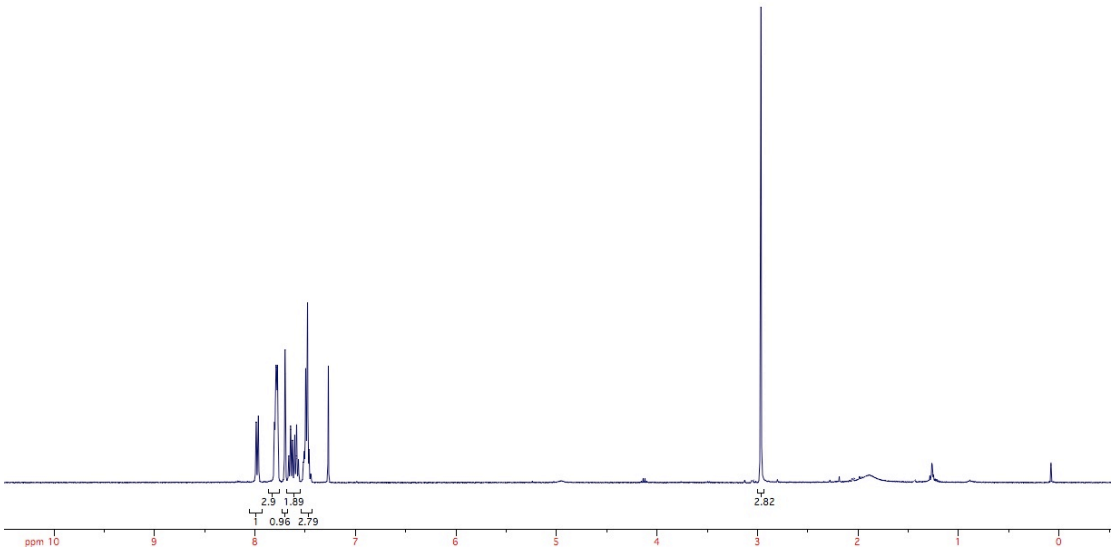


10 (^{13}C, 100 MHz, $CDCl_3$)

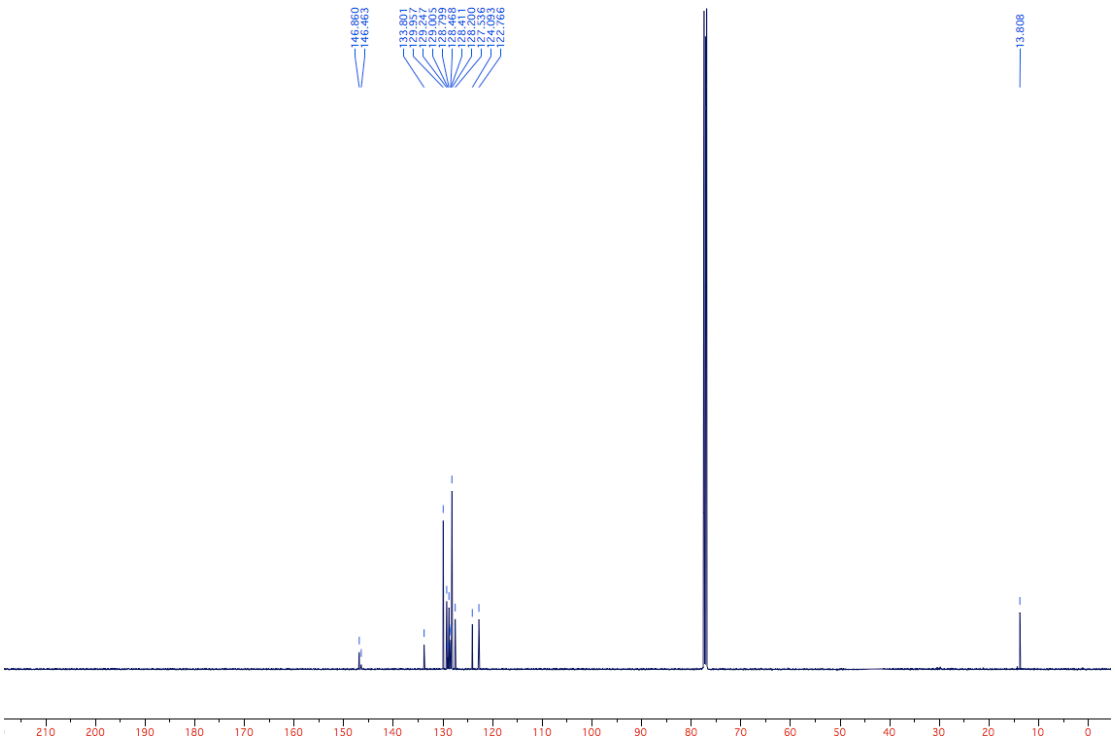


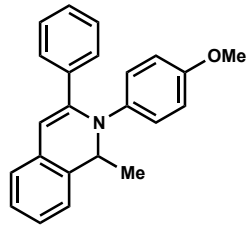


11 (^{1}H, 400 MHz, $CDCl_3$)

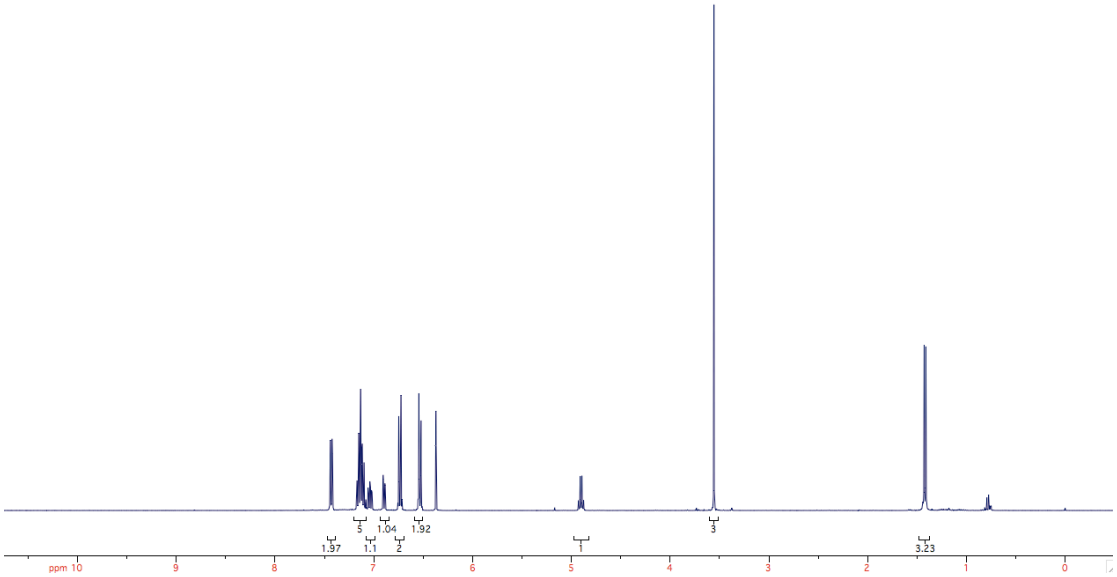


11 (^{13}C, 100 MHz, $CDCl_3$)

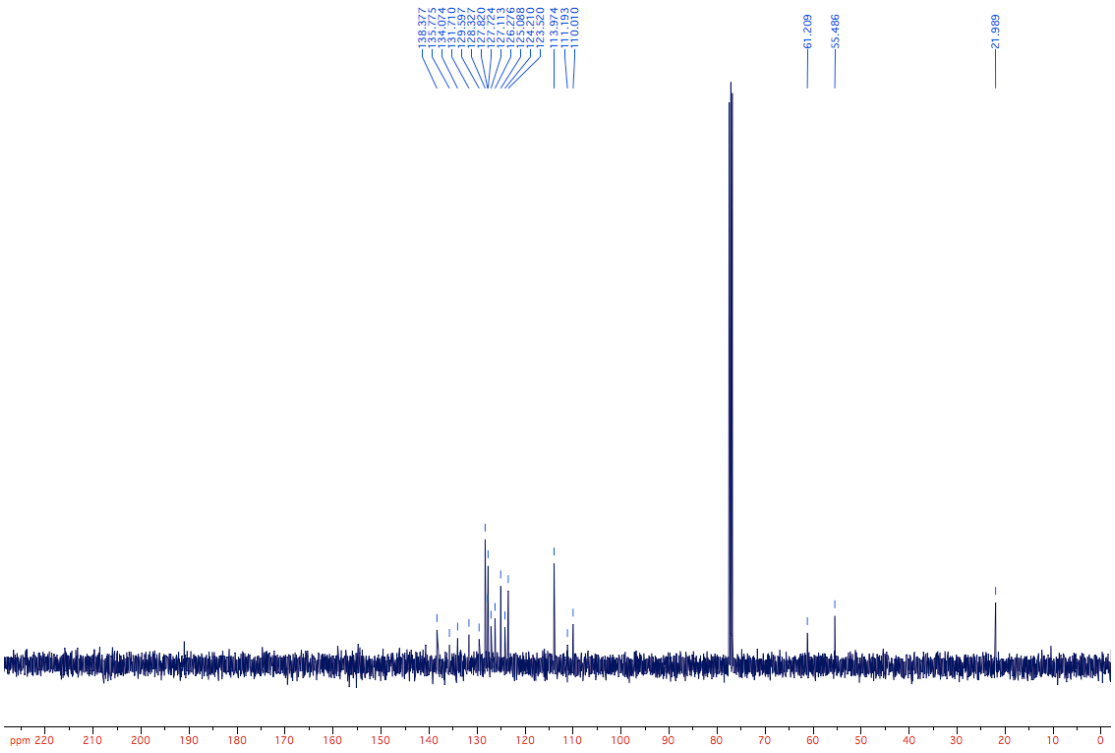


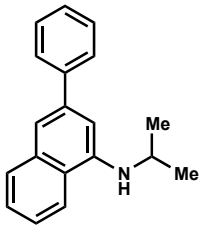


12 (^{1}H, 400 MHz, $CDCl_3$)

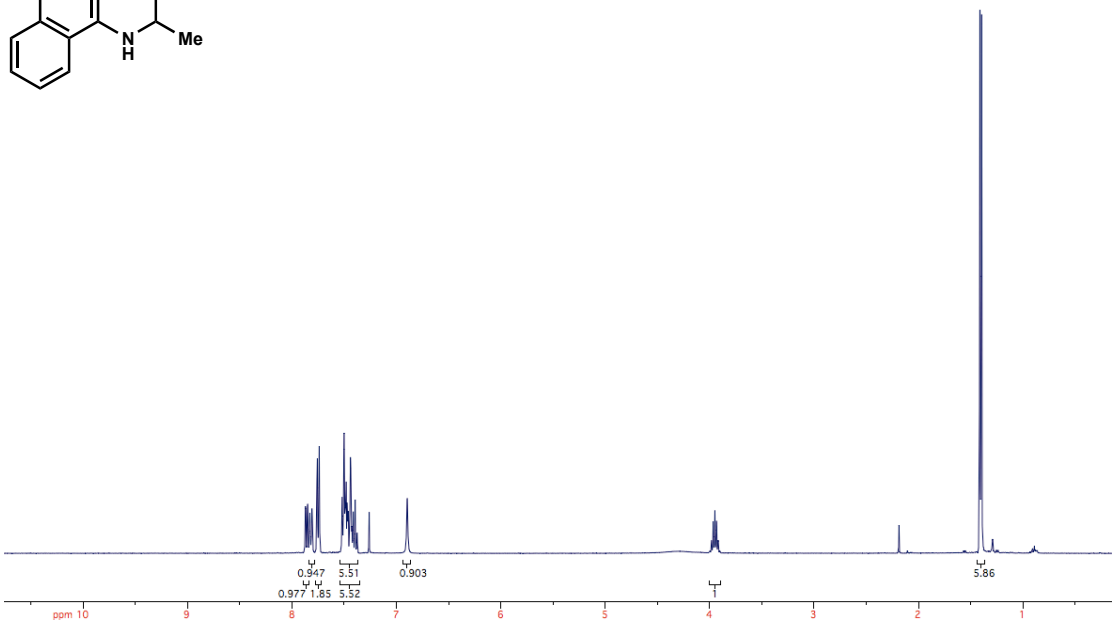


12 (^{13}C, 100 MHz, $CDCl_3$)

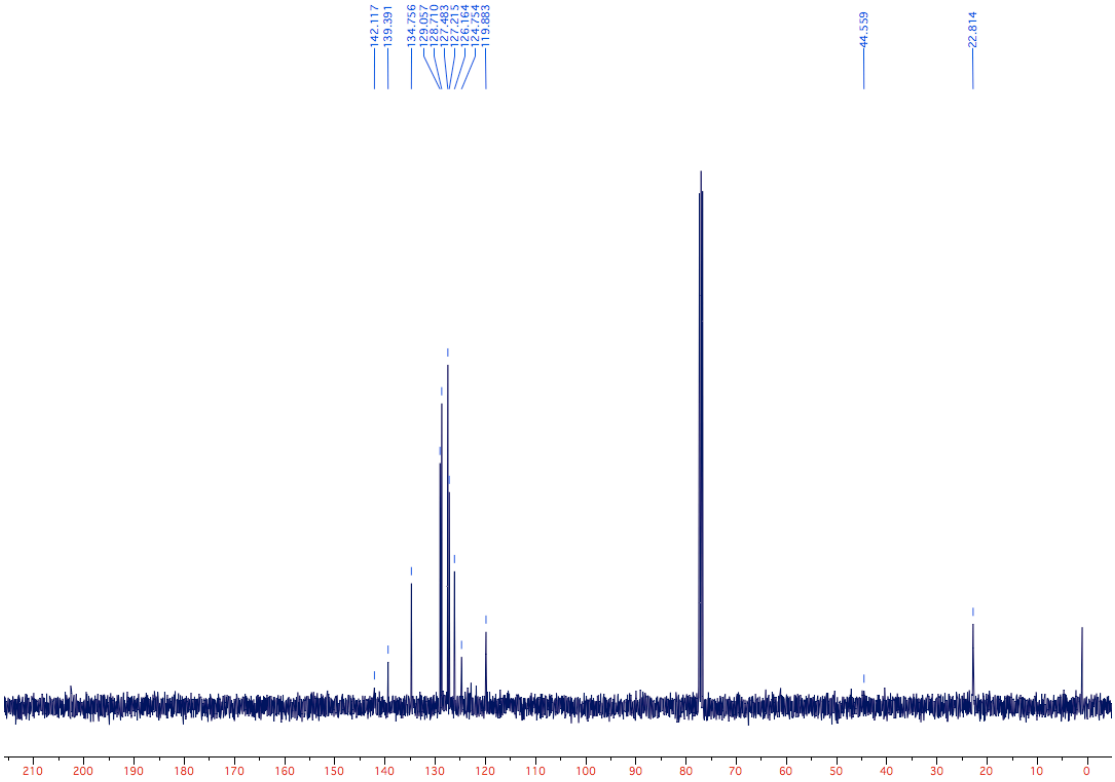




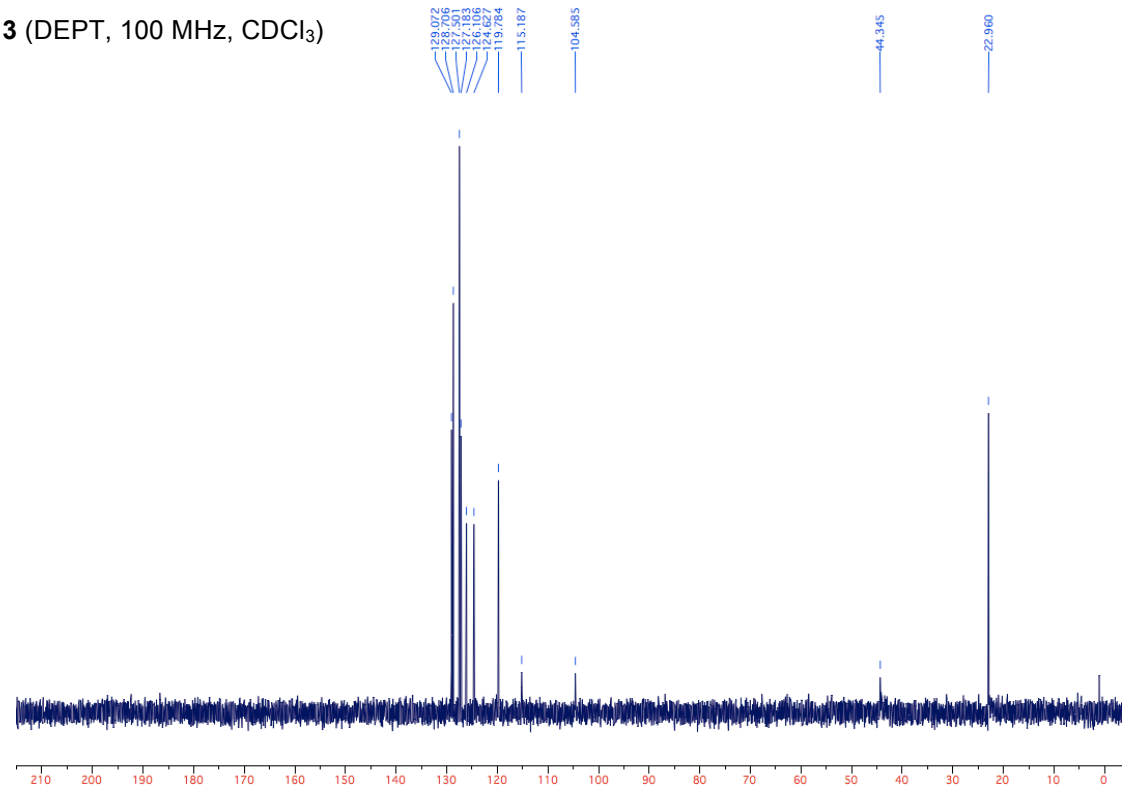
13 (^{1}H, 400 MHz, $CDCl_3$)

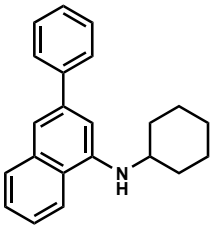


13 (^{13}C, 100 MHz, $CDCl_3$)



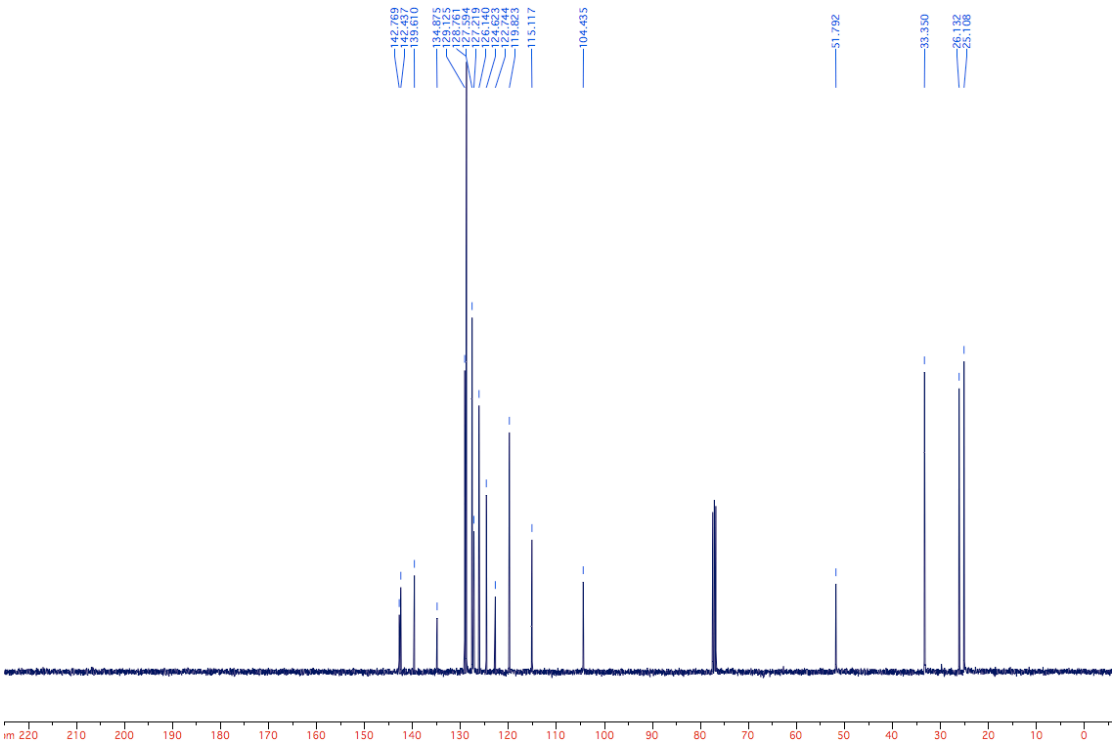
13 (DEPT, 100 MHz, $CDCl_3$)

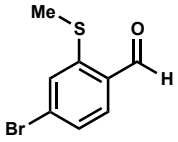




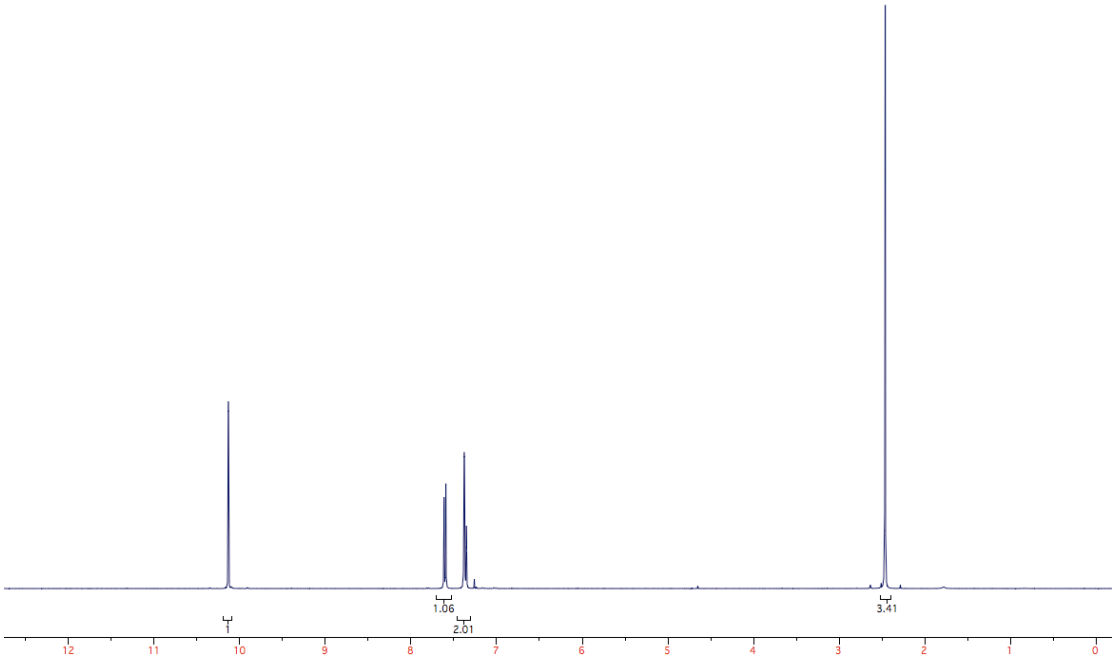
14 (^{1}H, 400 MHz, $CDCl_3$)

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

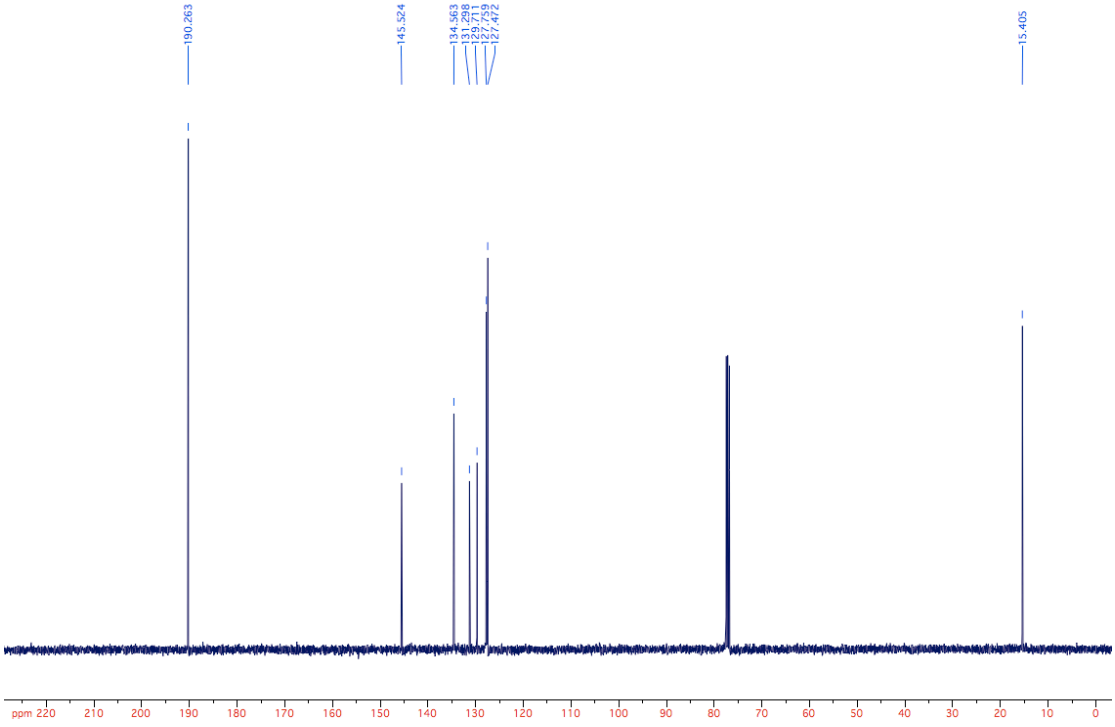


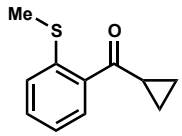


4-Bromo-2-(methylthio)benzaldehyde (^{1}H, 400 MHz, $CDCl_3$)

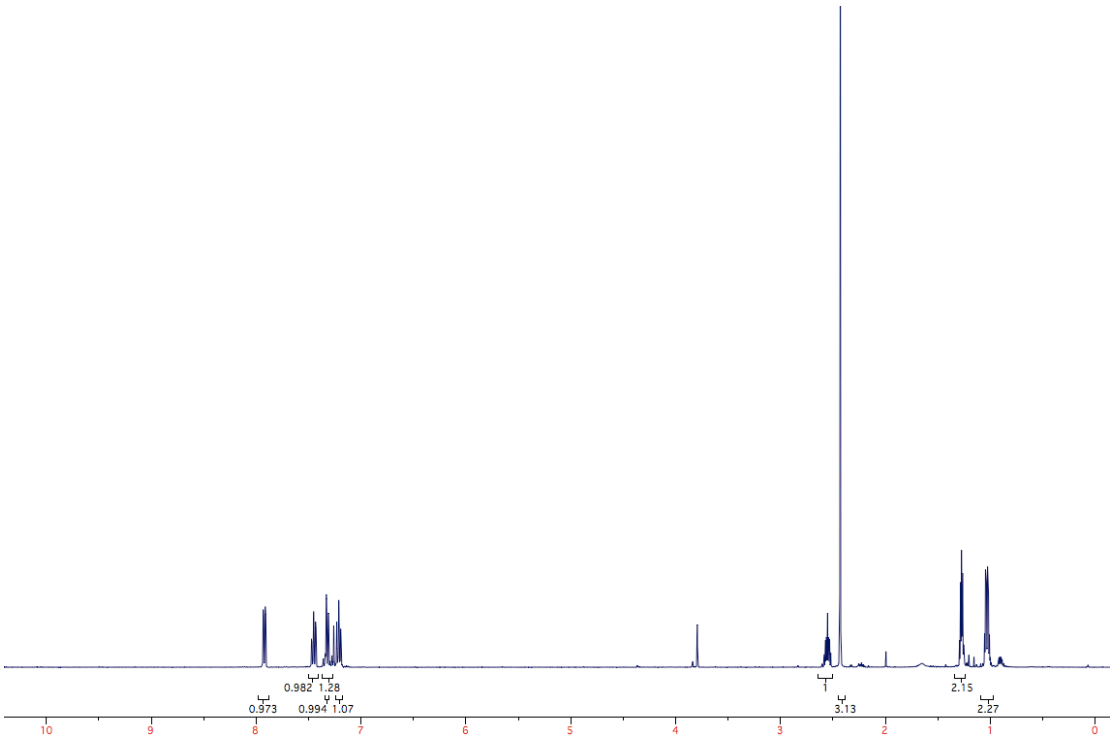


4-Bromo-2-(methylthio)benzaldehyde (^{13}C, 100 MHz, $CDCl_3$)

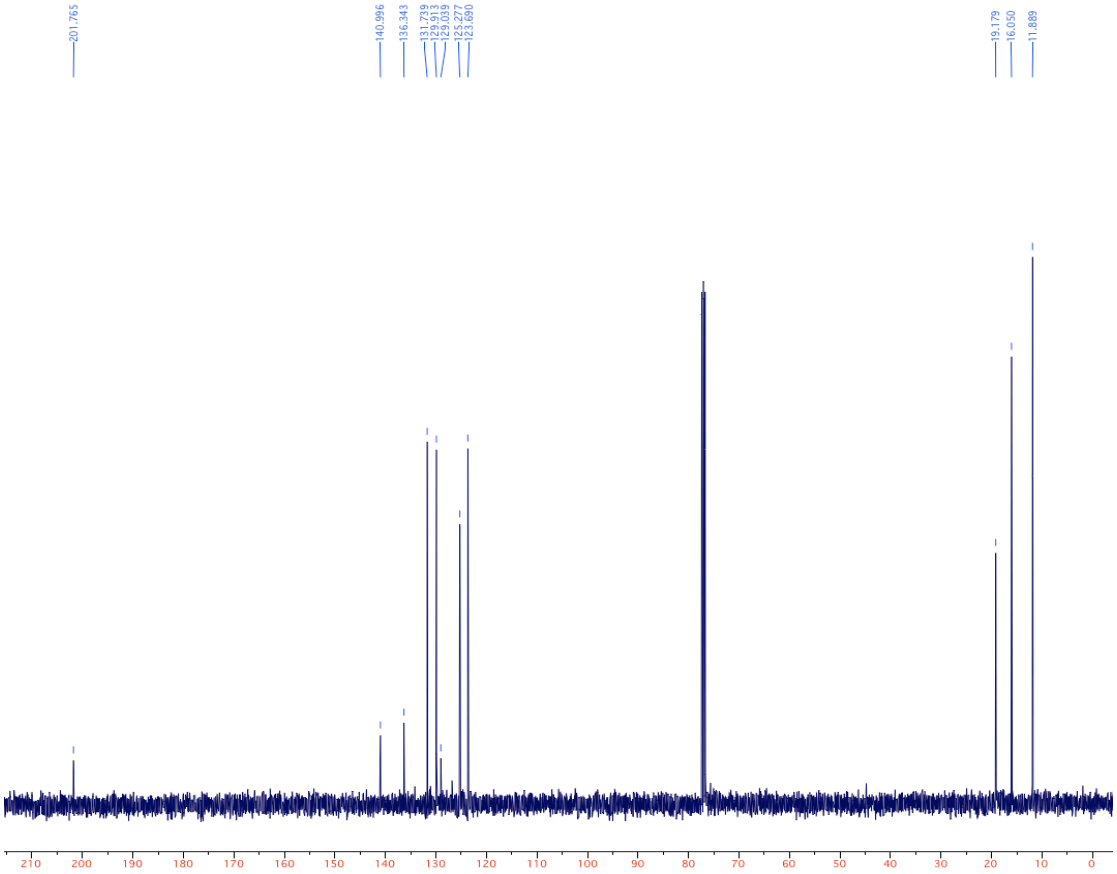


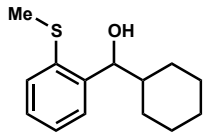


Cyclopropyl(2-(methylthio)phenyl)methanone (^{1}H, 400 MHz, $CDCl_3$)

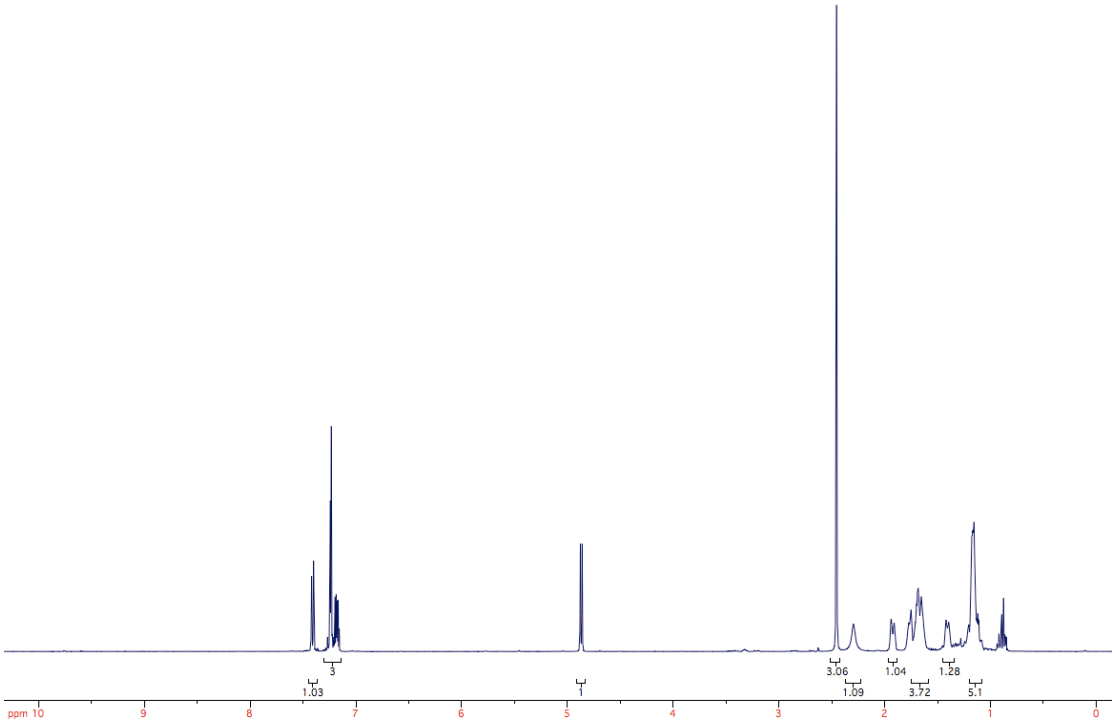


4-Bromo-2-(methylthio)benzaldehyde (^{13}C, 100 MHz, $CDCl_3$)

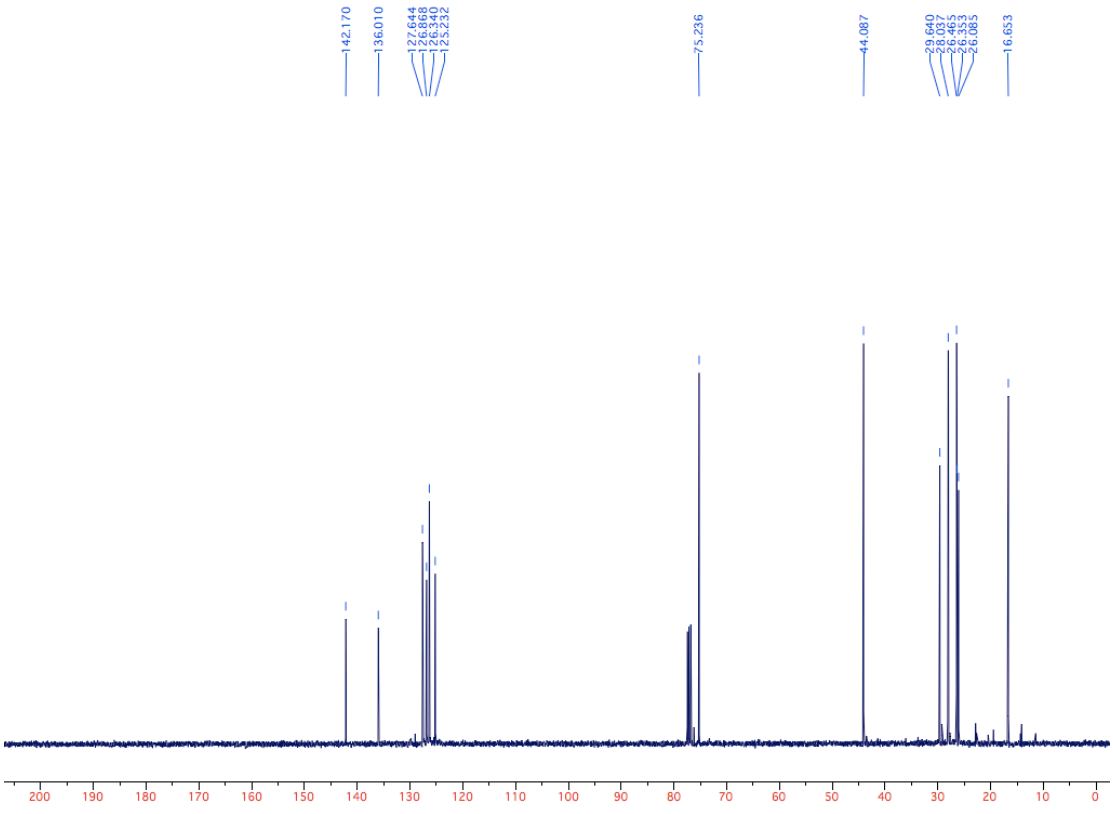


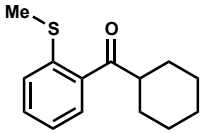


Cyclohexyl(2-(methylthio)phenyl)methanol (^{1}H, 400 MHz, $CDCl_3$)

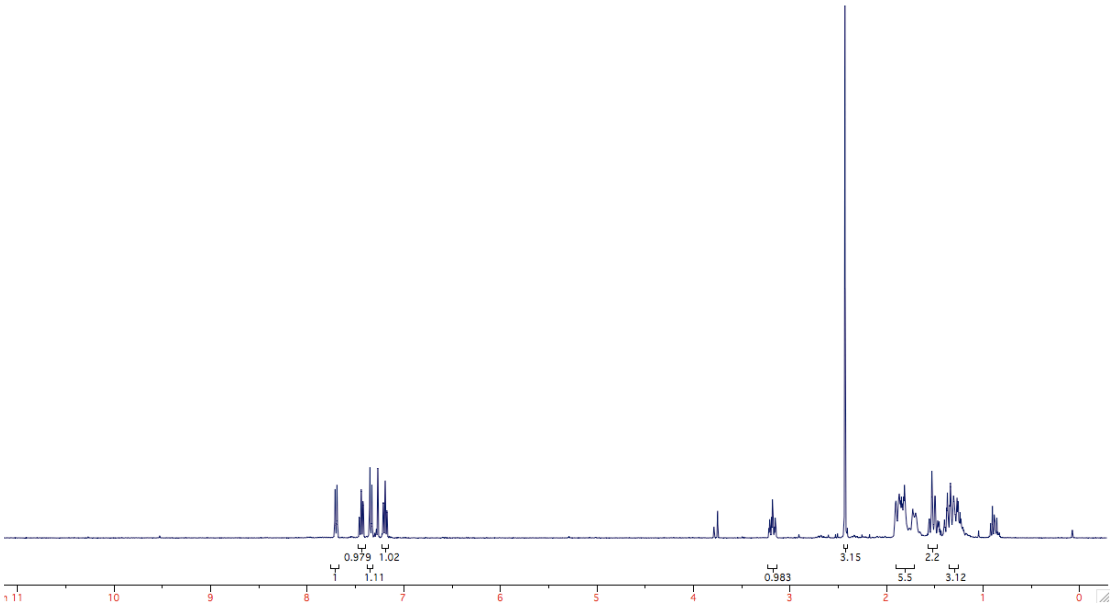


Cyclohexyl(2-(methylthio)phenyl)methanol (^{13}C, 100 MHz, $CDCl_3$)

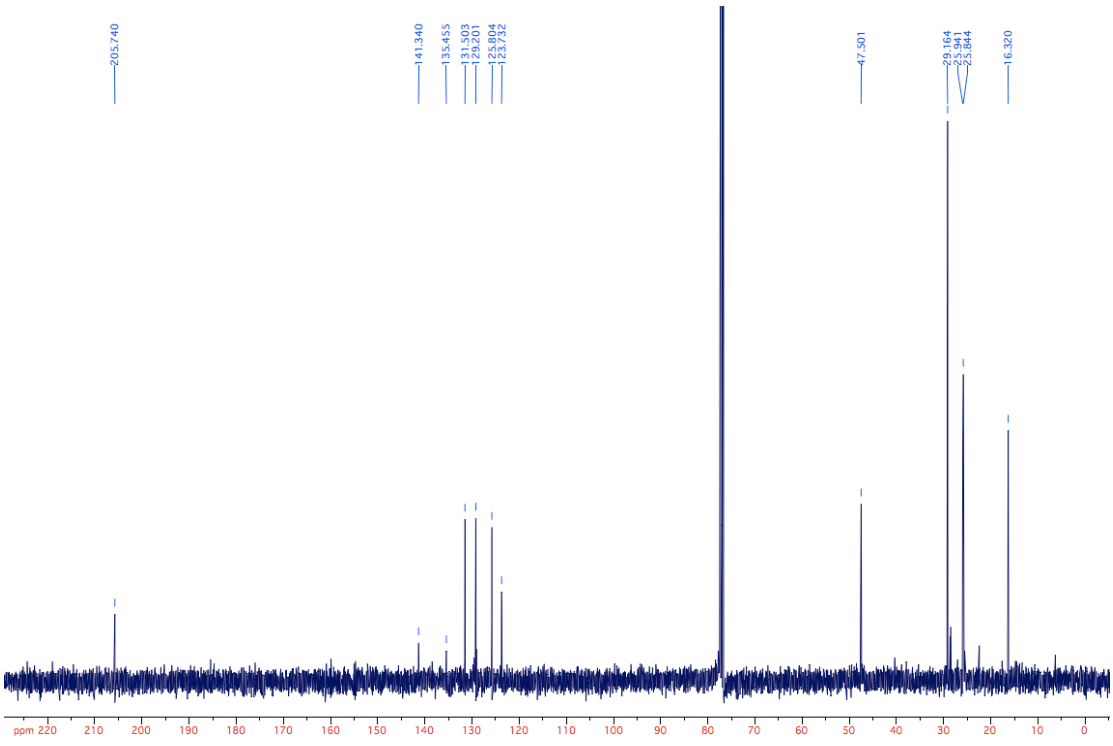


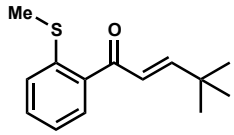


Cyclohexyl(2-(methylthio)phenyl)methanone (^{1}H, 400 MHz, $CDCl_3$)



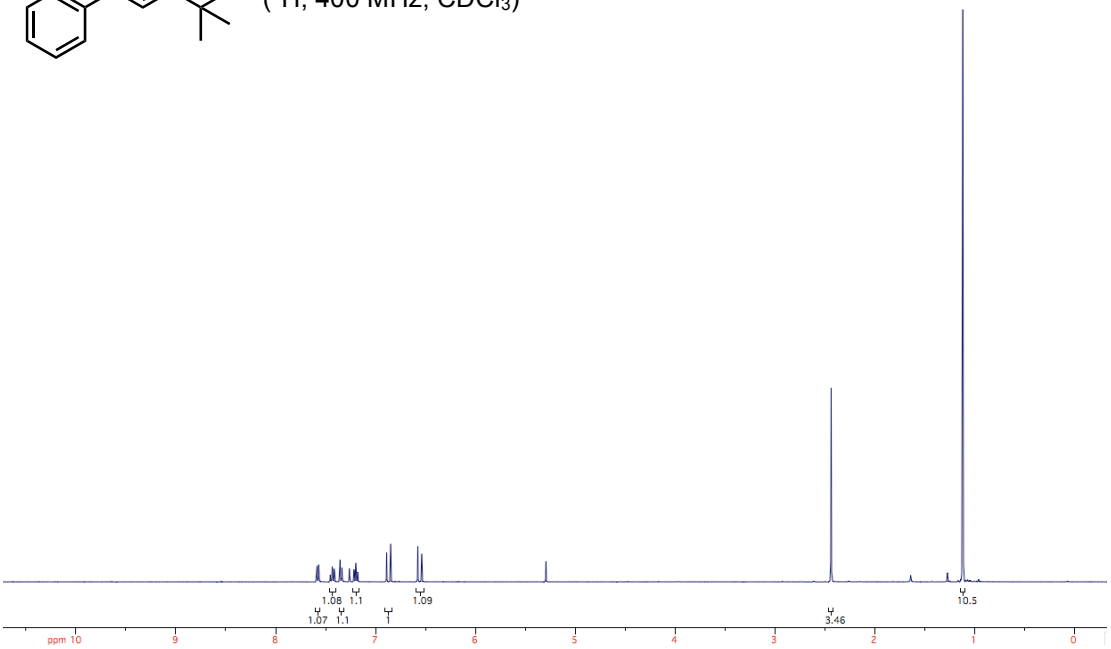
Cyclohexyl(2-(methylthio)phenyl)methanone (^{13}C, 100 MHz, $CDCl_3$)





(*E*)-4,4-Dimethyl-1-(2-(methylthio)phenyl)pent-2-en-1-one

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



(*E*)-4,4-Dimethyl-1-(2-(methylthio)phenyl)pent-2-en-1-one (^{13}C, 100 MHz, $CDCl_3$)