Electronic Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY INFORMATION

Highly regioselective synthesis of 2,4,5-(hetero)aryl substituted oxazoles by intermolecular[3+2]-cycloaddition of unsymmetrical internal alkynes

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General Experimental

Flash column chromatography: Fluorochem silica gel 60 (0.043-0.063 mm). Thin layer chromatography (TLC): Macherey Nagel silica gel 60F254 analytical plates which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid /Δ, potassium permanganate /Δ and vanillin /Δ. IR: Perkin–Elmer Spectrum 100 FTIR spectrometer. Only selected absorbencies (υ_{max}) are reported in cm^{-1}. MS and HRMS (EI): VG ProSpec or VG-ZabSpec at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant. MS and HRMS (ES): Micromass LCT using a methanol mobile phase. HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as *m/z* (relative intensity). Commercially available chemicals/reagents were purchased from Aldrich, Acros, Strem, Alfa Aesar and used without further purification unless reported. All catalysis reactions were carried out under argon in a heat gun-dried glassware. The solvents used were purified using a Pure Solv-MD solvent purification system and were transferred under argon. Anhydrous *m*-xylene was dried over 4 Å molecular sieves. The following cooling baths were used: 0 ^{o}C (ice/water), -78 ^{o}C (dry ice/acetone) and -40 ^{o}C (dry ice/acetonitrile). Asynt DrySyn heating blocks on stirrer hotplates were employed for reactions with temperature controlled *via* external probe. NMR: Spectra were recorded on Bruker AVIII300 (^{1}H = 300 MHz, ^{13}C = 75.5 MHz) and Bruker AVIII400 (^{1}H = 400 MHz, ^{13}C = 101 MHz) in the solvents indicated; $CDCl_3$ purchased from Aldrich and DMSO-d_6 from Goss Scientific. Chemical shifts (δ) are given in ppm relative to TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_c \equiv 77.16$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_c \equiv 7.26$ ppm). Coupling constants (J) are reported in Hz. Multiplicity is denoted in ^{1}H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). 1D ^{13}C NMR spectra were recorded using the UDEFT or PENDANT pulse sequences from the Bruker standard pulse program library. 2D ^{13}C NMR HSQC and HMBC spectra were recorded using the Bruker standard pulse program library.

Starting Materials

The following compounds were prepared according to literature procedures.

Chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold (Au-II)

(78%)[1] Data matches that reported in the literature.[1]

3-Iodo-1*H*-indole (S1)

(99%)[2] Data matches that reported in the literature.[2]

1-Methyl-1*H*-indole (S2)

(97%) Data matches that reported in the literature.[3]

3-Iodo-1-methyl-1H-indole (S3)

(76%)[4] Data matches that reported in the literature.[4]

1-Benzyl-3-iodo-1H-indole (S4)

(98%)[5] Data matches that reported in the literature.[5]

2-(2,2-Dibromovinyl)furan (S5)

(68%)[6a] Data matches that reported in the literature.[6b]

2-Ethynylfuran (S6)

(99%)[7a] Data matches that reported in the literature.[7b]

2-(2,2-Dibromovinyl)thiophene (S7)

(98%)[6a] Data matches that reported in the literature.[8]

2-Ethynylthiophene (S8)

(99%)[7a] Data matches that reported in the literature.[9]

((4-Methoxyphenyl)ethynyl)trimethylsilane (S9)

(71%)[10a] Data matches that reported in the literature.[10b]

1-Ethynyl-4-methoxybenzene (S10)

(99%)[11] Data matches that reported in the literature.[11]

1-(2,2-Dibromovinyl)-4-fluorobenzene (S11)

(98%)[6a] Data matches that reported in the literature.[12]

1-Ethynyl-4-fluorobenzene (S12)

(99%)[7a] Data matches that reported in the literature.[13]

((2-Bromophenyl)ethynyl)trimethylsilane (S13)

(99%)[10a] Data matches that reported in the literature.[14]

1-Bromo-2-ethynylbenzene (S14)

(99%)[11] Data matches that reported in the literature.[15]

5-Bromo-3-iodo-1H-indole (S15)

(92%)[16] Data matches that reported in the literature.[16]

Methyl 1H-indole-6-carboxylate (S16)

(72%)[17a] Data matches that reported in the literature.[17b]

Methyl 3-iodo-1H-indole-6-carboxylate (S17)

(98%)[18] Data matches that reported in the literature.[18]

4-Iodo-N,N-dimethylaniline (S18)

(71%)[19a] Data matches that reported in the literature.[19b]

4-(4-Iodophenyl)morpholine (S19)

(64%)[20a] Data matches that reported in the literature.[20b]

4-(Phenylethynyl)aniline (S20)

(58%)[21a] Data matches that reported in the literature.[21b]

3-(Phenylethynyl)aniline (S21)

(11%)[22a] Data matches that reported in the literature.[22b]

4-Methoxybenzoyl chloride (S21)

(99%)[23] Data matches that reported in the literature.[23]

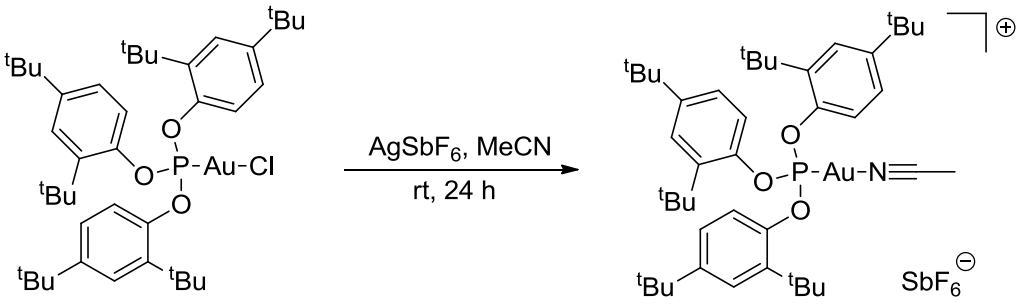
2-(2,4-Dinitrophenoxy)-1*H*-isoindole-1,3(2*H*)-dione (S22)

(97%)[24a,b] Data matches that reported in the literature.[24a,b]

***O*-(2,4-Dinitrophenyl)hydroxylamine (S23)**

(66%)[24a,b] Data matches that reported in the literature.[24a,b]

Synthesis of the gold-complex Au-III



Au-**II** Au-**III**

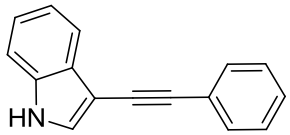
Following Echavarren's procedure,[25] a double-neck, round-bottom flask covered with aluminium foil was charged with $AgSbF_6$ (60.9 mg, 0.18 mmol, 1.2 equiv) dissolved in MeCN (10 mL). Au-**II** (131.7 mg, 0.15 mmol, 1.0 equiv) was added at room temperature to the reaction mixture forming a white suspension. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the white solid residue was redissolved in CH_2Cl_2 (15 mL). After filtration through a plug of silica, evaporation of the solvent and drying on the high vaccuum line for at least 3 hours, the gold complex Au-**III** was afforded as a white powder (140 mg, 83%); mp. 78-80 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.50-7.46 (m, 3H), 7.37 (dd, *J* = 8.5, 1.5 Hz, 3H), 7.25 (dd, *J* = 8.5, 1.5 Hz, 3H), 2.50 (s, 3H), 1.46 (s, 27H), 1.32 (s, 27H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.2 (3 × C), 147.1 (3 × C), 139.1 (3 × C), 125.9 (3 × CH), 124.7 (3 × CH), 119.2 (3 × CH), 35.3 (3 × C), 34.7 (3 × C), 31.4 (9 × CH_3), 30.5 (9 × CH_3), 2.9 (CH_3) ($C_{q.}$ of the CH_3CN is not obvious in the spectra); ^{31}P NMR (300 MHz, $CDCl_3$) δ 87.5; HRMS (ES) calcd. for $C_{44}H_{66}NO_3PAu$: 884.4446, found: 884.4436 $[M]^+$; IR ν_{max}/cm^{-1} 3379, 2206, 1615, 1499, 1415, 1097, 1071, 740, 683.

Synthesis of alkynes (1a-1l, 4a-4e and 6)

General Procedure 1 (GP1)

A mixture of the aryl iodide (1 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (3 mol%) and the terminal alkyne (1.2-3.0 equiv) in degassed Et_3N (0.4 M) was stirred at room temperature overnight. The reaction mixture was then filtered to remove the salts and the filterate was evaporated under reduced pressure. The crude residue was purified by silica flash column chromatography.

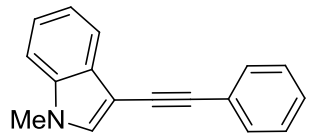
3-(Phenylethynyl)-1H-indole (1a)



Internal alkyne **1a** was synthesised according to **GP1** using 3-iodoindole **S1** (2.43 g, 10.0 mmol), phenyl acetylene (1.34 mL, 12.0 mmol), $PdCl_2(PPh_3)_2$ (351 mg, 5 mol%), CuI (64 mg, 3 mol%) and Et_3N (25 mL). After purification with silica flash column chromatography [Hexane:EtOAc (8:2)] the indole derivative was isolated as a brown solid (913 mg, 70%); mp. 140-142 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.58 (bs, NH), 7.78 (d, *J* = 2.7 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 2H), 7.47-7.30 (m, 4H), 7.24-7.01 (m, 2H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 135.5 (C), 130.8 (2 × CH), 129.7 (CH), 128.5 (2 × CH), 128.1 (C), 127.7 (C), 123.9 (CH), 122.4 (CH), 120.1 (CH), 119.0 (CH), 112.2 (CH), 96.1 (C), 90.6 (C), 84.4 (C); IR ν_{max}/cm^{-1} 3386, 2214, 1484, 1421, 1456, 1333, 1236, 1100, 819, 744, 688.

Data matches that reported in the literature.[26]

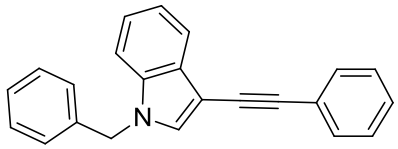
1-Methyl-3-(phenylethynyl)-1H-indole (1b)



Internal alkyne **1b** was synthesised according to **GP1** using *N*-methyl-3-iodoindole **S2** (514 mg, 2.0 mmol), phenyl acetylene (0.25 mL, 2.4 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 5 mol%), CuI (11.5 mg, 3 mol%) and Et_3N (5 mL). After purification with silica flash column chromatography [Hexane:Toluene (9:1)] the indole derivative was isolated as a brown oil (228 mg, 49%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.82 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.51 (m, 2H), 7.38-7.33 (m, 3H), 7.33-7.28 (m, 2H), 7.25-7.19 (m, 2H), 3.80 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 136.4 (C), 132.3 (CH), 131.4 (2 × CH), 129.3 (CH), 128.4 (2 × CH), 127.5 (CH), 124.5 (C), 122.8 (C), 120.5 (CH), 120.3 (CH), 109.7 (CH), 97.2 (C), 91.2 (C), 83.3 (C), 33.2 (CH_3); IR ν_{max}/cm^{-} 3052, 2932, 2209, 1596, 1487, 1424, 1155, 813, 737, 689.

Data matches that reported in the literature.[27]

1-Benzyl-3-(phenylethynyl)-1H-indole (1c)

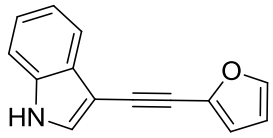


Internal alkyne **1c** was synthesised according to **GP1** using 1-benzyl-3-iodo-1*H*-indole **S4** (1.65 g, 5.0 mmol), phenyl acetylene (0.8 mL, 6.0 mmol), $PdCl_2(PPh_3)_2$ (150 mg, 5 mol%), CuI (63 mg, 3 mol%) and Et_3N (5 mL). After

purification with silica flash column chromatography [Hexane:EtOAc (7:3)] the indole derivative was isolated as a brown solid (616 mg, 40%); mp. 116-118 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.87-7.81 (m, 1H), 7.59-7.52 (m, 2H), 7.42 (s, 1H), 7.39-7.27 (m, 7H), 7.25-7.21 (m, 2H), 7.18-7.12 (m, 2H), 5.33 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 136.7 (C), 136.0 (C), 131.7 (CH), 131.4 (2 × CH), 129.5 (C), 129.0 (2 × CH), 128.4 (2 × CH), 128.1 (CH), 127.7 (CH), 127.1 (2 × CH), 124.4 (C), 123.0 (CH), 120.8 (CH), 120.5 (CH), 110.2 (CH), 97.9 (C), 91.4 (C), 83.1 (C), 50.4 (CH_2); IR ν_{max}/cm^{-1} 3388, 2216, 1598, 1496, 1214, 831, 741.

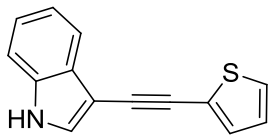
Data matches that reported in the literature.[28]

3-(Furan-2-ylethynyl)-1H-indole (1d)



Internal alkyne **1d** was synthesised according to **GP1** using 3-iodoindole **S1** (729 mg, 3.0 mmol), 2-ethynylfuran **S6** (5.0 mmol), $PdCl_2(PPh_3)_2$ (131 mg, 5 mol%), CuI (19 mg, 3 mol%) and Et_3N (8 mL). After purification with silica flash column chromatography [Hexane:EtOAc (9:1)] the indole derivative was isolated as a dark brown oil (98 mg, 16%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.29 (bs, NH), 7.80 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 2.7 Hz, 1H), 7.37 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.35-7.30 (m, 1H), 7.22-7.13 (m, 2H), 6.64 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.44 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.3 (CH), 138.1 (C), 135.3 (C), 128.7 (CH), 128.4 (C), 123.5 (CH), 121.1 (CH), 120.3 (CH), 114.5 (CH), 111.5 (CH), 111.1 (CH), 98.2 (C), 87.1 (C), 81.0 (C); HRMS (EI) calcd. for $C_{14}H_9NO$: 207.0684, found: 207.0686 $[M]^+$; IR ν_{max}/cm^{-1} 3376, 3059, 1615, 1514, 1488, 1239, 1114, 923, 766, 685.

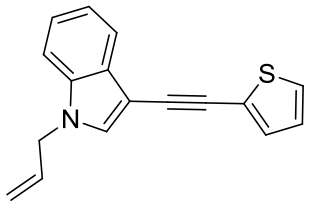
3-(Thiophen-2-ylethynyl)-1H-indole (1e)



Internal alkyne **1e** was synthesised according to **GP1** using 3-iodoindole **S1** (729 mg, 3.0 mmol), 2-ethynylthiophene **S8** (0.5 mL, 5.0 mmol), $PdCl_2(PPh_3)_2$ (131 mg, 5 mol%), CuI (19 mg, 3 mol%) and Et_3N (8 mL). After purification with silica flash column chromatography [Hexane:EtOAc (8:2)] the indole derivative was isolated as a dark brown solid (670 mg, 42%); mp. 69-71 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.27 (bs, NH), 7.82 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.42-7.38 (m, 1H), 7.31-7.27 (m, 2H), 7.25-7.20 (m, 2H), 7.02 (dd, *J* = 5.2, 3.6 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 135.3 (C), 131.2

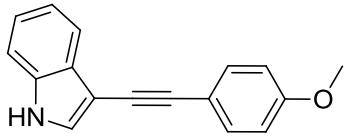
(CH), 128.5 (C), 128.1 (CH), 127.1 (CH), 126.5 (CH), 124.5 (C), 123.4 (CH), 121.0 (CH), 120.3 (CH), 111.4 (CH), 98.8 (C), 86.8 (C), 84.1 (C); HRMS (ES) calcd. for $C_{14}H_{10}NS$: 224.0534, found: 224.0523 $[M+H]^+$; IR ν_{max}/cm^{-1} 3382, 2206, 1457, 1255, 1098, 815, 742, 682.

1-Allyl-3-(thiophen-2-ylethynyl)-1H-indole (1f)



Internal alkyne **1e** (67 mg, 0.3 mmol), allyl bromide (0.03 mL, 0.3 mmol) and NaOH (25 mg, 0.6 mmol) were dissolved in DMSO (0.3 mL) and the reaction mixture was stirring at room temperature for 3h. The reaction mixture was diluted with EtOAc (5 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL), and the combined organic phase was dried over Na_2SO_4. Filtration, evaporation of the solvents in reduced pressure and purification by silica column chromatography (Hexane) afforded **1f** as a viscus yellow oil (71 mg, 90%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.83-7.78 (m, 1H), 7.39 (s, 1H), 7.36-7.28 (m, 3H), 7.26-7.19 (m, 2H), 7.01 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.07-5.92 (m, 1H), 5.25 (ddd, *J* = 10.3, 2.6, 1.4 Hz, 1H), 5.12 (ddd, *J* = 17.1, 2.6, 1.7 Hz, 1H), 4.74 (dt, *J* = 5.4, 1.7 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 135.8 (C), 132.8 (CH), 131.6 (CH), 131.1 (CH), 129.3 (C), 127.1 (CH), 126.4 (CH), 124.6 (C), 123.0 (CH), 120.8 (CH), 120.5 (CH), 118.2 CH), 110.0 (CH_2), 97.4 (C), 87.0 (C), 84.1 (C), 49.2 (CH_2); HRMS (ES) calcd. for $C_{17}H_{14}NS$: 264.0847, found: 264.0846 $[M+H]^+$; IR ν_{max}/cm^{-1} 2920, 2199, 1551, 1504, 1382, 1214, 1158, 925, 739, 701.

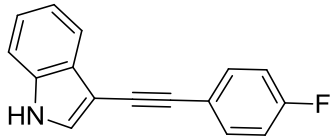
3-[(4-Methoxyphenyl)ethynyl]-1H-indole (1g)



Internal alkyne **1g** was synthesised according to **GP1** using 3-iodoindole **S1** (486 mg, 2.0 mmol), 1-ethynyl-4-methoxybenzene **S10** (0.39 mL, 3.0 mmol), $PdCl_2(PPh_3)_2$ (87 mg, 5 mol%), CuI (13 mg, 3 mol%) and Et_3N (8 mL). After purification with silica flash column chromatography [Hexane:EtOAc (8:2)] the indole derivative was isolated as a brown solid (196 mg, 40%); mp. 128-130 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.19 (bs, NH), 7.82 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.29-7.19 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.1 (C), 135.4 (C), 133.0 (2 × CH), 130.9 (C), 128.6 (C),

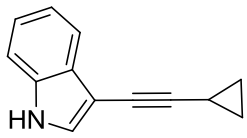
127.5(CH), 123.3 (CH), 120.8 (CH), 120.3 (CH), 116.5 (C), 114.1 (2 × CH), 111.4 (CH), 91.0 (C), 81.4 (C), 55.5 (CH_3); IR ν_{max}/cm^{-1} 3379, 1456, 1242, 1028, 815, 743, 707. Data matches that reported in the literature.[29]

3-[(4-Fluorophenyl)ethynyl]-1H-indole (1h)



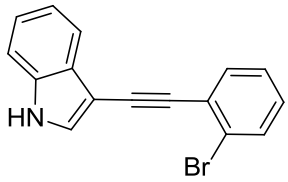
Internal alkyne **1h** was synthesised according to **GP1** using 3-iodoindole **S1** (600 mg, 2.5 mmol), 1-ethynyl-4-fluorobenzene **S12** (0.49 mL, 4.3 mmol), $PdCl_2(PPh_3)_2$ (109 mg, 5 mol%), CuI (16 mg, 3 mol%) and Et_3N (5 mL). After purification with silica flash column chromatography [Hexane:EtOAc (8:2)] the indole derivative was isolated as a dark brown solid (323 mg, 55%); mp. 170-172 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.24 (bs, NH), 7.81 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.57-7.51 (m, 2H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.28 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.25-7.21 (m, 1H), 7.08-7.02 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 250.1 Hz, C), 135.2 (C), 133.3 (d, J_{C-F} = 7.8 Hz, *meta*-2 × CH), 130.6 (C), 128.6 (C), 127.9 (CH), 123.4 (CH), 121.0 (CH), 120.2 (CH), 115.7 (d, J_{C-F} = 22.1 Hz, *ortho*-2 × CH), 112.3 (C), 111.5 (CH), 91.9 (C), 90.1 (C); HRMS (EI) calcd. for $C_{16}H_{10}NF$: 235.0797, found: 235.0796 $[M]^+$; IR ν_{max}/cm^{-1} 3388, 2217, 1599, 1497, 1457, 1215, 1089, 831, 741, 627.

3-(Cyclopropylethynyl)-1H-indole (1i)



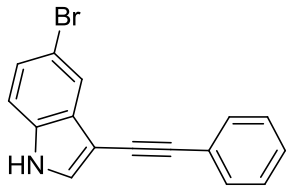
Internal alkyne **1i** was synthesised according to **GP1** using 3-iodoindole **S1** (972 mg, 4.0 mmol), cyclopropyl acetylene (1.0 mL, 11.8 mmol), $PdCl_2(PPh_3)_2$ (114 mg, 5 mol%), CuI (23 mg, 3 mol%) and Et_3N (10 mL). After purification with silica flash column chromatography [Hexane:Toluene (9:1)] the indole derivative was isolated as a dark brown oil (707 mg, 98%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.09 (bs, NH), 7.73 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.40-7.36 (m, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.26-7.24 (m, 1H), 7.22 (dd, *J* = 8.2, 1.5 Hz, 1H), 1.58-1.50 (m, 1H), 0.92-0.80 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 135.3 (C), 129.0 (C), 127.4 (CH), 123.0 (CH), 120.6 (CH), 120.1 (CH), 111.3 (CH), 99.5 (C), 94.8 (C), 68.6 (C), 8.8 (2 × CH_2), 0.5 (CH); HRMS (ES) calcd. for $C_{13}H_{12}N$: 182.0970, found: 182.0969 $[M+H]^+$;IR ν_{max}/cm^{-1} 3380, 1607, 1485, 1432, 1174, 930, 830, 736, 697.

3-((2-Bromophenyl)ethynyl)-1H-indole (1j)



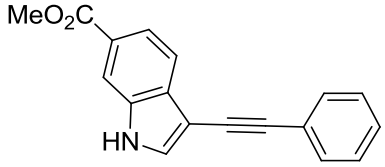
Internal alkyne **1j** was synthesised according to **GP1** using methyl 3-iodo-1*H*-indole **S1** (729 mg, 3.0 mmol), 1-bromo-2-ethynylbenzene **S14** (6.0 mmol), $PdCl_2(PPh_3)_2$ (131 mg, 5 mol%), CuI (19 mg, 3 mol%) and Et_3N (5 mL). After purification with silica flash column chromatography [Hexane:EtOAc (9:1)] the indole derivative was isolated as a brown oil (171 mg, 19%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31 (bs, NH), 7.95-7.90 (m, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.54 (d, *J* = 2.7 Hz, 1H), 7.44-7.40 (m, 1H), 7.35-7.27 (m, 3H), 7.19-7.12 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 209.7 (C), 135.4 (C), 132.9 (CH), 132.5 (CH), 128.7 (CH), 128.2 (CH), 127.1 (CH), 126.5 (C), 125.1 (C), 123.4 (CH), 121.1 (CH), 120.5 (CH), 111.5 (CH), 98.8 (C), 90.0 (C), 88.2 (C); HRMS (ES) calcd. for $C_{16}H_{11}NBr$: 296.0075, found: 296.0061 $[M+H]^+$; IR ν_{max}/cm^{-1} 3395, 3258, 2206, 1456, 1229, 1098, 1025, 838, 739.

5-Bromo-3-(phenylethynyl)-1H-indole (1k)



Internal alkyne **1k** was synthesised according to **GP1** using methyl 5-bromo-3-iodo-1*H*-indole **S15** (258 g, 0.8 mmol), phenyl acetylene (0.15 mL, 1.1 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 5 mol%), CuI (5 mg, 3 mol%) and Et_3N (3 mL). After purification with silica flash column chromatography [Hexane:EtOAc (9:1)] the indole derivative was isolated as a brown solid (169 mg, 71%); mp. 96-98 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.28 (bs, NH), 7.95 (d, *J* = 1.6 Hz, 1H), 7.58-7.55 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.41-7.29 (m, 5H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 134.0 (C), 131.5 (2 × CH), 130.3 (C), 128.8 (CH), 128.5 (2 × CH), 128.0 (CH), 126.3 (CH), 123.9 (C), 122.9 (CH), 114.4 (C), 113.0 (CH), 99.0 (C), 91.5 (C), 82.1 (C); HRMS (EI) calcd. for $C_{16}H_{10}NBr$: 294.9997, found: 294.9993 $[M]^+$; IR ν_{max}/cm^{-1} 3414, 2211, 1448, 1285, 1098, 872, 757, 692.

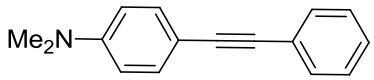
Methyl 3-(phenylethynyl)-1H-indole-6-carboxylate (1l)



Internal alkyne **1l** was synthesised according to **GP1** using methyl 3-iodo-1*H*-indole-6-carboxylate **S17** (753 mg, 2.5 mmol), phenyl acetylene (0.34 mL, 3.0

mmol), $PdCl_2(PPh_3)_2$ (109 mg, 5 mol%), CuI (16 mg, 3 mol%) and Et_3N (5 mL). After purification with silica flash column chromatography [Hexane:EtOAc (7:3)] the indole derivative was isolated as a dark brown solid (337 mg, 49%); mp. 166-168 ^oC; ^1H-NMR (300 MHz, $CDCl_3$) δ 8.57 (bs, NH), 8.17 (dd, *J* = 1.4, 0.7 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 2.7 Hz, 1H), 7.60-7.55 (m, 2H), 7.41-7.33 (m, 3H), 3.95 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.0 (C), 134.8 (C), 132.2 (C), 131.5 (2 × CH), 130.8 (CH), 128.5 (2 × CH), 128.0 (CH), 125.2 (C), 123.9 (C), 121.9 (CH), 120.0 (CH), 113.4 (CH), 99.7 (C), 91.7 (C), 82.1 (C), 52.2 (CH_3); HRMS (ES) calcd. for $C_{18}H_{14}NO_2$: 276.1025, found: 276.1027 $[M+H]^+$; IR ν_{max}/cm^{-1} 3316, 2216, 1697, 1284, 1223, 756, 688.

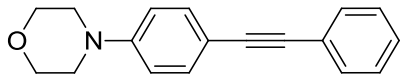
N,N-Dimethyl-4-(phenylethynyl)aniline (4a)



Internal alkyne **4a** was synthesised according to **GP1** using 4-iodo-*N,N*-dimethyl aniline **S18** (879 mg, 3.6 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 1 mol%), CuI (20 mg, 1 mol%) and the phenyl acetylene (0.44 mL, 4.3 mmol) in degassed Et_3N (8 mL). The reaction mixture was stirred at 50 ^oC overnight. After purification with silica flash column chromatography [Hexane:EtOAc (99:1)], the product was isolated as a light brown solid (175 mg, 22%); mp. 108-110 ^oC; ^1H-NMR (300 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.35-7.27 (m, 3H), 6.66 (d, *J* = 9.0 Hz, 2H), 2.99 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.2 (C), 132.9 (2 × CH), 131.4 (2 × CH), 128.4 (CH), 127.6 (2 × CH), 124.3 (C), 112.0 (2 × CH), 110.0 (C), 90.6 (C), 86.9 (C), 40.4 (2 × CH_3); IR ν_{max}/cm^{-1} 3378, 2206, 1607, 1522, 1441, 1227, 1102, 1071, 745.

Data matches that reported in the literature.[30]

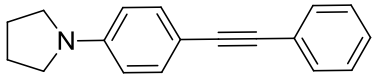
4-[4-(Phenylethynyl)phenyl]morpholine (4b)



Internal alkyne **4b** was synthesised according to **GP1** using 4-(4-iodophenyl)morpholine aniline **S19** (925 mg, 3.2 mmol), $PdCl_2(PPh_3)_2$ (22 mg, 1 mol%), CuI (18 mg, 1 mol%) and the phenyl acetylene (0.40 mL, 3.8 mmol) in degassed Et_3N (7.5 mL) The reaction mixture was stirred at 50 ^oC overnight. Purification with silica flash column chromatography [Hexane:EtOAc (3:1)], afforded the aniline derivative as a light brown solid (432 mg, 51%); mp. 178-180 ^oC; ^1H-NMR (300 MHz, $CDCl_3$) δ 7.54-7.48 (m, 2H), 7.45 (d, *J* = 8.9

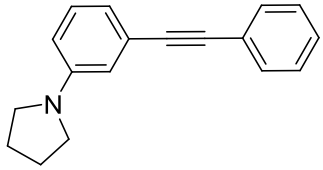
Hz, 2H), 7.38-7.28 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.91-3.80 (m, 4H), 3.26-3.16 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.0 (C), 132.9 (2 × CH), 131.6 (2 × CH), 128.4 (2 × CH), 127.9 (CH), 123.9 (C), 115.0 (2 × CH), 114.0 (C), 89.9 (C), 88.1 (C), 66.9 (2 × CH_2), 48.7 (2 × CH_2); HRMS (ES) calcd. for $C_{18}H_{18}NO$: 264.1388, found: 264.1381 $[M+H]^+$; IR ν_{max}/cm^{-1} 2961, 2855, 2830, 2208, 1607, 1592, 1444, 1382, 1263, 1236, 1068, 818, 760.

1-[4-(Phenylethynyl)phenyl]pyrrolidine (4c)



4-(Phenylethynyl)aniline **S20** (773 mg, 4.0 mmol) was disolved in toluene (5 mL), 1,4-dibromobutane (0.86 mL, 7.2 mmol) and DIPEA (1.68 mL, 9.6 mmol) were added to the reaction mixture. After refluxing for 16 h at 120 ^{o}C, the mixture was allowed to cool and the inorganic salts formed were removed by filtration and washed with EtOAc. Evaporation of the solvent under reduced pressure and purification of the crude residue with silica flash column chromatography [Hexane:EtOAc (9:1)] afforded the aniline derivative as an orange solid (940 mg, 95%); mp. 168-172 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.35-7.28 (m, 3H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.31 (t, *J* = 6.6 Hz, 4H), 2.06-1.97 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.1 (C), 132.8 (2 × CH), 131.4 (2 × CH), 128.4 (2 × CH), 127.3 (C),127.5 (CH), 126.7 (C), 111.5 (2 × CH), 77.2 (C), 73.5 (C), 47.6 (2 × CH_2), 25.6 (2 × CH_2); HRMS (EI) calcd. for $C_{18}H_{17}N$: 247.1361, found: 247.1362 $[M]^+$; IR ν_{max}/cm^{-1} 2962, 2869, 1608, 1518, 1159, 1026, 957, 812, 750.

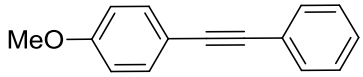
1-(3-(Phenylethynyl)phenyl)pyrrolidine (4d)



3-(Phenylethynyl)aniline **S21** (218 mg, 1.2 mmol) was disolved in toluene (3 mL), 1,4-dibromobutane (0.24 mL, 2.0 mmol) and DIPEA (0.46 mL, 2.7 mmol) were added to the reaction mixture. After refluxing for 16 h at 120 ^{o}C, the mixture was allowed to cool and the inorganic salts formed were removed by filtration and washed with EtOAc. Evaporation of the solvent under reduced pressure and purification of the crude residue with silica flash column chromatography (Hexane) afforded the aniline derivative as a yellow oil (112 mg, 41%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.61-7.51 (m, 2H), 7.41-7.30 (m, 3H), 7.20 (app. t, *J* = 7.9 Hz, 1H), 6.89-6.83 (m, 1H), 6.76-6.43 (m,

1H), 6.59-6.52 (m, 1H), 3.37-3.24 (m, 4H), 2.08-1.96 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 147.8 (C), 131.8 (2 × CH), 129.2 (CH), 128.4 (2 × CH), 128.1 (CH), 123.7 (C), 119.0 (CH), 114.6 (CH), 112.2 (CH), 90.7 (C), 88.3 (C), 47.7 (2 × CH_2), 25.6 (2 × CH_2); HRMS (ES) calcd. for $C_{18}H_{18}N$: 248.1439, found: 247.1441 $[M+H]^+$;IR ν_{max}/cm^{-1} 2965, 2834, 1592, 1439, 1373, 1173, 1009, 837, 753, 684.

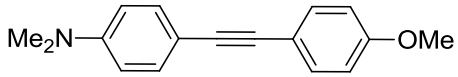
1-Methoxy-4-(phenylethynyl)benzene (4e)



Internal alkyne **4e** was synthesised according to **GP1** using *p*-iodoanisole (1.17 g, 5.0 mmol), $PdCl_2(PPh_3)_2$ (176 mg, 5 mol%), CuI (96 mg, 10 mol%) and phenyl acetylene (0.63 mL, 6.0 mmol) in degassed Et_3N (10 mL). The reaction mixture was stirred at room temperature overnight. After purification with silica flash column chromatography (Hexane), the product was isolated as a yellow solid (824 mg, 80%); mp. 54-56 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.31-7.22 (m, 3H), 6.84-6.78 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.8 (C), 133.2 (2 × CH), 131.6 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 123.8 (C), 115.6 (C), 114.2 (2 × CH), 88.5 (C), 88.2 (C), 55.5 (CH_3); IR ν_{max}/cm^{-1} 2994, 2217, 1594, 1508, 1439, 1243, 1178, 1027, 832, 752, 690.

Data matches that reported in the literature.[31]

4-((4-Methoxyphenyl)ethynyl)-N,N-dimethylaniline (6)



Following a known procedure,[32] a mixture of *p*-iodoanisole (749 mg, 3.2 mmol, 1.0 equiv), 4-ethynyl-*N,N*-dimethylaniline (3.8 mmol, 1.4 equiv), $NiCl_2(PPh_3)_2$ (105 mg, 5 mol%), CuI (61 mg, 10 mol%) and K_2CO_3 (883 mg, 6.4 mmol, 2.0 equiv) in dioxane (13 mL) and water (5 mL) was stirred under argon at reflux for 2 hours. Filtration through a silica pad, evaporation of the solvent and purification with silica column chromatography [Hexane:EtOAc (9:1)] to yield the aniline derivative as a yellow solid (300 mg, 37%); mp. 118-120 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.68 (bd, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.00 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.2 (C), 150.1 (C), 132.8 (2 × CH), 132.7 (2 × CH), 116.5 (C), 114.0 (2 × CH), 112.0 (2 × CH), 110.6 (C), 89.2 (C), 87.3 (C), 55.4 (CH_3), 40.4 (CH_3), IR ν_{max}/cm^{-1} 3217, 1609, 1525, 1496, 1238, 1024, 817.

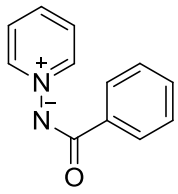
Data matches that reported in the literature.[33]

Synthesis of N-substituted iminopyridinium ylides (2a-2f and 2aI-2aV)

General Procedure 2 (GP2)

N-Aminopyridinium iodide (1.0 equiv) was added to an aqueous solution of 10% aq. NaOH at 0°C and stirred for 10 min. Acid chloride (2.0 equiv) was added at this temperature and the mixture stirred overnight at room temperature. The resulting suspension was then extracted with CH_2Cl_2 (3 times) and the organic layer dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the desired ylides which, if necessary, were purified by recrystallisation.

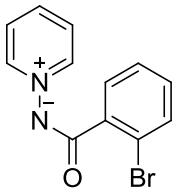
Benzoyl(pyridin-1-ium-1-yl)amide (2a/2a-I)



Ylide **2a** was synthesised according to **GP2** using *N*-aminopyridinium iodide (888 mg, 4.0 mmol) and benzoyl chloride (0.9 mL, 8.0 mmol) in 10% aq. NaOH (20 mL). Recrystallisation of the crude residue from CH_2Cl_2/Et_2O afforded the desired ylide as off-white needles (605 mg, 76%); mp. 187-189 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) 8.84 (dd, *J* = 6.8, 1.2 Hz, 2H), 8.23-8.14 (m, 2H), 8.01-7.91 (m, 1H), 7.69-7.71 (m, 2H), 7.51-7.39 (m, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.7 (C), 143.6 (2 × CH), 137.2 (C), 137.0 (CH), 130.4 (CH), 128.0 (2 × CH), 128.1 (2 × CH), 126.0 (2 × CH); HRMS (ES) calcd for $C_{12}H_{10}N_2ONa$: 221.0691, found: 221.0694 $[M+Na]^+$.

Data matches that reported in the literature.[34]

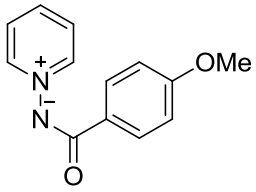
(2-Bromobenzoyl)(pyridin-1-ium-1-yl)amide (2b)



Ylide **2b** was synthesised according to **GP2** using *N*-aminopyridinium iodide (444 mg, 2.0 mmol) and 2-bromobenzoyl chloride (0.55 mL, 4.0 mmol) in 10% aq. NaOH (10 mL). Recrystallisation of the crude residue from CH_2Cl_2/Et_2O afforded the desired ylide as off-white needles (411 mg, 74%); mp. 102-103 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 6.9, 1.3 Hz, 2H), 8.05-7.94 (m, 1H), 7.79-7.70 (m, 2H), 7.67-7.57 (m, 2H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 7.25-7.18 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 172.6 (C), 143.3 (2 × CH), 140.5 (C), 137.6 (CH), 133.1 (CH), 129.8 (CH), 129.4 (CH), 127.3 (CH), 126.4 (2 × CH), 120.9 (C); IR ν_{max}/cm^{-1} 1584, 1465, 1347, 1256, 1022, 751.

Data matches that reported in the literature.[34]

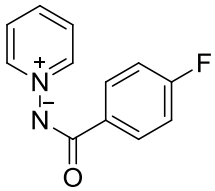
(4-Methoxybenzoyl)(pyridin-1-ium-1-yl)amide (2c)



Ylide **2c** was synthesised according to **GP2** using *N*-aminopyridinium iodide (444 mg, 2.0 mmol) and 2-methoxybenzoyl chloride **S21** (0.5 mL, 4.0 mmol) in 10% aq. NaOH (10 mL). Recrystallisation of the crude residue from CH_2Cl_2/Et_2O afforded the desired ylide as white needles (302 mg, 66%); mp. 148-150 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 6.9, 1.2 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 7.88 (tt, *J* = 7.7, 6.9 Hz, 1H), 7.64 (app t, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.5 (C), 161.5 (C), 143.5 (2 × CH), 136.6 (CH), 129.7 (2 × CH, C), 126.0 (2 × CH), 113.2 (2 × CH), 55.4 (OCH_3); IR ν_{max}/cm^{-1} 3596, 3060, 1606, 1547, 1463, 1331, 1242, 1179, 1032, 843, 762.

Data matches that reported in the literature.[35]

(4-Fluorobenzoyl)(pyridin-1-ium-1-yl)amide (2d)



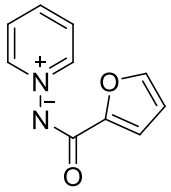
Ylide **2d** was synthesised according to **GP2** using *N*-aminopyridinium iodide (444 mg, 2.0 mmol) and 4-fluorobenzoyl chloride (0.6 mL, 5.0 mmol) in NaOH (10%, 10 mL). Recrystallisation of the crude residue from CH_2Cl_2/Et_2O afforded the desired ylide as off-white needles (280 mg, 65%); mp. 183-184 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.84-8.79 (m, 2H), 8.20-8.12 (m, 2H), 7.99-7.92 (m, 1H), 7.74-7.66 (m, 2H), 7.13-7.04 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.0 (C), 164.4 (d, J_{C-F} = 250.1 Hz, *ipso*-C_q), 143.4 (2 × CH), 137.0 (CH), 133.4 (d, J_{C-F} = 3.2 Hz, *para*-C), 130.3 (d, J_{C-F} = 8.4 Hz, *meta*-2 × CH), 126.2 (2 × CH), 114.8 (d, J_{C-F} = 22.4 Hz, *ortho*- 2 × CH); HRMS (ES) calcd for $C_{12}H_{10}N_2OF$: 217.0777, found: 217.0772 $[M+H]^+$; IR ν_{max}/cm^{-1} 3116, 3061, 1607, 1555, 1325, 1213, 1170, 860, 765.

General Procedure 3 (GP3)

N-Aminopyridinium iodide (1.0 equiv) was suspended in MeOH, followed by addition of K_2CO_3 (2.4 equiv) and the corresponding acyl chloride (1.2 equiv). The reaction mixture was stirred at room temperature for 3 days. Undisolved salts removed by filtration through a filter paper and the filterate was evaporated under reduced

pressure. The resulting crude mixture was purified by column chromatography using neutral or basic Al_2O_3 (5% MeOH/CH_2Cl_2).

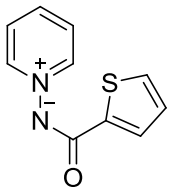
N-2-Furoyliminopyridinium ylide (2e)



Ylide **2e** was synthesised according to **GP3** using *N*-aminopyridinium iodide (1.11 g, 5.0 mmol), K_2CO_3 (1.74 g, 12.0 mmol) and 2-furoyl chloride (0.6 mL, 6.0 mmol). After purification by column chromatography using Al_2O_3 (5% MeOH/CH_2Cl_2) the ylide was isolated as an off-white solid (872 mg, 93%); mp. 182-184 ^oC; ^1H-NMR (300 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 7.1, 1.3 Hz, 2H), 8.00-7.92 (m, 1H), 7.70 (t, *J* = 7.1 Hz, 2H), 7.51 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.11 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.6 (C), 151.2 (C), 143.4 (2 × CH), 143.2 (CH), 136.9 (CH), 126.0 (2 × CH), 112.8 (CH), 111.1 (CH); MS (ES): m/z 211.2 ([M+Na], 100%).

Data matches that reported in the literature.[34]

Pyridin-1-ium-1-yl(thiophene-2-carbonyl)amide (2f)



Ylide **2f** was synthesised according to **GP3** by using *N*-aminopyridinium iodide (444 mg, 2.0 mmol), K_2CO_3 (663 mg, 4.8 mmol) and 2-thiophenecarbonyl chloride (0.26 mL, 2.4 mmol). After purification by filtration over a plug of Al_2O_3, washing (3 times) with (5% MeOH/CH_2Cl_2) and evaporation of the solvent under reduced pressure, the title compound was isolated as an off-white solid (403 mg, 98%); mp. 224-226 ^oC; ^1H-NMR (300 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 7.0, 1.3 Hz, 2H), 7.98-7.86 (m, 1H), 7.76 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.66-7.57 (m, 2H), 7.38 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.7 (C), 143.4 (CH), 136.9 (CH), 133.6 (C), 129.2 (CH), 128.4 (CH), 127.3 (2 × CH), 126.1 (2 × CH); IR ν_{max}/cm^{-1} 3065, 1555, 1466, 1422, 1357, 1294, 1170, 858, 711.

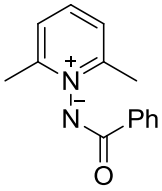
Data matches that reported in the literature.[36]

General Procedure 4 (GP4)

Using a modification of published procedure,[25] the substituted pyridine (1.0 equiv) and *O*-(2,4-dinitrophenyl)hydroxylamine (1.1 equiv) were dissolved in a 1:1 mixture of THF:H_2O (2.8 M). The reaction mixture was stirred at 40 ^oC for 12 h. Then, the mixture was cooled to room temperature and poured into aq. NaOH (2.5M). Benzoyl

chloride (1.5 equiv) was added dropwise and the reaction mixture stirred for 4 h at room temperature. Subsequently the mixture was diluted with water and extracted (3 times) with $CHCl_3$. The organic layer washed with aq. NaOH (2.5 M), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography to afford the pure ylide.

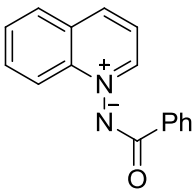
Benzoyl(2,6-dimethylpyridin-1-ium-1-yl)amide (2a-II)



Ylide **2a-II** was synthesised according to **GP4** by using 2,4-lutidine (0.14 mL, 1.2 mmol), *O*-(2,4-dinitrophenyl)hydroxylamine **23** (272 mg, 1.4 mmol) in THF:H_2O (1:1, 0.5 mL) and benzoyl chloride (0.22 mL, 1.8 mmol). The crude mixture was purified by flash column chromatography [Hexane:EtOAc (5:5)-MeOH] to yield a yellow oil. Recrystallisation with Hexane/Et_2O afforded the formation of yellow needles (107 mg, 40%); mp. 128-130 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.19-8.12 (m, 2H), 7.79-7.71 (m, 1H), 7.47-7.36 (m, 5H), 2.65 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 169.1 (C), 154.8 (C), 137.4 (CH), 130.0 (CH), 128.1 (2 × CH), 125.4 (2 × CH), 109.5 (2 × CH), 109.4 (2 × C), 20.0 (2 × CH_3); MS (ES): m/z 227.2 ([M+H], 100%).

Data matches that reported in the literature.[24a,b]

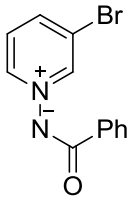
Benzoyl(quinolin-1-ium-1-yl)amide (2a-III)



Ylide **2a-III** was synthesised according to **GP4** using quinoline (0.15 mL, 1.2 mmol) and the *O*-(2,4-dinitrophenyl)hydroxylamine **23** (272 mg, 1.4 mmol) in THF:H_2O (1:1, 0.5 mL). After the addition of base and benzoyl chloride (0.22 mL, 1.8 mmol) the reaction mixture was stirred for 8 h. The crude mixture was purified by flash column chromatography [Hexane:EtOAc (5:5)-MeOH] to yield a brown solid (116 mg, 40%); mp. 155-158 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.16 (dd, *J* = 5.9, 1.2 Hz, 1H), 8.78 (d, *J* = 8.6 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 8.34-8.25 (m, 2H), 8.01 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.94-7.85 (m, 1H), 7.76 (ddd, *J* = 8.1, 5.7, 1.1 Hz, 1H), 7.68 (dd, *J* = 8.3, 5.9 Hz, 1H), 7.52-7.41 (m, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.5 (C), 145.9 (CH), 139.9 (C), 138.2 (CH), 137.5 (C), 133.4 (CH), 130.2 (CH), 130.3 (C), 129.5 (CH), 128.7 (CH), 128.3 (2 × CH), 128.0 (2 × CH), 120.6 (2 × CH); MS (ES): m/z 271.1 ([M+Na], 100%).

Data matches that reported in the literature.[24a,b]

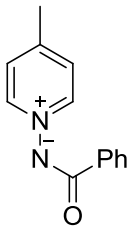
Benzoyl(3-bromopyridin-1-ium-1-yl)amide (2a-IV)



Ylide **2a-IV** was synthesised according to **GP4** using 3-bromopyridine (0.12 mL, 1.2 mmol), the *O*-(2,4-dinitrophenyl)hydroxylamine **23** (272 mg, 1.4 mmol) in THF:H_2O (1:1, 0.5 mL) and benzoyl chloride (0.215 mL, 1.8 mmol). The crude mixture was purified by flash column chromatography [Hexane:EtOAc (5:5)-MeOH] to afford a yellow solid (186 mg, 54%); mp. 121-123 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.20 (bs, 1H), 8.84 (d, *J* = 6.4, 1H), 8.15 (dd, *J* = 8.0, 1.6 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 8.3, 6.4 Hz, 1H), 7.51-7.36 (m, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.8 (C), 144.5 (CH), 141.5 (CH), 139.0 (CH), 136.9 (C), 130.6 (CH), 128.5 (2 × CH), 128.2 (2 × CH), 126.2 (CH), 120.9 (C); MS (ES): m/z 279.0 ([M+H], 100%).

Data matches that reported in the literature.[24a,b]

Benzoyl(4-methylpyridin-1-ium-1-yl)amide (2a-V)



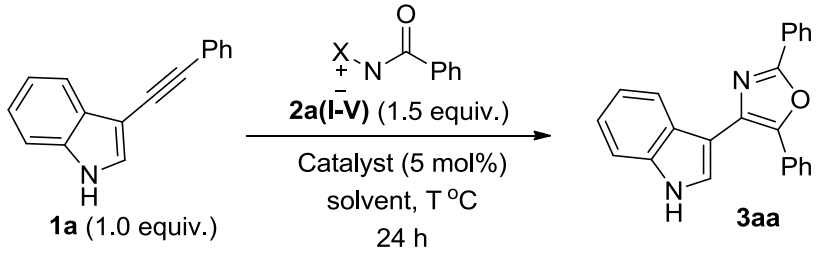
Ylide **2a-V** was synthesised according to **GP4** using 4-picoline (0.12 mL, 1.2 mmol), the *O*-(2,4-dinitrophenyl)hydroxylamine **23** (272 mg, 1.4 mmol) in THF:H_2O (1:1, 5 mL) and benzoyl chloride (0.22 mL, 1.8 mmol). The crude mixture was purified by flash column chromatography [Hexane:EtOAc (5:5)-MeOH] to afford an orange solid (150 mg, 57%); mp. 65-67 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.8 Hz, 2H), 8.22-7.97 (m, 2H), 7.53-7.32 (m, 5H), 2.57 (s, 3H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 171.2 (C), 150.2 (C), 143.0 (2 × CH), 137.4 (C), 130.2 (2 × CH), 128.1 (2 × CH), 126.5 (2 × CH), 126.6 (CH), 21.5 (CH_3); MS (ES): m/z 213.1 ([M+H], 100%).

Data matches that reported in the literature.[37]

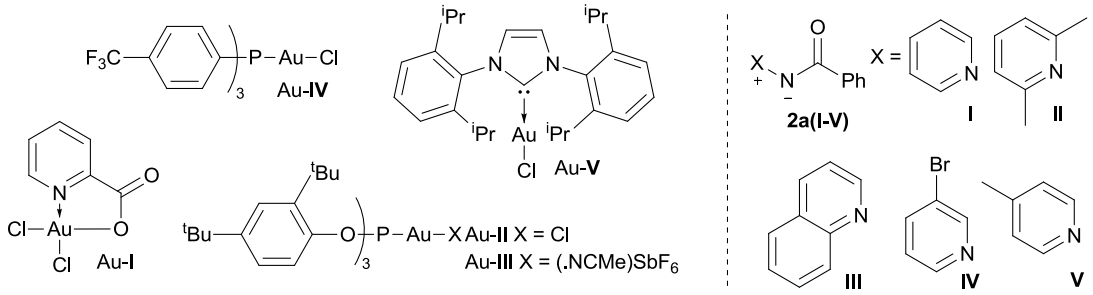
Reaction optimisation survey:

The free indole derivative **1a** reacted to give **3aa** in low yield and conversion using a Au(III) precatalyst Au-**S-I** (Supplementary Table 1, Entry 1). The use of more electrophilic cationic gold(I) species, generated *in situ* from ligated gold chloride and silver triflate led to improved conversion with a variety of ligands (Table 1, Entries 2-5).

Supplementary Table 1 Full reaction study screening.



Entry	Catalyst	2a	C (M)	Solvent	T (°C)	3aa (%)[a]
1	Au-**I**	**I**	0.1	Toluene	90	12
2	$Ph_3PAuCl/AgOTf$	**I**	0.1	Toluene	90	24
3	Au-**IV**/AgOTf	**I**	0.1	Toluene	90	37
4	Au-**II**/AgOTf	**I**	0.1	Toluene	90	38
5	Au-**V**/AgOTf	**I**	0.1	Toluene	90	46
6	Au-**II**/AgOTf	**I**	0.05	Toluene	90	35
7	Au-**II**/AgOTf	**I**	0.2	Toluene	90	54
8	Au-**II**/$AgNTf_2$	**I**	0.2	Toluene	90	44
9	Au-**II**/AgOTs	**I**	0.2	Toluene	90	37
10	Au-**II**/$AgBF_4$	**I**	0.2	Toluene	90	41
11	Au-**II**/$AgSbF_6$	**I**	0.2	Toluene	90	58
12	Au-**V**/AgOTf	**I**	0.2	*m*-Xylene	120	65
13	Au-**V**/$AgSbF_6$	**I**	0.2	*m*-Xylene	120	61
14	Au-**II**/$AgSbF_6$	**I**	0.2	*m*-Xylene	120	73 (64[b])
15	-	**I**	0.2	*m*-Xylene	120	0
16	TfOH	**I**	0.2	*m*-Xylene	120	0[c]
17	$AgSbF_6$	**I**	0.2	*m*-Xylene	120	25
18	Au-**II**	**I**	0.2	*m*-Xylene	120	61
19	Au-**III**	**I**	0.2	*m*-Xylene	120	78[d] (48[e])
20	Au-**III**	**I**	0.2	*p*-Xylene	120	63
21	Au-**III**	**I**	0.2	*o*-Xylene	120	76
22	Au-**III**	**II**	0.2	*m*-Xylene	120	21
23	Au-**III**	**III**	0.2	*m*-Xylene	120	18
24	Au-**III**	**IV**	0.2	*m*-Xylene	120	75
25	Au-**III**	**V**	0.2	*m*-Xylene	120	50



[a] Isolated yields after flash chromatography. [b] **2a** (1.0 equiv). [c] immediate degradation of the starting material at 5 mol% loading. [d] average yield across 3 runs. [e] 1 mol% catalyst loading.

Higher concentration (Entry 7 vs. 4 and 6) proved beneficial, with triflate or hexafluoroantimonate the most effective of the counterions tested (Entries 7-11).

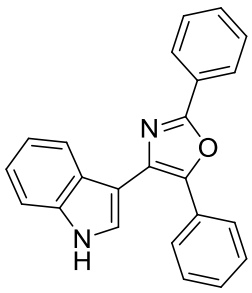
Conversion and product yield were increased at higher temperature in *m*-xylene, with the phosphite gold complex Au-**III** affording better yields than the carbene-gold complex Au-**IV** (Entries 12-14). Comparable results were seen in *o*- and *m*-xylene whilst *p*-xylene gave a less clean reaction and a lower yield (Entries 19-21).

Formation of 2,4,5-trisubstituted oxazoles 3(a-l)(a-f), 5(a-e)a and 7

General Procedure 5 (GP5)

Initially, the internal alkyne (1.0 equiv), the pyridinium ylide (1.5 equiv) and the gold complex Au-**III** were combined in a Schlenk tube; *m*-xylene (0.2M) was added and the reaction mixture was stirred at 120 ^{o}C for 24 h. The reactions were monitored by TLC until 8 h showing the formation of the product and unreacted starting material. After 24 h (TLC indicates either consumption of the starting material or trace of it) the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (Toluene:EtOAc) to afford the pure oxazole.

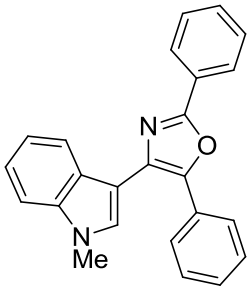
4-(1H-Indol-3-yl)-2,5-diphenyloxazole (3aa)



Oxazole **3aa** was synthesised according to **GP5** using indole derivative **1a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (52 mg, 78%); mp. 150-153 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.4 (bs, 1H), 8.17-8.09 (m, 2H), 7.73-7.70 (m, 2H), 7.70 (s, 1H), 7.62-7.55 (m, 3H), 7.48 (d, J = 8.1 Hz, 1H), 7.46-7.38 (m, 3H), 7.37-7.32 (m, 1H), 7.16 (app. td, *J* = 7.5, 1.0 Hz, 1H), 7.00 (app. td, *J* = 7.5, 0.7 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 159.1 (C), 144.2 (C), 136.2 (C), 131.9 (C), 130.6 (CH), 129.2 (2 × CH), 128.7 (2 × CH), 128.6 (C), 128.1 (CH), 126.9 (C), 126.0 (2 × CH), 125.5 (2 × CH), 125.4 (C), 125.1 (CH), 121.6 (CH), 120.1 (CH), 119.3 (CH), 111.9 (CH), 106.5 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2ONa$: 359.1160, found: 359.1165 $[M+Na]^+$; IR ν_{max}/cm^{-1} 3412, 2925, 2856, 1628, 1487, 1448, 1344, 1248, 1097, 1016, 934, 744, 700.

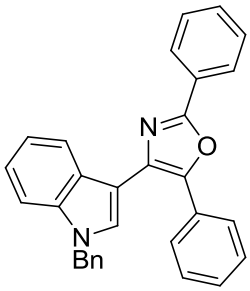
When run at 0.4 mmol scale the oxazole was afforded in 79% (106 mg).

4-(1-Methyl-1H-indol-3-yl)-2,5-diphenyloxazole (3ba)



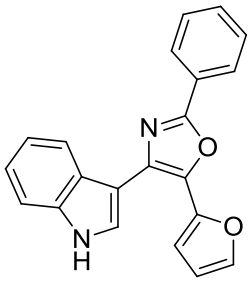
Oxazole **3ba** was synthesised according to **GP5** using indole derivative **1b** (69 mg, 0.3 mmol, 1.0 equiv) and ylide **2a** (89 mg, 0.45 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (61 mg, 58%); mp. 158-160 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.53-7.44 (m, 2H), 7.33-7.27 (m, 4H), 7.17 (m, 1H), 7.25-7.23 (d, *J* = 8.2 Hz, 5H), 6.85 (t, *J* = 7.5 Hz, 1H), 3.65 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.1 (C), 145.1 (C), 137.3 (C), 131.6 (C), 130.4 (CH), 129.4 (C), 128.9 (2 × CH), 128.8 (CH), 128.6 (2 × CH), 128.0 (CH), 127.6 (C), 126.6 (2 × CH), 126.4 (C), 126.0 (2 × CH), 122.1 (CH), 121.5 (CH), 120.0 (CH), 109.5 (CH), 107.2 (C), 33.2 (CH_3); HRMS (ES) calcd. for $C_{24}H_{19}N_2O$: 351.1497, found: 351.1486 $[M+H]^+$;IR ν_{max}/cm^{-1} 3381, 2206, 1414, 1359, 1324, 1235, 740, 681.

4-(1-Benzyl-1H-indol-3-yl)-2,5-diphenyloxazole (3ca)



Oxazole **3ca** was synthesised according to **GP5** using indole derivative **1c** (62 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow solid (30 mg, 35%); mp. 220-222 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.72 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.62 (bd, *J* = 8.2 Hz, 1H), 7.54 (s, 1H), 7.42-7.56 (m, 3H), 7.38-7.28 (m, 7H), 7.25-7.19 (m, 3H), 7.10 (app. td, *J* = 7.6, 1.0 Hz, 1H), 5.4 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.1 (C), 145.2 (C), 137.2 (C), 136.8 (C), 131.8 (C), 130.3 (CH), 129.4 (C), 129.0 (2 × CH), 128.9 (2 × CH), 128.6 (2 × CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (C), 127.1 (2 × CH), 126.9 (C), 126.6 (2 × CH), 126.0 (2 × CH), 122.4 (CH), 121.6 (CH), 120.3 (CH), 110.0 (CH), 108.0 (C), 50.4 (CH_2); HRMS (ES) calcd. for $C_{30}H_{23}N_2O$: 427.1810, found: 427.1815 $[M+H]^+$; IR ν_{max}/cm^{-1} 3284, 1603, 1333, 1191, 1012, 770, 739, 695.

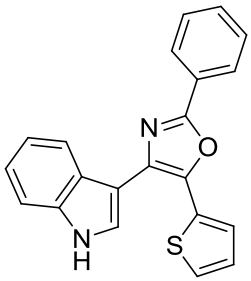
5-(Furan-2-yl)-4-(1H-indol-3-yl)-2-phenyloxazole (3da)



Oxazole **3da** was synthesised according to **GP5** using indole derivative **1d** (42 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (44 mg, 67%); mp. 180-183 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.52 (bs, NH), 8.19-8.07 (m, 3H), 7.98 (d, *J* = 2.8 Hz, 1H), 7.92 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.66-7.56 (m, 2H), 7.50-7.45 (m, 1H), 7.24-7.23 (m, 1H), 7.17 (dd, J = 8.1, 1.2 Hz, 1H), 7.11 (dd, J = 8.1 Hz, 1.1 Hz, 1H), 6.93 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.73 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 159.0 (C), 143.2 (C), 143.6 (CH), 136.2 (C), 135.8 (C), 132.9 (C), 130.8 (CH), 126.5 (C), 129.2 (2 × CH), 126.1 (2 × CH), 125.9 (C), 125.2 (CH), 121.7 (CH), 121.0 (CH), 119.6 (CH), 112.0 (CH), 111.7 (CH), 109.0 (CH), 106.0 (C); HRMS (ES) calcd. for $C_{21}H_{15}N_2O_2$: 327.1134, found: 327.1144 $[M+H]^+$; IR ν_{max}/cm^{-1} 3675, 2972, 2901, 1607, 1493, 1456, 1068, 746, 737.

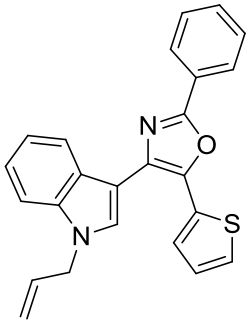
When run at 0.5 mmol scale the oxazole was afforded in 72% (166 mg).

4-(1H-Indol-3-yl)-2-phenyl-5-(thiophen-2-yl)oxazole (3ea)



Oxazole **3ea** was synthesised according to **GP5** using indole derivative **1e** (45 mg, 0.2 mmol, 1 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (46 mg, 67%); mp. 180-183 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.53 (bs, NH), 8.11 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.80 (d, *J* = 2.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.61-7.55 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.27-7.18 (m, 3H), 7.11 (app. td, *J* = 7.5, 0.8 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 158.8 (C), 140.2 (C), 136.2 (C), 131.7 (C), 130.7 (CH), 129.5 (C), 129.2 (2 × CH), 128.9 (C), 128.2 (C), 127.8 (CH), 126.7 (CH), 126.0 (2 × CH), 125.8 (CH), 125.3 (CH), 121.7 (CH), 120.3 (CH), 119.5 (CH), 111.7 (CH), 105.6 (C); HRMS (ES) calcd. for $C_{21}H_{14}N_2OSNa$: 365.0725, found: 365.0724 $[M+Na]^+$; IR ν_{max}/cm^{-1} 3203, 1628, 1611, 1541, 1189, 850, 744, 697 678.

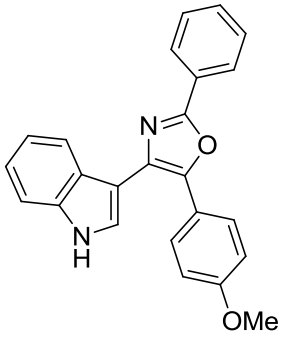
4-(1-Allyl-1H-indol-3-yl)-2-phenyl-5-(thiophen-2-yl)oxazole (3fa)



Oxazole **3fa** was synthesised according to **GP5** using indole derivative **1f** (53 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography (Toluene) the oxazole was isolated as a yellow viscous oil (26 mg, 34%, ~90% purity); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.54-7.49 (m, 3H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32-7.27 (m, 2H), 7.14 (app. td, *J* = 7.5, 0.9 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.05 (ddt, *J* = 17.0, 10.5, 5.4 Hz, 1H), 5.26 (dd, *J* = 10.5, 1.2 Hz, 1H), 5.18 (dd, *J* = 17.0, 1.2 Hz, 1H), 4.81 (dt, *J* = 5.4 Hz, 1.4 Hz, 2H);^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.8 (C), 141.3 (C), 137.9 (C), 136.7 (C), 133.3 (CH), 130.8 (C), 130.4 (CH), 128.9 (2 × CH), 128.0 (CH), 127.5 (CH), 126.9 (C), 126.6 (2 × CH), 126.2 (C), 125.4 (CH), 125.3 (CH), 122.3 (CH), 121.5 (CH), 120.2 (CH), 117.9 (CH_2), 109.9 (CH), 106.9 (C), 49.2 (CH_2); HRMS (ES) calcd. for $C_{24}H_{19}N_2OS$: 383.1218, found: 383.1225 $[M+H]^+$; IR ν_{max}/cm^{-1} 3079, 2921, 1637, 1468, 1186, 923, 744, 690.

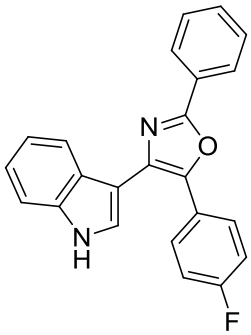
*Attempts to remove final traces of toluene led to degradation of the product.

4-(1H-Indol-3-yl)-5-(4-methoxyphenyl)-2-phenyloxazole (3ga)



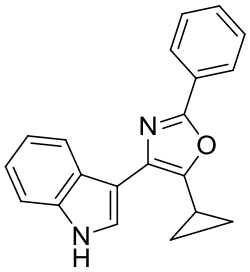
Oxazole **3ga** was synthesised according to **GP5** by using indole derivative **1g** (50 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (60 mg, 82%); mp. 110-115 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.45 (bs, NH), 8.12 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.67 (d, *J* = 2.6 Hz, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.60-7.53 (m, 3H), 7.50-7.45 (m, 2H), 7.17 (app. td, *J* = 7.5, 0.9 Hz, 1H), 7.02-6.98 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 159.2 (C), 158.5 (C), 144.4 (C), 136.2 (C), 130.6 (C), 130.4 (CH), 129.2 (2 × CH), 127.3 (2 × CH), 127.0 (C), 125.9 (2 × CH), 125.6 (C), 124.8 (CH), 121.6 (CH), 121.2 (C), 120.2 (CH), 119.3 (CH), 114.3 (2 × CH), 111.8 (CH), 106.6 (C)., 55.2 (OCH_3); HRMS (ES) calcd. for $C_{24}H_{19}N_2O_2$: 367.1447, found: 367.1442 $[M+H]^+$; IR ν_{max}/cm^{-1} 3376, 2207, 1607, 1337, 1241, 1228, 1170, 743.

5-(4-Fluorophenyl)-4-(1H-indol-3-yl)-2-phenyloxazole (3ha)



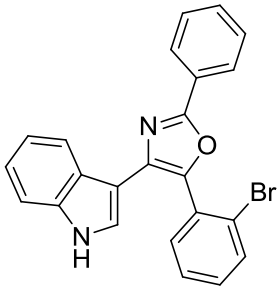
Oxazole **3ha** was synthesised according to **GP5** using indole derivative **1h** (47 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (48 mg, 64%); mp. 158-160 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.45 (bs, NH), 8.22-8.14 (m, 2H), 7.70-7.63 (m, 2H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.54-7.41 (m, 5H), 7.25-7.17 (m, 1H), 7.13-7.08 (m, 1H), 7.08-7.00 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.7 (d, J_{C-F} = 245.9 Hz, *ipso*-C), 160.1 (C), 144.6 (C), 136.4 (C), 131.4 (C), 130.4 (CH), 128.9 (2 × CH), 127.9 (d, J_{C-F} = 8.1 Hz, *meta*-2 × CH), 127.7 (C), 126.6 (2 × CH), 125.9 (C), 125.6 (C), 124.1 (CH), 122.8 (CH), 121.2 (CH), 120.5 (CH), 115.7 (d, J_{C-F} = 22.1 Hz, *ortho*-2 × CH), 111.4 (CH), 108.8 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2OF$: 355.1247, found: 355.1243 $[M+H]^+$; IR ν_{max}/cm^{-1} 3254, 3062, 1491, 1228, 936, 838, 724.

5-Cyclopropyl-4-(1H-indol-3-yl)-2-phenyloxazole (3ia)



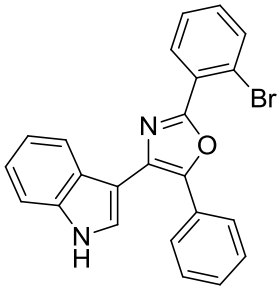
Oxazole **3ia** was synthesised according to **GP5** using indole derivative **1i** (56 mg, 0.3 mmol, 1.0 equiv) and ylide **2a** (89 mg, 0.45 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (31 mg, 35%); mp. 150-152 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.46 (bs, NH), 8.18 (dd, *J* = 6.9, 1.9 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.52-7.45 (m, 2H), 7.44-7.37 (m, 3H), 7.26-7.20 (m, 2H), 2.13 (tt, J = 7.2, 6.2 Hz, 1H), 1.21-1.02 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 158.7 (C), 147.5 (C), 136.3 (C), 131.8 (C), 129.8 (CH), 128.7 (2 × CH), 128.1 (C), 126.6 (C), 126.2 (2 × CH), 122.9 (CH), 122.6 (CH), 121.3 (CH), 120.3 (CH), 111.2 (CH), 108.9 (C), 7.5 (2 × CH_2), 7.4 (CH); HRMS (ES) calcd. for $C_{20}H_{17}N_2O$: 301.1341, found: 301.1343 $[M+H]^+$; IR ν_{max}/cm^{-1} 3377, 3058, 1615, 1514, 1445, 1238, 766, 685.

5-(2-Bromophenyl)-4-(1H-indol-3-yl)-2-phenyloxazole (3ja)



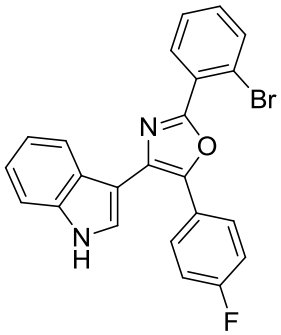
Oxazole **3ja** was synthesised according to **GP5** using indole derivative **1j** (60 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (50 mg, 60%); mp. 56-58 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.32 (bs, NH), 8.25-8.19 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75-7.71 (m, 1H), 7.52-7.46 (m, 3H), 7.34-7.25 (m, 4H), 7.22-7.16 (m, 2H), 7.11-7.06 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.9 (C), 142.9 (C), 136.2 (C), 134.6 (C), 133.7 (CH), 132.5 (CH), 131.1 (C), 130.7 (CH), 130.4 (CH), 128.9 (2 × CH), 127.8 (C), 127.5 (CH), 126.7 (2 × CH), 125.9 (C), 124.2 (C), 123.4 (CH), 122.5 (CH), 121.4 (CH), 120.4 (CH), 111.2 (CH), 108.5 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2OBr$: 415.0446, found: 415.0439 $[M+H]^+$; IR ν_{max}/cm^{-1} 3403, 3057, 1484, 1335, 1092, 1026, 930, 742, 688.

2-(2-Bromophenyl)-4-(1H-indol-3-yl)-5-phenyloxazole (3ab)



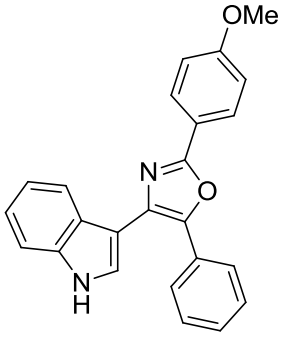
Oxazole **3ab** was synthesised according to **GP5** using indole derivative **1a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2b** (83 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (60 mg, 72%); mp. 198-200 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.42 (bs, NH), 8.18 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.78-7.67 (m, 3H), 7.64-7.33 (m, 7H), 7.21-7.13 (m, 1H), 7.05-6.98 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 158.6 (C), 145.9 (C), 136.2 (C), 134.6 (CH), 131.4 (CH), 131.4 (C), 131.0 (CH), 129.1 (C), 128.6 (2 × CH), 128.4 (C), 128.1 (CH), 127.4 (CH), 126.0 (2 × CH), 125.9 (C), 124.0 (CH), 122.6 (CH), 121.3 (CH), 121.0 (C), 120.4 (CH), 111.2 (CH), 108.7 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2OBr$: 415.0446, found: 415.0447 $[M+H]^+$; IR ν_{max}/cm^{-1} 3170, 2836, 1607, 1494, 1432, 1250, 1174, 1020, 831, 688.

2-(2-Bromophenyl)-5-(4-fluorophenyl)-4-(1H-indol-3-yl)oxazole (3hb)



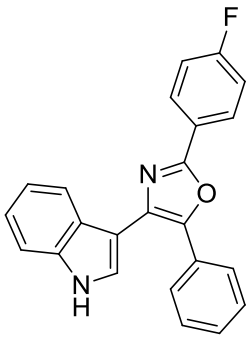
Oxazole **3hb** was synthesised according to **GP5** using indole derivative **1h** (47 mg, 0.2 mmol, 1.0 equiv) and ylide **2b** (83 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a light brown solid (59 mg, 68%); mp. 176-178 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.53 (bs, NH), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.77-7.75 (m, 1H), 7.75-7.70 (m, 2H), 7.59 (td, *J* = 7.6, 1.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.52-7.45 (m, 2H), 7.31-7.25 (m, 2H), 7.14-7.19 (m, 1H), 7.02 (dd, *J* = 7.8, 7.2 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 161.9 (d, $J_{C\text{-}F}$ = 249.7 Hz, *ipso*-C), 157.7 (C), 143.7 (C), 136.2 (C), 134.5 (CH), 132.0 (CH), 131.6 (C), 131.3 (CH), 128.9 (C), 128.1 (CH), 128.0 (d, $J_{C\text{-}F}$ = 8.4 Hz, *meta*-2 × CH), 127.5 (C), 125.5 (C), 125.1 (CH), 121.7 (CH), 120.2 (CH), 120.1 (C), 119.5 (CH), 115.9 (d, $J_{C\text{-}F}$ = 21.5 Hz, *ortho*-2 × CH), 111.9 (CH), 105.9 (C); HRMS (ES) calcd. for $C_{23}H_{15}N_2OFBr$: 433.0352, found: 433.0354 $[M+H]^+$; IR ν_{max}/cm^{-1} 3257, 1627, 1492, 1228, 1163, 936, 838, 763, 724.

5-(4-Bromophenyl)-4-(1H-indol-3-yl)-2-(4-methoxyphenyl)oxazole (3ac)



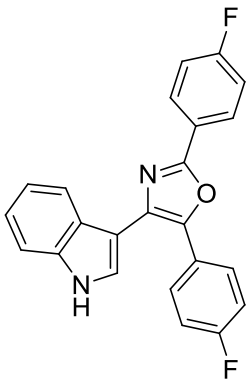
Oxazole **3ac** was synthesised according to **GP5** using indole derivative **1a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2c** (69 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow solid (58 mg, 79%); mp. 194-196 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.44 (bs, NH), 8.15 (d, *J* = 8.9 Hz, 2H), 7.68 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38-7.28 (m, 3H), 7.25-7.19 (m, 1H), 7.12-7.05 (m, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.5 (C), 160.2 (C), 157.6 (C), 144.9 (C), 142.6 (C), 136.4 (C), 129.5 (C), 128.6 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 126.1 (C), 125.9 (2 × CH), 124.2 (CH), 122.8 (C), 122.6 (CH), 121.3 (CH), 120.4 (CH), 114.4 (2 × CH), 111.3 (CH), 108.9 (C), 55.6 (OCH_3); HRMS (ES) calcd. for $C_{24}H_{19}N_2O_2$: 367.1447, found: 367.1441 $[M+H]^+$; IR ν_{max}/cm^{-1} 3079, 2920, 1637, 1465, 1186, 845, 743, 620.

5-(2-Bromophenyl)-2-(4-fluorophenyl)-4-(1H-indol-3-yl)oxazole (3ad)



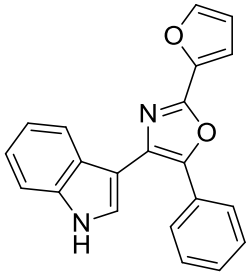
Oxazole **3ad** was synthesised according to **GP5** using indole derivative **1a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2d** (65 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (55 mg, 78%); mp. 162-164 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.43 (bs, NH), 8.23-8.15 (m, 2H), 7.71-7.69 (m, 2H), 7.58-7.54 (m, 2H), 7.43 (d, *J* = 8.2, Hz, 1H), 7.39-7.27 (m, 3H), 7.27-7.16 (m, 3H), 7.10 (app. td, *J* = 7.5, 0.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 250.5 Hz, *ipso*-C), 159.3 (C), 145.4 (C), 136.4 (C), 131.7 (C), 129.3 (2 × C), 128.8 (C), 128.7 (d, $J_{C\text{-}F}$ = 8.1 Hz, *meta*-2 × CH), 128.7 (2 × CH), 128.1 (CH), 126.0 (2 × CH), 124.1 (CH), 122.7 (CH), 121.3 (CH), 120.5 (CH), 116.2 (d, $J_{C\text{-}F}$ = 22.3 Hz, *ortho*-2 × CH) , 111.4 (CH), 108.9 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2OF$: 355.1247, found: 355.1251 $[M+H]^+$; IR ν_{max}/cm^{-1} 3254, 2962, 1624, 1466, 1440, 1260, 1172, 737, 696.

2,5-Bis(4-fluorophenyl)-4-(1H-indol-3-yl)oxazole (3hd)



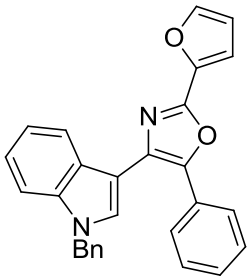
Oxazole **3hd** was synthesised according to **GP5** using indole derivative **1h** (47 mg, 0.2 mmol, 1.0 equiv) and ylide **2d** (65 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (53 mg, 70%); mp. 192-194 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.53 (bs, NH), 8.27-8.12 (m, 2H), 7.78-7.68 (m, 3H), 7.52-7.38 (m, 4H), 7.31-7.22 (m, 2H), 7.19-7.18 (m, 1H), 7.00 (app. t, *J* = 7.5 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 163.8 (d, $J_{C\text{-}F}$ = 250.1 Hz, *ipso*-C), 161.3 (d, $J_{C\text{-}F}$ = 250.5 Hz, *ipso*-C), 143.5 (C), 136.2 (C), 131.7 (C), 129.1 (C), 128.5 (d, $J_{C\text{-}F}$ = 8.0 Hz, *meta*-2 × CH), 128.0 (d, $J_{C\text{-}F}$ = 8.0 Hz, *meta*-2 × CH), 126.0 (d, $J_{C\text{-}F}$ = 3.0 Hz, *para*-C), 125.4 (C), 125.0 (CH), 123.5 (d, $J_{C\text{-}F}$ = 3.0 Hz, *para*-C), 121.6 (CH), 120.0 (CH), 119.4 (CH), 116.3 (d, $J_{C\text{-}F}$ = 21.9 Hz, *meta*-2 × CH), 115.8 (d, $J_{C\text{-}F}$ = 22.0 Hz, *meta*-2 × CH), 111.9 (CH), 106.2 (C); HRMS (ES) calcd. for $C_{23}H_{15}N_2OF_2$: 373.1152, found: 373.1153 $[M+H]^+$; IR ν_{max}/cm^{-1} 3415, 1601, 1499, 1219, 1088, 928, 756, 663.

2-(Furan-2-yl)-4-(1H-indol-3-yl)-5-phenyloxazole (3ae)



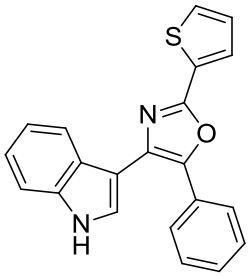
Oxazole **3ae** was synthesised according to **GP5** using indole derivative **1a** (65 mg, 0.3 mmol, 1.0 equiv) and ylide **2e** (84 mg, 0.45 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brownish solid (81 mg, 83%); mp. 138-140 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.49 (bs, 1H), 7.66 (dd, J = 8.1, 1.4 Hz, 2H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.60 (d, *J* = 2.6 Hz, 1H), 7.42 (app. t, J = 8.3 Hz, 2H), 7.35-7.27 (m, 3H), 7.21 (app. td, J = 7.6, 0.9 Hz, 1H), 7.14 (dd, J = 3.4, 0.5 Hz, 1H), 7.06 (app. td, J = 7.6, 0.8 Hz, 1H), 6.53 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.1 (C), 144.9 (C), 144.5 (CH), 143.3 (C), 136.3 (C), 131.4 (C), 129.0 (C), 128.6 (2 × CH), 128.2 (CH), 126.1 (2 × CH), 125.8 (C), 124.5 (CH), 122.6 (CH), 121.3 (CH), 120.4 (CH), 112.1 (CH), 111.6 (CH), 111.4 (CH), 108.6 (C); HRMS (ES) calcd. for $C_{21}H_{15}N_2O_2$: 327.1134, found: 327.1137 $[M+H]^+$; IR ν_{max}/cm^{-1} 3398, 3057, 2924, 1625, 1447, 1067, 1010, 930, 739, 690.

4-(1-Benzyl-1H-indol-3-yl)-5-phenyl-2-(thiophen-2-yl)oxazole (3ce)



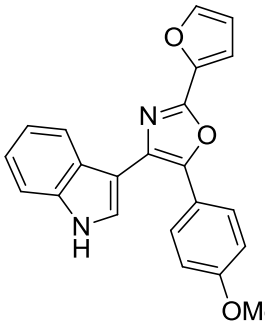
Oxazole **3ce** was synthesised according to **GP5** using indole derivative **1c** (62 mg, 0.2 mmol, 1.0 equiv) and ylide **2e** (56 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (27 mg, 33%); mp. 124-126 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.60 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.56 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36-7.31 (m, 3H), 7.32-7.27 (m, 4H), 7.23-7.16 (m, 3H), 7.13 (dd, *J* = 3.5, 0.6 Hz, 1H), 7.05 (app. td, *J* = 7.5, 1.0 Hz, 1H), 6.58 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.37 (s, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 153.2 (C), 144.8 (C), 143.3 (C), 137.3 (C), 136.8 (C), 131.6 (C), 129.1 (C), 128.7 (2 × CH), 128.6 (2 × CH), 128.2 (CH), 128.0 (CH), 127.2 (2 × CH), 126.6 (C), 126.2 (2 × CH), 122.4 (CH), 121.7 (CH), 121.1 (CH), 120.3 (CH), 112.1 (CH), 111.7 (CH), 110.1 (CH), 144.6 (CH), 107.7 (C), 50.6 (CH_2); HRMS (ES) calcd. for $C_{28}H_{21}N_2O_2$: 417.1603, found: 417.1607 $[M+H]^+$; IR ν_{max}/cm^{-1} 3255, 1624, 1528, 1469, 1442, 1099, 725, 690.

4-(1H-Indol-3-yl)-5-phenyl-2-(thiophen-2-yl)oxazole (3af)



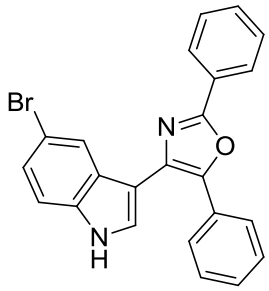
Oxazole **3af** was synthesised according to **GP5** using indole derivative **1a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2f** (61 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brownish solid (44 mg, 64%); mp. 167-170 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.53 (bs, NH), 7.91 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.88 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.67-7.61 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.43-7.33 (m, 4H), 7.28 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.14 (app. td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (app. td, *J* = 7.5, 1.0 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 155.5 (C), 143.6 (C), 136.2 (C), 131.8 (C), 129.7 (CH), 129.1 (C), 128.9 (C), 128.7 (2 × CH), 128.6 (C), 128.4 (CH), 128.2 (2 × CH), 125.5 (2 × CH), 125.3 (CH), 121.6 (CH), 120.1 (CH), 119.4 (CH), 111.9 (CH), 106.2 (C); HRMS (ES) calcd. for $C_{21}H_{14}N_2ONaS$: 365.0725, found: 365.0720 $[M+Na]^+$; IR ν_{max}/cm^{-1} 3376, 3058, 1614, 1488, 1445, 1239, 825, 690.

2-(Furan-2-yl)-4-(1H-indol-3-yl)-5-(4-methoxyphenyl)oxazole (3ge)



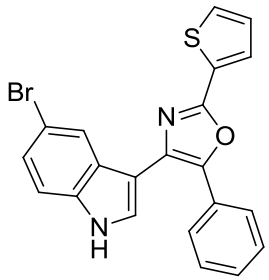
Oxazole **3ge** was synthesised according to **GP5** using indole derivative **1g** (50 mg, 0.2 mmol, 1.0 equiv) and ylide **2e** (56 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (61 mg, 86%); mp. 90-93 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.47 (bs, NH), 7.63-7.53 (m, 4H), 7.44-7.38 (m, 2H), 7.21 (app t, *J* = 7.7 Hz, 1H), 7.11 (dd, *J* = 3.4, 0.7 Hz, 1H), 7.05 (app t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 3.4, 1.7 Hz, 1H), 3.80 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.6 (C), 152.6 (C), 145.0 (C), 144.3 (CH), 143.4 (C), 136.3 (C), 130.0 (C), 127.8 (2 × CH), 125.8 (C), 124.4 (CH), 122.5 (CH), 121.7 (C), 121.3 (CH), 120.3 (CH), 114.1 (2 × CH), 112.4 (CH), 112.0 (CH), 111.3 (CH), 108.8 (C), 55.4 (OCH_3); HRMS (ES) calcd. for $C_{22}H_{17}N_2O_3$: 357.1239, found: 357.1229 $[M+H]^+$; IR ν_{max}/cm^{-1} 3373, 2107, 1407, 1236, 1222, 1215, 1170, 842, 750.

4-(5-Bromo-1H-indol-3-yl)-2,5-diphenyloxazole (3ka)



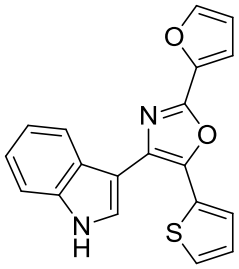
Oxazole **3ka** was synthesised according to **GP5** using indole derivative **1k** (59 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow solid (33 mg, 40%); mp. 78-80 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.70 (bs, NH), 8.14 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.77 (d, *J* = 2.6 Hz, 1H), 7.72-7.68 (m, 2H), 7.63 (d, *J* = 1.7 Hz, 1H), 7.61-7.56 (m, 2H), 7.48-7.41 (m 3H), 7.27 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.26-7.21 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.3 (C), 145.7 (C), 135.0 (C), 131.0 (C), 130.5 (CH), 129.8 (C), 129.1 (C), 129.0 (2 × CH), 128.9 (2 × CH), 128.4 (CH), 127.6 (C), 126.6 (2 × CH), 126.1 (2 × CH), 125.7 (CH), 125.0 (CH), 123.9 (CH), 113.4 (C), 112.8 (CH), 108.7 (C); HRMS (ES) calcd. for $C_{23}H_{16}N_2OBr$: 415.0446, found: 415.0454 $[M+H]^+$; IR ν_{max}/cm^{-1} 2922, 2852, 1592, 1447, 1260, 1070, 796, 690.

4-(5-Bromo-1H-indol-3-yl)-5-phenyl-2-(thiophen-2-yl)oxazole (3kf)



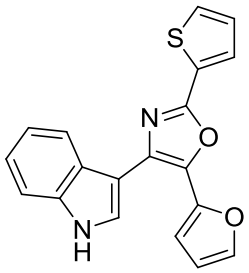
Oxazole **3kf** was synthesised according to **GP5** using indole derivative **1k** (59 mg, 0.2 mmol, 1.0 equiv) and ylide **2f** (61 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow solid (57 mg, 68%); mp. 180-182 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.70 (bs, NH), 7.88-7.84 (m, 1H), 7.83 (bs, 1H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.65 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.56 (bs, 1H), 7.47-7.38 (m, 4H), 7.30-7.25 (m, 2H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 155.7 (C), 143.8 (C), 134.9 (C), 131.1 (C), 129.8 (CH), 129.0 (C), 128.8 (2 × CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.7 (C), 127.2 (C), 126.7 (CH), 125.7 (2 × CH), 124.2 (CH), 122.4 (CH), 114.0 (CH), 112.0 (C), 105.9 (C); HRMS (ES) calcd. for $C_{21}H_{14}N_2OSBr$: 421.0010, found: 421.0018 $[M+H]^+$; IR ν_{max}/cm^{-1} 3165, 2922, 1583, 1450, 1106, 884, 799, 705.

2-(Furan-2-yl)-4-(1H-indol-3-yl)-5-(thiophen-2-yl)oxazole (3fe)



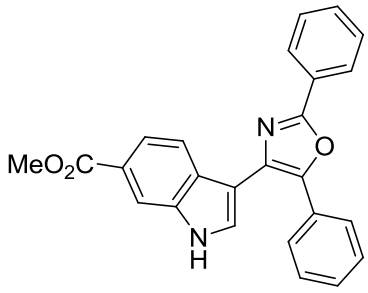
Oxazole **3fe** was synthesised according to **GP5** using indole derivative **1f** (45 mg, 0.2 mmol, 1.0 equiv) and ylide **2e** (56 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow powder (47 mg, 71%); mp. 197-200 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.54 (bs, NH), 8.00 (d, *J* = 1.0 Hz, 1H), 7.79 (bd, *J* = 2.3 Hz, 1H), 7.65-7.58 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.28 (d, *J* = 3.5 Hz, 1H), 7.21-7.11 (m, 2H), 7.04 (app td, *J* = 7.4, 0.5 Hz, 1H), 6.77 (dd, *J* = 3.5, 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 151.8 (C), 145.7 (CH), 141.9 (C), 139.4 (C), 136.2 (C), 131.5 (C), 129.2 (C), 127.8 (CH), 126.9 (CH), 125.9 (CH), 125.6 (C), 125.5 (CH), 121.7 (CH), 120.2 (CH), 119.5 (CH), 112.5 (CH), 112.3 (CH), 111.9 (CH), 105.3 (C); HRMS (ES) calcd. for $C_{19}H_{12}N_2O_2NaS$: 355.0517, found: 355.0518 $[M+Na]^+$; IR ν_{max}/cm^{-1} 3143, 1613, 1523, 1455, 1071, 971, 743, 692.

5-(Furan-2-yl)-4-(1H-indol-3-yl)-2-(thiophen-2-yl)oxazole (3ef)



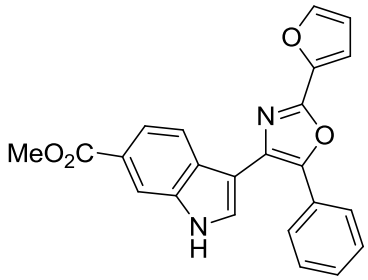
Oxazole **3ef** was synthesised according to **GP5** using indole derivative **1e** (42 mg, 0.2 mmol, 1.0 equiv) and ylide **2f** (61 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (40 mg, 61%); mp. 157-160 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.51 (bs, NH), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 2.7 Hz, 1H), 7.90 (d, *J* = 1.5 Hz, 1H), 7.87-7.83 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.17 (app. td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (app. td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.71 (dd, *J* = 3.5, 1.5 Hz, 1H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 155.4 (C), 143.7 (CH), 143.0 (C), 136.1 (C), 135.2 (C), 132.8 (C), 130.1 (CH), 128.7 (C), 128.7 (CH), 128.4 (CH), 125.8 (C), 125.3 (CH), 121.7 (CH). 120.7 (CH), 119.6 (CH), 112.0 (CH), 111.8 (CH), 109.1 (CH), 105.3 (C); HRMS (ES) calcd. for $C_{19}H_{13}N_2O_2S$: 333.0698, found: 333.0695 $[M+H]^+$; IR ν_{max}/cm^{-1} 3379, 3145, 2929, 1607, 1455, 1242, 1072, 884, 742.

Methyl 3-(2,5-diphenyloxazol-4-yl)-1H-indole-6-carboxylate (3la)



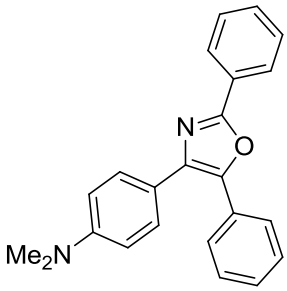
Oxazole **3la** was synthesised according to **GP5** using indole derivative **1l** (55 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (59 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (62 mg, 79%); mp. 188-190 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.99 (bs, NH), 8.22-8.18 (m, 2H), 8.17 (d, *J* = 1.1 Hz, 1H), 7.77 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.69 (d, *J* = 2.7 Hz, 1H), 7.68-7.64 (m, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.54-7.45 (m, 3H), 7.36-7.28 (m, 3H), 3.93 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.2 (C), 160.3 (C), 145.7 (C), 135.8 (C), 131.0 (C), 130.5 (CH), 129.5 (C), 129.1 (C), 129.0 (2 × CH), 128.8 (2 × CH), 128.3 (CH), 127.5 (CH), 127.6 (C), 126.6 (2 × CH), 126.1 (2 × CH), 124.4 (C), 121.4 (CH), 120.9 (CH), 113.9 (CH), 109.3 (C), 52.1 (CH_3); HRMS (ES) calcd. for $C_{25}H_{19}N_2O_3$: 395.1396, found: 395.1397 $[M+H]^+$; IR ν_{max}/cm^{-1} 3376, 3231, 1712, 1504, 1290, 1248, 1028, 745, 690.

Methyl 3-(2-(furan-2-yl)-5-phenyloxazol-4-yl)-1H-indole-6-carboxylate (3le)



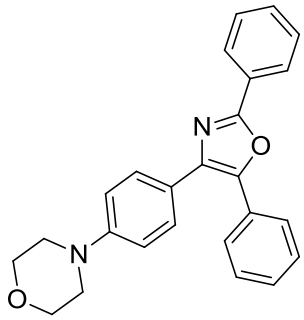
Oxazole **3la** was synthesised according to **GP5** using indole derivative **1l** (55 mg, 0.2 mmol, 1.0 equiv) and ylide **2e** (56 mg, 0.3 mmol, 1.5 equiv). After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a brown solid (45 mg, 59%); mp. 122-124 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.92 (bs, NH), 8.15 (s, 1H), 7.94-7.76 (m, 2H), 7.70-7.56 (m, 3H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.44-7.33 (m, 3H), 7.31 (bs, 1H), 6.77 (bs, 1H), 3.86 (s, 3H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 167.1 (C), 152.3 (C), 145.7 (CH), 143.8 (C), 142.0 (C), 135.5 (C), 130.9 (C), 129.1 (CH), 128.9 (2 × CH and C), 128.5 (CH), 128.1 (C), 125.7 (2 × CH), 122.8 (C), 120.0 (2 × CH), 114.0 (CH), 112.4 (CH), 112.3 (CH), 106.8 (C), 51.8 (CH_3); HRMS (ES) calcd. for $C_{23}H_{17}N_2O_4$: 385.1188, found: 385.1186 $[M+H]^+$; IR ν_{max}/cm^{-1} 3219, 1704, 1437, 1290, 933, 741, 688.

4-(2,5-Diphenyloxazol-4-yl)-N,N-dimethylaniline (5aa)



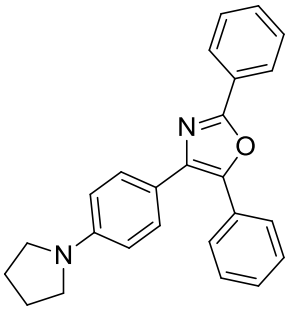
Oxazole **5aa** was synthesised according to **GP5** using aniline derivative **4a** (44 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (90 mg, 0.45 mmol, 2.25 equiv). The reaction mixture was quenched after 48 h. After purification with flash column chromatography (Toluene) the oxazole was isolated as a yellow powder (43 mg, 63%); mp. 128-130 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.20-8.13 (m, 2H), 7.78-7.68 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.51-7.45 (m, 3H), 7.43-7.30 (m, 3H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.00 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.0 (C), 150.5 (C), 144.3 (C), 137.5 (C), 130.2 (CH), 129.7 (C), 129.1 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 128.1 (CH), 127.8 (C), 126.6 (2 × CH), 126.4 (2 × CH), 120.5 (C), 112.4 (2 × CH), 40.6 (2 × CH_3); HRMS (ES) calcd. for $C_{23}H_{20}N_2ONa$: 363.1473, found: 363.1469 $[M+Na]^+$; IR ν_{max}/cm^{-1} 3691, 3619, 2919, 2852, 1607, 1455, 1242, 1008, 911, 692.

4-(4-(2,5-Diphenyloxazol-4-yl)phenyl)morpholine (5ba)



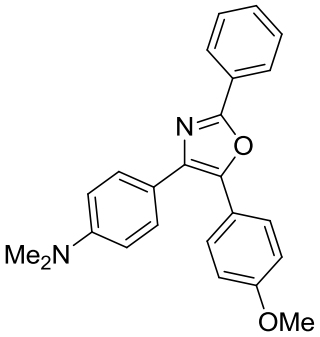
Oxazole **5ba** was synthesised according to **GP5** using aniline derivative **4b** (53 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (90 mg, 0.45 mmol, 2.25 equiv). The reaction mixture was quenched after 48 h. After purification with flash column chromatography [Toluene:EtOAc (9:1)] the oxazole was isolated as a yellow powder (45 mg, 59%); mp. 140-142 ^{o}C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.13-8.06 (m, 2H) 7.72-7.66 (m, 2H), 7.61- 7.53 (m, 4H), 7.53-7.38 (m, 4H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.79-3.70 (m, 4H), 3.22-3.14 (m, 4H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 159.2 (C), 150.9 (C), 144.0 (C), 136.3 (C), 130.7 (CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.7 (CH), 128.6 (C), 128.4 (2 × CH), 126.7 (C), 126.2 (2 × CH), 126.0 (2 × CH), 122.0 (C), 114.6 (2 × CH), 66.0 (2 × CH_2), 47.8 (2 × CH_2); HRMS (ES) calcd. for $C_{25}H_{23}N_2O_2$: 383.1760, found: 383.1764 $[M+H]^+$; IR ν_{max}/cm^{-1} 3377, 3059, 1615, 1514, 1445, 1260, 1239, 923, 824, 740, 685.

2,5-Diphenyl-4-(4-(pyrrolidin-1-yl)phenyl)oxazole (5ca)



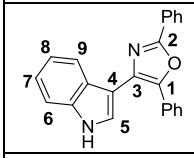
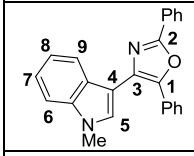
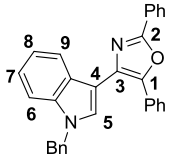
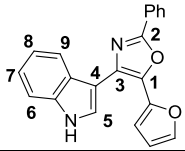
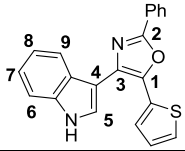
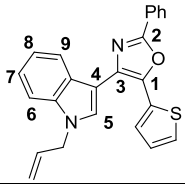
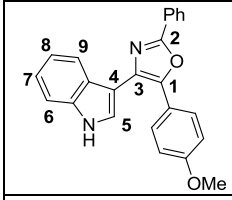
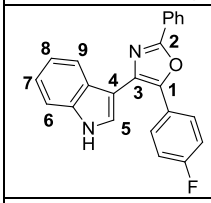
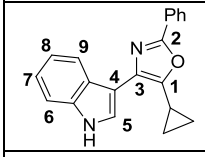
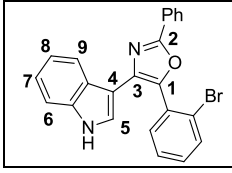
Oxazole **5ca** was synthesised according to **GP5** using aniline derivative **4c** (50 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (90 mg, 0.45 mmol, 2.25 equiv). The reaction mixture was quenched after 48 h. After purification with flash column chromatography (Toluene) the oxazole was isolated as a brown solid (25 mg, 34%); mp. 130-135 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.21-8.17 (m, 2H), 7.77-7.70 (m, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.52-7.43 (m, 3H), 7.40-7.35 (m, 2H), 7.36-7.31 (m, 1H), 6.59 (d, *J* = 8.7 Hz, 2H), 3.34 (t, *J* = 6.6, 4H), 2.06-2.02 (m, 4H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 159.9 (C), 147.9 (C), 144.1 (C), 137.7 (C), 130.1 (CH), 129.8 (C), 129.2 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 128.0 (CH), 127.9 (C), 126.6 (2 × CH), 126.4 (2 × CH), 119.4 (C), 111.7 (2 × CH), 47.7 (2 × CH_2), 25.6 (2 × CH_2); HRMS (ES) calcd. for $C_{25}H_{23}N_2O$: 367.1810, found: 367.1812 $[M+H]^+$; IR ν_{max}/cm^{-1} 2851, 1614, 1378, 1112, 765, 686.

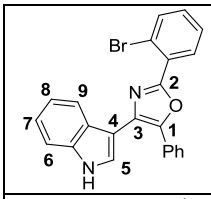
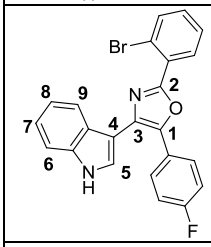
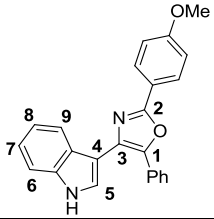
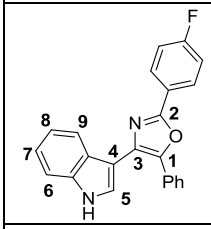
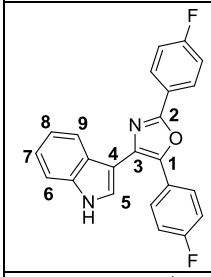
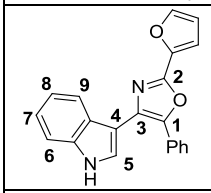
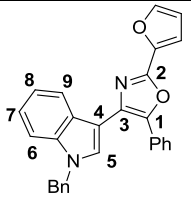
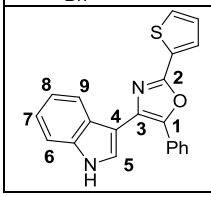
4-(5-(4-Methoxyphenyl)-2-phenyloxazol-4-yl)-N,N-dimethylaniline (7)

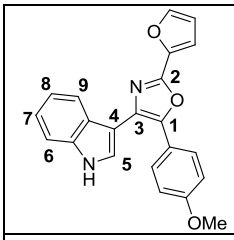
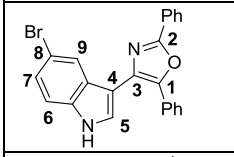
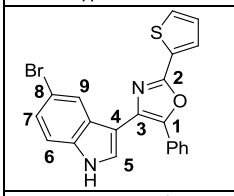
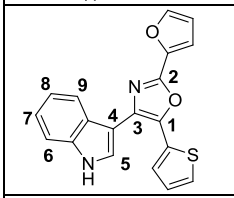
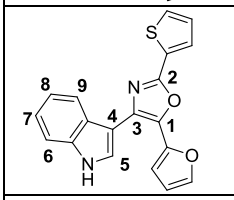
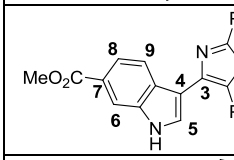
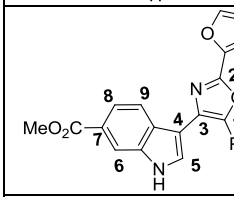
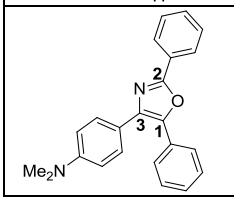
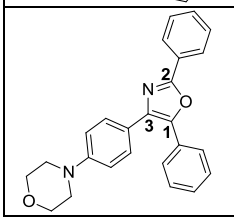


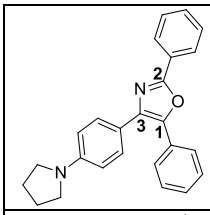
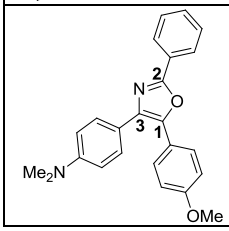
Oxazole **7** was synthesised according to GP4 using aniline derivative **6** (50 mg, 0.2 mmol, 1.0 equiv) and ylide **2a** (90 mg, 0.45 mmol, 2.25 equiv). The reaction mixture was quenched after 48 h. After purification with flash column chromatography (Toluene) the oxazole was isolated as a yellow powder (63 mg, 84%); mp. 117-120 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.18 (m, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.51-7.41 (m, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.00 (s, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.6 (C), 159.5 (C), 150.4 (C), 144.4 (C), 136.2 (C), 130.1 (CH), 129.0 (2 × CH), 128.8 (2 × CH), 128.1 (2 × CH), 127.9 (C), 126.5 (2 × CH), 122.4 (C), 120.7 (C), 114.2 (2 × CH), 112.5 (2 × CH), 55.5 (OCH_3), 40.6 (2 × CH_3); HRMS (ES) calcd. for $C_{24}H_{23}N_2O_2$: 371.1760, found: 371.1755 $[M+H]^+$; IR ν_{max}/cm^{-1} 2902, 1615, 1500, 1250, 1174, 1029, 827, 686.

^{13}C-NMR comparison table for characteristic peaks

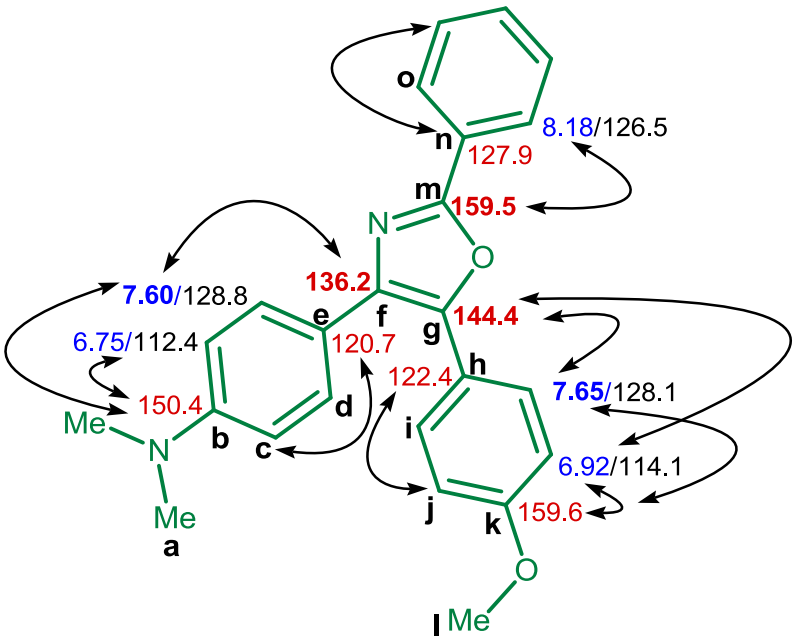
Compound	NMR solvent	C1	C2	C3	C4	C5	C6	C7	C8	C9
 **3aa**	DMSO-d_6	144.2	159.1	136.2	106.5	125.1	111.9	121.6	119.3	120.1
 **3ba**	$CDCl_3$	145.1	160.1	137.3	107.2	128.0	109.5	122.1	120.0	121.5
 **3ca**	$CDCl_3$	145.2	160.1	136.7	108.0	127.9	110.0	122.4	120.3	121.6
 **3da**	DMSO-d_6	143.2	159.0	136.2	106.0	125.2	112.0	121.7	119.6	121.0
 **3ea**	DMSO-d_6	140.2	158.8	136.2	105.6	125.3	111.7	121.7	119.5	120.3
 **3fa**	$CDCl_3$	145.1	160.1	137.3	107.2	128.0	109.5	122.1	120.0	121.5
 **3ga**	DMSO-d_6	144.4	159.2	136.2	106.6	124.8	111.8	121.6	119.3	120.2
 **3ha**	$CDCl_3$	144.6	160.1	136.4	108.8	124.1	111.4	122.8	120.5	121.2
 **3ia**	$CDCl_3$	147.5	158.7	136.3	108.9	122.6	111.2	122.6	120.3	121.3
 **3ja**	$CDCl_3$	142.9	160.9	136.2	108.5	127.5	111.2	122.5	120.4	121.4

 **3ab**	$CDCl_3$	145.9	158.6	136.2	108.7	124.0	111.2	122.6	120.4	121.3
 **3hb**	DMSO-d_6	143.7	157.7	136.2	105.9	125.1	111.9	121.7	119.5	120.2
 **3ac**	DMSO-d_6	144.9	160.2	136.4	108.9	124.2	111.3	122.6	120.4	121.3
 **3ad**	$CDCl_3$	145.4	159.3	136.4	108.9	124.1	111.4	122.7	120.5	121.3
 **3hd**	DMSO-d_6	143.5	163.5	136.2	106.2	125.0	111.9	121.6	119.4	120.0
 **3ae**	$CDCl_3$	144.9	153.1	136.3	108.6	124.5	111.4	122.6	120.4	121.3
 **3ce**	$CDCl_3$	144.8	153.2	136.8	107.7	126.6	111.7	122.4	120.3	121.7
 **3af**	DMSO-d_6	143.6	155.5	136.2	106.2	125.3	111.9	121.6	119.4	120.1

 **3ge**	$CDCl_3$	144.3	159.3	136.3	108.8	124.4	111.3	122.5	120.3	121.3
 **3ka**	$CDCl_3$	145.7	160.3	135.0	108.7	125.9	112.8	123.9	128.4	130.5
 **3kf**	DMSO-d_6	143.8	155.7	134.9	105.9	126.7	114.0	128.6 or 128.5	127.7	129.8
 **3fe**	DMSO-d_6	141.9	151.8	136.2	105.3	125.5	111.9	121.7	119.5	120.2
 **3ef**	DMSO-d_6	143.0	155.4	136.1	105.3	125.3	111.8	121.7	119.6	120.7
 **3la**	$CDCl_3$	145.7	160.3	135.8	109.3	127.5	113.9	131.0	120.9	121.4
 **3le**	DMSO-d_6	143.8	152.3	135.5	106.8	128.5	112.3	130.9	128.5	120.0
 **5aa**	$CDCl_3$	144.3	160.0	137.5	-	-	-	-	-	-
 **5ba**	DMSO-d_6	144.0	159.2	136.3	-	-	-	-	-	-

 **5ca**	$CDCl_3$	144.1	159.9	137.7	-	-	-	-	-	-
 **7**	$CDCl_3$	144.4	159.5	136.2	-	-	-	-	-	-

Compound 7 (2D-Spectra Analysis)



Key correlations from HMBC and HSQC studies for the determination of structure **7** are described below (Chemical shifts are shown in blue (H), black (C) and red (quaternary carbon):

- For the substituent at the 4-position of the oxazole ring: H_a is coupled with the quaternary C_b which in turn is coupled with H_c. H_d is coupled with C_c and the quaternary C_f through a ^{3}J-coupling.
- For the substituent at the 5-position of the oxazole ring: H_l is coupled with the quaternary C_k which in turn is coupled with H_j. H_i is coupled with C_j and the quaternary Cg_f through a ^{3}J-coupling.
- For the substituent at the 2-position of the oxazole ring: H_o is coupled with C_m.
- The assignment of the quaternary carbons at the oxazole ring (C_f, C_g, C_m) is in agreement with data reported in the literature.[38]

Crystal Data for 3aa

$C_{23}H_{16}N_2O$, M = 336.38, Monoclinic, a = 12.0222(2), b = 7.2396 (1), c = 20.9825(3) Å, β= 106.482(1), U= 1751.19(5) Å^3, T = 120(2) K, space group $P2_1/c$, Z = 4, 11907 reflections measured, 3042 unique (R_{int} = 0.0655) which were used in all calculations. The final $R1$ was 0.0525 ($I>2\sigma(I)$) and $wR(F_2)$ was 0.1537 (all data).

Suitable crystals were selected and a dataset was measured on a Bruker SMART 6000 diffractometer ($\lambda_{Cu\text{-}K\alpha}$ = 1.5418 Å). The data collection was driven by SMART[39] and processed by SAINTPLUS[40] and an absorption correction was applied using SADABS.[41] The structures was solved using ShelXS-97[42] and refined by a full-matrix least-squares procedure on F^2 in ShelXL-97.[42] All non-hydrogen atoms were refined with anisotropic displacement parameters. The N-bound hydrogen atom was located in the electron density and the position refined freely. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model and the isotropic displacement parameters for all hydrogen atoms are based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2.[43]

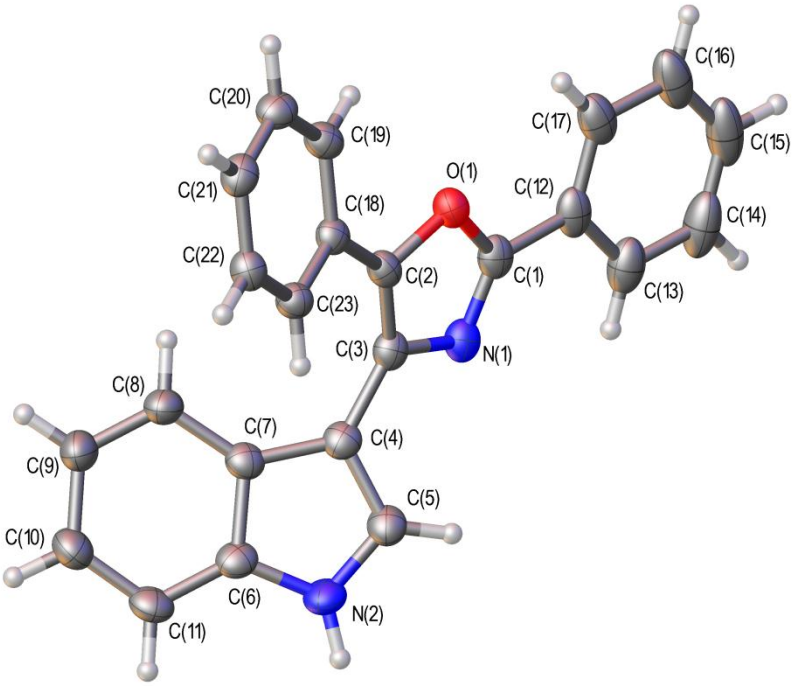


Figure S1 Crystal structure of oxazole **3aa** with ellipsoids drawn at the 50 % probability level.

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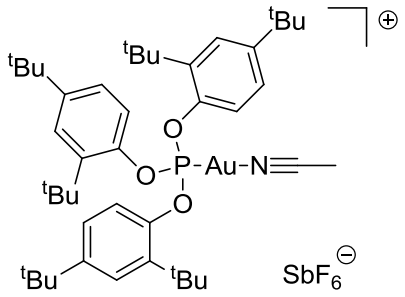
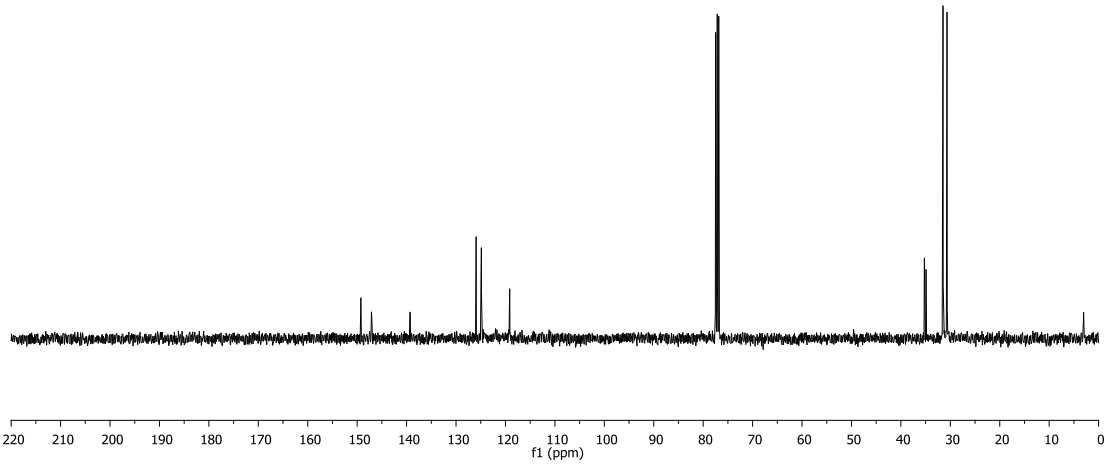
^{1}H and ^{13}C-NMR spectra for all immediate precursors and catalysis products

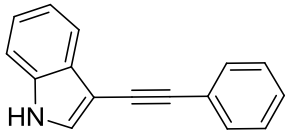
Catalyst Au-III



Au-**III**



Compound 1a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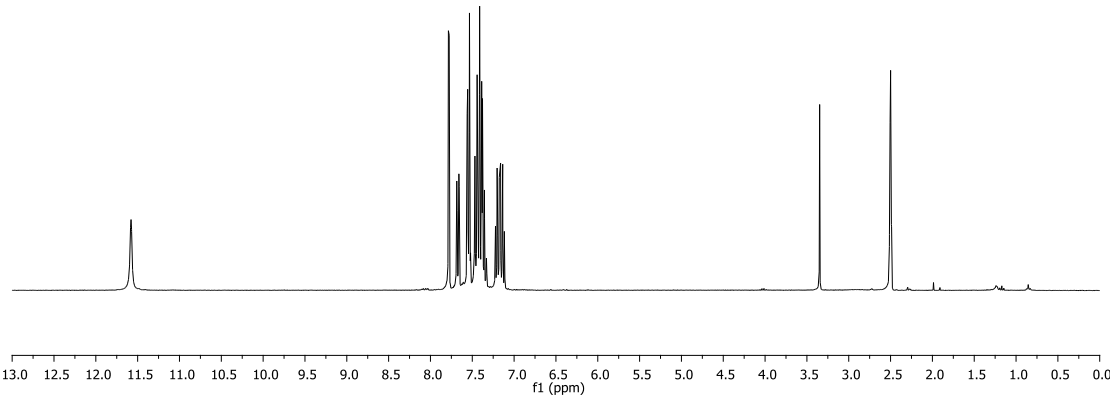
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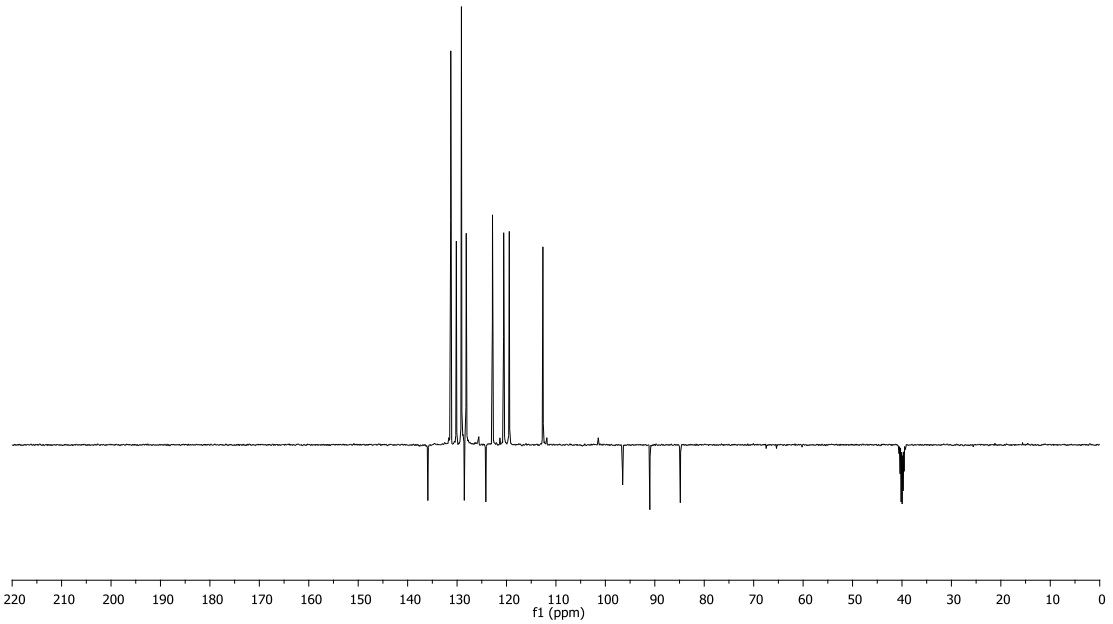
f1 (ppm)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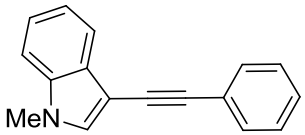
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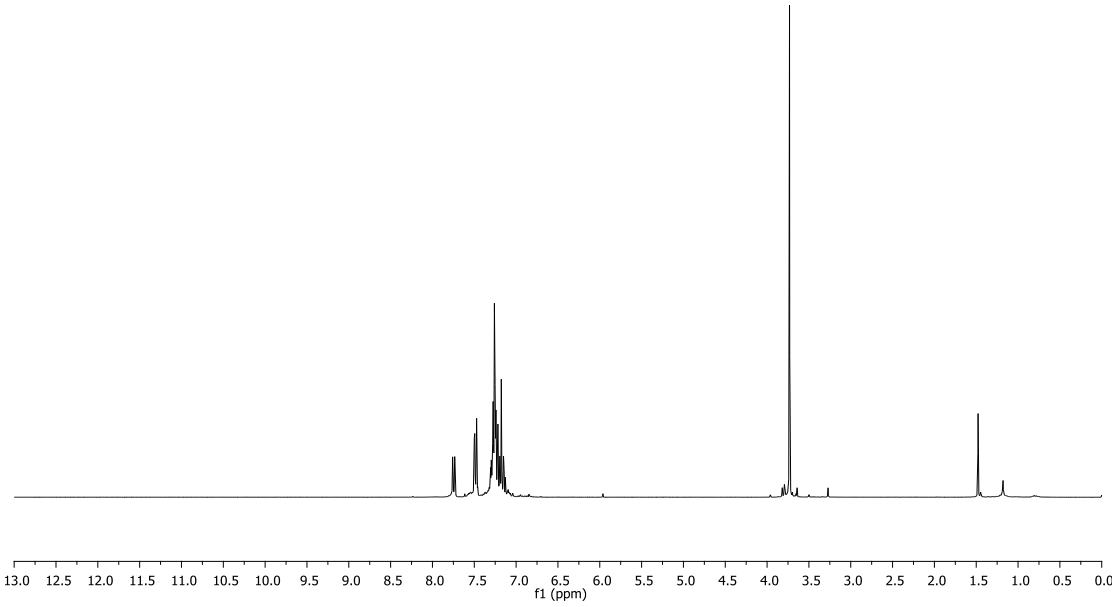
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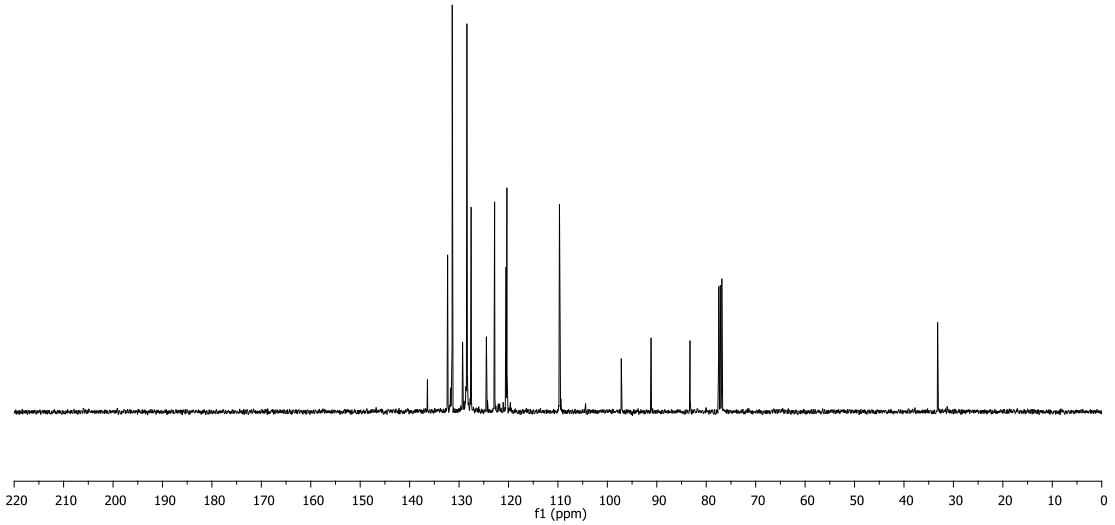
f1 (ppm)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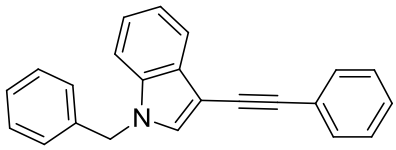
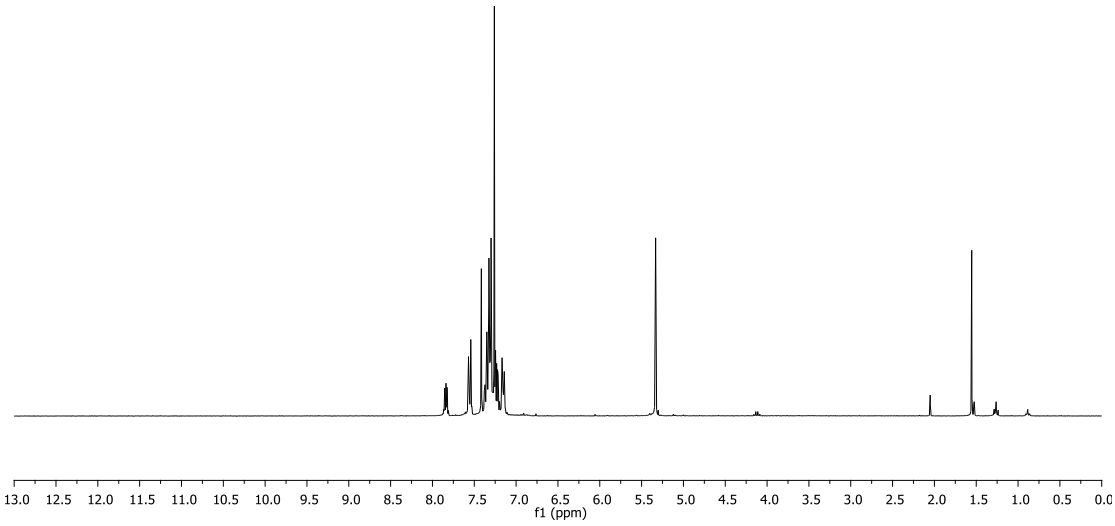
f1 (ppm)

Compound 1c

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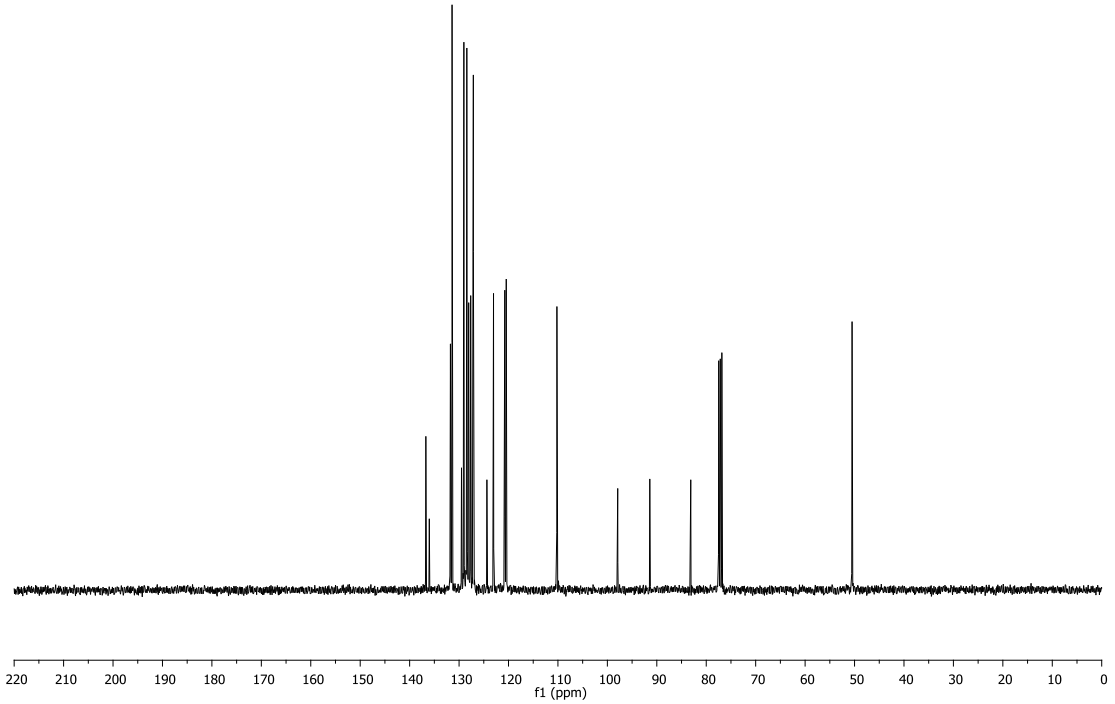
f1 (ppm)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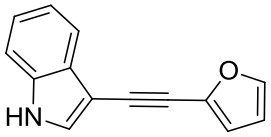
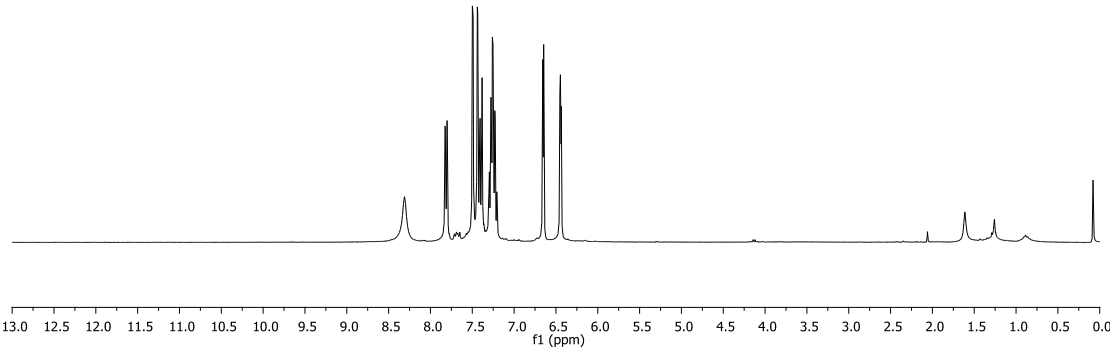
Compound 1d


HN
O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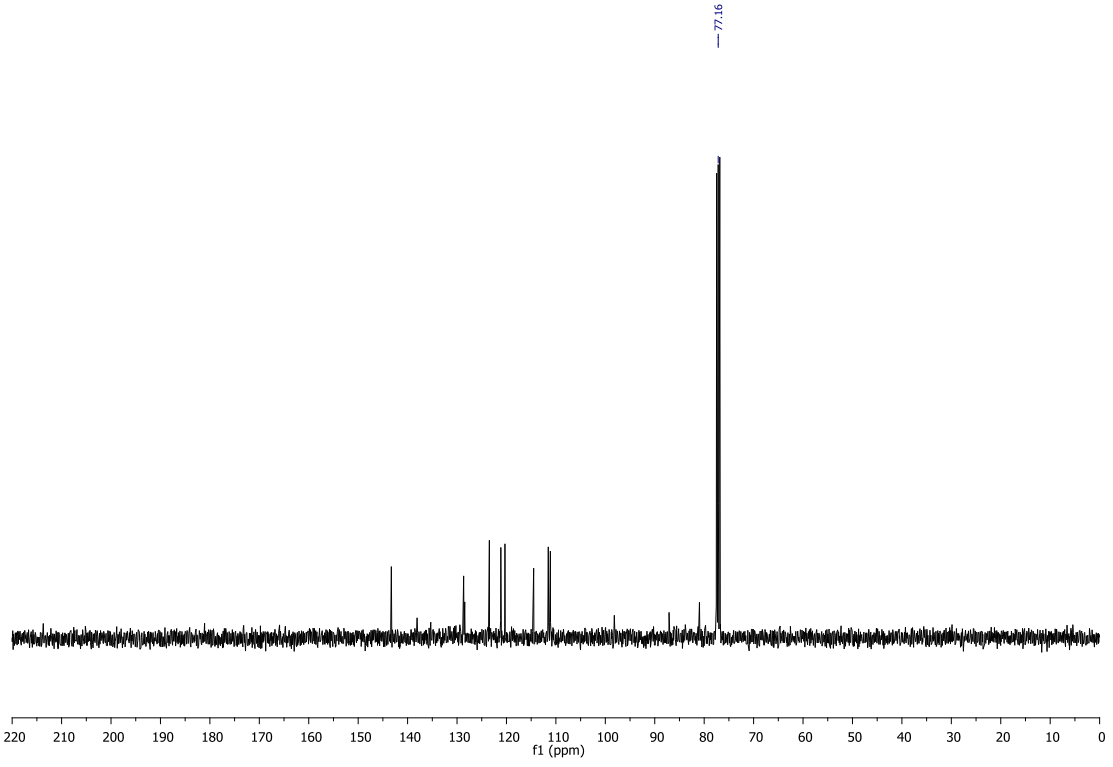
f1 (ppm)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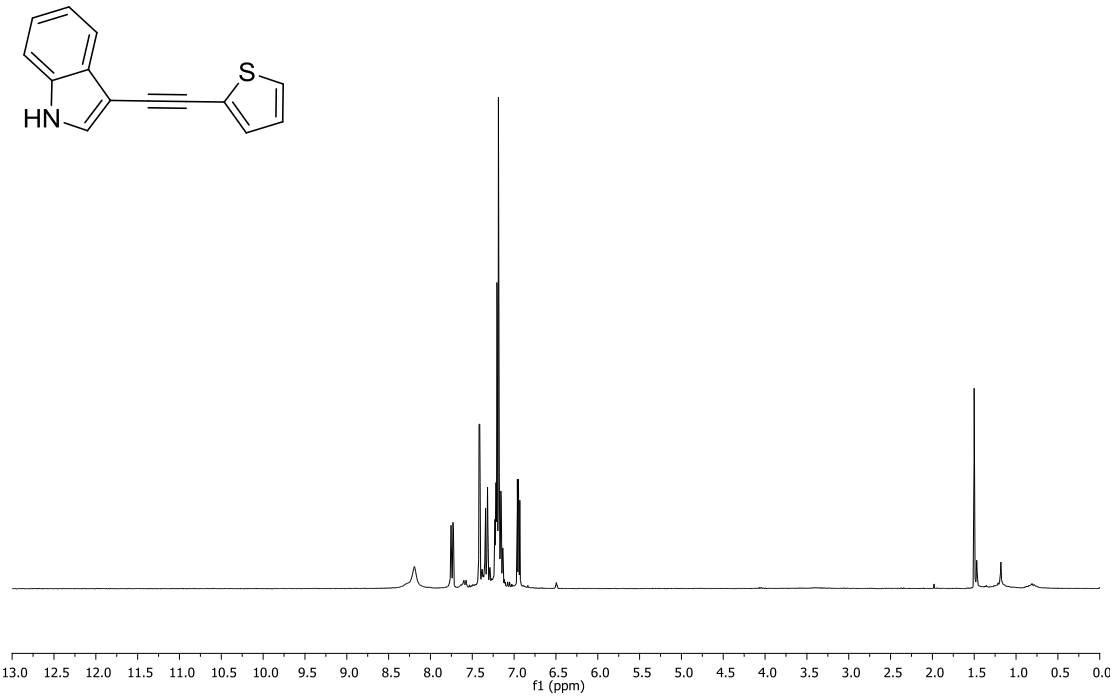
Compound 1e


S
HN
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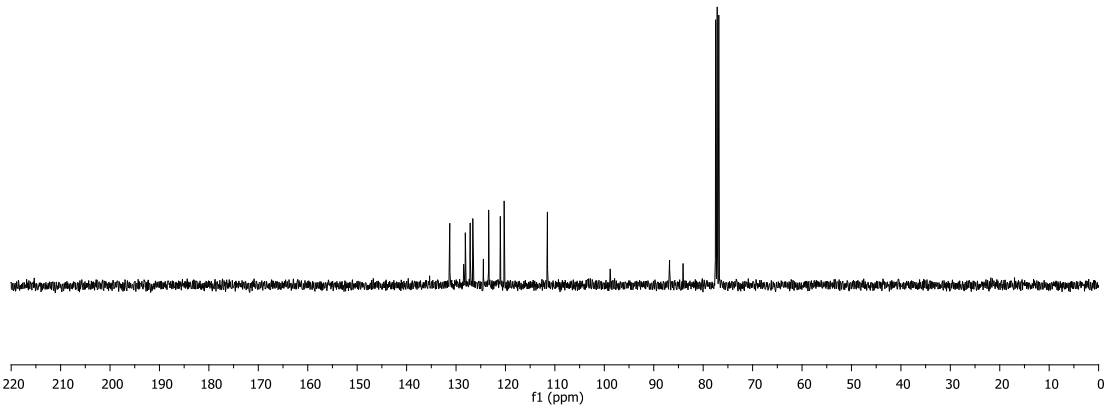
f1 (ppm)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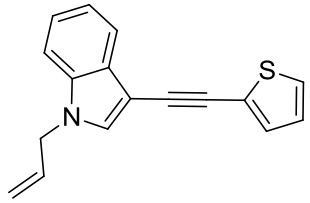
Compound 1f


S
N

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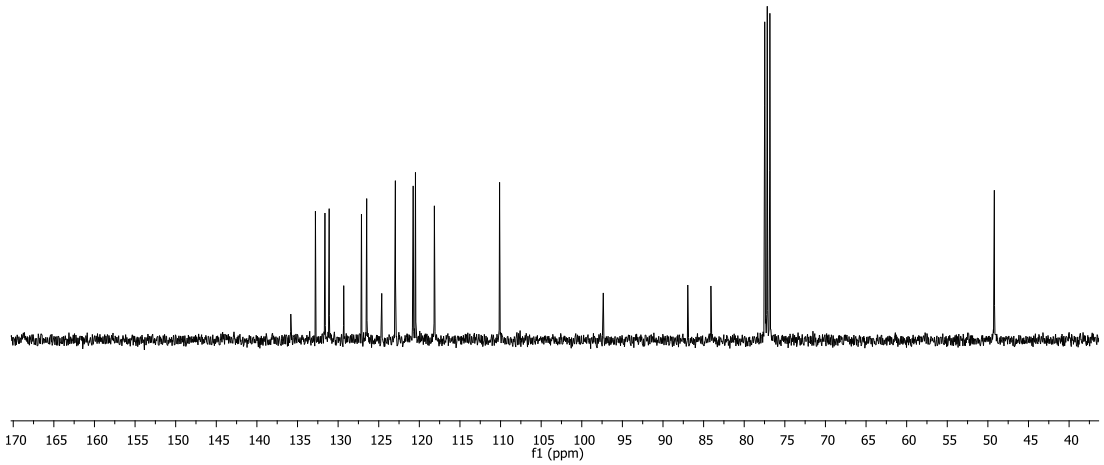
f1 (ppm)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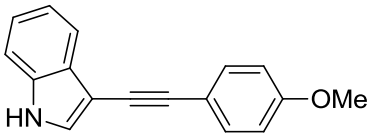
Compound 1g


HN
OMe

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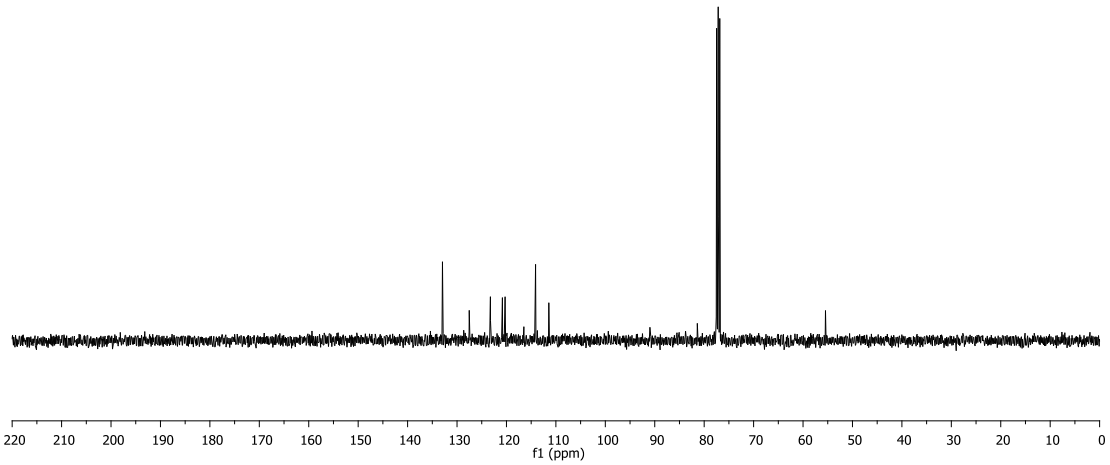
f1 (ppm)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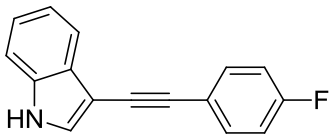
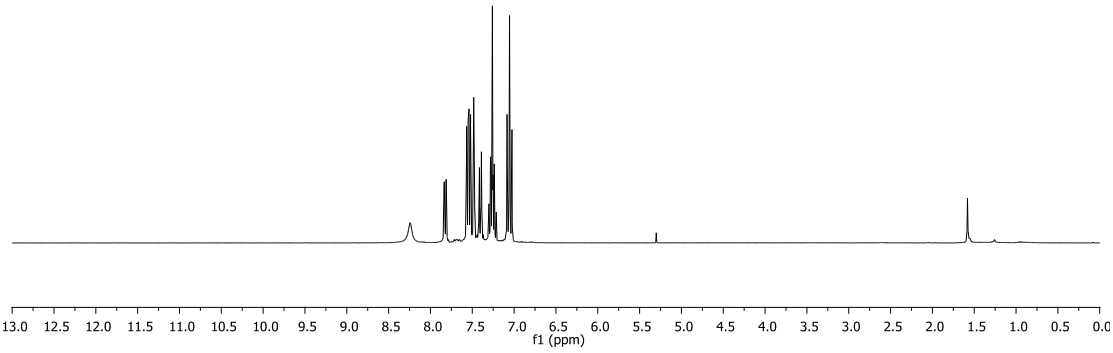
f1 (ppm)

Compound 1h


HN
F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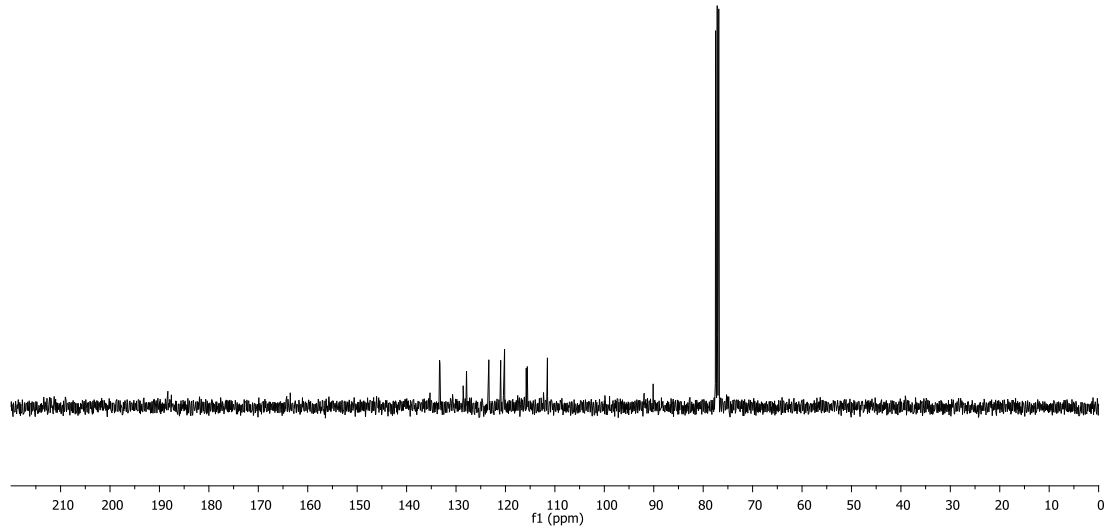
f1 (ppm)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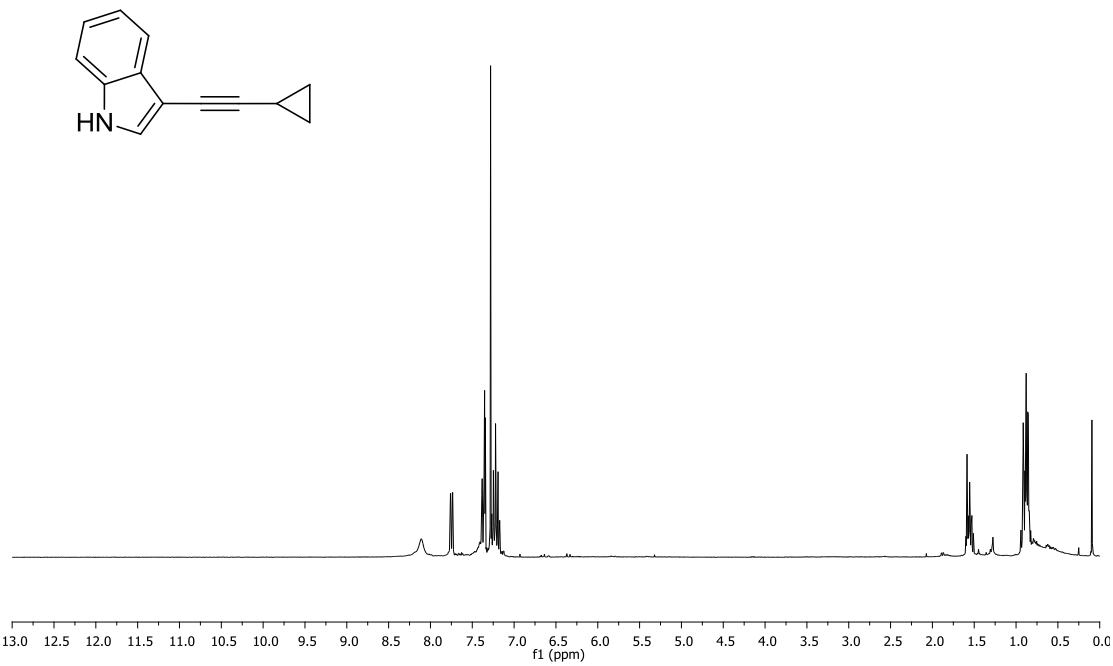
Compound 1i


HN
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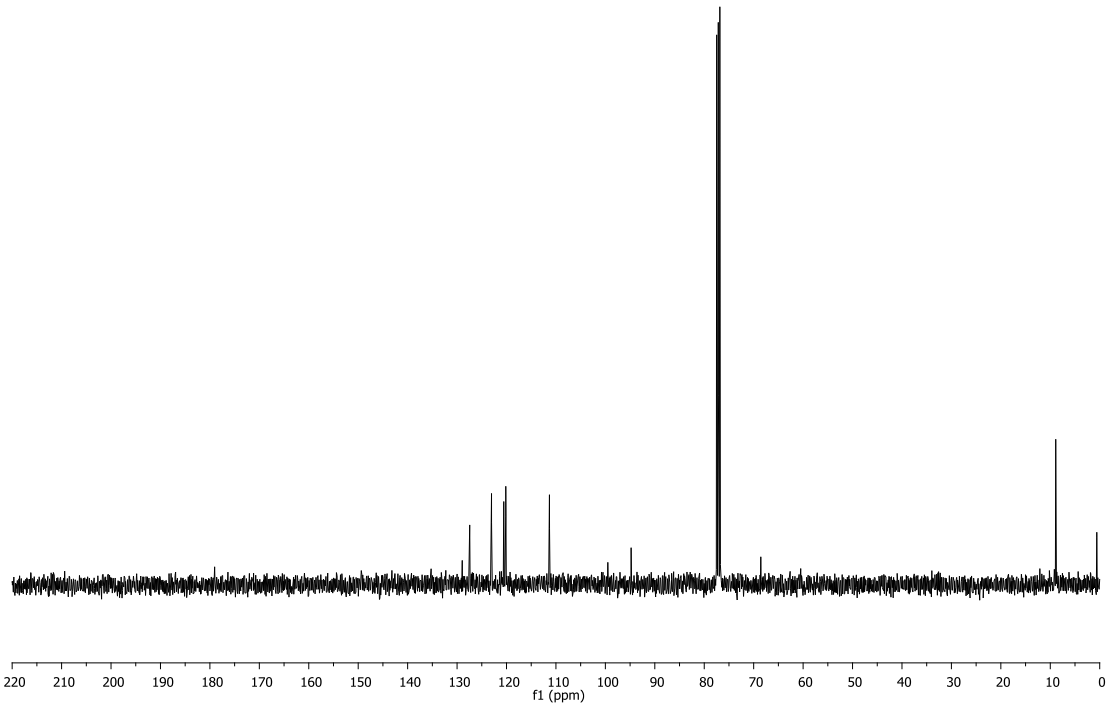
f1 (ppm)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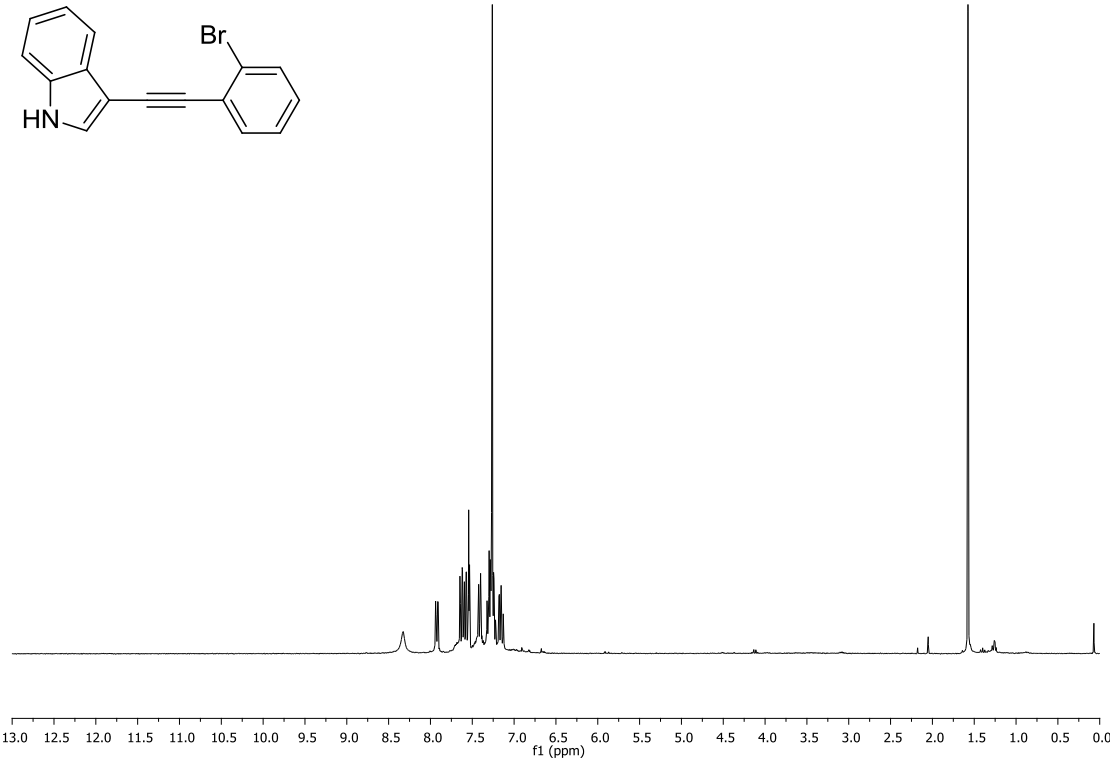
f1 (ppm)

Compound 1j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HN
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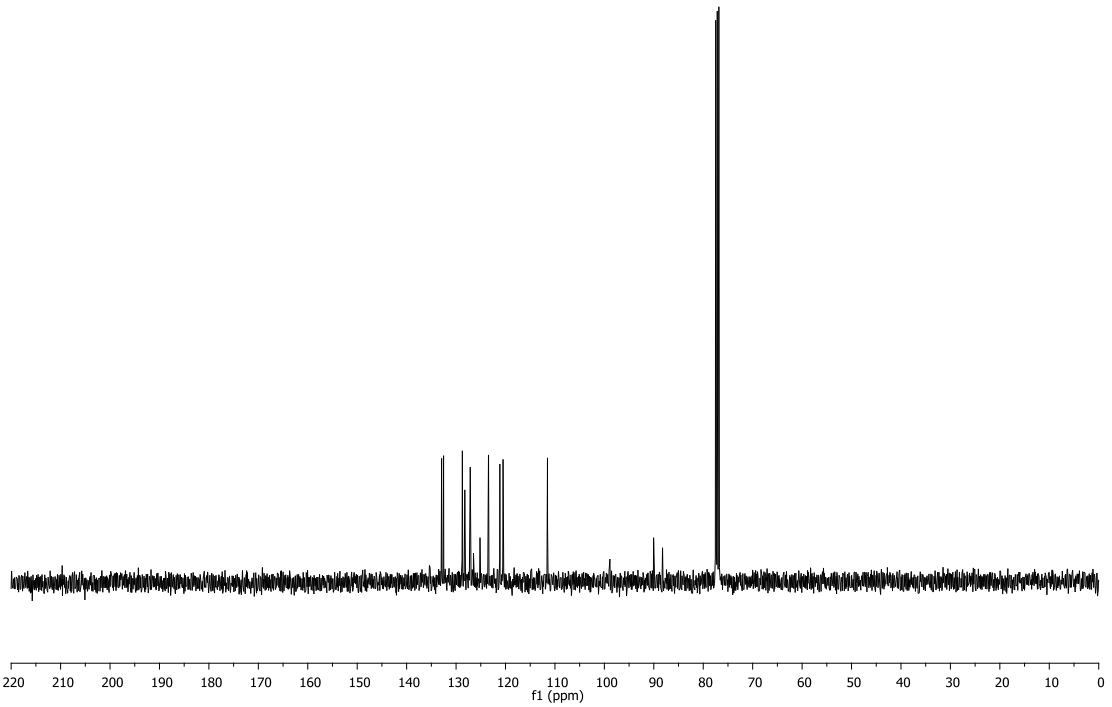
f1 (ppm)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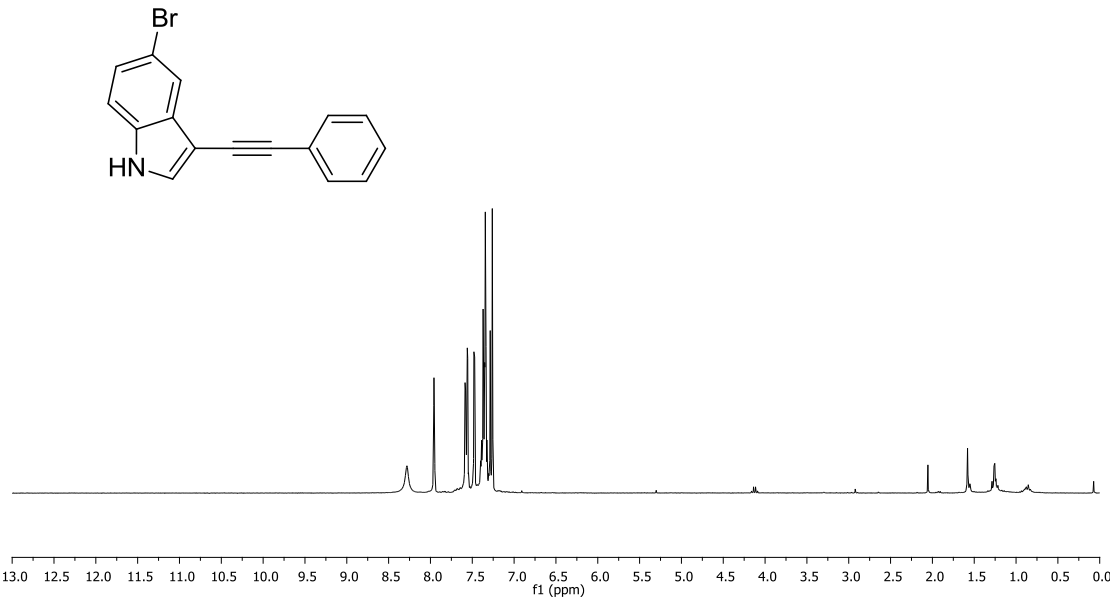
Compound 1k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HN
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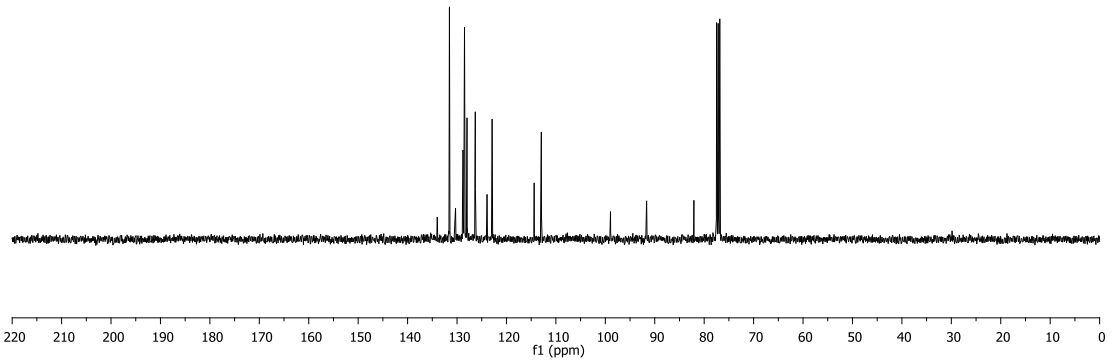
f1 (ppm)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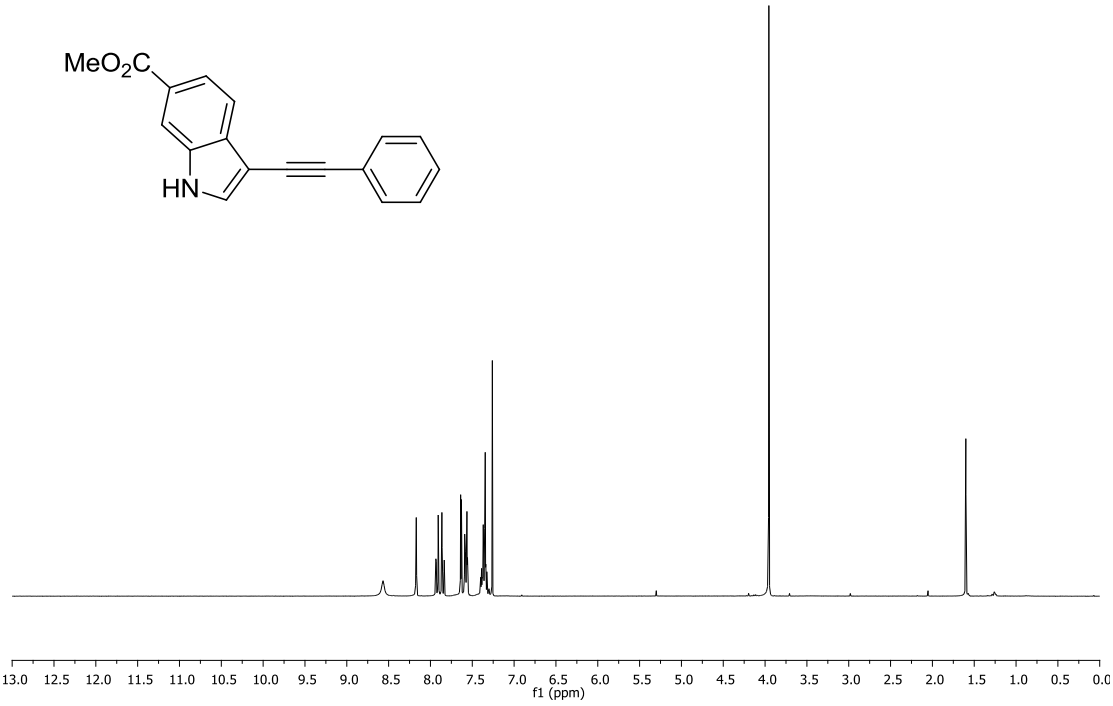
Compound 1l


MeO2C
HN
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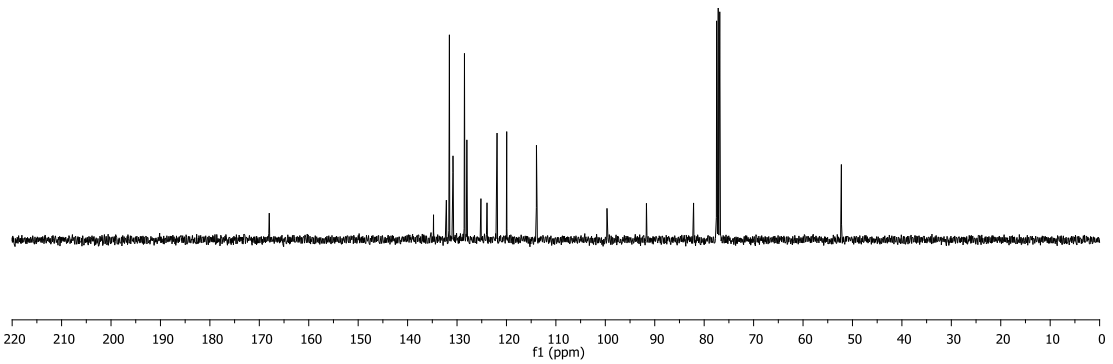
f1 (ppm)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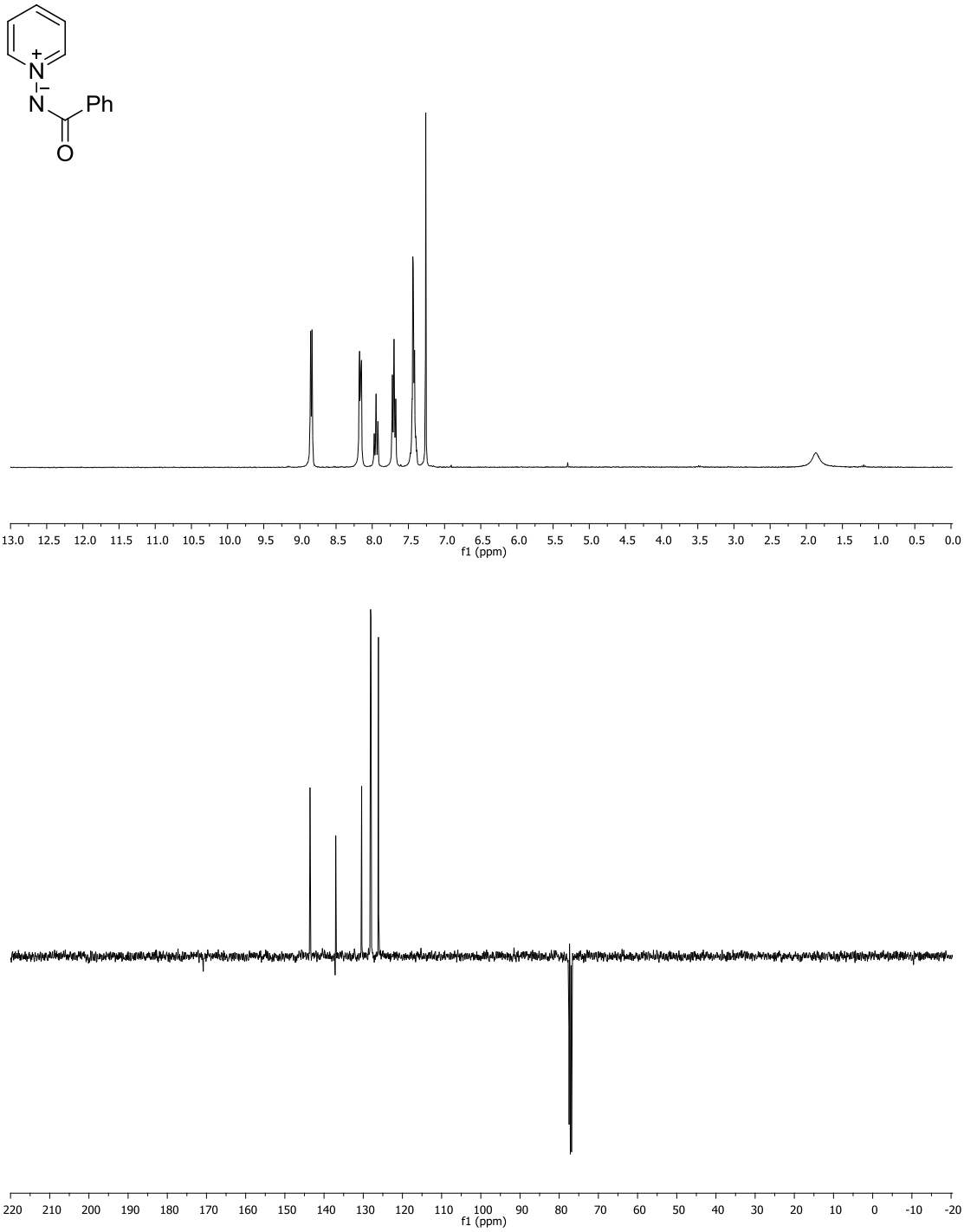
Compound 2a


N
N
Ph
O
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f1 (ppm)
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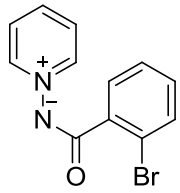
f1 (ppm)

Compound 2b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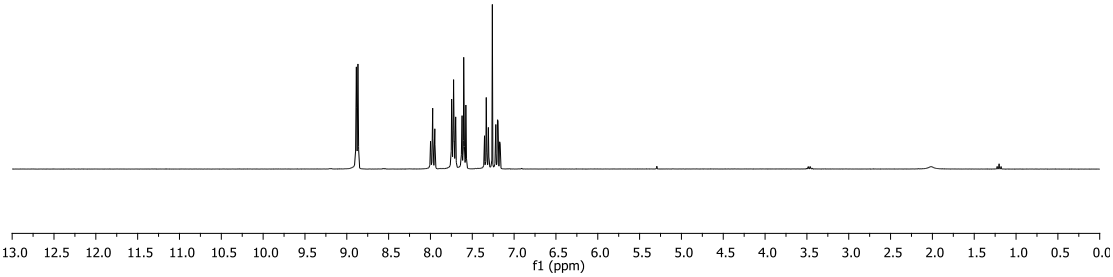
N
O
Br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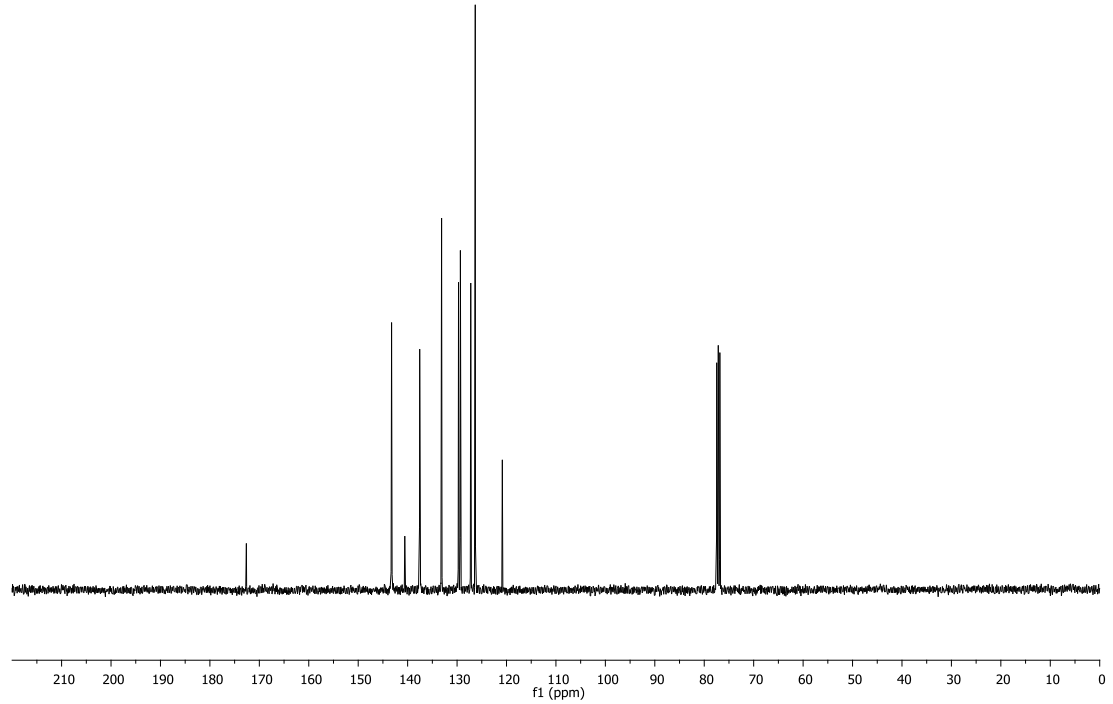
f1 (ppm)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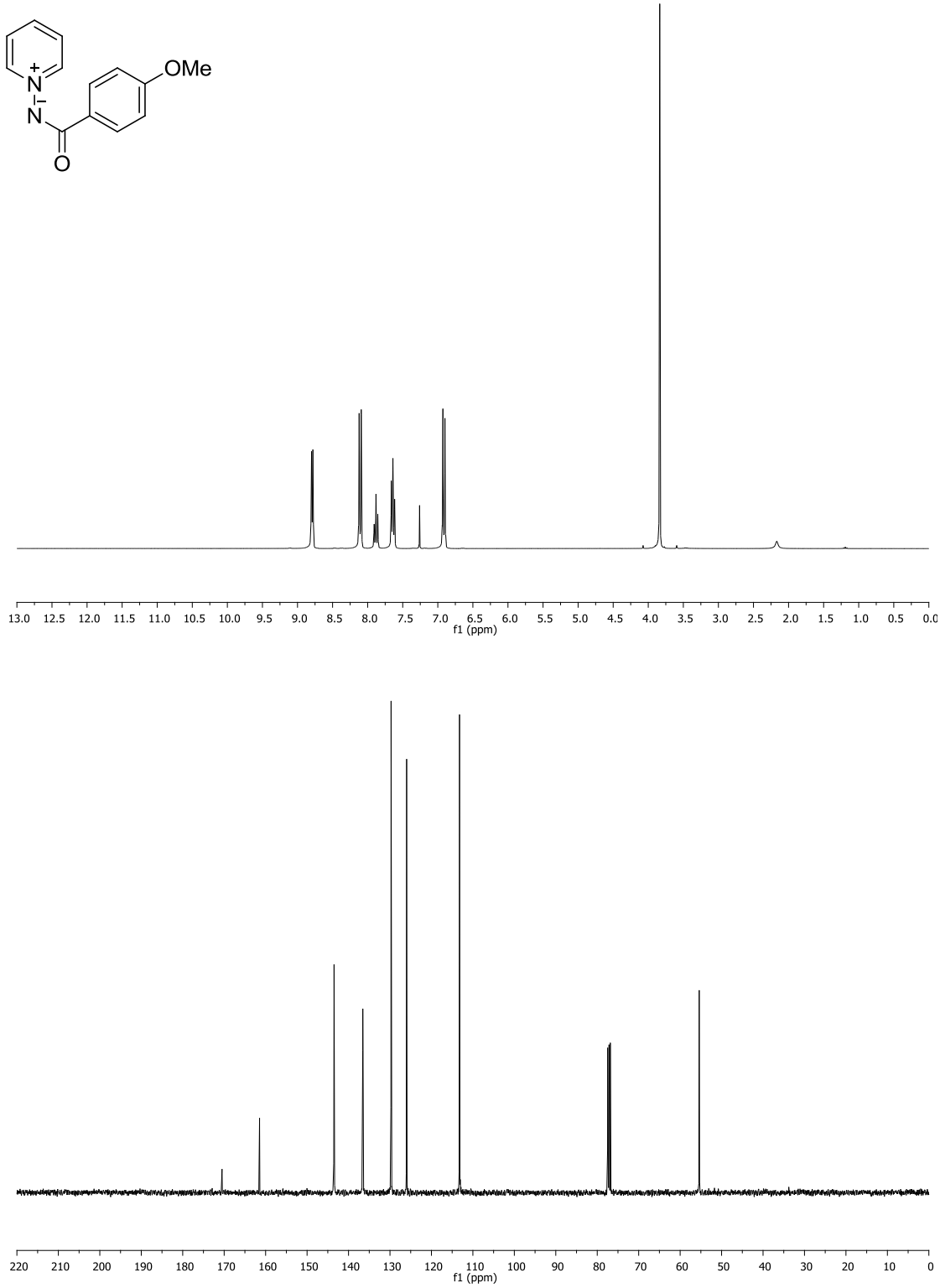
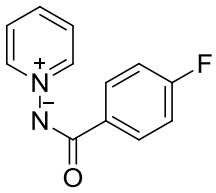
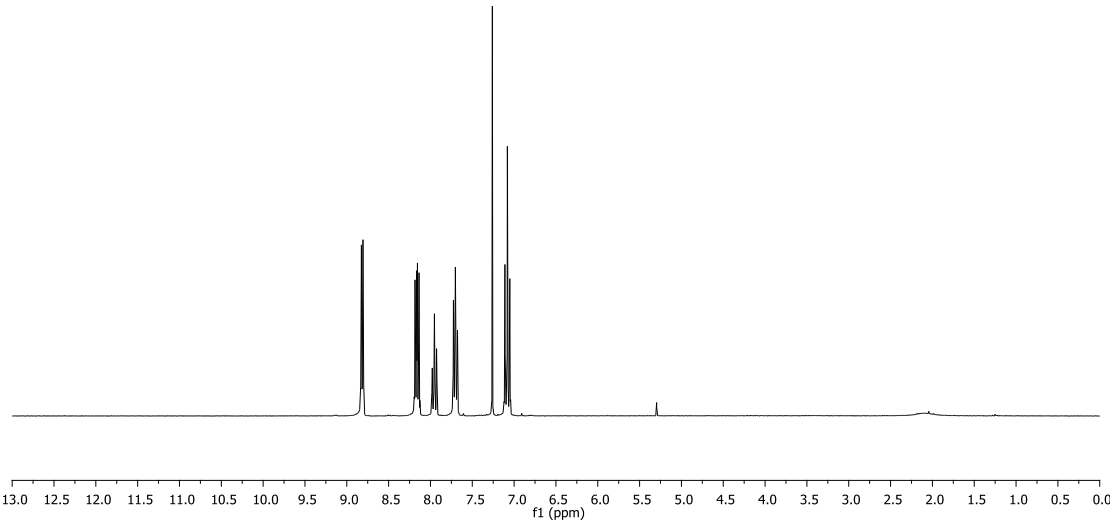
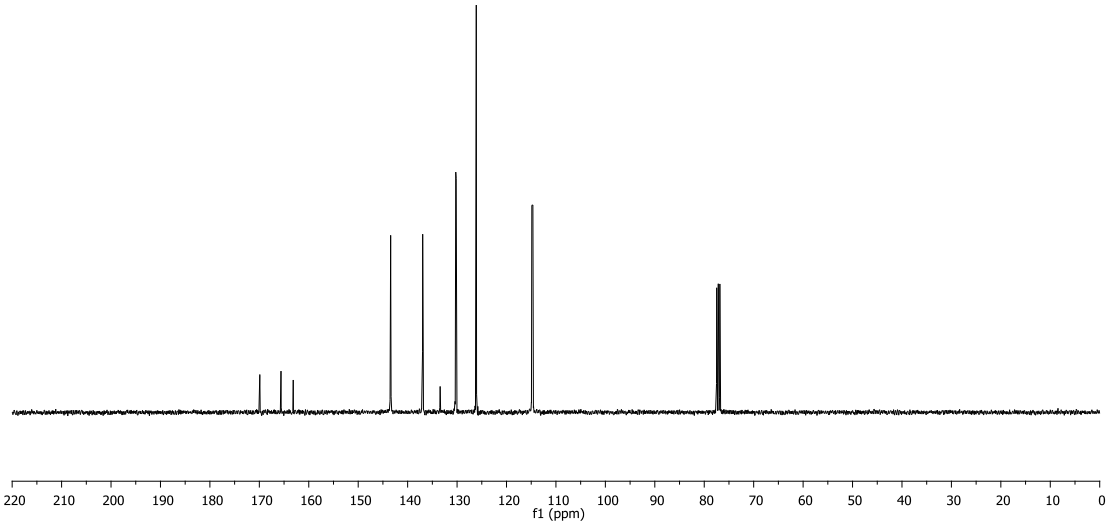
Compound 2c


OMe
N
N
O
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

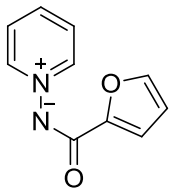
Compound 2d


F
N
N
O

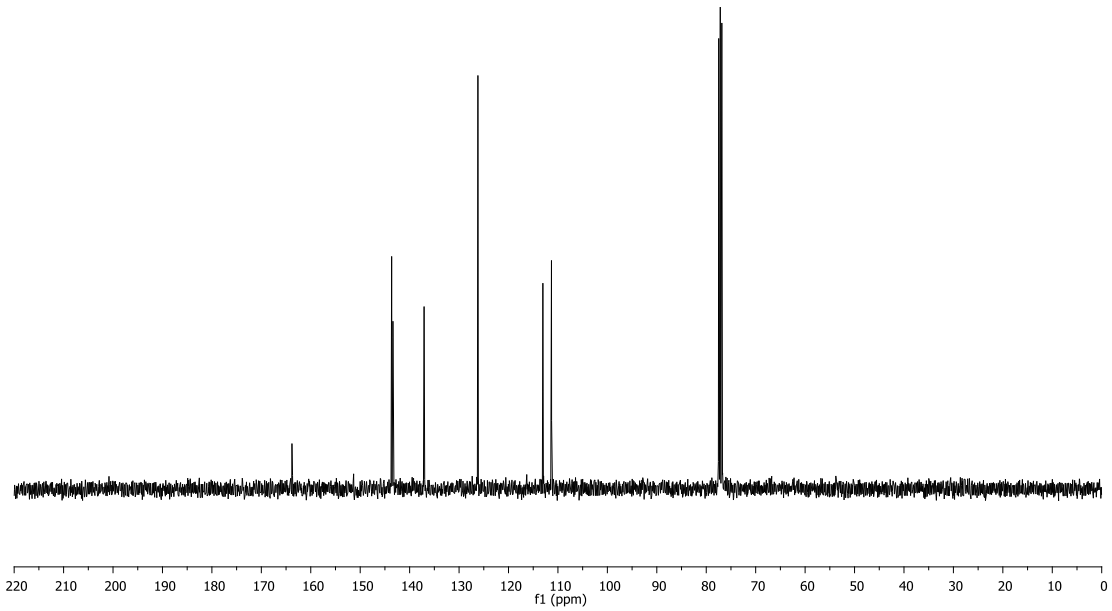

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

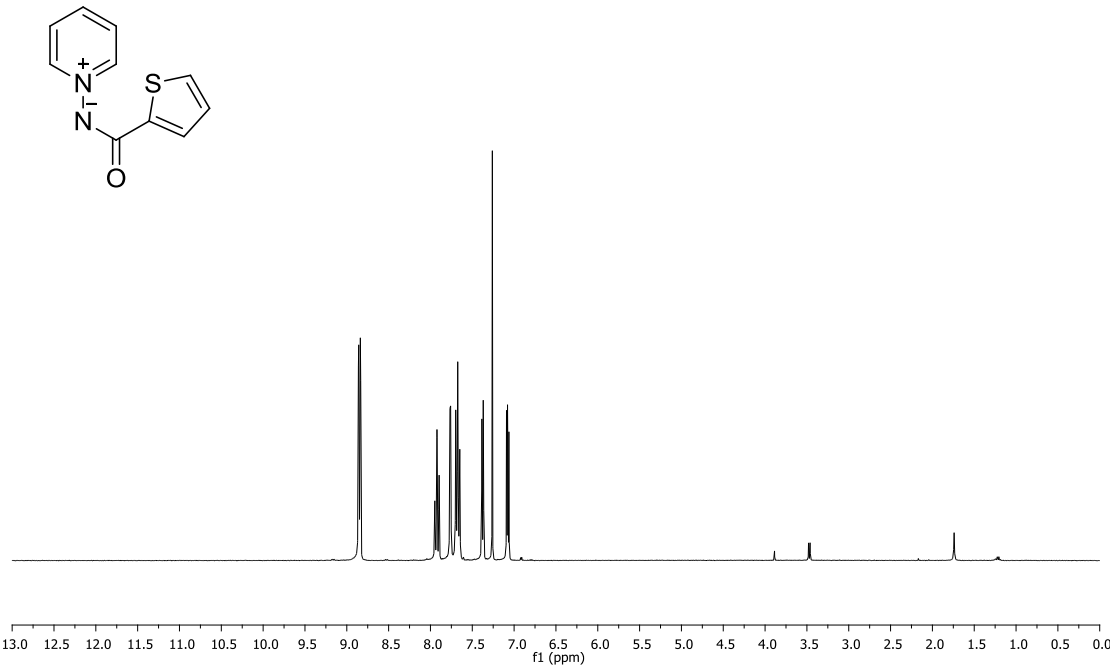
Compound 2e

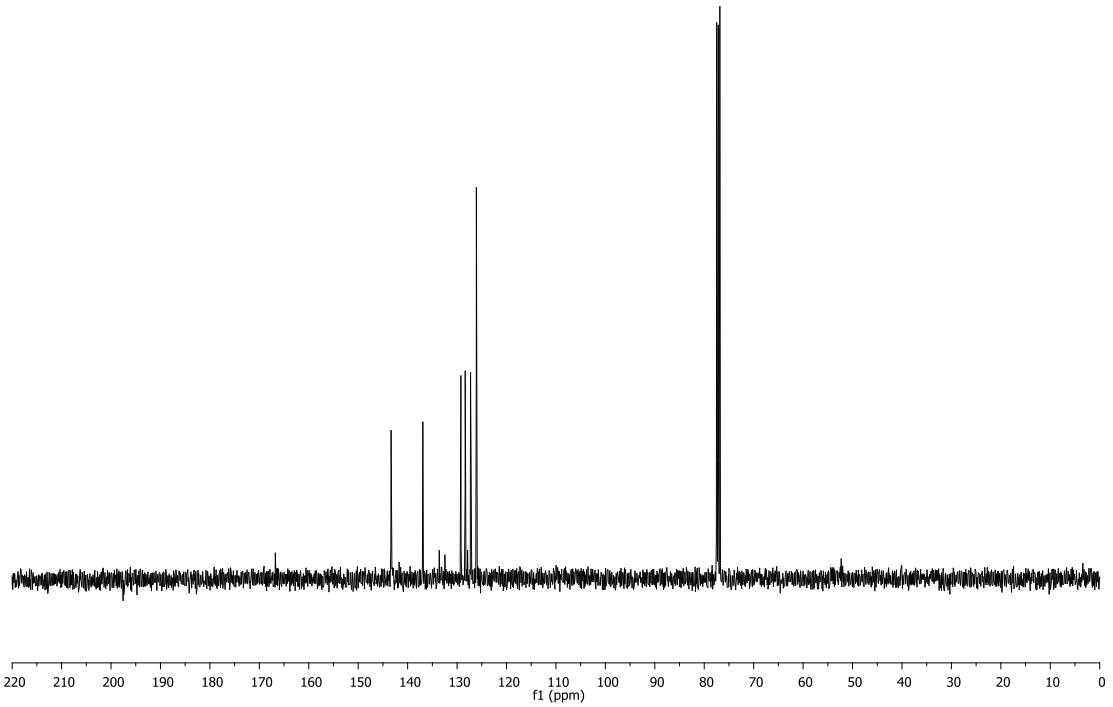

N
N
O
O

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

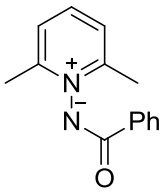

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

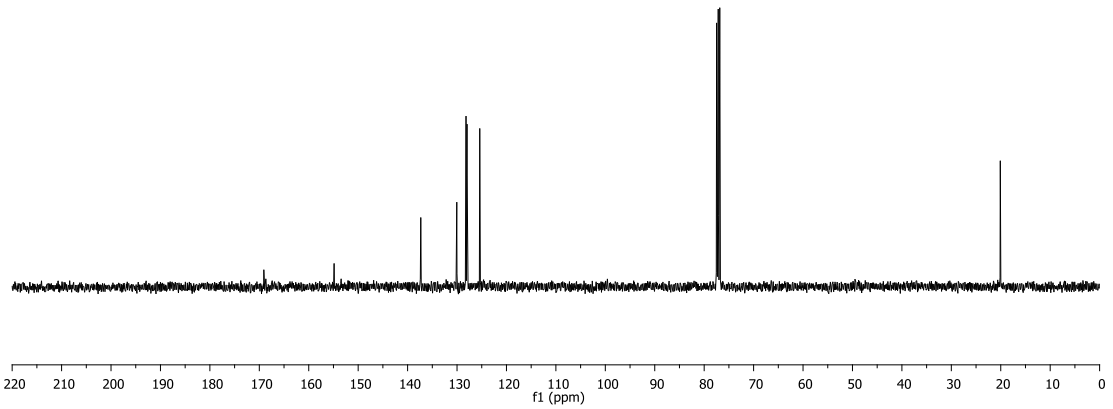
Compound 2f


13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

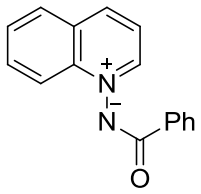

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

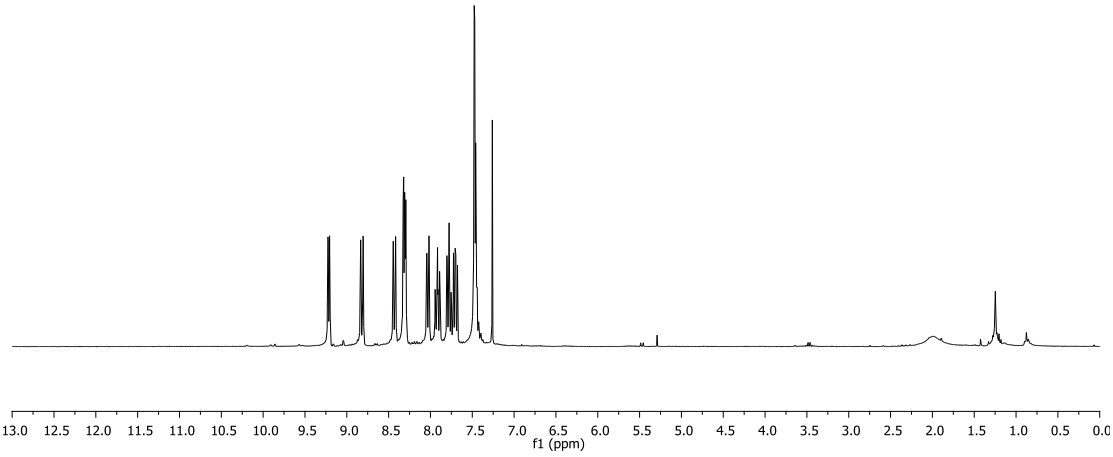
Compound 2aII

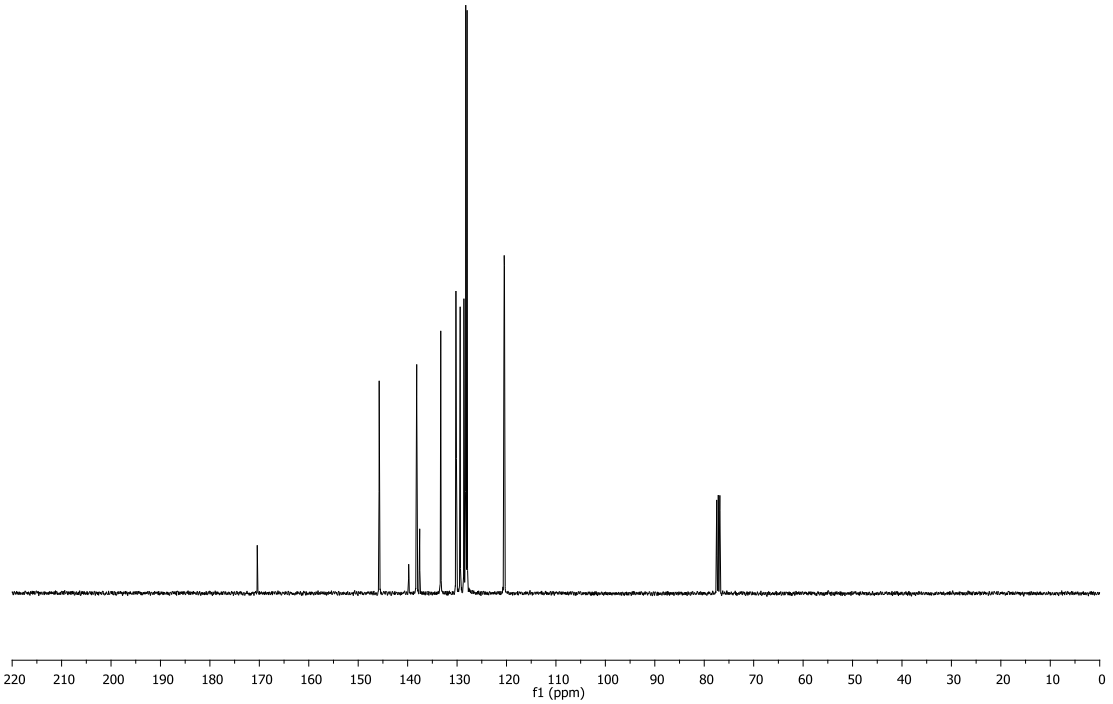




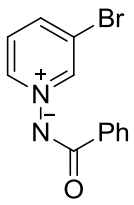
Compound 2aIII

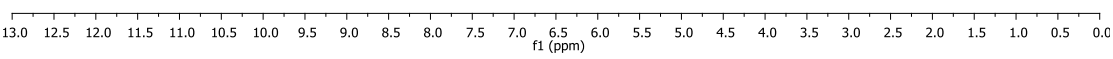


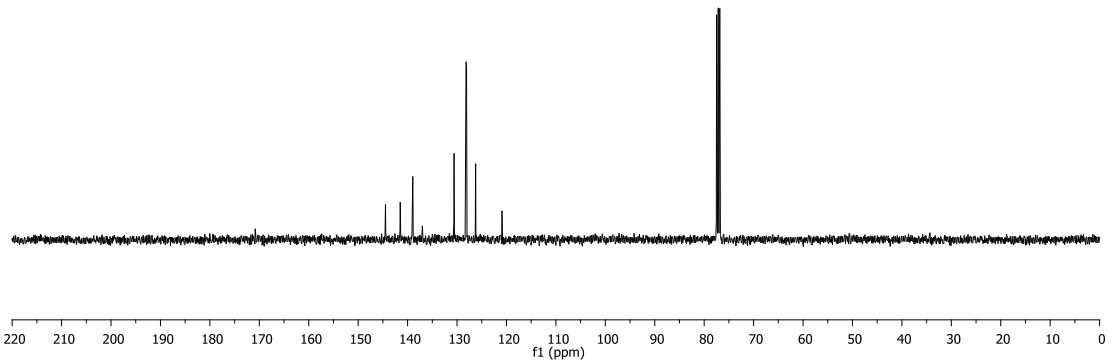




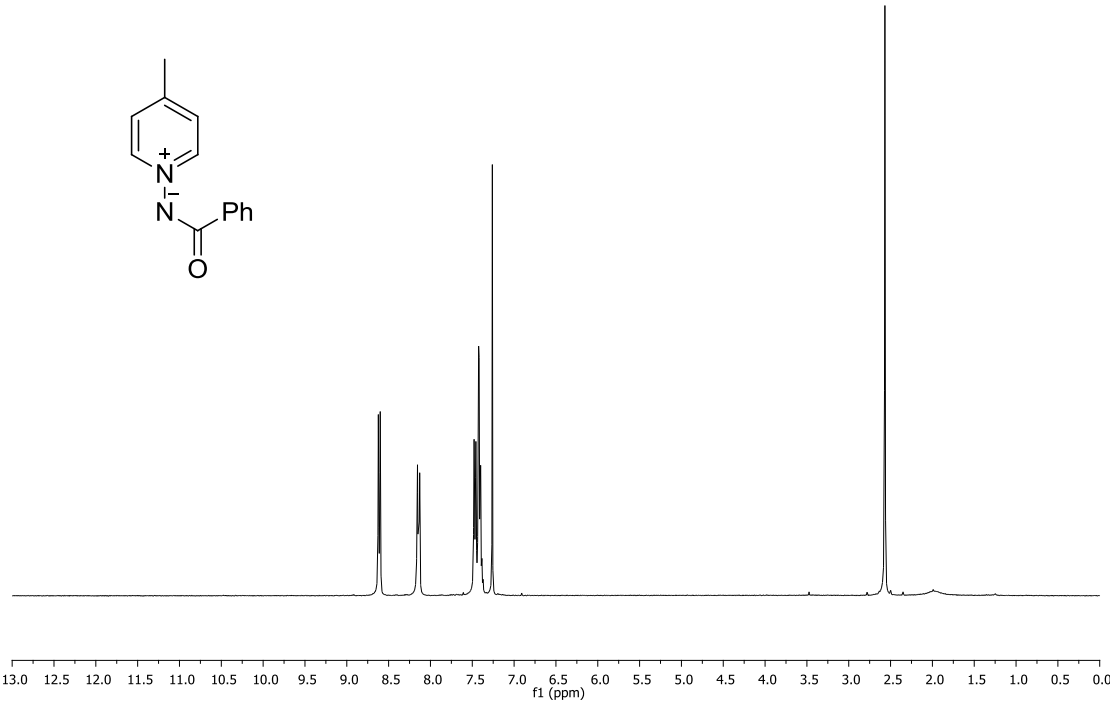
Compound 2aIV

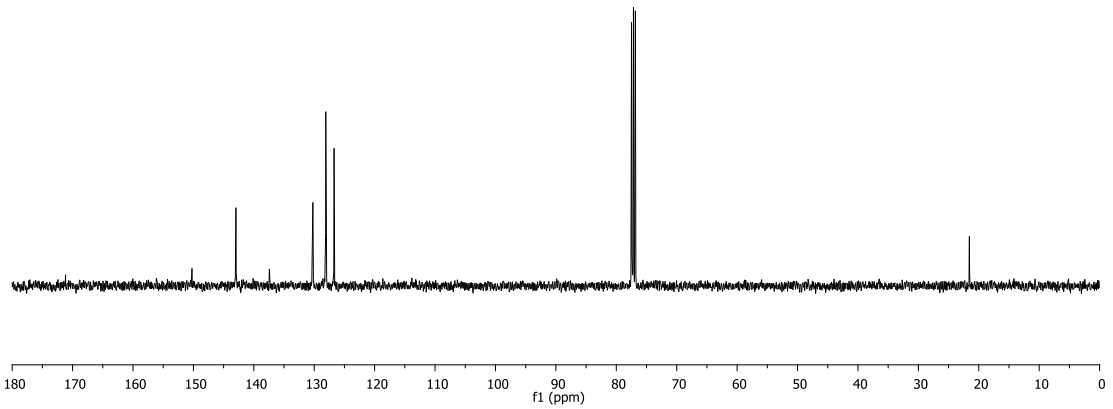




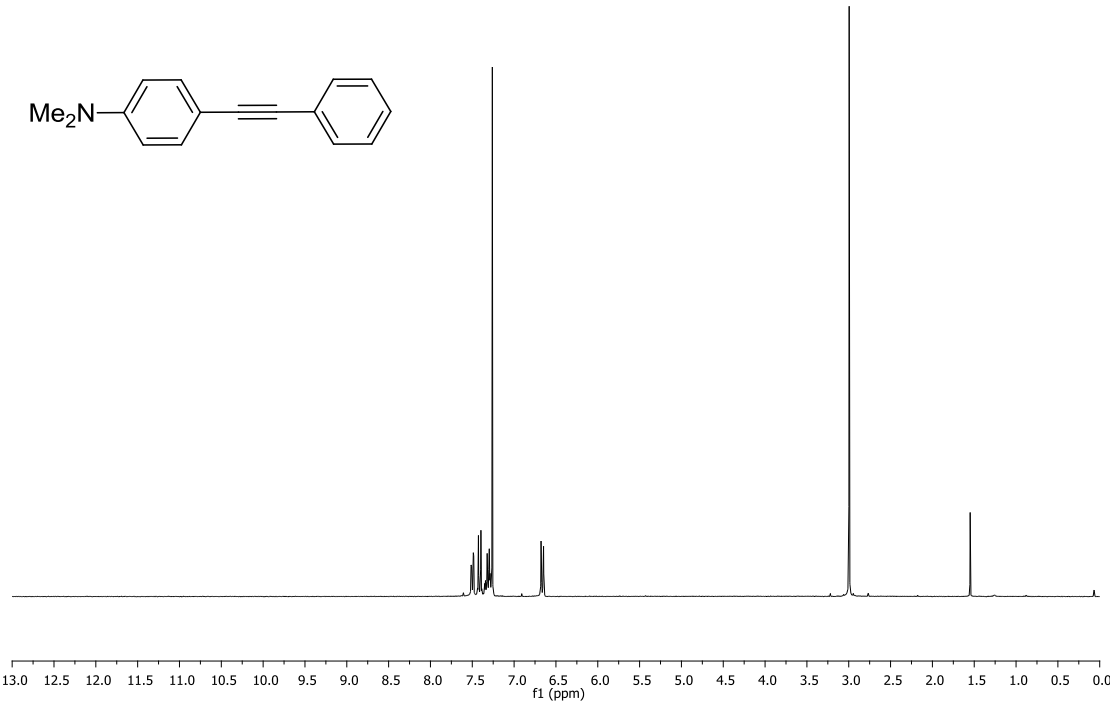


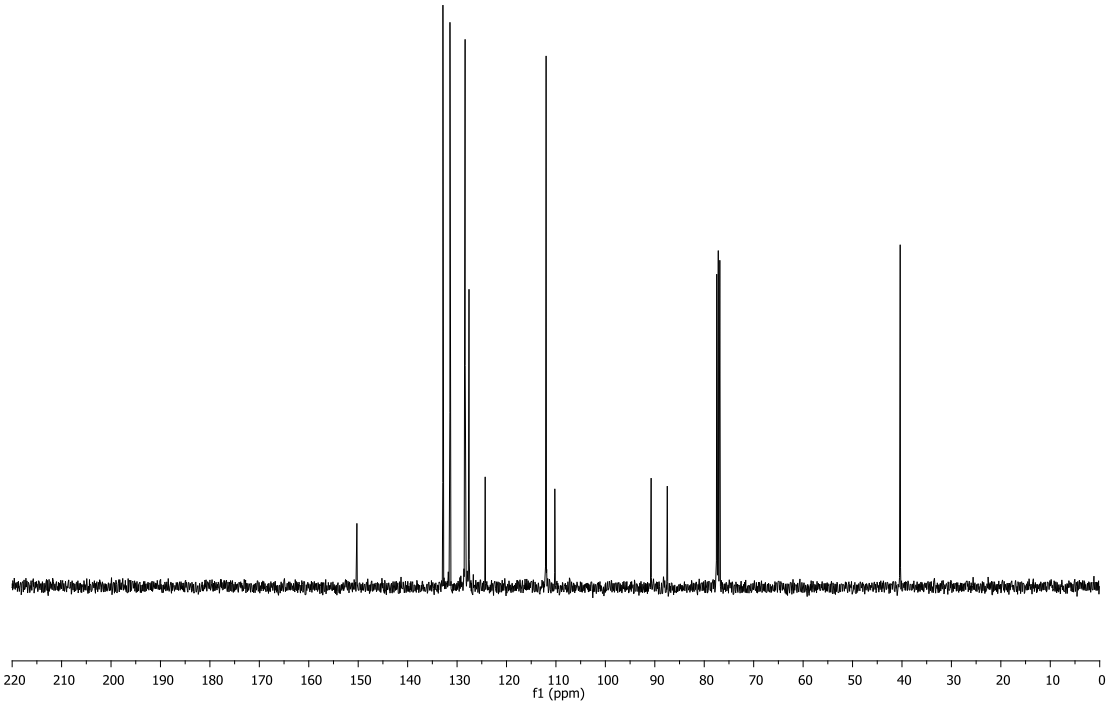
Compound 2aV



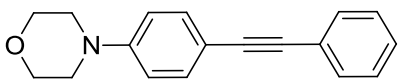


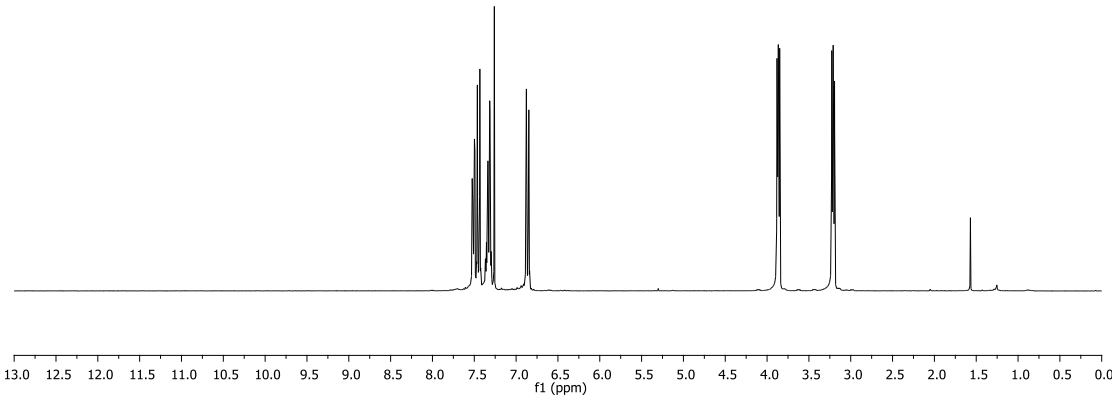
Compound 4a

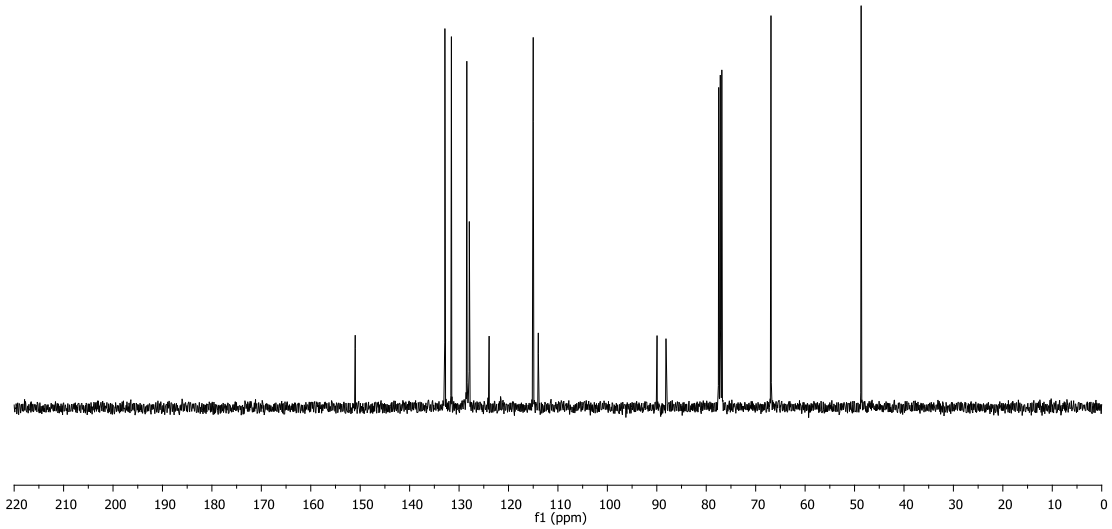

Me2N
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

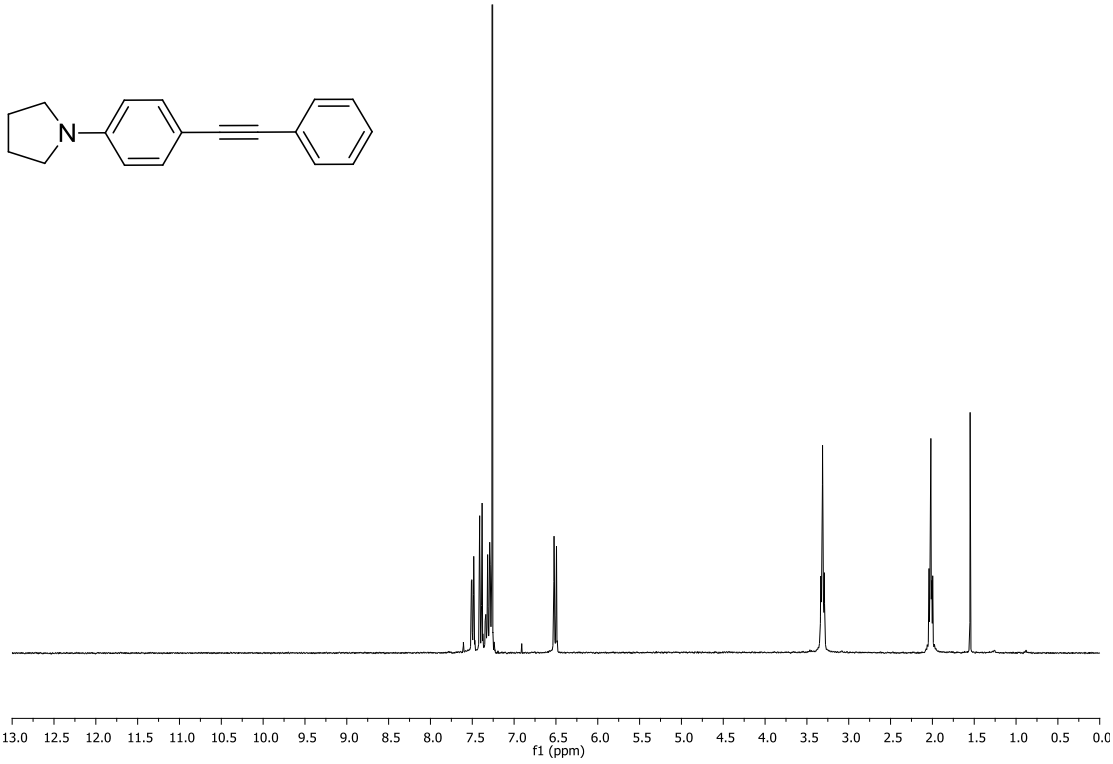
Compound 4b

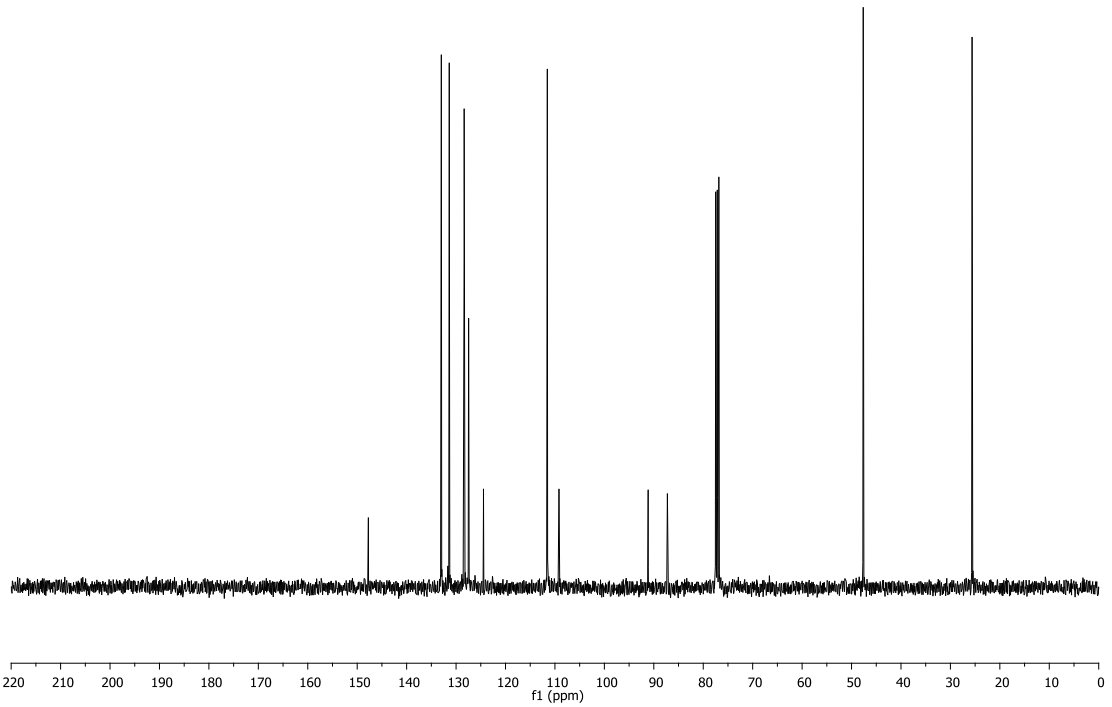

O
N


13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

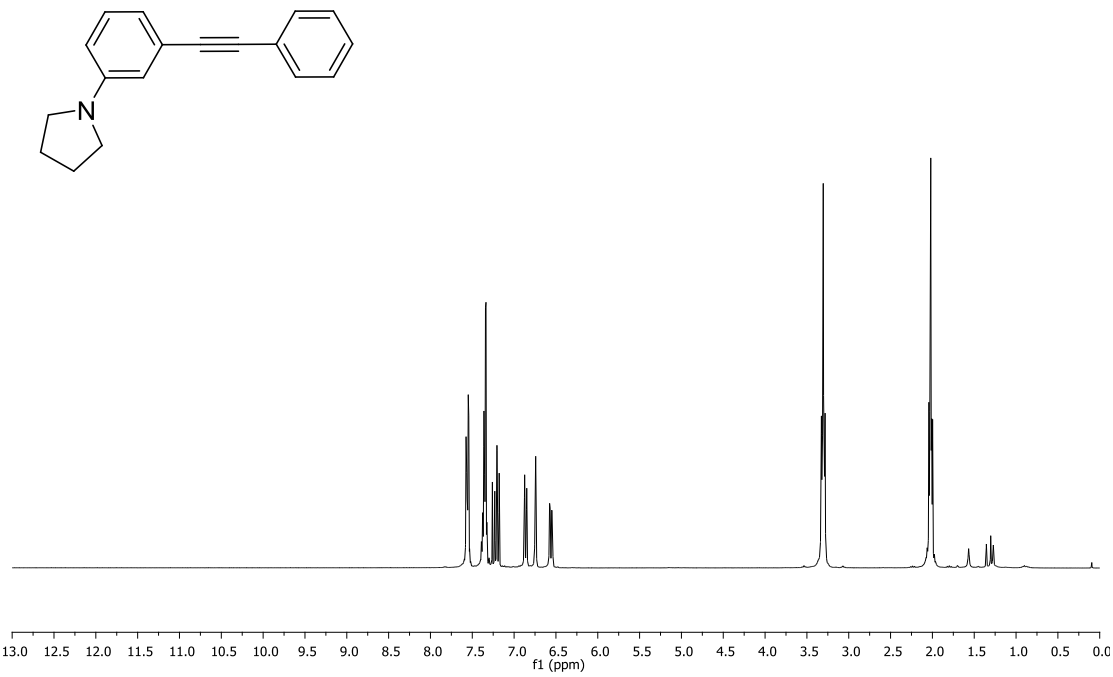

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

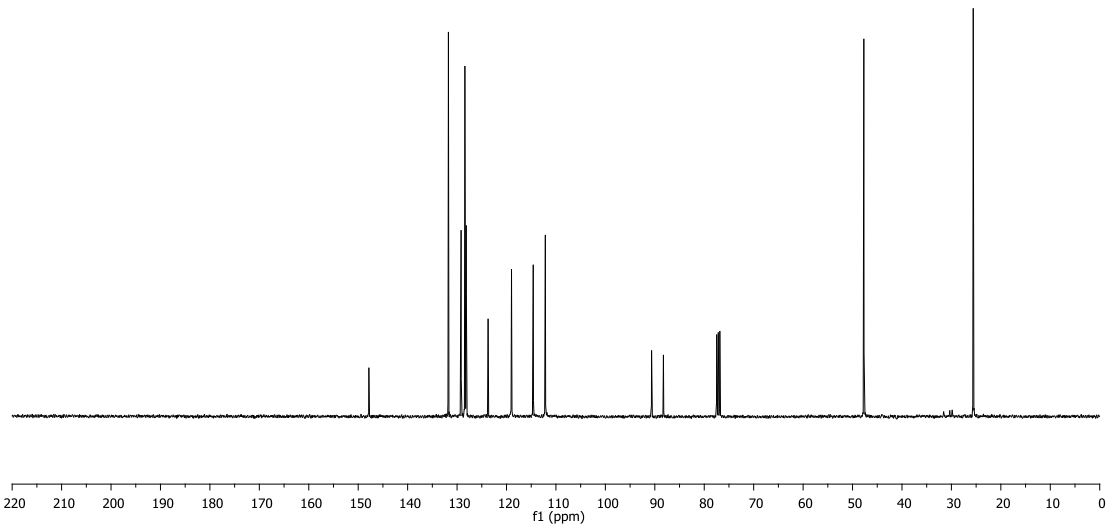
Compound 4c


N
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

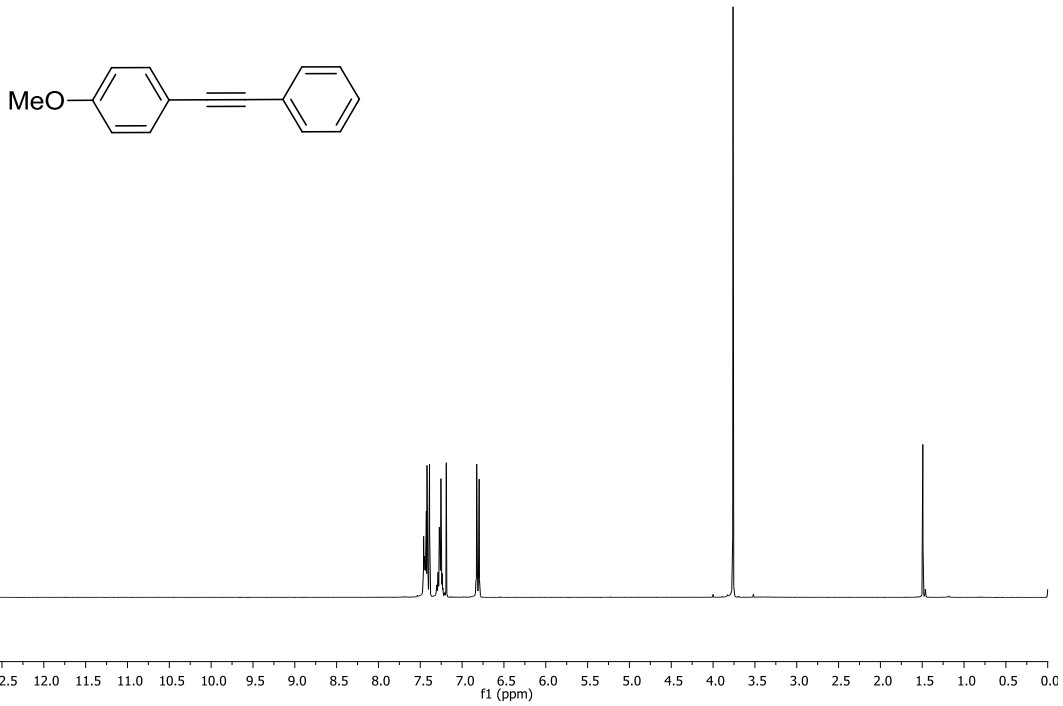

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

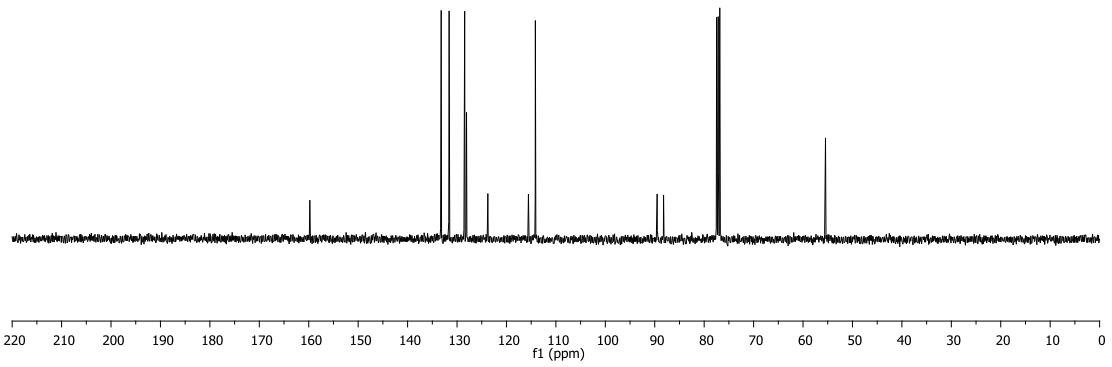
Compound 4d


N
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

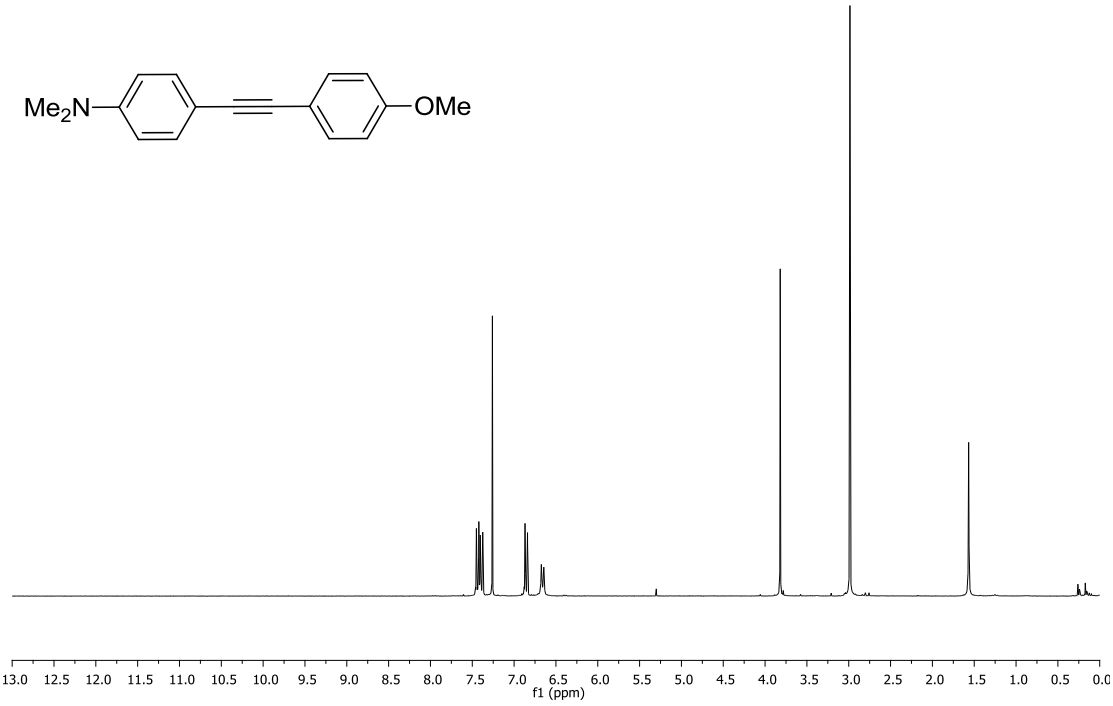

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

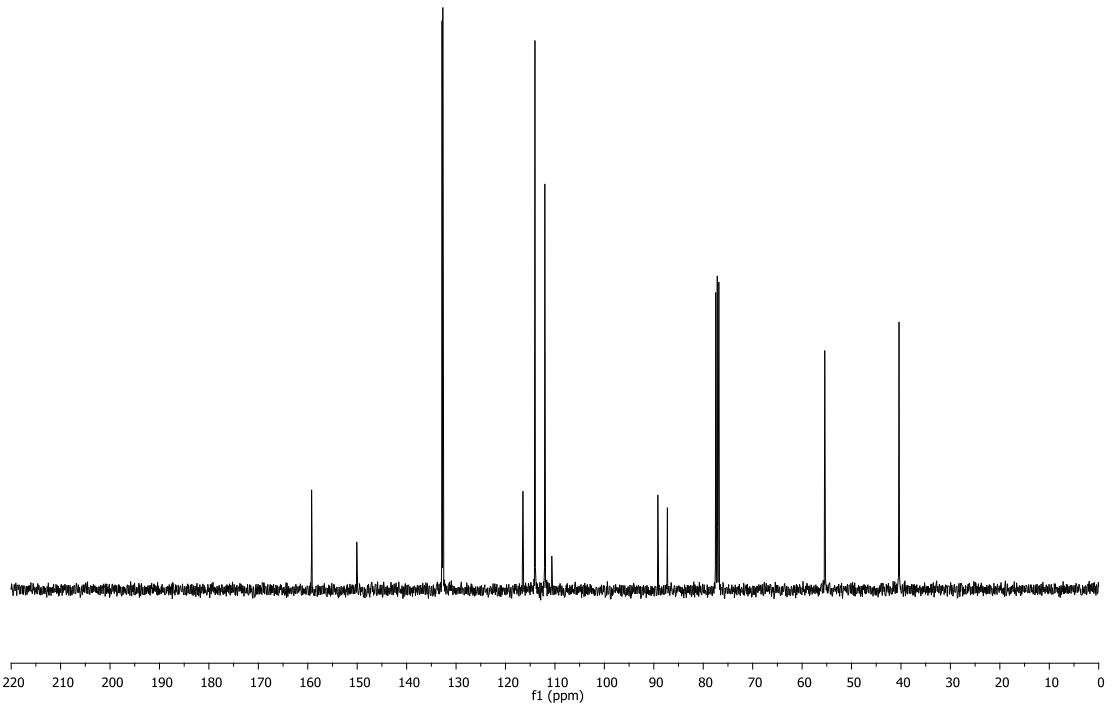
Compound 4e


MeO
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

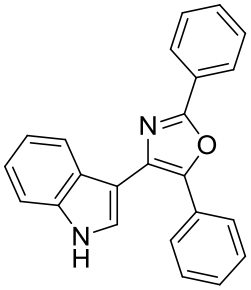

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

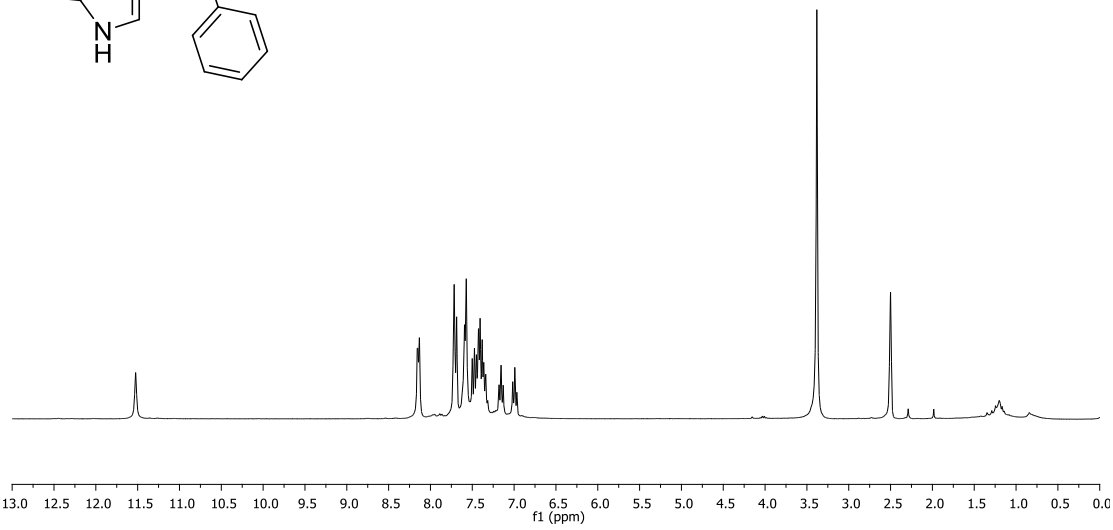
Compound 6

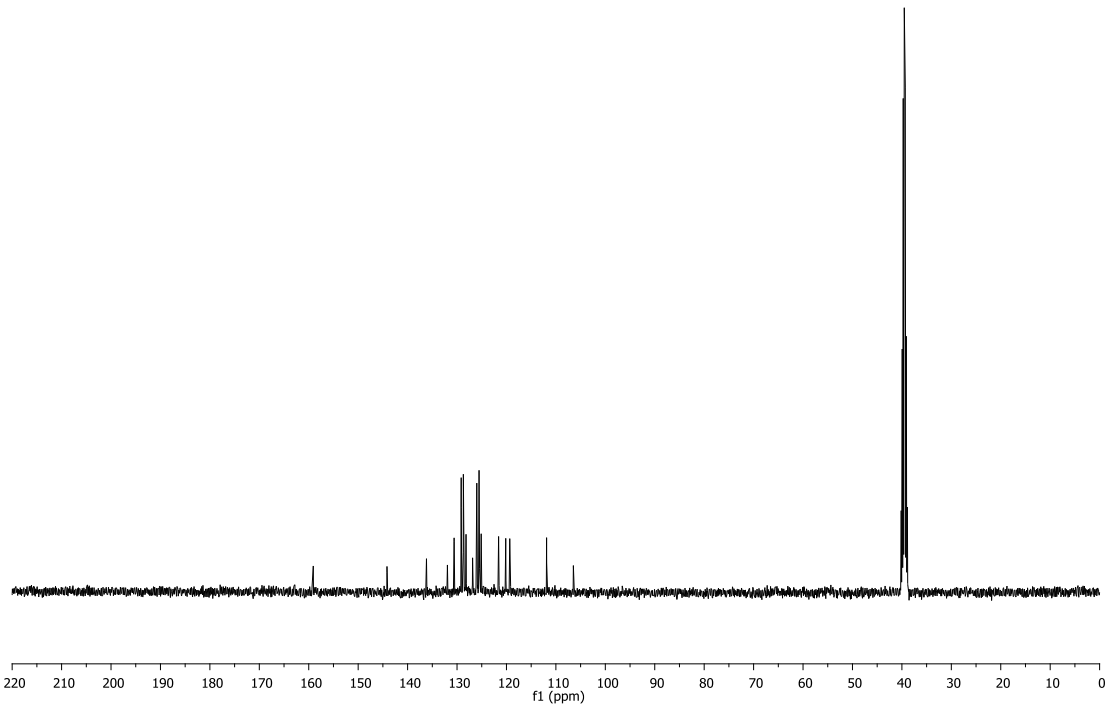

Me2N
OMe
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

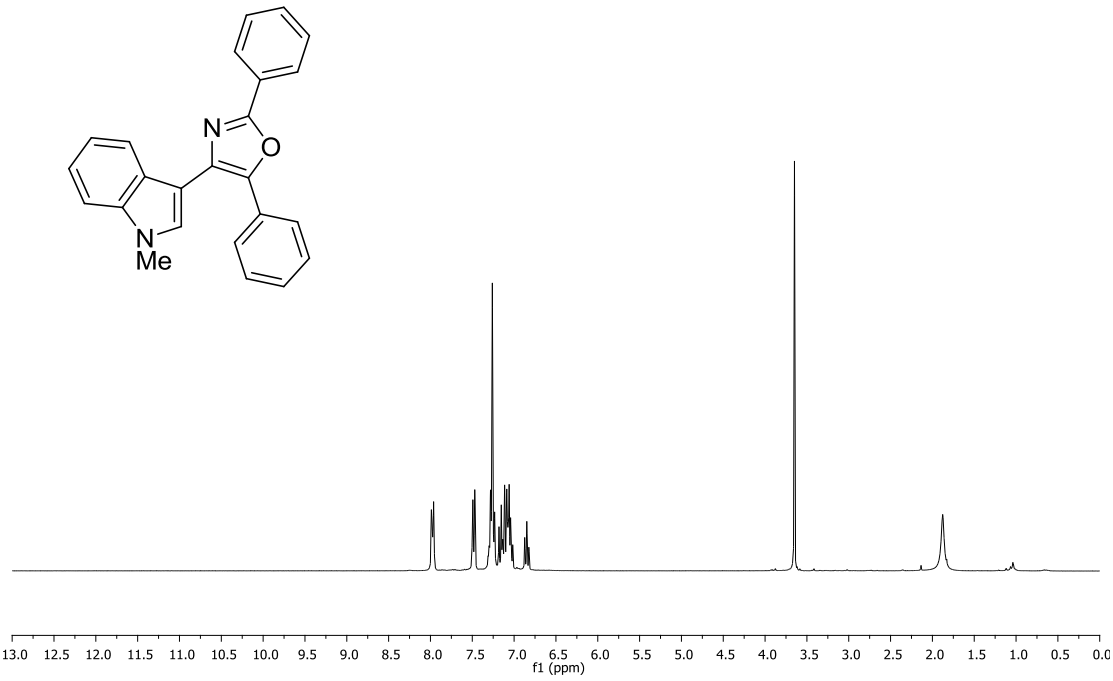
Compound 3aa

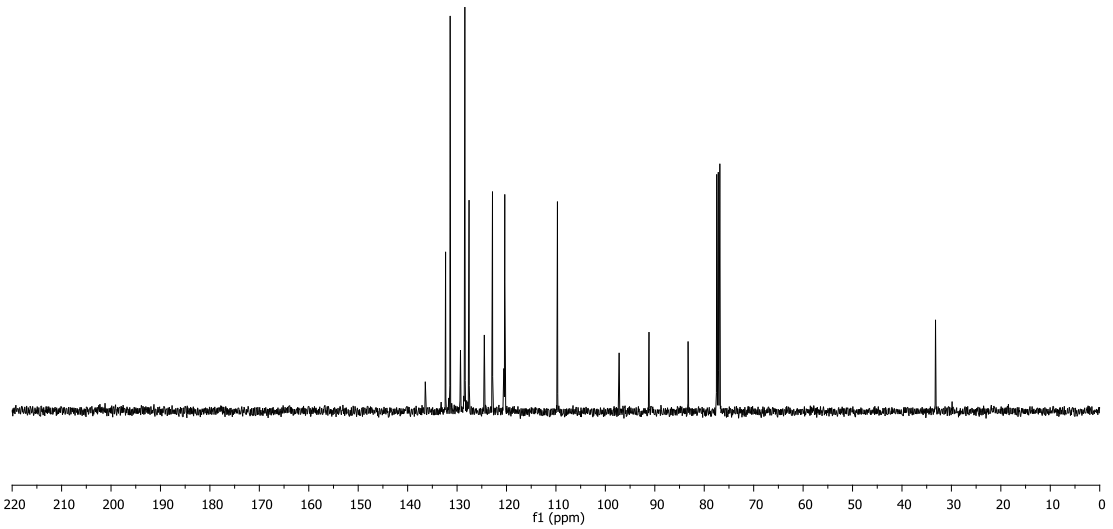




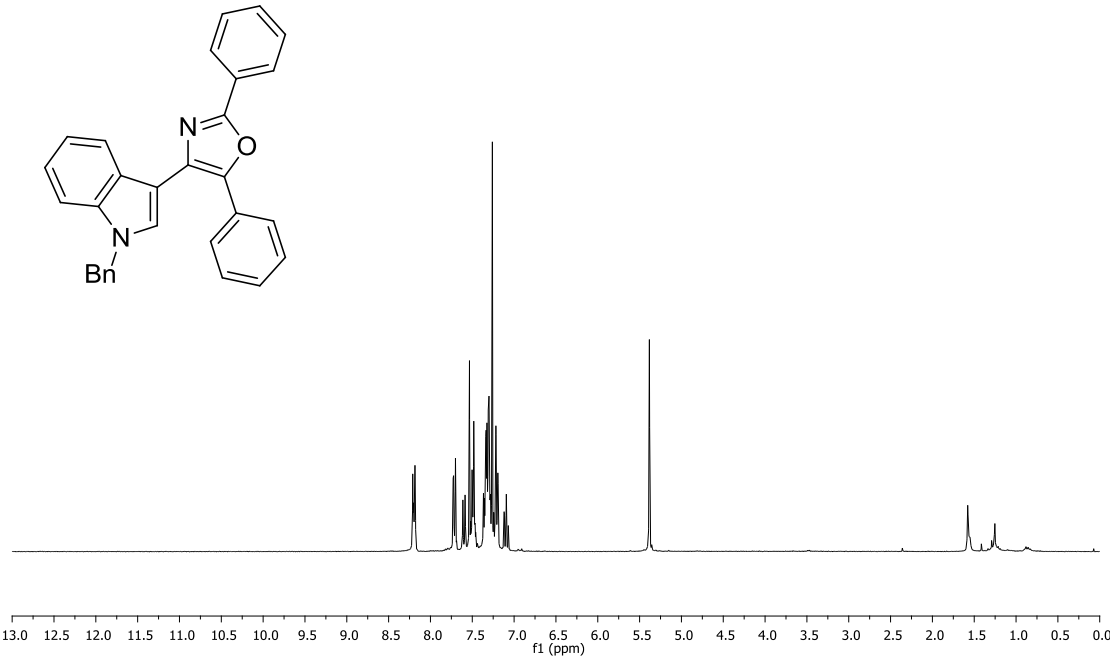


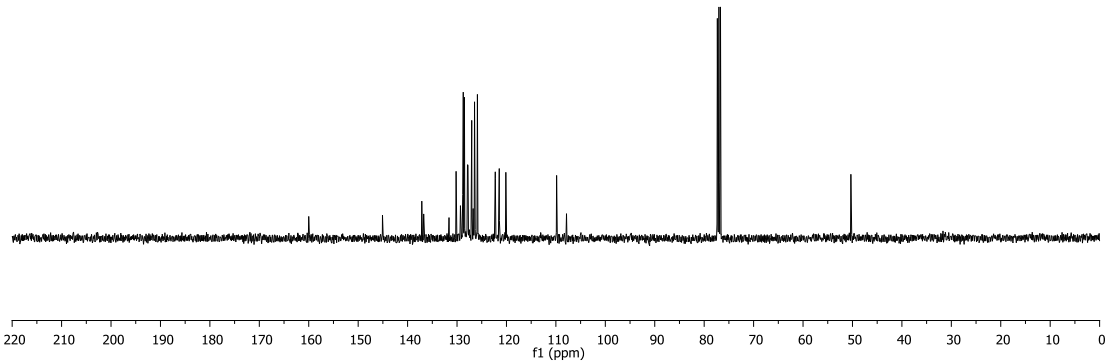
Compound 3ba



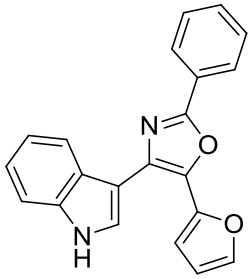


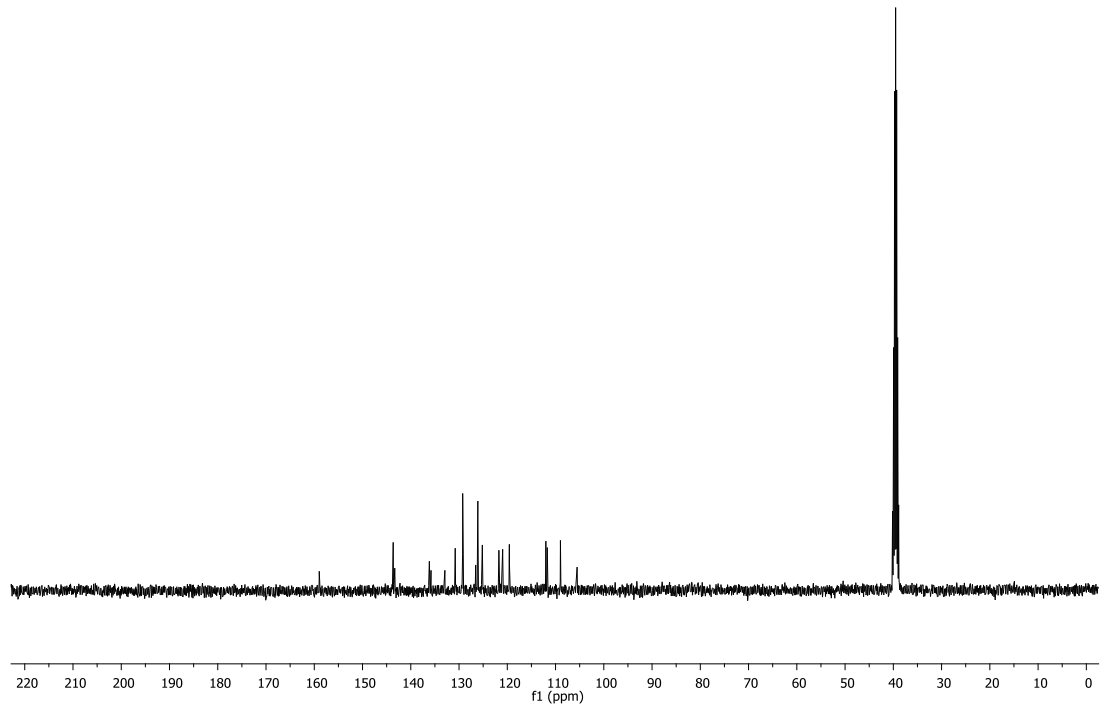
Compound 3ca



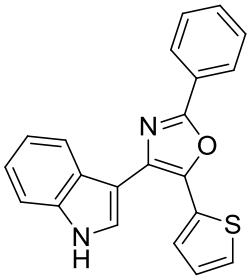


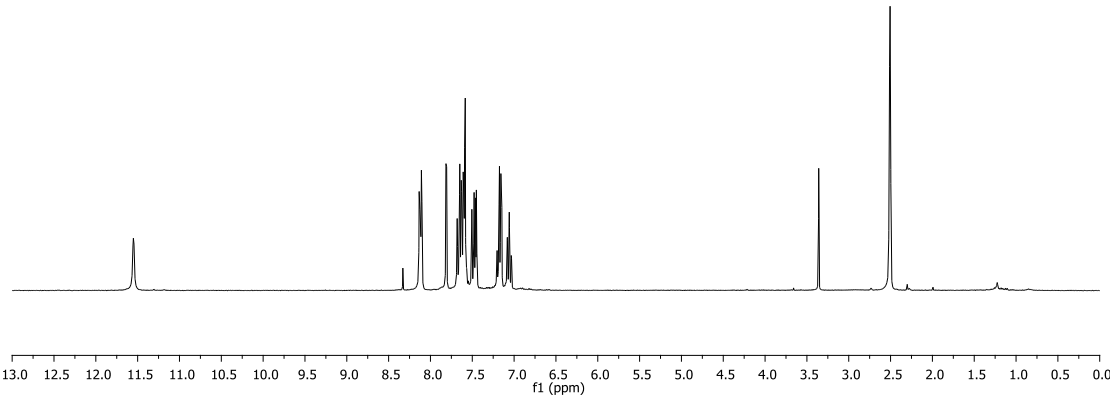
Compound 3da

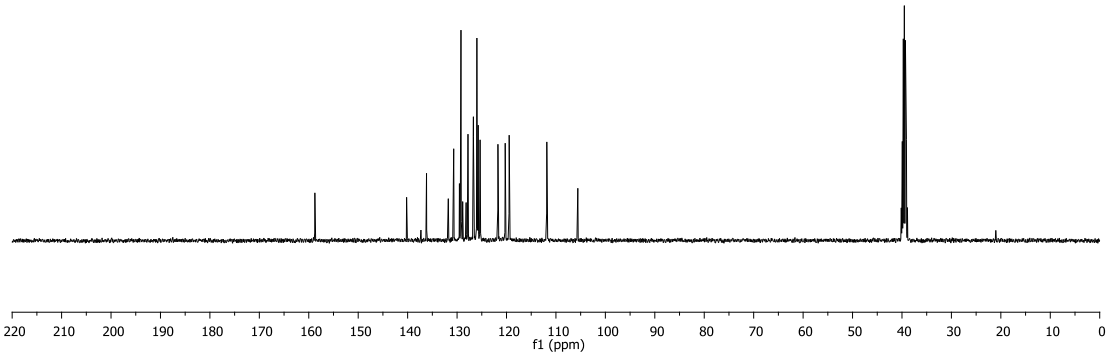




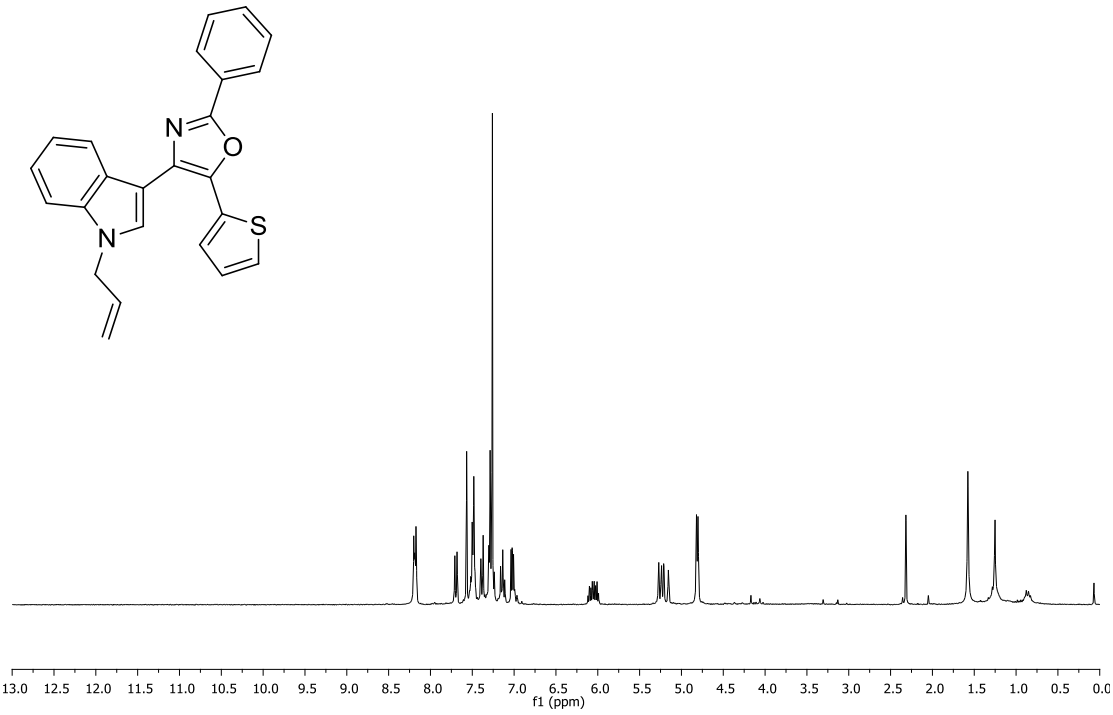
Compound 3ea

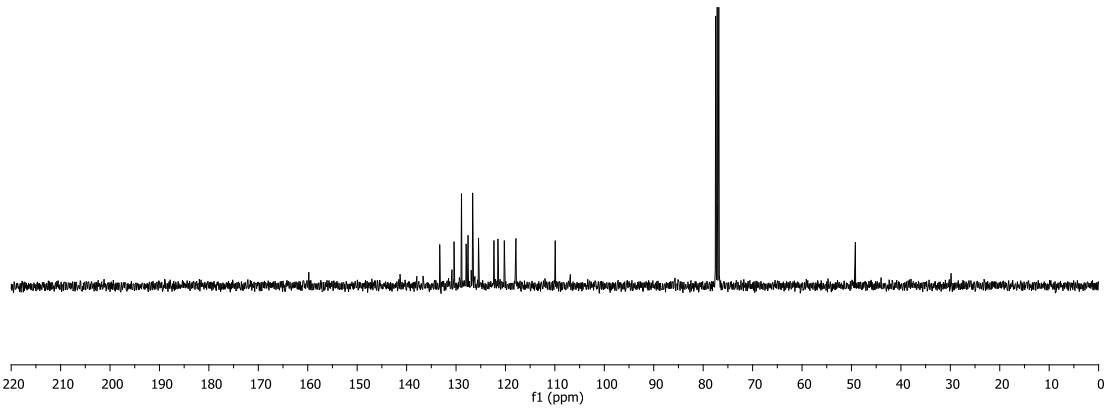




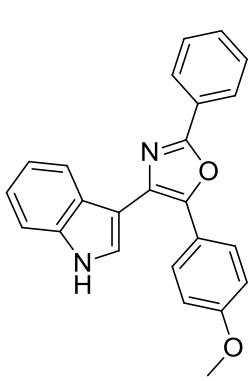


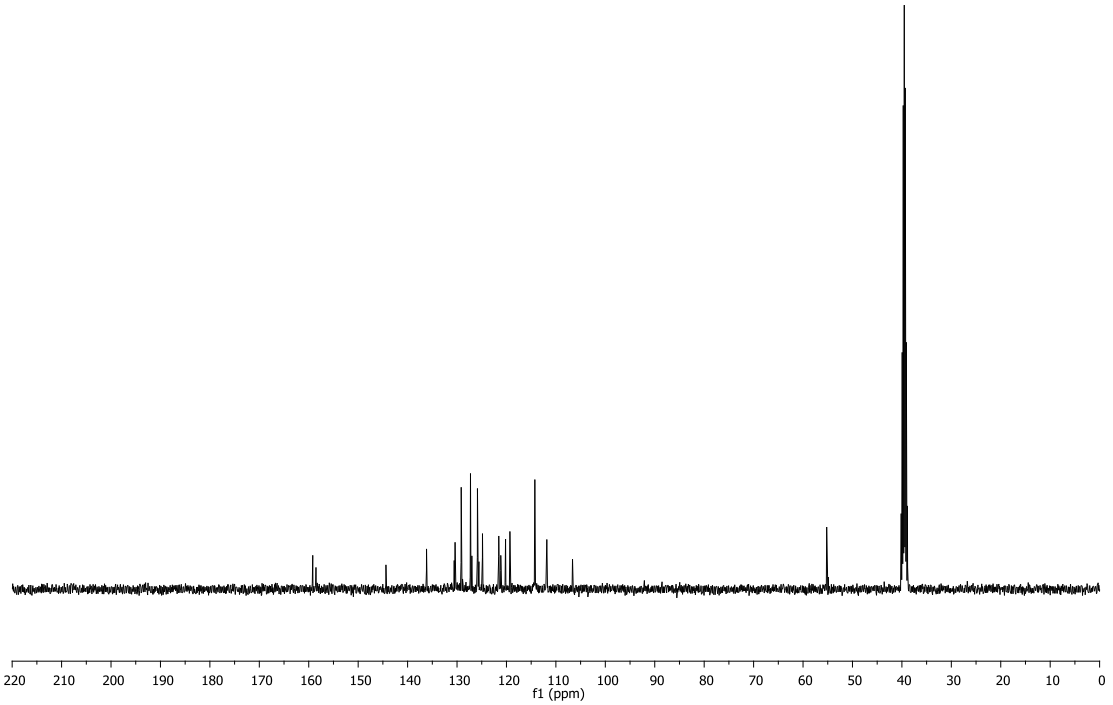
Compound 3fa



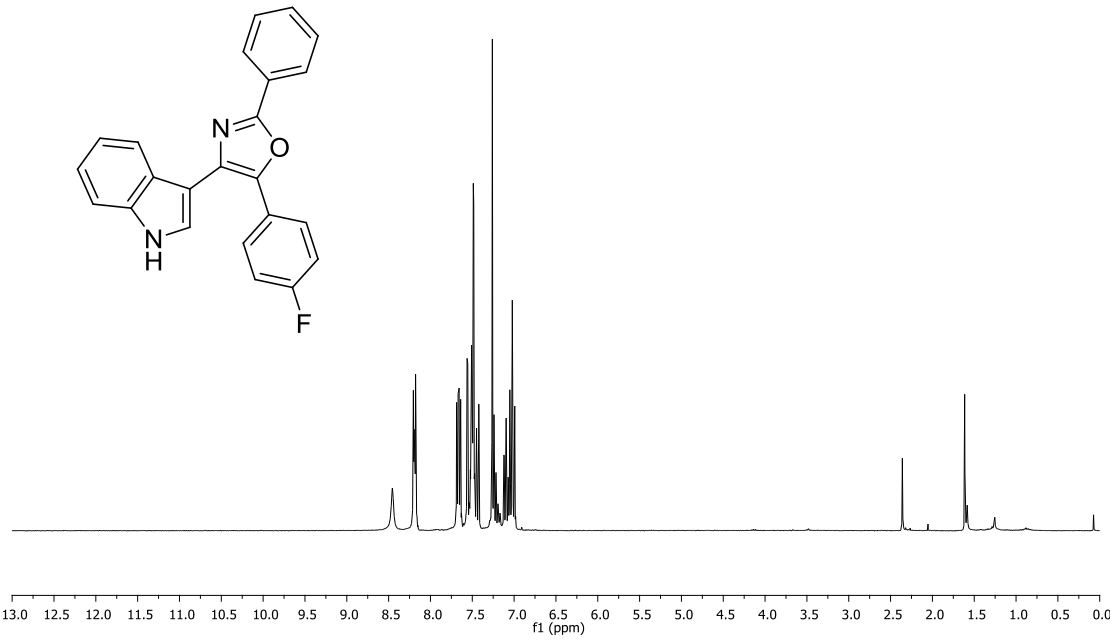


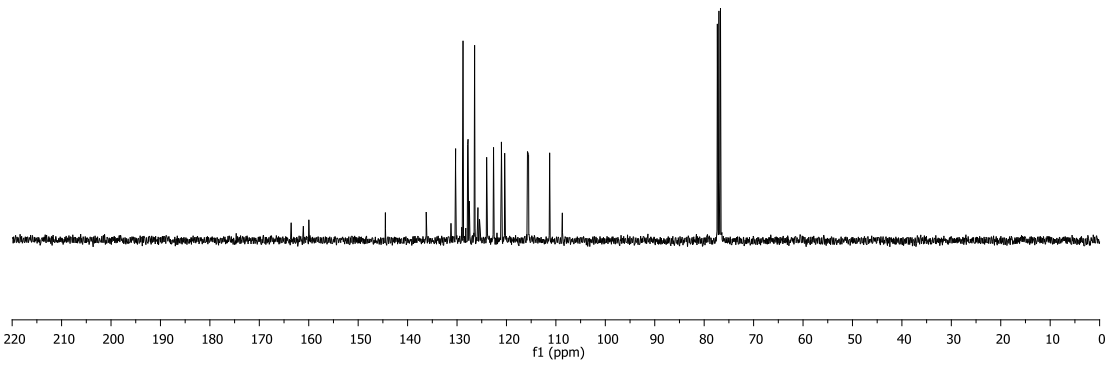
Compound 3ga



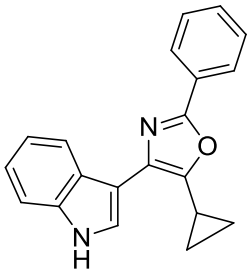


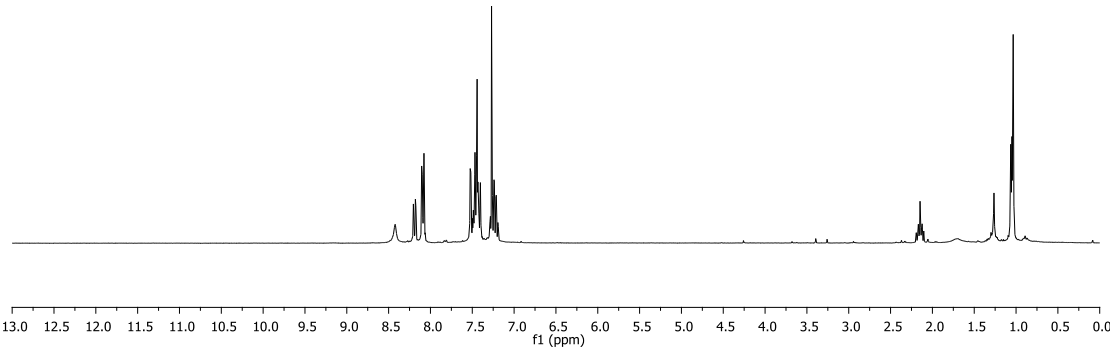
Compound 3ha

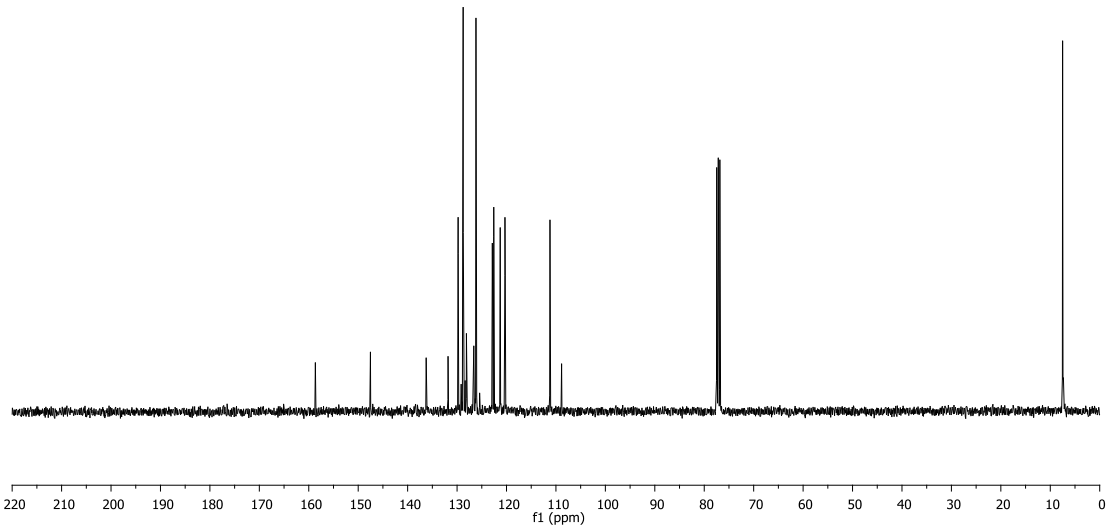




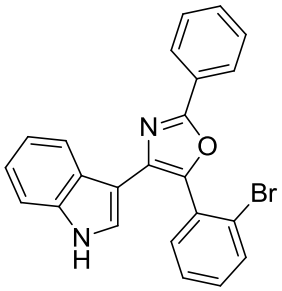
Compound 3ia

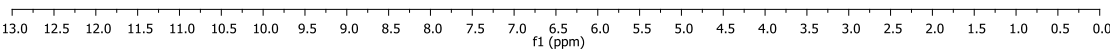


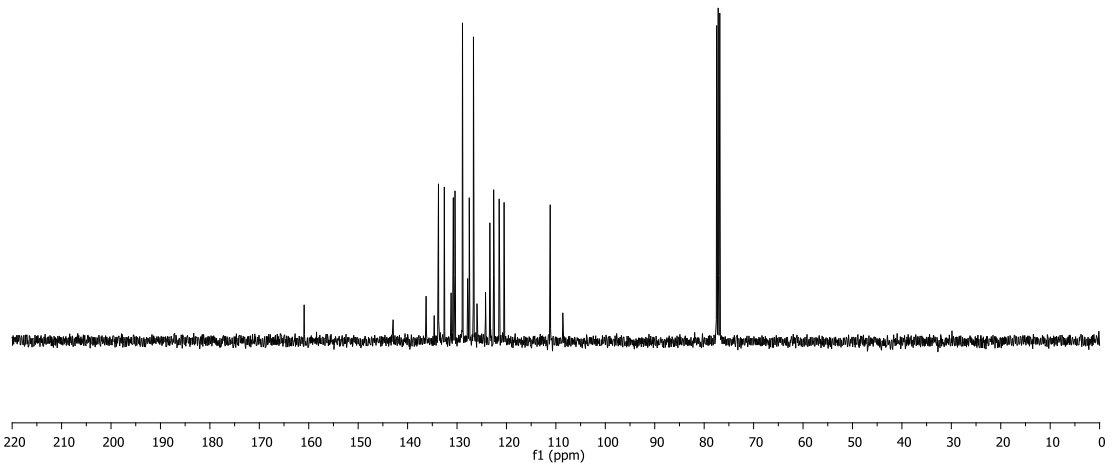




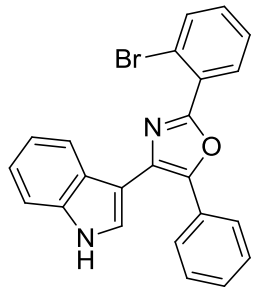
Compound 3ja

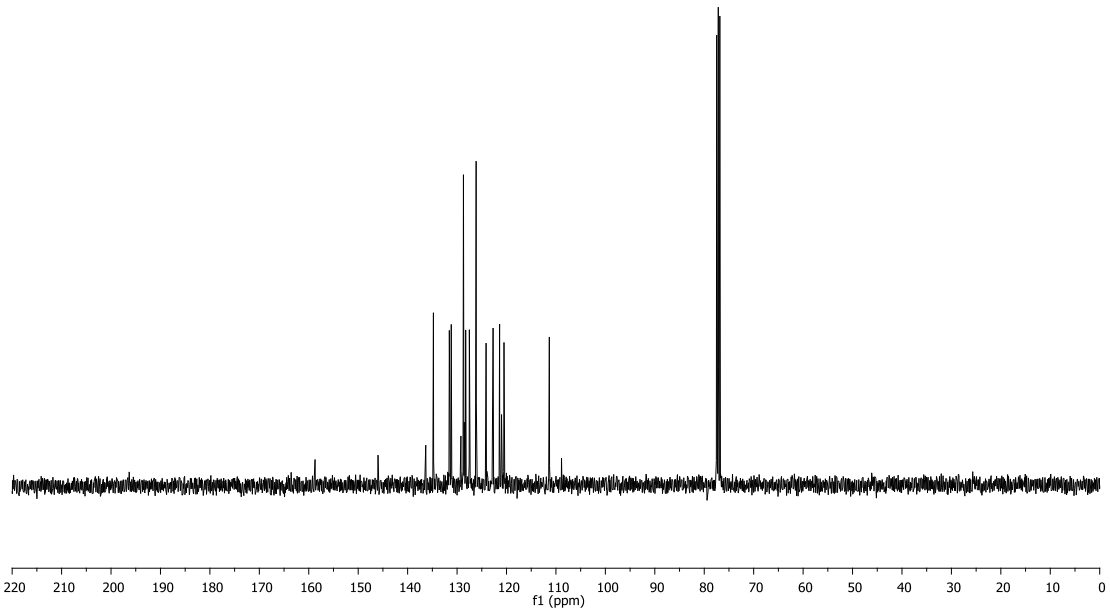




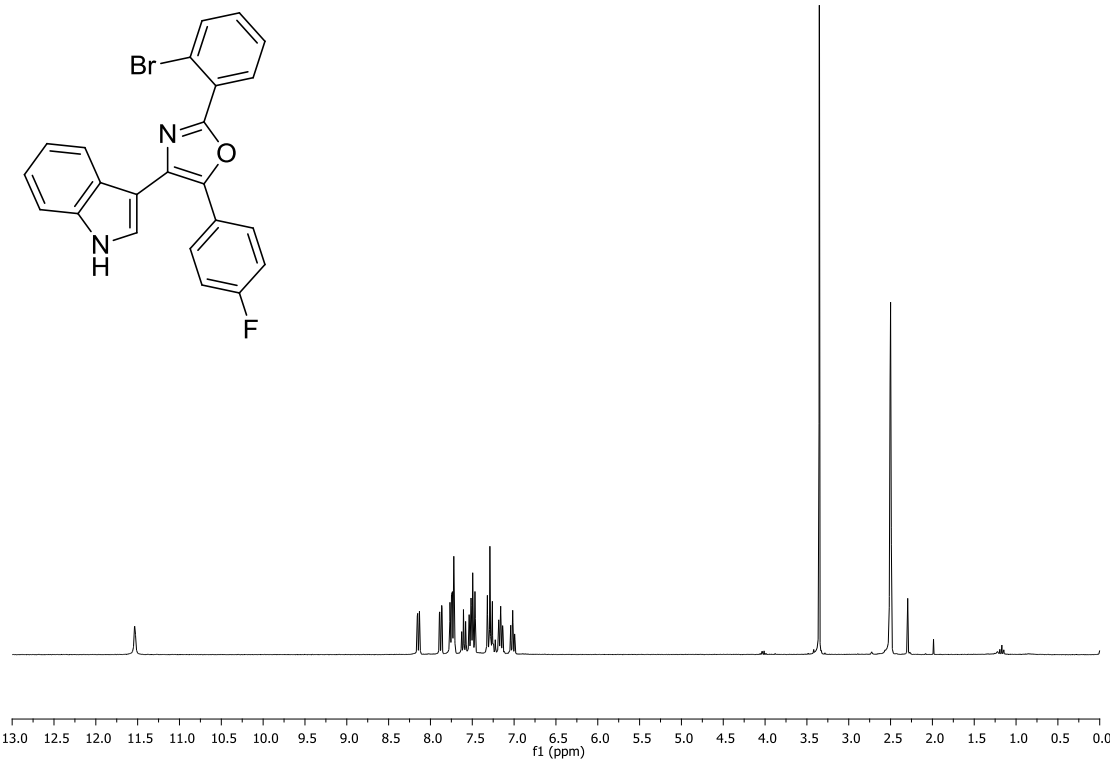


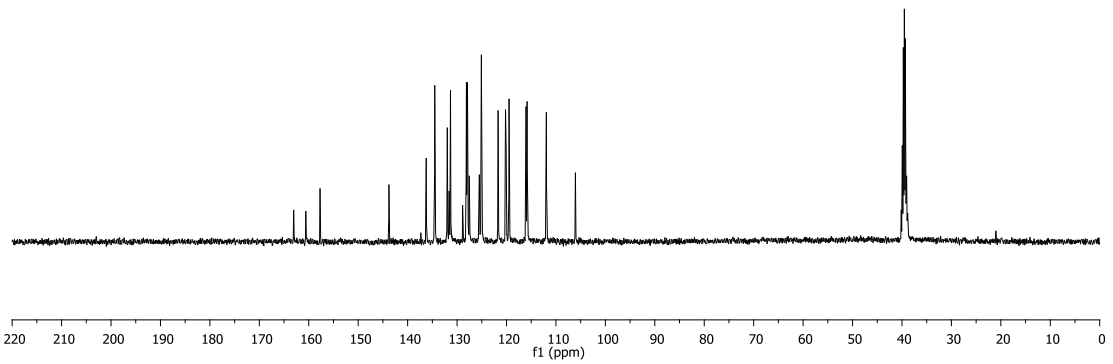
Compound 3ab



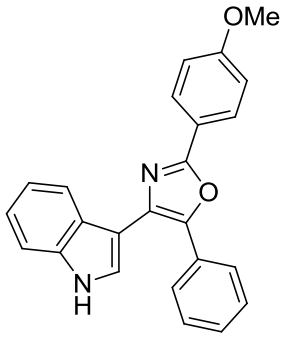


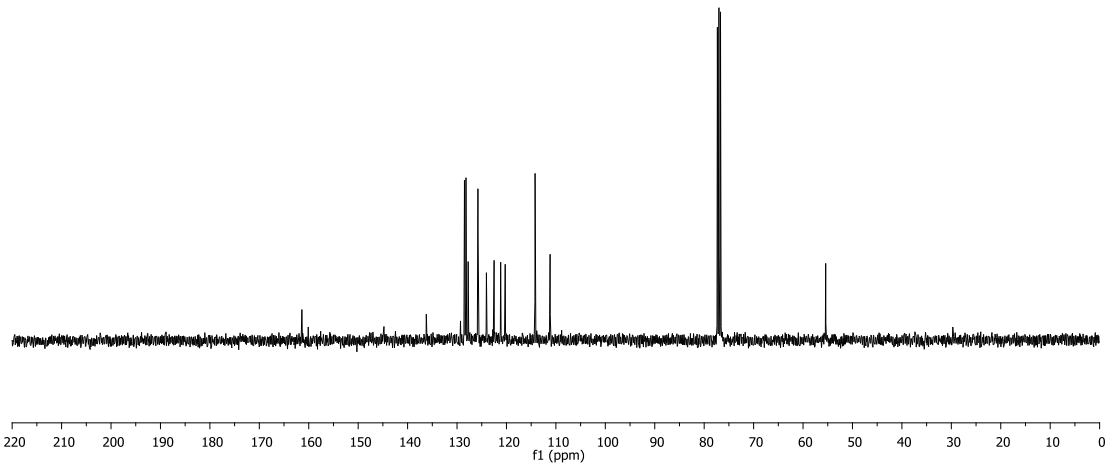
Compound 3hb





Compound 3ac





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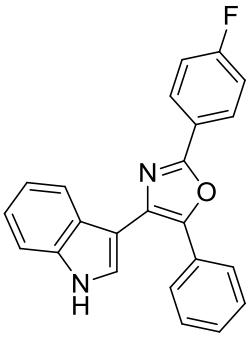
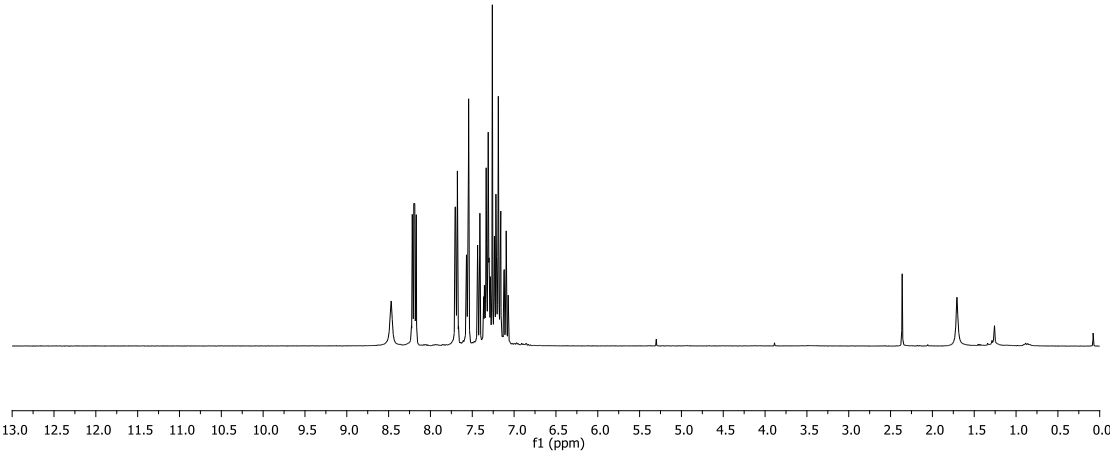
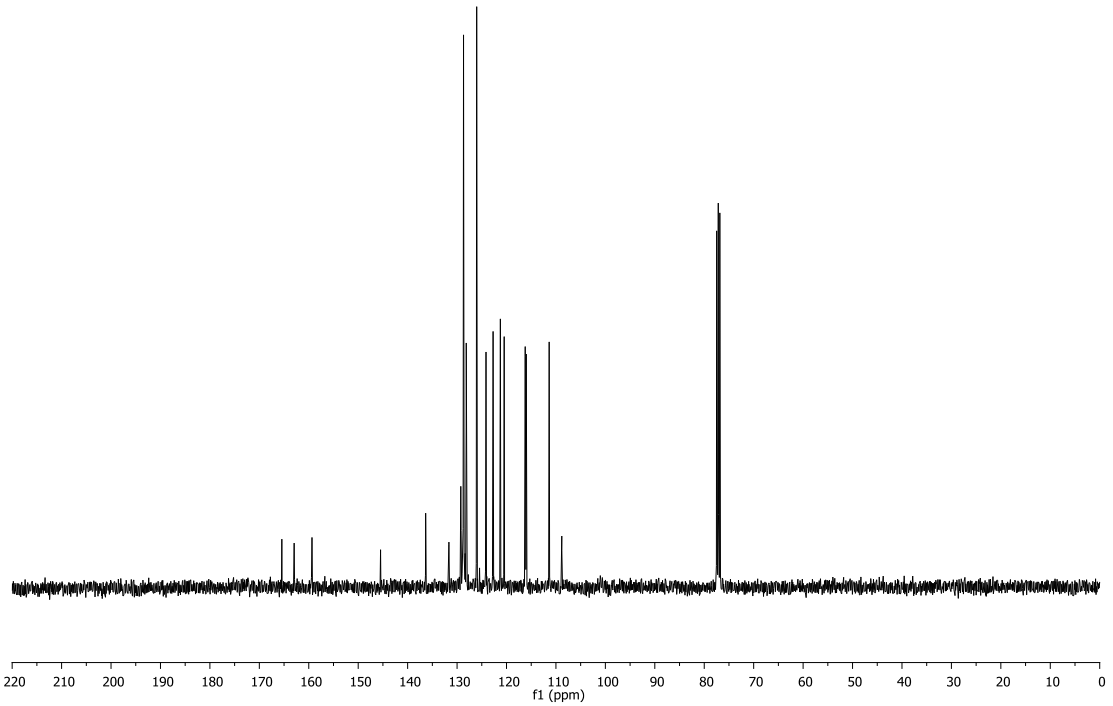
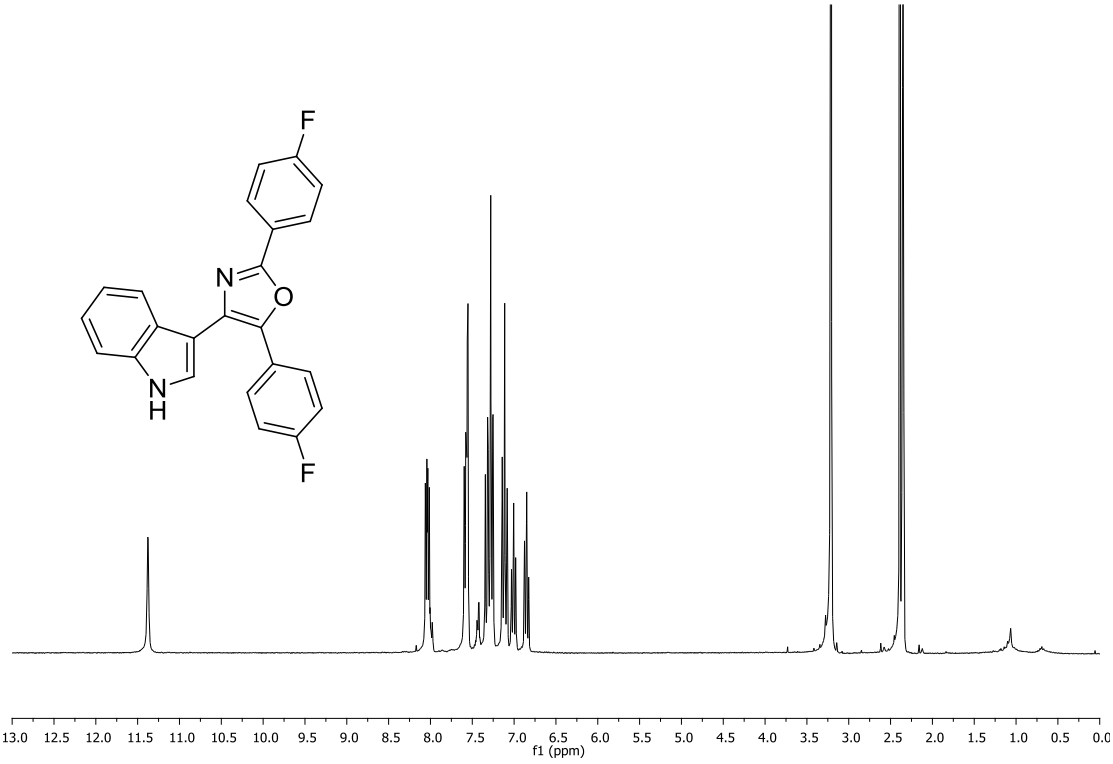
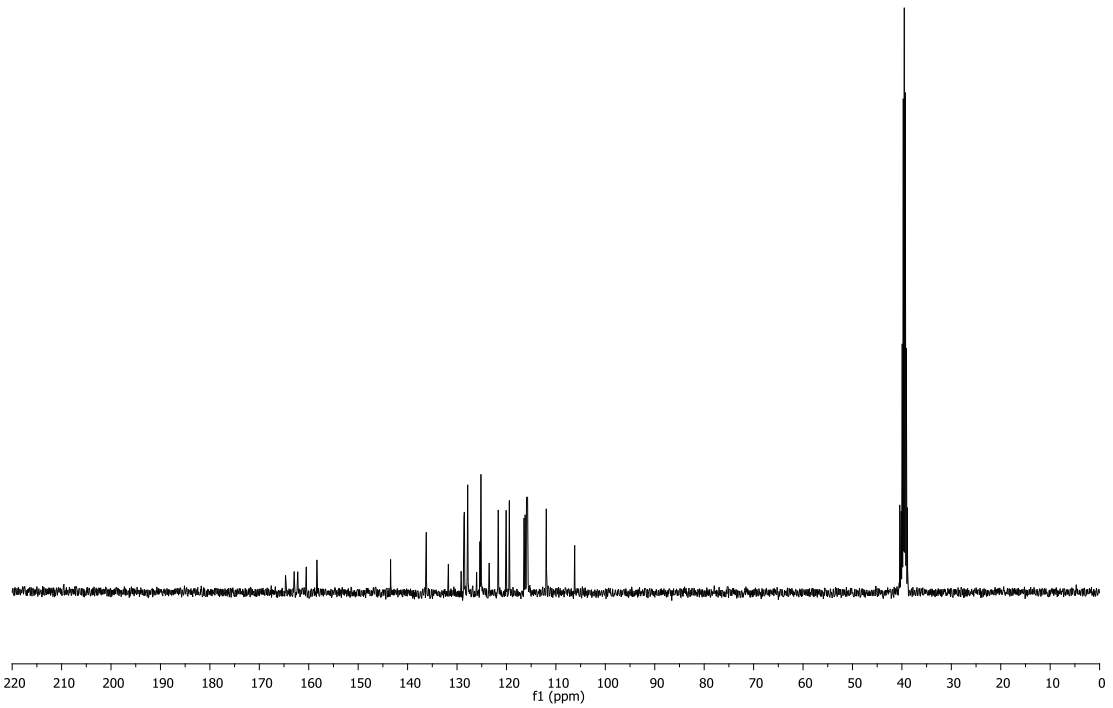






Compound 3hd





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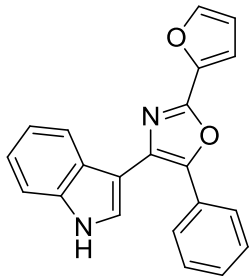
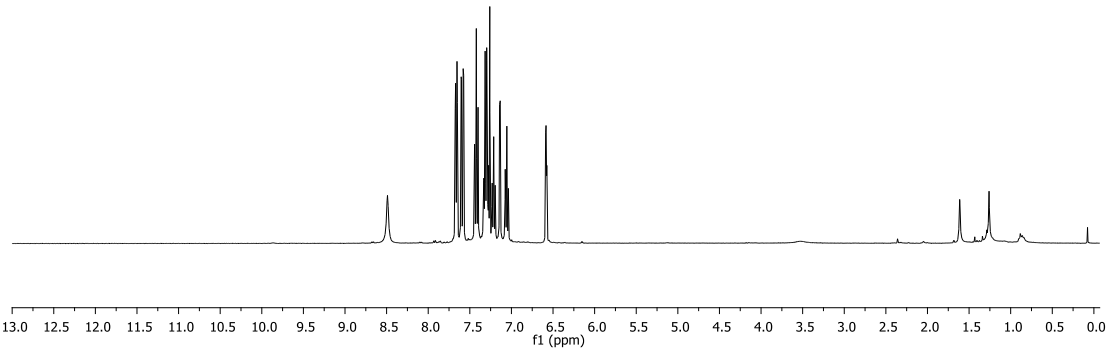
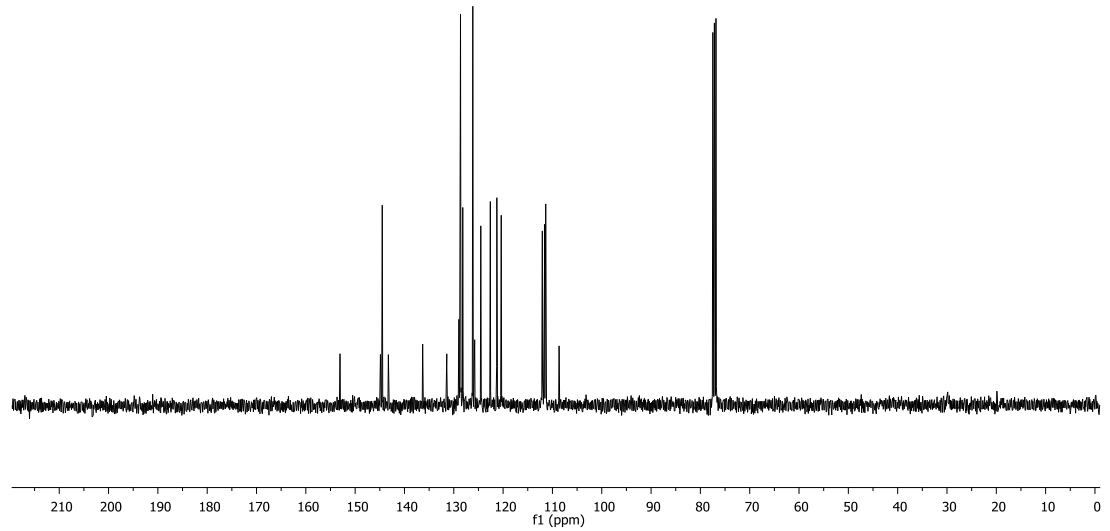
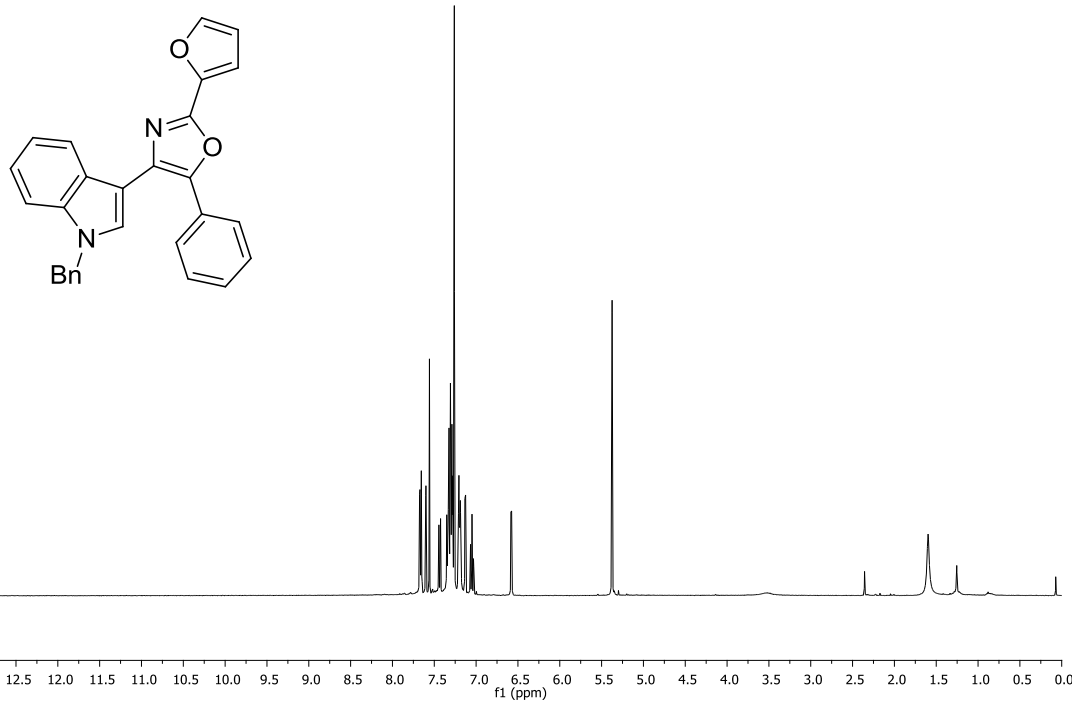
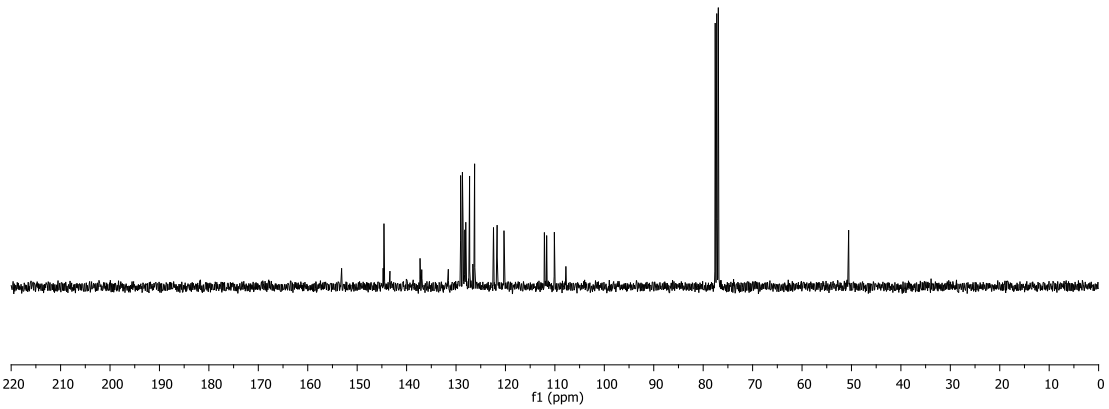






Compound 3ce





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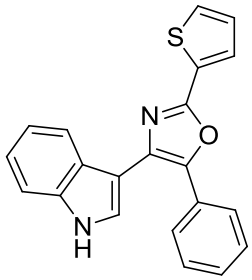

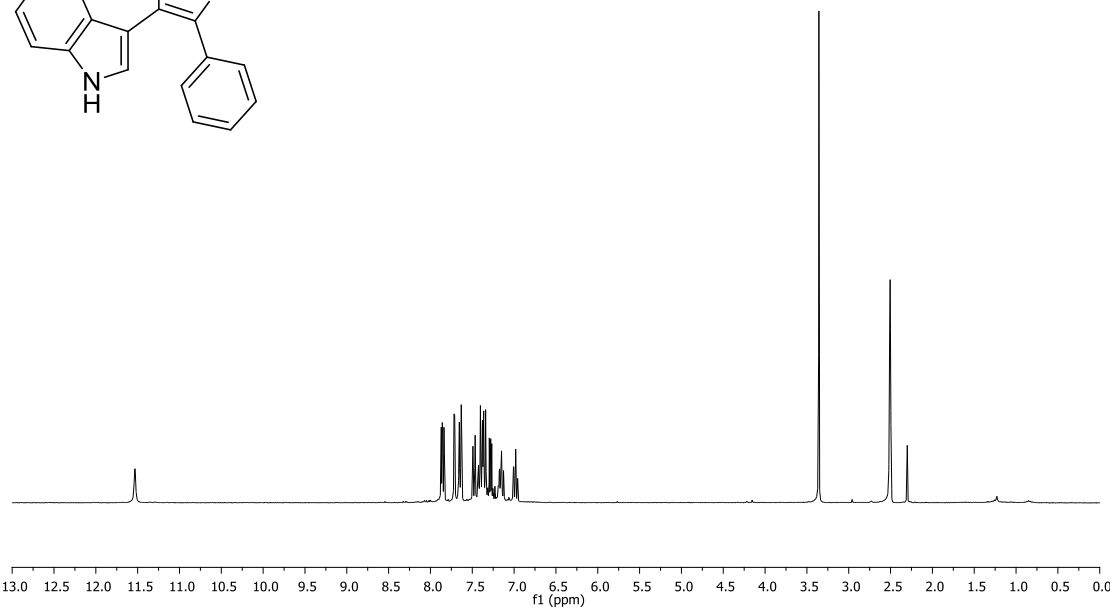

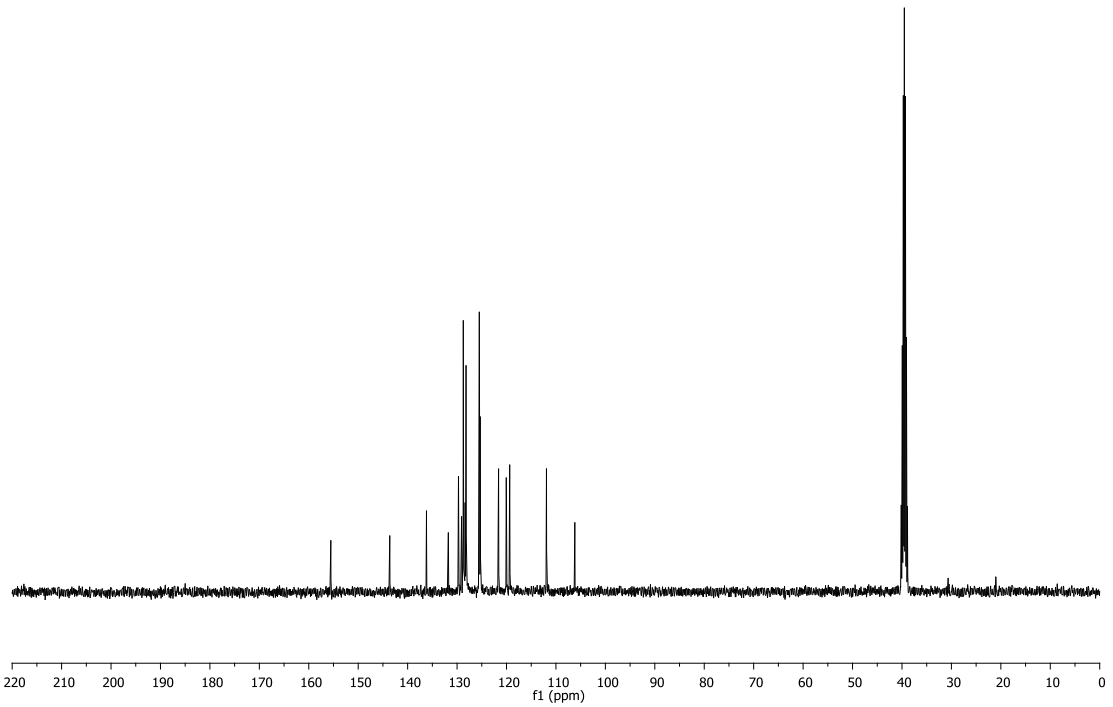

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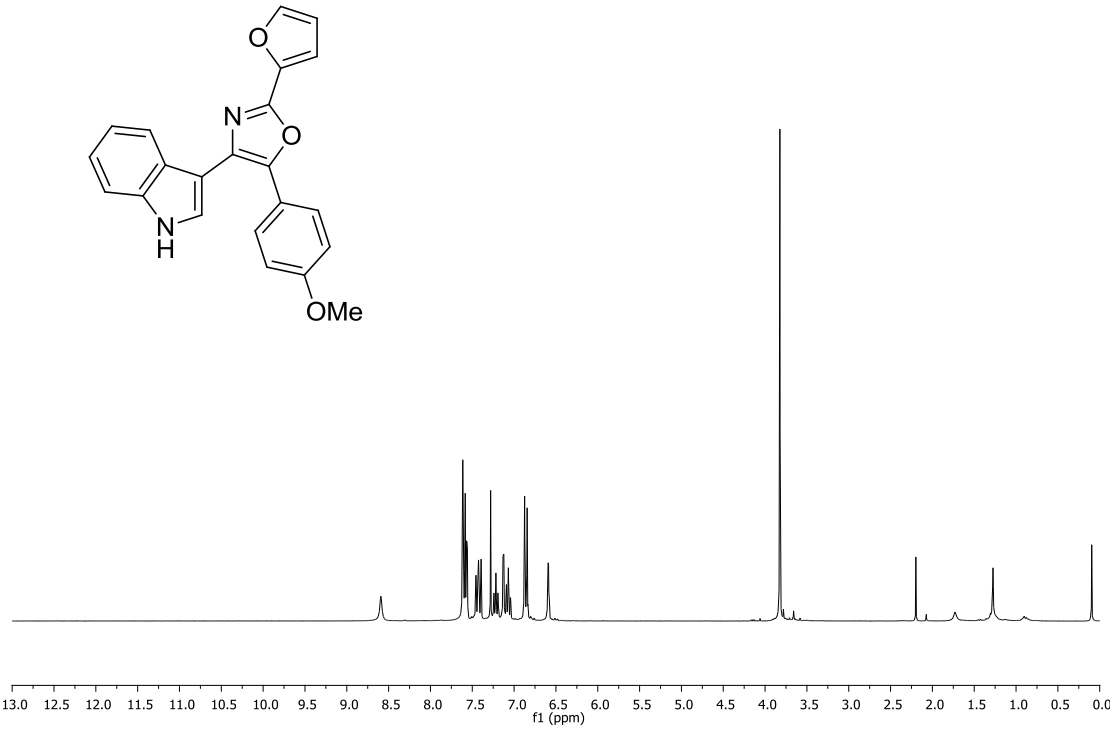

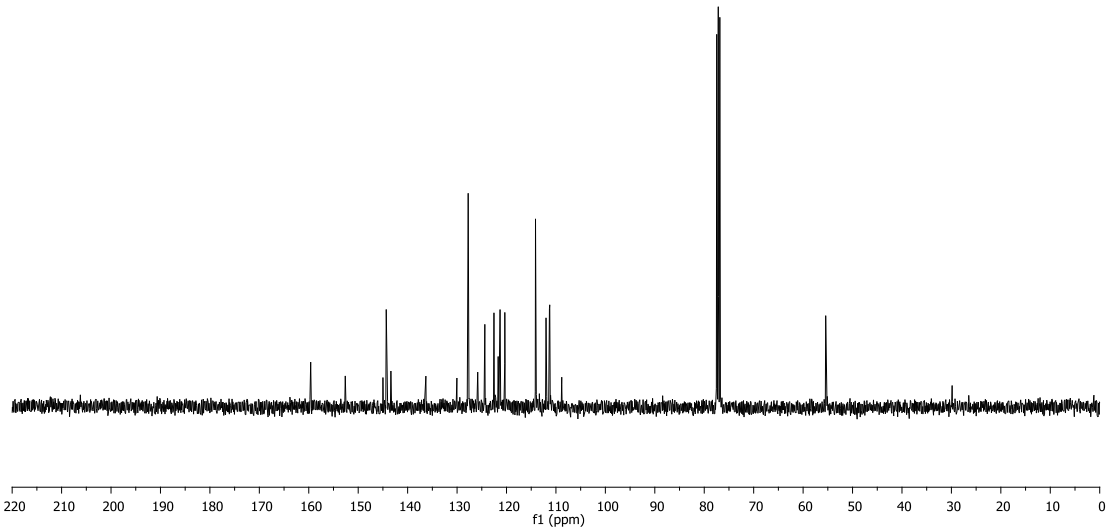

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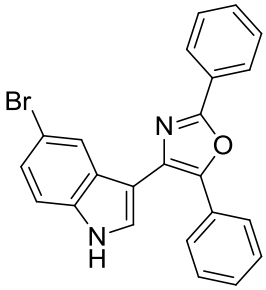

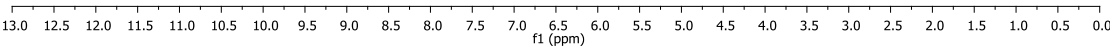

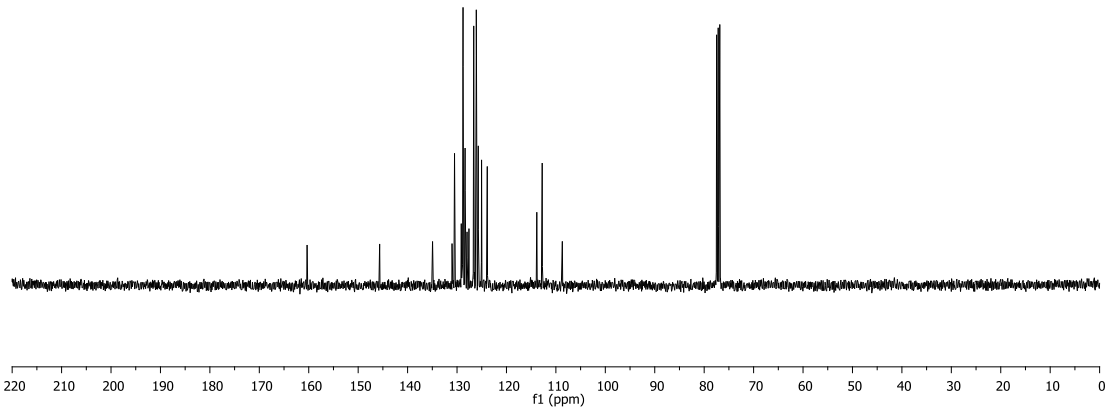

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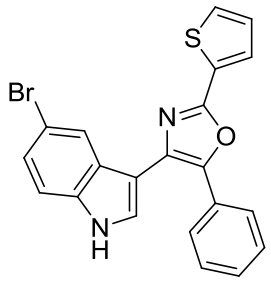
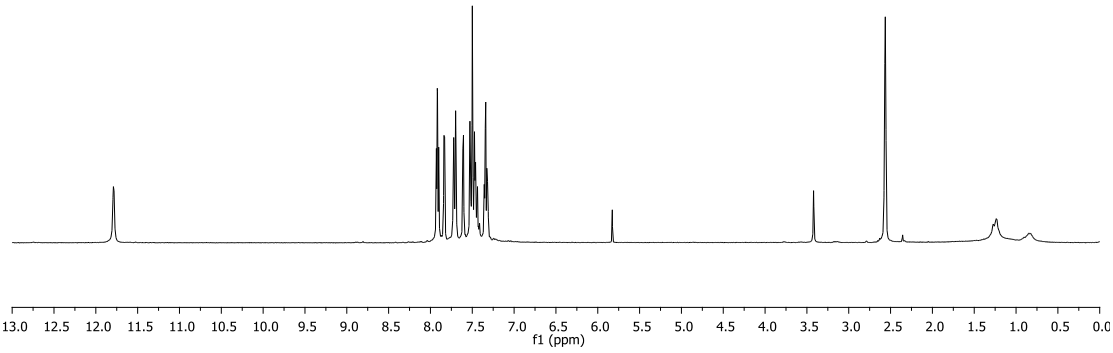
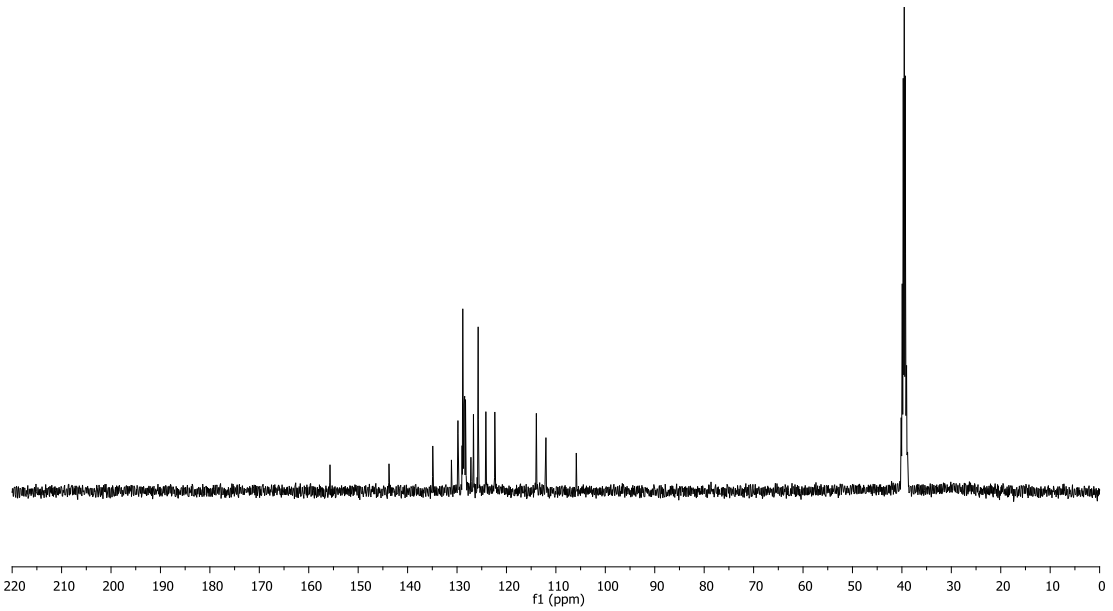
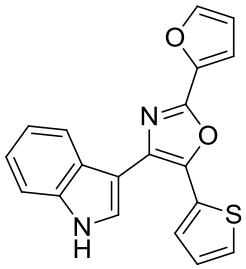
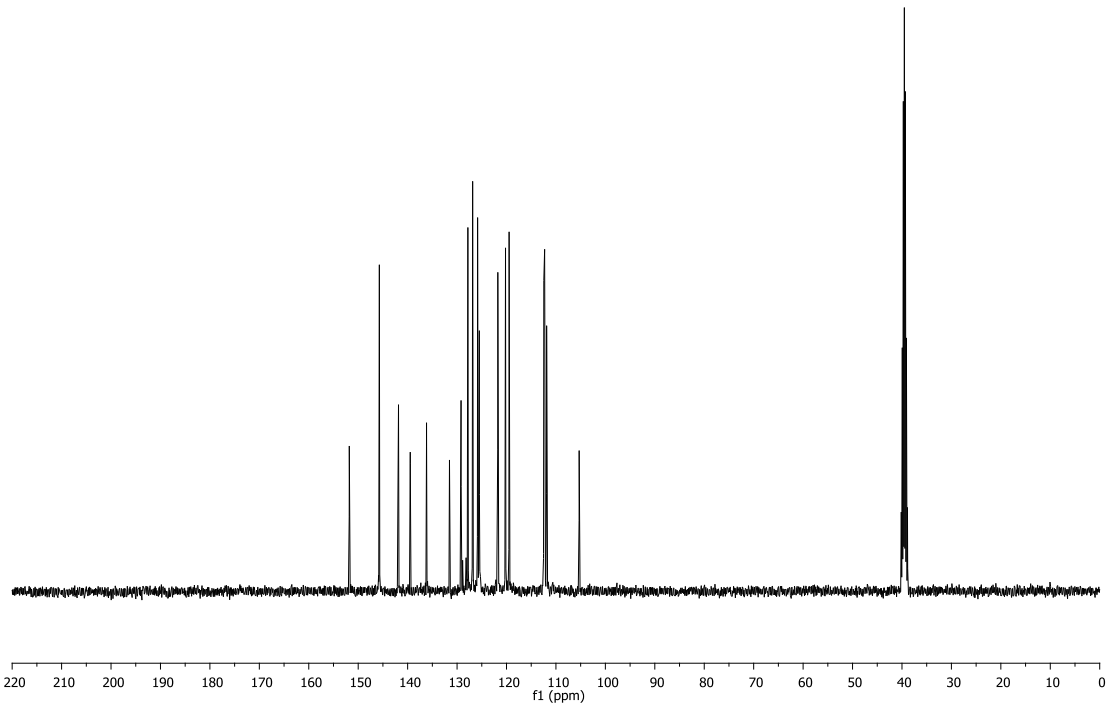






Compound 3fe





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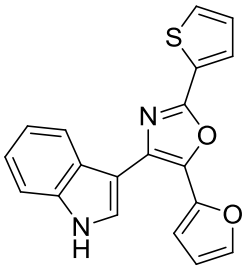
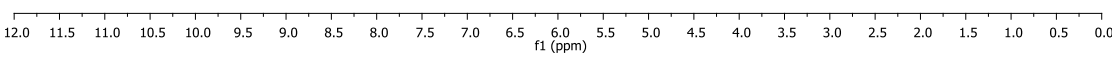
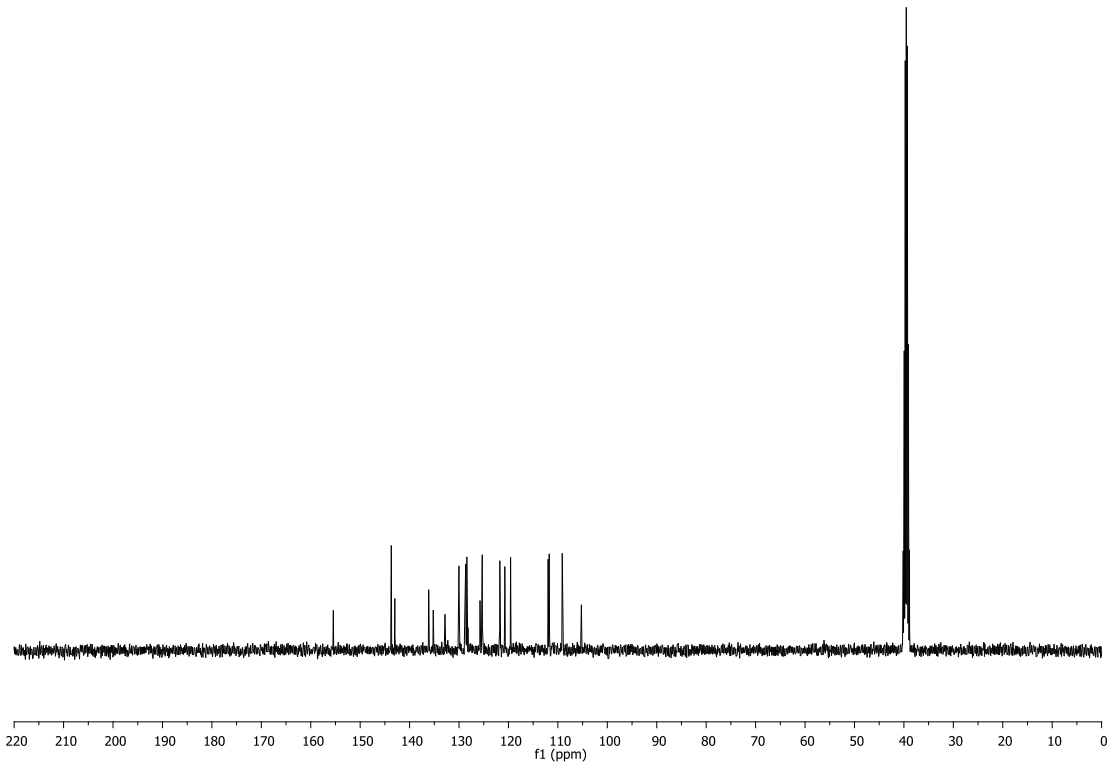
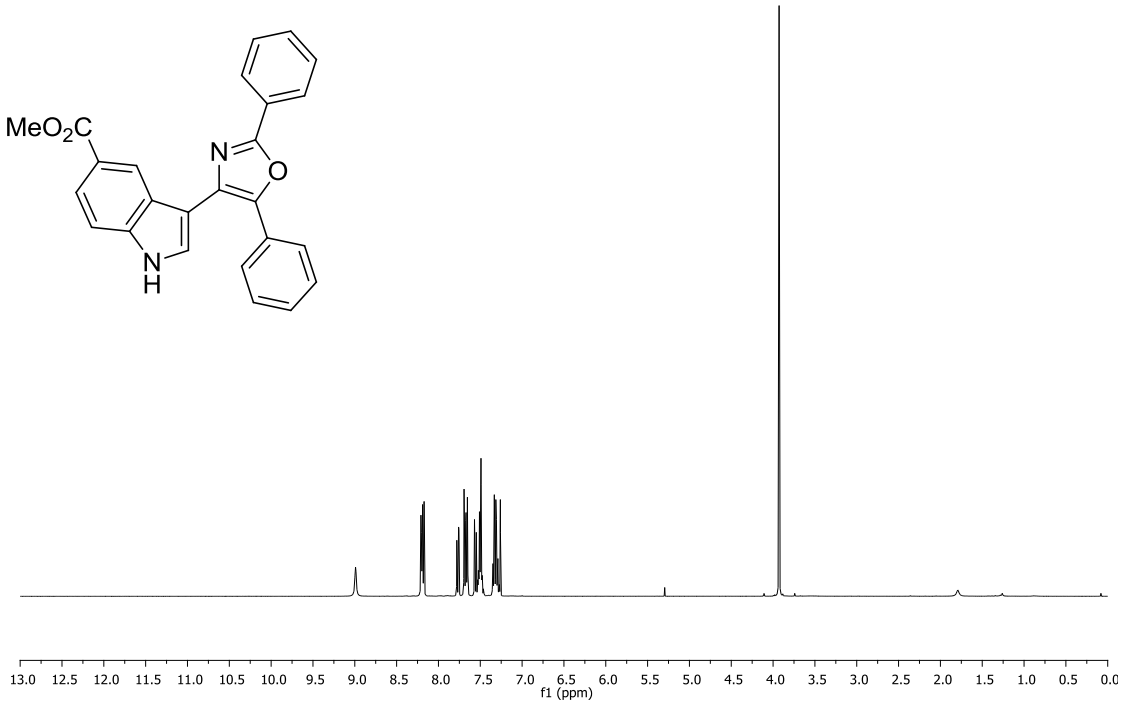
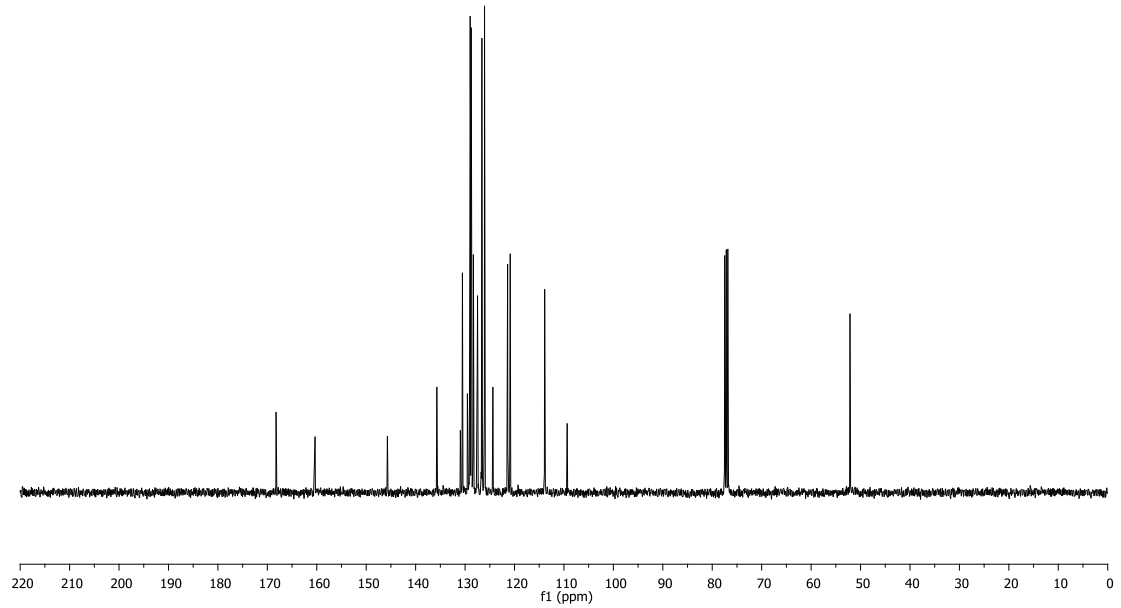






Compound 3la





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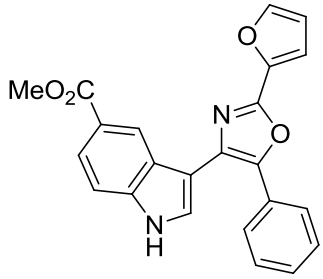

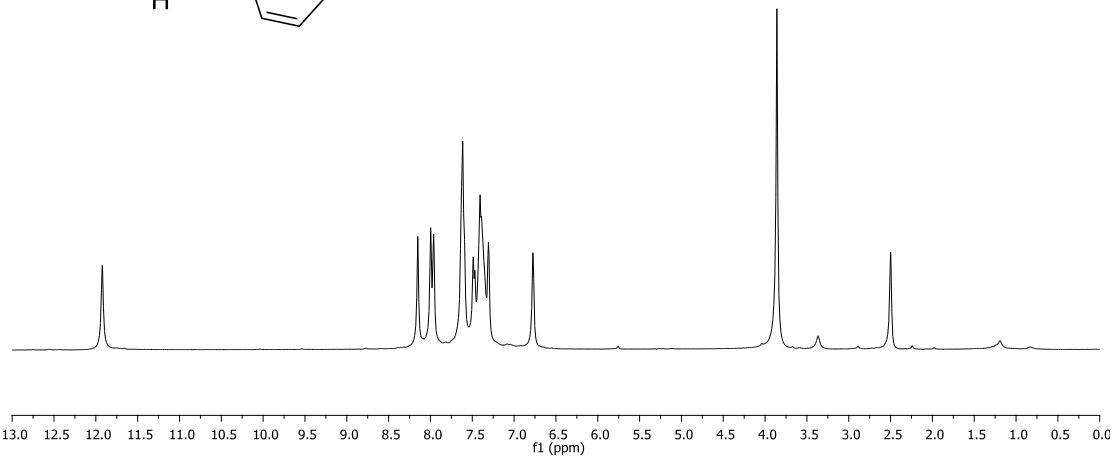

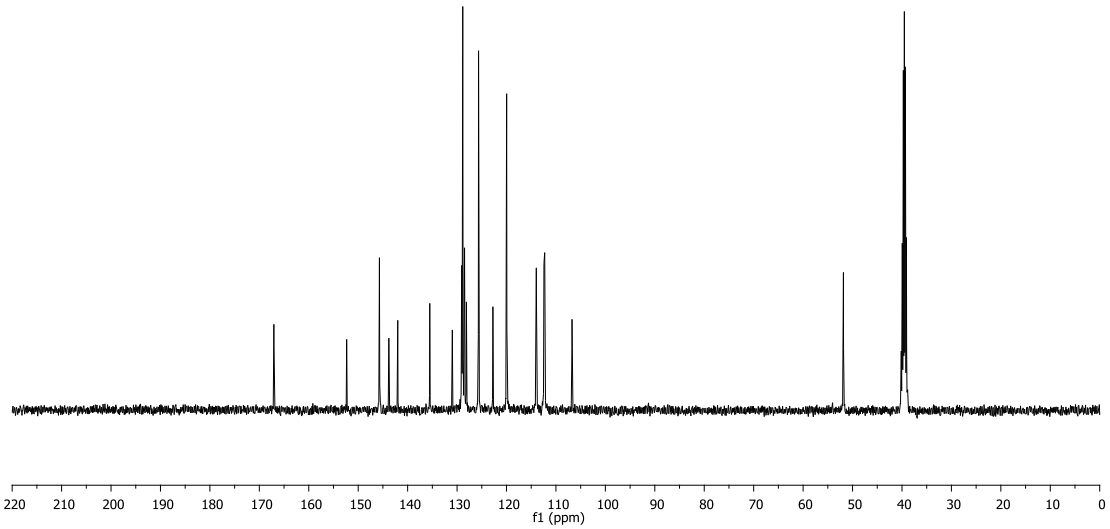

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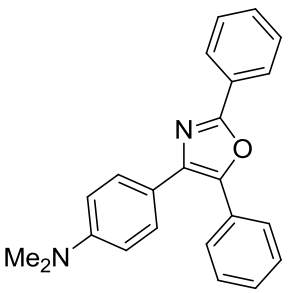
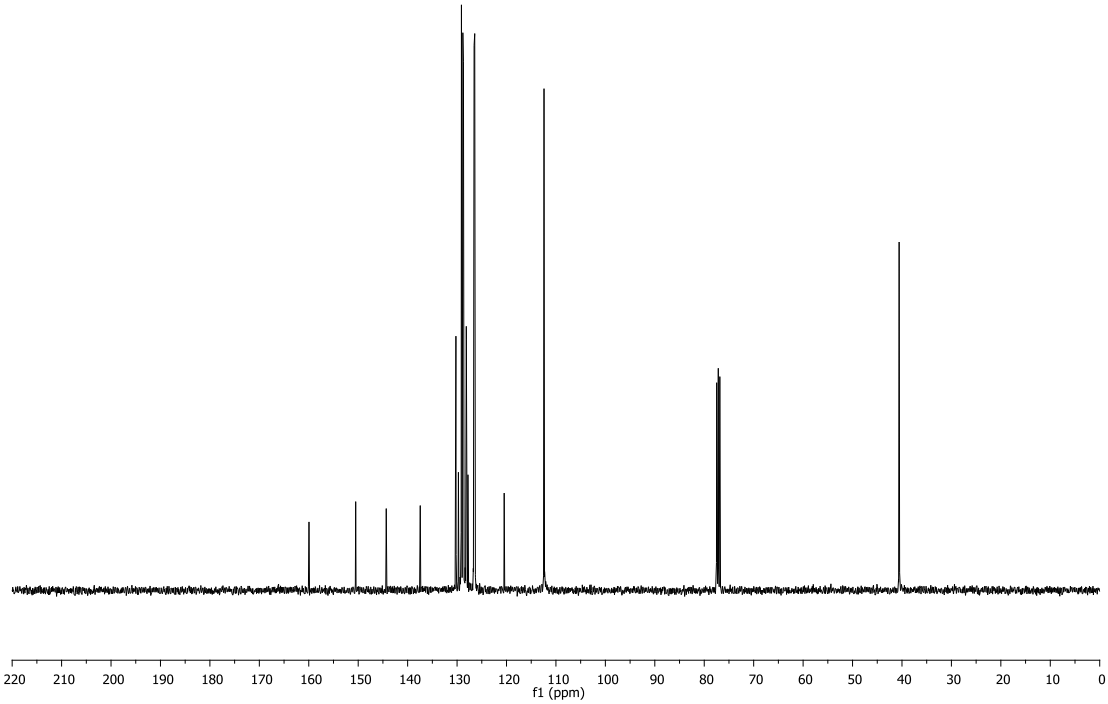
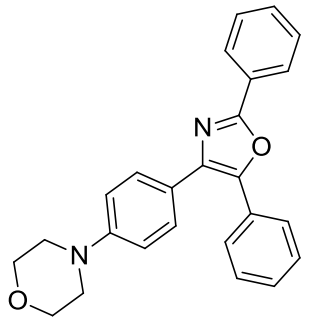
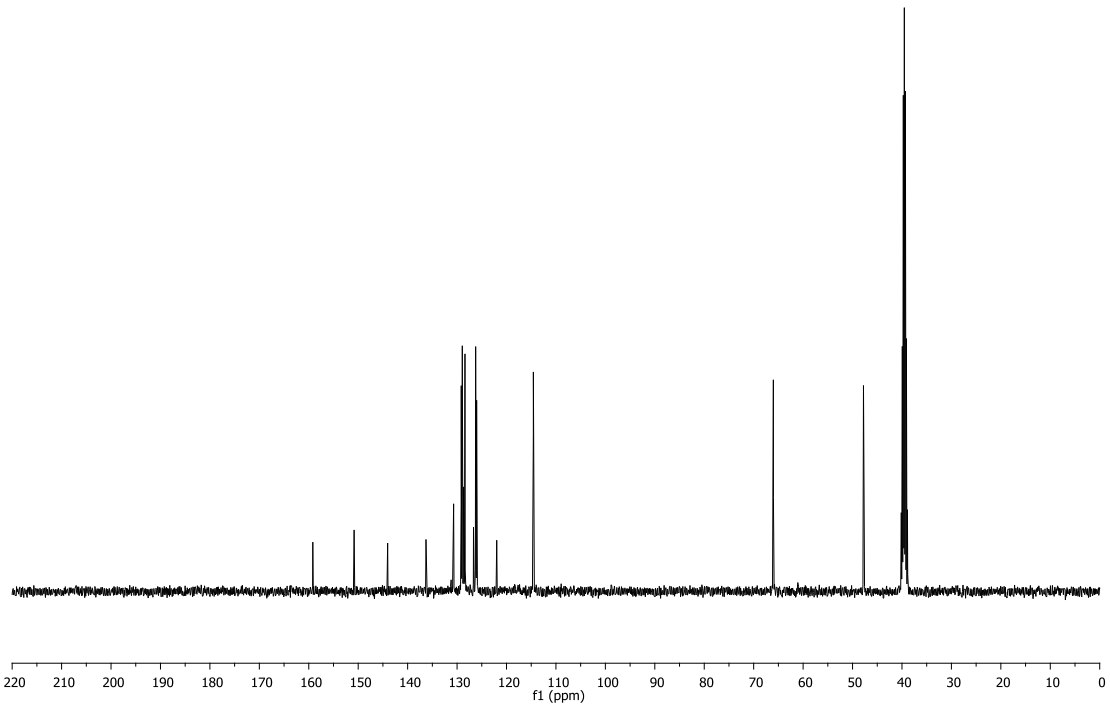


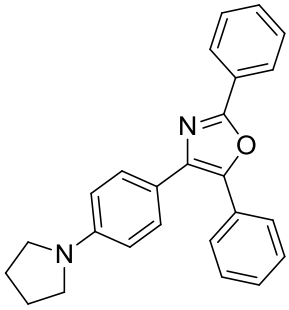


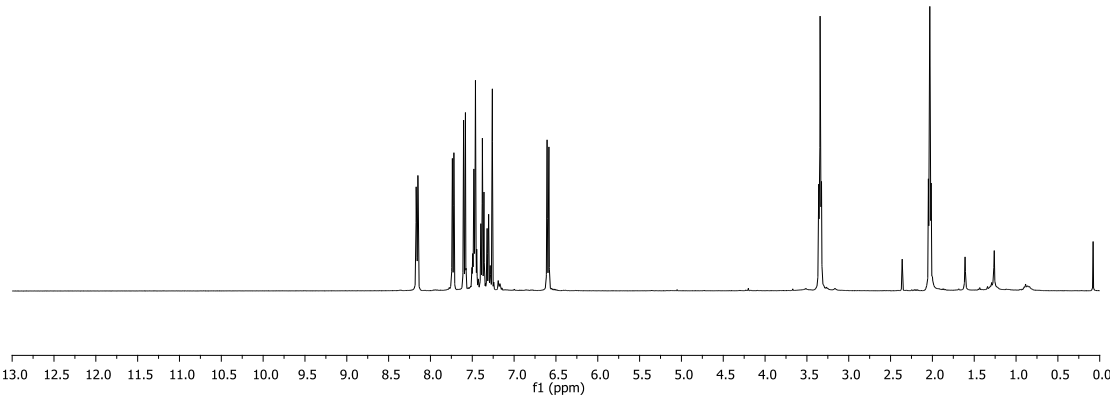
Compound 5ba

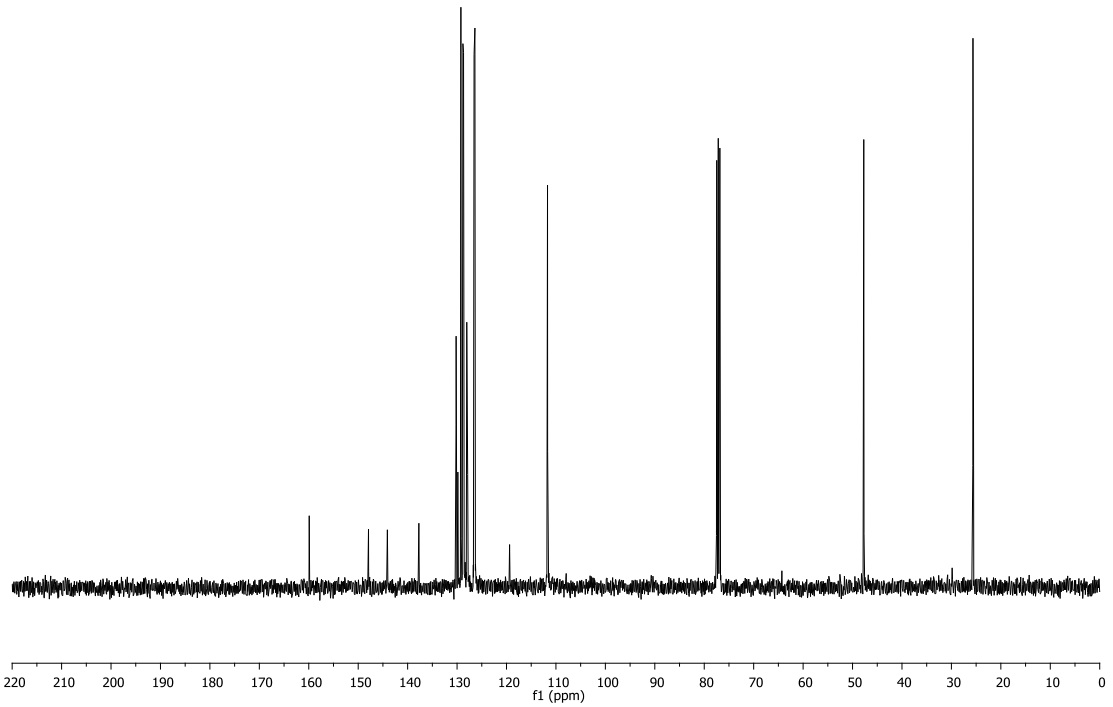




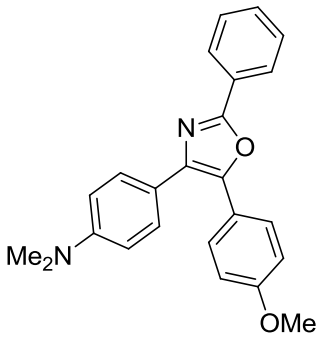
Compound 5ca



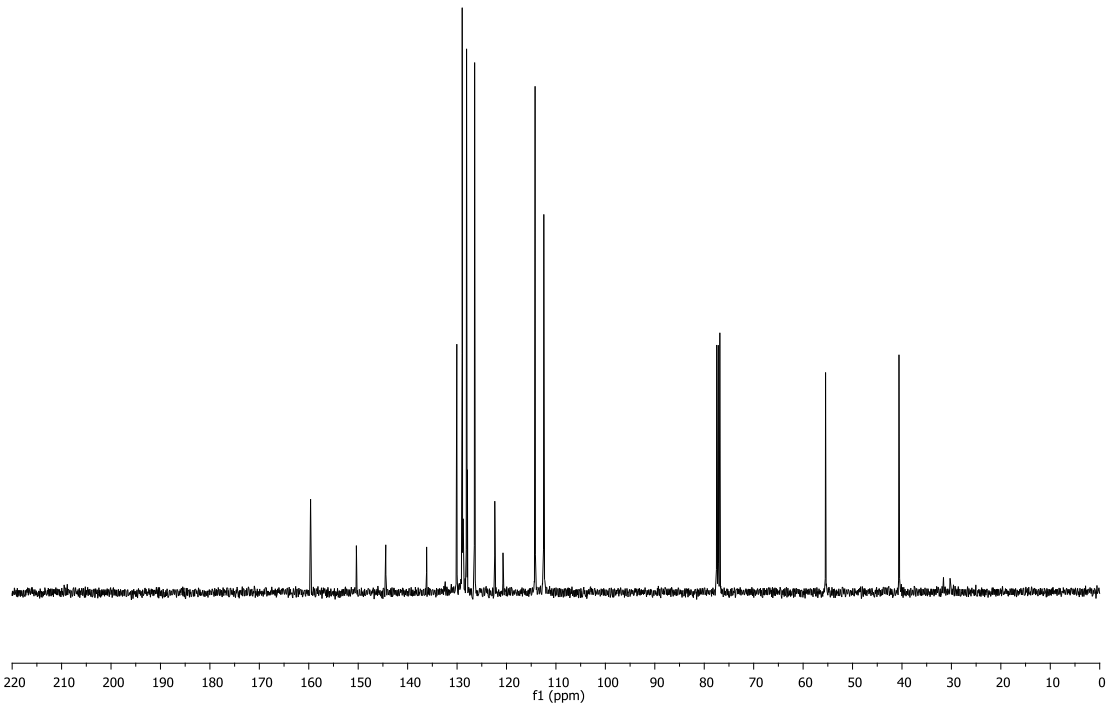




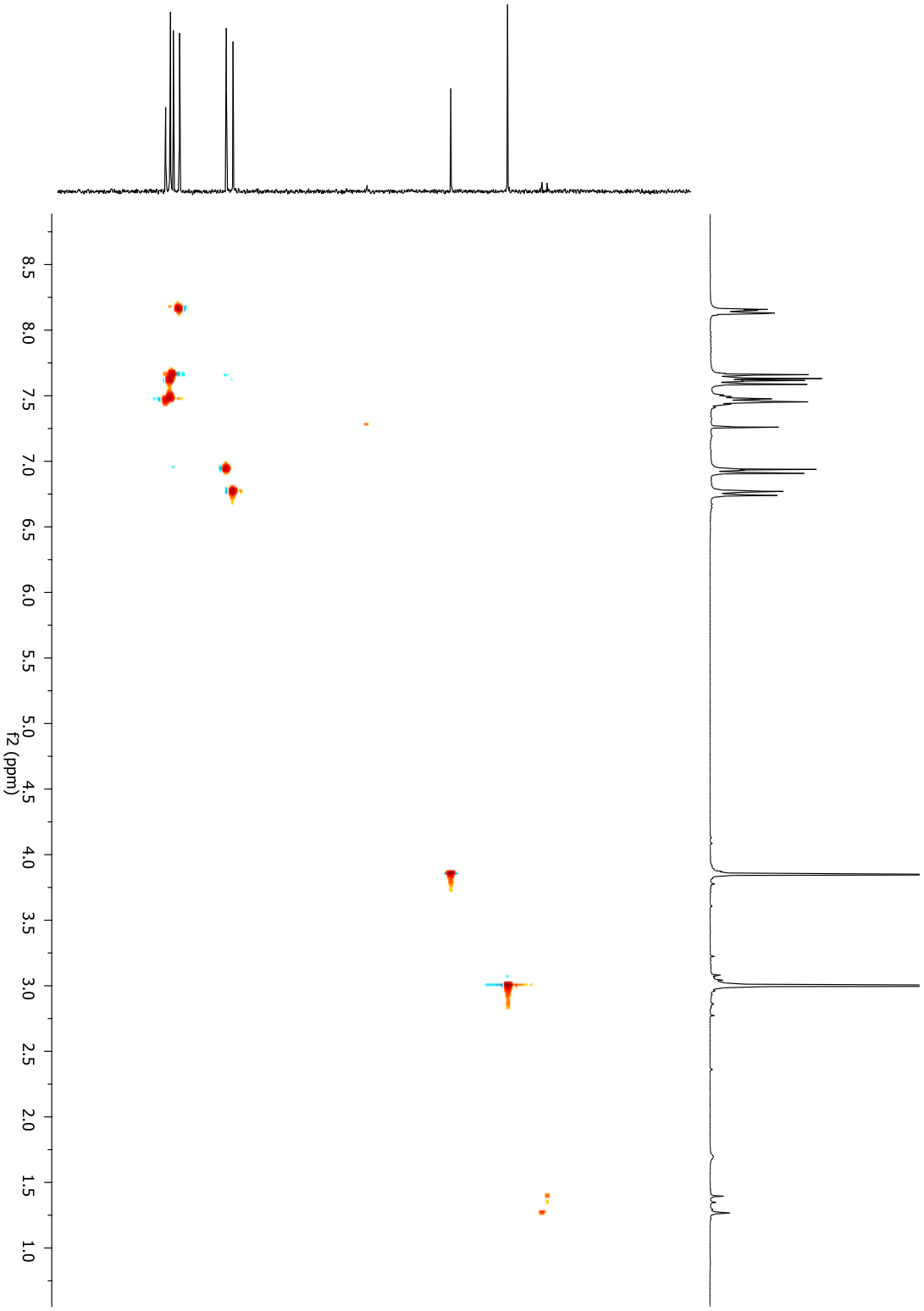
Compound 7


N
O
Me2N
OMe

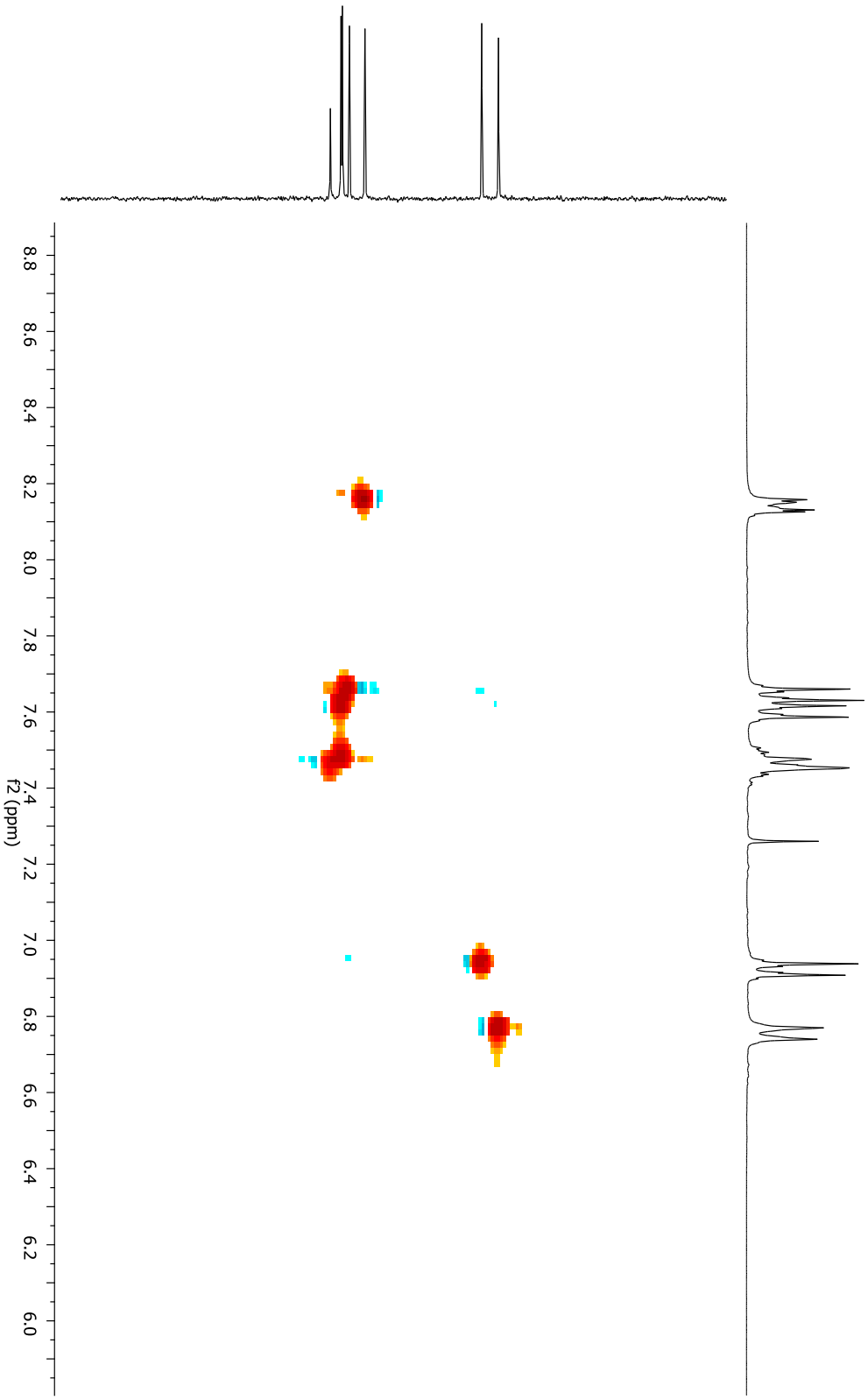
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

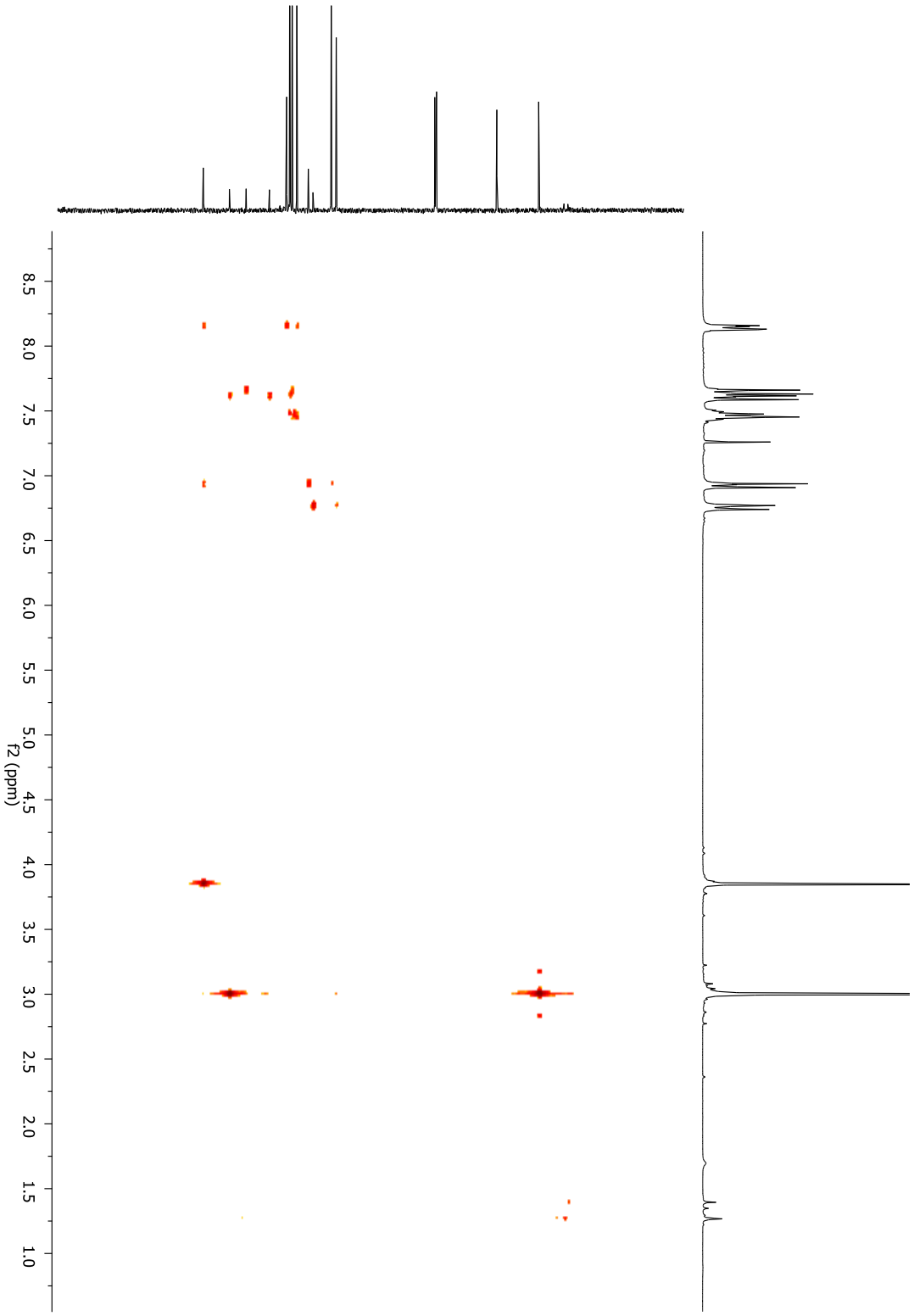
Compound 7 (HSQC spectrum)



Compound 7 (HSQC spectrum-expanded version)



Compound 7 (HMBC spectrum)



Compound 7 (HMBC spectrum-expanded version)