Supporting Information for Publication

Regioselective One-Pot, Three-Component Synthesis of Substituted 2*H*-Indazoles from 2-Nitroarylaldehyde, Alkyne and Amine Catalyzed by CuBr/$Zn(OTf)_2$ System

Ramanjaneyulu Unnava,[a] Kiran Indukuri,[a] Sujit Sarkar,[a] and Anil K. Saikia*[a]

Contents:

General experimental methods: Solvents were distilled before use. All starting materials were used as received without further purification unless otherwise indicated. The combined organic layers were dried over Na_2SO_4. Solvents were evaporated under reduced pressure. All yields given refer to isolated yields. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 600, 400 and 150, 100 MHz NMR spectrometer, respectively using TMS as internal standard. HRMS spectra were recorded using a TOF mass spectrometer. IR spectra were recorded either neat or as film on KBr pellets on a FT-IR spectrometer. Melting points were measured in open capillary tubes and are uncorrected. For thin-layer chromatography (TLC) silica gel GF_{254} was used. Column chromatography was carried out using silica gel 60-120 mesh. X-ray analysis was done on single crystal X-ray diffractometer. All the reactions were performed under nitrogen atmosphere.

General procedure for the Synthesis of 2*H*-Indazoles: To a mixture of CuBr (30 mol%), *o*-nitrobenzaldehyde (0.5 mmol), and $Zn(OTf)_2$ (10 mol%) in 3 mL of dry toluene, amine (0.55 mmol) and alkyne (1.0mmol) were added by dissolving in 5 mL of toluene and the reaction mixture was refluxed for specified time. After completion of the reaction, the reaction was cooled, the solvent was removed under rotary evaporator, diluted with water and then extracted with ethyl acetate. The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-2*H*-indazole (4a):

Red solid; mp118-120 ^oC; R_f (hexane/EtOAc 4:1) 0.52; yield 159 mg, 83%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (t, *J* = 9.2 Hz, 2 H), 7.53 (s, 2 H), 7.40 (s, 3 H), 7.73 (t, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.74 (s, 2 H), 6.43 (s, 1 H), 4.77 (t, *J* = 6.8 Hz, 2 H), 3.79 (s, 3 H), 3.56 (s, 3 H), 3.27 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 148.2, 148.0, 131.6, 130.4, 129.2, 128.6, 126.7, 124.2, 122.8, 122.3, 120.9, 120.1, 119.1, 117.9, 112.0, 111.5, 100.3, 77.0, 55.9, 55.6, 53.6, 36.7; IR (KBr, neat) 2925, 2853, 1592, 1516, 1464, 1263, 1238, 1156, 1139, 1028, 751, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}N_2O_2$ $(M + H)^+$ 383.1754, found 383.1761.

2-(3,4-Dimethoxyphenethyl)-6-nitro-3-(phenylethynyl)-2*H*-indazole (4b):

Yellow solid; mp160-162 ^{o}C; R_f (hexane/EtOAc 7:3) 0.50; yield 160 mg, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1 H), 7.98 (d, *J* = 9.2 Hz, 1 H), 7.84 (d, *J* = 9.2 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.43 (d, *J* = 5.6 Hz, 3 H), 6.75-6.69 (m, 2 H), 6.48 (s, 1 H), 4.84 (t, *J* = 6.8 Hz, 2 H), 3.80 (s, 3 H), 3.60 (s, 3 H), 3.31 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.3, 147.3, 146.3, 131.8, 129.9, 129.8, 128.9, 126.4, 121.7, 121.6, 121.0, 120.7, 116.7, 116.0, 112.0, 111.7, 101.5, 75.7, 56.1, 55.8, 54.4, 36.6; IR (KBr, neat) 2923, 1561, 1529, 1519, 1503, 1346, 1267, 1235, 1159, 1029, 837, 754 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{22}N_3O_4$ $(M + H)^+$ 428.1605, found 428.1613.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-6-(trifluoromethyl)-2*H*-indazole (4c):

Paleyellow solid; mp 94-96 ^{o}C; R_f (hexane/EtOAc 7:3) 0.55; yield 178 mg, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.57-7.53 (m, 2 H), 7.42 (s, 3 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 6.75-6.70 (m, 2 H), 6.45 (s, 1 H), 4.81 (t, *J* = 6.8 Hz, 2 H), 3.80 (s, 3 H), 3.58 (s, 3 H), 3.29 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.2, 148.2, 146.7, 131.7, 130.1, 129.6, 129.1 (q, *J* = 33.0 Hz), 128.8, 125.2, 124.6 (q, *J* = 271.5 Hz), 122.0, 121.5, 121.0, 120.0, 118.6, 116.5 (q, *J* = 4.5 Hz), 112.0, 111.6, 101.0, 76.2, 56.0, 55.7, 54.0, 36.7; ^{19}F NMR (376 MHz, C_6F_6/$CDCl_3$): δ 99.44. IR (KBr, neat) 2934, 2202, 1516, 1463, 1337, 1253, 1160, 1121, 1045, 808, 755, 688 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{22}F_3N_2O_2$ $(M + H)^+$ 451.1628, found 451.1628.

5-Chloro-2-(3,4-dimethoxyphenethyl)-3-(phenylethynyl)-2*H*-indazole (4d):

Pale yellow solid; mp 83-85 ^{o}C; R_f (hexane/EtOAc 4:1) 0.51; yield 148 mg, 71%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1 H), 7.68 (d, *J* = 9.2 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.43-7.39 (m, 3 H), 7.28-7.24 (m, 1 H), 6.75–6.69 (m, 2 H), 6.46 (s, 1 H), 4.75 (t, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.59 (s, 3 H), 3.27 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 148.5, 146.9, 132.0, 130.5, 130.0, 129.8, 129.1, 128.4, 124.9, 122.4, 121.3, 119.8, 119.4, 119.3, 112.3, 112.0, 101.1, 76.7, 56.3, 56.0, 54.1, 37.0; IR (KBr, neat) 2932, 2834, 1515, 1463, 1327, 1263, 1237,

1157, 1028, 804, 756, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{22}ClN_2O_2$ $(M + H)^+$ 417.1364, found 417.1366.

5-(Benzyloxy)-2-(3,4-dimethoxyphenethyl)-3-(phenylethynyl)-2*H*-indazole (4e):

Pale yellow semisolid; R_f (hexane/EtOAc 4:1) 0.51; yield 73 mg, 30%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.2 Hz, 1 H), 7.56–7.53 (m, 2 H), 7.49 (d, *J* = 7.2 Hz, 2 H), 7.43–7.34 (m, 6 H), 7.11 (d, *J* = 8.8 Hz, 1 H), 7.04 (s, 1 H), 6.75 (s, 2 H), 6.45 (s, 1 H), 5.11 (s, 2 H), 4.73 (t, *J* = 7.6 Hz, 2 H), 3.81 (s, 3 H), 3.58 (s, 3 H), 3.26 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.5, 149.2, 148.1, 145.0, 137.1, 131.7, 130.6, 129.2, 128.8, 128.7, 128.2, 127.9, 124.5, 122.6, 121.7, 121.0, 119.5, 118.4, 112.2, 111.6, 100.3, 98.3, 77.4, 70.6, 56.1, 55.7, 53.6, 36.8; IR (KBr, neat) 2925, 2850, 1633, 1516, 1464, 1262, 1236, 1189, 1027, 807, 756 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{29}N_2O_3$ $(M + H)^+$ 489.2173, found 489.2171.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-2*H*-indazol-5-yl acetate (4f):

Pale yellow semisolid; R_f (hexane/EtOAc 7:3) 0.54; yield 77 mg, 35%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 9.2 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.45-7.38 (m, 4 H), 7.06 (d, *J* = 8.8 Hz, 1 H), 6.76-6.72 (m, 2 H), 6.48 (s, 1 H), 4.77 (t, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.61 (s, 3 H), 3.27 (t, *J* = 7.6 Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1, 149.2, 148.2, 146.5, 146.4, 131.7, 130.3, 129.4, 128.8, 123.9, 122.8, 122.3, 121.0, 119.8, 119.3, 112.1, 111.6, 111.2, 100.8, 76.7, 56.1, 55.8, 53.9, 36.8, 21.3; IR (KBr, neat) 2921, 2851, 1757, 1655, 1516, 1465, 1261, 1208, 1158, 1028, 806, 757, 668 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{25}N_2O_4$ $(M + H)^+$ 441.1809, found 441.1811.

2-(3,4-Dimethoxyphenethyl)-3-(*p*-tolylethynyl)-2*H*-indazole (4g):

Red solid; mp 74-76 ^oC; R_f (hexane/EtOAc 4:1) 0.55; yield 119 mg, 60%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 6.73 (s, 2 H), 6.43 (s, 1 H), 4.75 (t, *J* = 7.2 Hz, 2 H), 3.79 (s, 3 H), 3.55 (s, 3 H), 3.25 (t, *J* = 7.2 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 148.2, 148.0, 139.6, 131.6, 130.5, 129.5, 126.7, 124.1, 122.7, 121.0, 120.2, 119.4, 119.3,

117.9, 112.0, 111.5, 100.6, 76.4, 56.0, 55.7, 53.6, 36.7, 21.8; IR (KBr, neat) 2925, 2853, 1625, 1515, 1464, 1263, 1238, 1139, 1028, 815, 748 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{25}N_2O_2$ $(M + H)^+$ 397.1911, found 397.1915.

3-((4-(*tert*-Butyl)phenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2*H*-indazole (4h):

Pale yellow semisolid; R_f (hexane/EtOAc 4:1) 0.56; yield 125 mg, 57%; ^1H NMR (600 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.42 (d, *J* = 7.8 Hz, 2 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 6.75 (s, 2 H), 6.48 (s, 1 H), 4.77 (t, *J* = 7.8 Hz, 2 H), 3.81 (s, 3 H), 3.58 (s, 3 H), 3.28 (t, *J* = 7.2 Hz, 2 H), 1.35 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.9, 149.2, 148.3, 148.1, 131.5, 130.5, 126.8, 125.8, 124.2, 122.8, 121.0, 120.2, 119.5, 119.5, 118.0, 112.1, 111.6, 100.7, 76.5, 56.1, 55.7, 53.7, 36.8, 35.2, 31.4 (3C); IR (KBr, neat) 2920, 1630, 1516, 1464, 1263, 1028, 747, 600 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{31}N_2O_2$ $(M + H)^+$ 439.2380, found 439.2385.

3-((4-Chlorophenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2*H*-indazole (4i):

Colorless solid; mp 112-114°C; R_f (hexane/EtOAc 4:1) 0.52; yield 129 mg, 62%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 9.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.44 (d, *J* = 8.8 Hz, 2 H), 7.39-7.32 (m, 3 H), 7.17 (t, *J* = 6.8 Hz, 1 H), 6.75–6.70 (m, 2 H), 6.38 (s, 1 H), 4.76 (t, *J* = 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.55 (s, 3 H), 3.27 (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.1, 148.4, 148.1, 135.4, 132.8, 130.5, 129.1 (2C), 126.9, 124.4, 123.1, 121.0, 120.9, 120.1, 118.1, 112.1, 111.6, 99.2, 78.1, 56.1, 55.7, 53.8, 36.8; IR (KBr, neat) 2916, 2844, 1633, 1516, 1468, 1263, 1027, 789, 748 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{22}ClN_2O_2$ $(M + H)^+$ 417.1364, found 417.1364.

3-((4-Bromophenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2*H*-indazole (4j):

Pale yellow semisolid; mp104-106 °C; R_f (hexane/EtOAc 4:1) 0.53; yield 150 mg, 65%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.8 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.38-7.31 (m, 3 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.75-6.69 (m, 2 H), 6.38 (s, 1 H), 4.76 (t, *J* = 7.2 Hz, 2 H), 3.79 (s, 3 H), 3.55 (s, 3 H), 3.27 (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 148.3, 148.1, 132.9, 132.0, 130.4, 126.8, 124.3, 123.6, 123.0, 121.3, 120.9,

120.0, 118.9, 118.1, 112.1, 111.6, 99.2, 78.2, 56.0, 55.7, 53.7, 36.7; IR (KBr, neat) 2932, 1624, 1515, 1463, 1263, 1139, 1010, 821, 747 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{22}BrN_2O_2$ $(M + H)^+$ 461.0859, found 461.0856.

2-(3,4-Dimethoxyphenethyl)-3-((4-nitrophenyl)ethynyl)-2*H*-imidazole (4k):

Yellow solid; mp154-156 ^oC; R_f (hexane/EtOAc 7:3) 0.55; yield 173 mg, 81%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.22 (t, *J* = 7.2 Hz, 1 H), 6.72 (s, 2 H), 6.33 (s, 1 H), 4.79 (t, *J* = 6.8 Hz, 2 H), 3.77 (s, 3 H), 3.53 (s, 3 H), 3.29 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 148.3, 148.2, 147.5, 133.6, 132.1, 130.3, 129.2, 127.0, 124.7, 123.9, 123.6, 120.9, 119.8, 118.3, 112.1, 111.5, 98.4, 82.2, 56.0, 55.7, 53.9, 36.7; IR (KBr, neat) 2927, 2851, 2202, 1592, 1516, 1463, 1342, 1262, 1238, 1140, 1107, 1028, 855, 748, cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{22}N_3O_4$ $(M + H)^+$ 428.1605, found 428.1600.

2-Phenethyl-3-(phenylethynyl)-2*H*-indazole (4l):

Red solid; mp 70-72 ^oC; R_f (hexane/EtOAc 4:1) 0.60; yield 126 mg, 78%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.73 (m, 2 H), 7.58-7.54 (m, 2 H), 7.43-7.40 (m, 3 H), 7.36-7.16 (m, 7 H), 4.80 (t, *J* = 8.0 Hz, 2 H), 3.35 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 137.9, 131.7, 129.2, 129.0, 128.9, 128.8, 127.0, 126.7, 124.3, 122.9, 122.4, 120.1, 118.9, 118.1, 100.6, 77.1, 53.5, 37.2; IR (KBr, neat) 2926, 1518, 1493, 1464, 1364, 1283, 1076, 747, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{19}N_2$ $(M + H)^+$ 323.1543, found 323.1550.

2-Benzyl-3-(phenylethynyl)-2*H*-indazole (4m):

Colorless solid; mp 78-80 ^oC; R_f (hexane/EtOAc 9:1) 0.62; yield 74 mg, 48%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 7.6 Hz, 2 H), 7.58-7.54 (m, 2 H), 740–7.27 (m, 9 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 5.76 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 136.2, 131.7, 129.3, 129.0, 128.8, 128.7, 128.3, 128.2, 126.8, 124.7, 123.0, 122.4, 120.2, 118.3, 101.0, 77.5, 55.9; IR (KBr, neat) 2952, 2852, 1494, 1455, 1443, 1283, 1172, 1097, 748, 706, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{17}N_2$ $(M + H)^+$ 309.1386, found 309.1396.

2-Allyl-3-(phenylethynyl)-2*H*-indazole (4n):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.59; yield 76 mg, 59%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (t, *J* = 8.4 Hz, 2 H), 7.61-7.58 (m, 2 H), 7.43-7.40 (m, 3 H), 7.35-7.31 (m, 1 H), 7.20-7.16 (m, 1 H), 6.19–6.09 (m, 1 H), 5.34–5.28 (m, 2 H), 5.21 (d, *J* = 6.0 Hz 2 H); ^{13}C NMR(150 MHz, $CDCl_3$): δ 148.4, 132.3, 131.7, 129.3, 128.8, 126.8, 124.7, 123.0, 122.5, 120.1, 119.2, 118.9, 118.3, 100.9, 77.2, 54.6; IR (KBr, neat) 2924, 2853, 1529, 1465, 1364, 1218, 1091, 927, 748, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{15}N_2$ $(M + H)^+$ 259.1230, found 259.1236.

2-Cyclohexyl-3-(phenylethynyl)-2*H*-indazole (4o):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.61; yield 99 mg, 66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.77 (d, *J* = 8.8 Hz, 2 H), 7.62-7.58 (m, 2 H), 7.45-7.39 (m, 3 H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1 H), 4.82–4.74 (m, 1 H), 2.22-2.12 (m, 4 H), 2.32-1.95 (m, 2 H), 1.82-1.76 (m, 1 H), 1.57-1.34 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 131.6, 129.2, 129.0, 128.8, 126.4, 124.4, 122.7, 120.0, 118.2, 117.7, 100.8, 77.5, 61.4, 33.2, 25.9, 25.5; IR (KBr, neat) 2931, 2854, 1452, 1352, 1280, 1211, 1010, 746, 868 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{21}N_2$ $(M + H)^+$ 301.1699, found 301.1696.

2-Isopropyl-3-(phenylethynyl)-2*H*-indazole (4p):

Pale yellow semi solid; R_f (hexane/ EtOAc 9:1) 0.62; yield 83 mg, 64%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80-7.77 (m, 2 H), 7.62 (t, *J* = 4.2 Hz, 2 H), 7.44-7.39 (m, 3 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 5.26–5.20 (m, 1 H), 1.71 (d, *J* = 7.2 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.9, 131.6, 129.2, 128.8, 126.4, 124.5, 122.7, 122.6, 120.0, 118.2, 117.6, 100.8, 77.3, 53.8, 22.9; IR (KBr, neat) 2923, 1641, 1459, 1347, 1276, 1235, 1082, 746, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{17}N_2$ $(M + H)^+$ 261.1386, found 261.1389.

2-Butyl-3-(phenylethynyl)-2*H*-indazole (4q):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.64; yield 96 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 9.6 Hz, 2 H), 7.62-7.59 (m, 2H), 7.43-7.40 (m, 3 H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1 H), 4.60 (t, *J* = 7.6 Hz, 2 H), 2.05 (p, *J* = 7.2 Hz, 2 H), 1.44–1.36 (m, 2

H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 131.6, 129.2, 128.8, 126.5, 124.4, 122.8, 122.5, 120.0, 118.8, 118.1, 100.6, 77.4, 51.8, 32.7, 20.1, 13.8; IR (KBr, neat) 2958, 2929, 2871, 2659, 2206, 2107, 1625, 1597, 1492, 1464, 1364, 1284, 1084, 746, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}N_2$ $(M + H)^+$ 275.1543, found 275.1552.

2-Butyl-3-(*p*-tolylethynyl)-6-(trifluoromethyl)-2*H*-indazole (4r):

Pale yellow solid; mp 84-86 °C; R_f (hexane/EtOAc 9:1) 0.58; yield 107 mg, 60%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (s, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 9.0 Hz, 1 H), 7.23 (d, *J* = 7.8 Hz, 2 H), 4.62 (t, *J* = 7.2 Hz, 2 H), 2.41 (s, 3 H), 2.05 (p, *J* = 7.2 Hz, 2 H), 1.43-1.38 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.6, 140.0, 131.7, 129.6, 128.7 (q, *J* = 33.0 Hz), 125.3, 124.7 (q, *J* = 270.0 Hz), 121.5, 119.8, 119.0, 118.4, 116.5 (q, *J* = 4.5 Hz), 101.5, 75.9, 52.2, 32.6, 21.8, 20.0, 13.8; ^{19}F NMR (376 MHz, C_6F_6/$CDCl_3$): δ 99.43; IR (KBr, neat) 2926, 1653, 1455, 1337, 1252, 1164, 1123, 1084, 1045, 809 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{20}F_3N_2$ $(M + H)^+$ 357.1573, found 357.1572.

2-(*tert*-Butyl)-3-(phenylethynyl)-2*H*-indazole (4s):

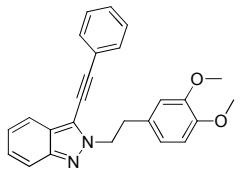
Pale yellow solid; mp 92-94 °C; R_f (hexane/EtOAc 9:1) 0.70; yield 70 mg, 51%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2 H), 7.62-7.58 (m, 2 H), 7.44-7.39 (m, 3 H), 7.33-7.28 (m, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 1.97 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 131.3, 129.1, 128.8, 128.7, 126.8, 126.3, 123.0, 122.8, 119.8, 118.4, 101.3, 79.5, 63.1, 30.1; IR (KBr, neat) 2925, 1653, 1456, 1369, 1343, 1261, 1205, 1028, 746, 688, 668 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}N_2$ $(M + H)^+$ 275.1543, found 275.1544.

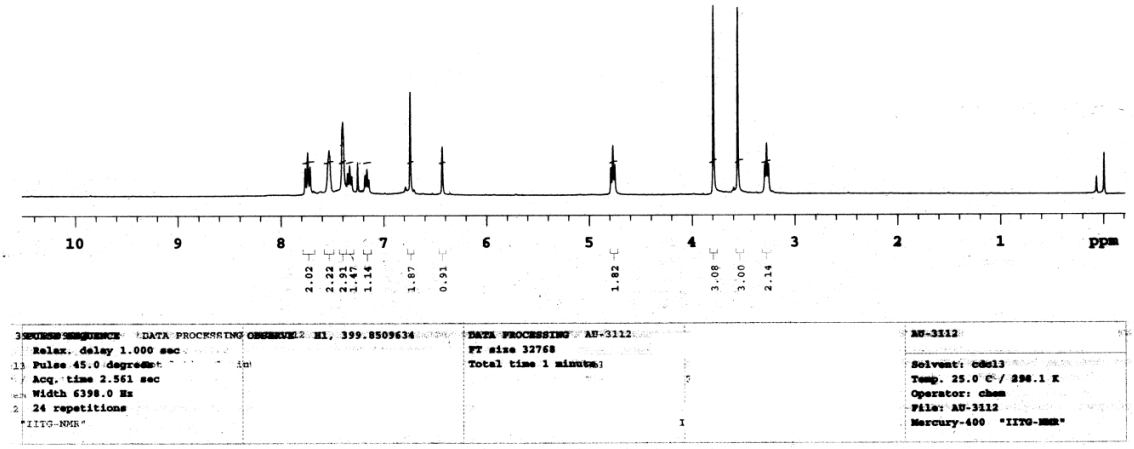
2-Octadecyl-3-(phenylethynyl)-2*H*-indazole (4t):

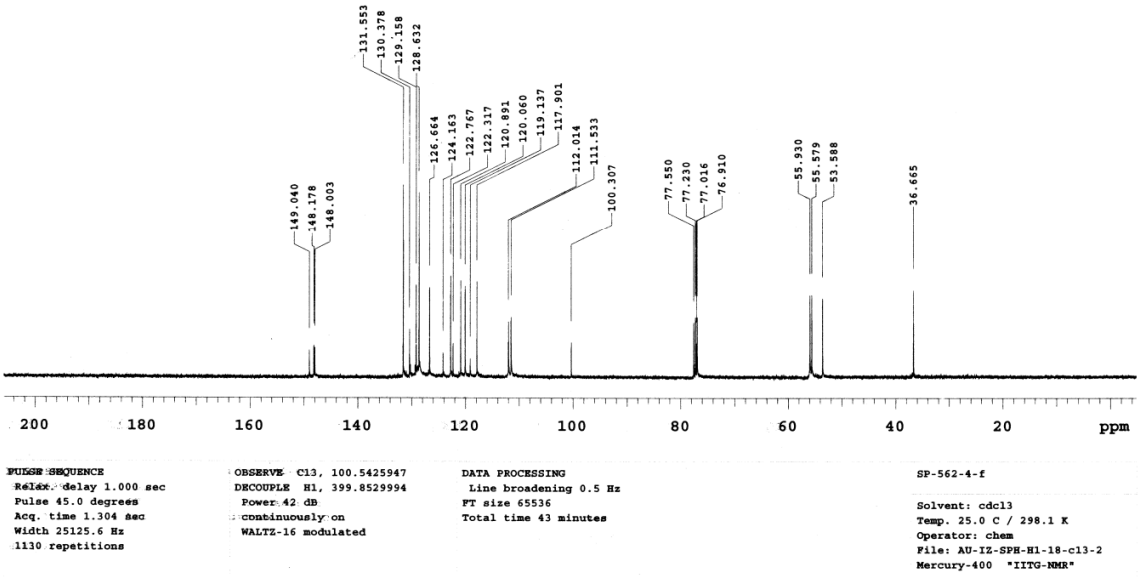
Pale yellow solid; mp 81-83 °C; R_f (hexane/EtOAc 9:1) 0.78; yield 132 mg, 56%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 9.2 Hz, 2 H), 7.63–7.58 (m, 2 H), 7.43-7.39 (m, 3 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 4.59 (t, *J* = 6.8 Hz, 2 H), 2.09-2.03 (m, 2 H), 1.37-1.21 (m, 30 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 131.6, 129.2, 128.8, 126.5, 124.4, 122.8, 122.6, 120.1, 118.7, 118.1, 100.6, 77.4, 52.1, 32.1, 30.7, 29.9 (4C), 29.8 (3C),

29.82, 29.8, 29.7, 29.6, 29.3, 26.8, 22.9, 14.3; IR (KBr, neat) 2920, 2852, 2213, 1641, 1465, 1368, 1279, 1025, 745, 688 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{47}N_2$ $(M + H)^+$ 471.3734, found 471.3721.

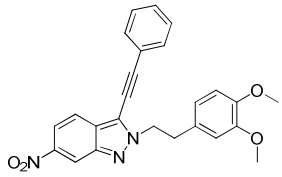
^{1}H and ^{13}C spectra of compound **4a**

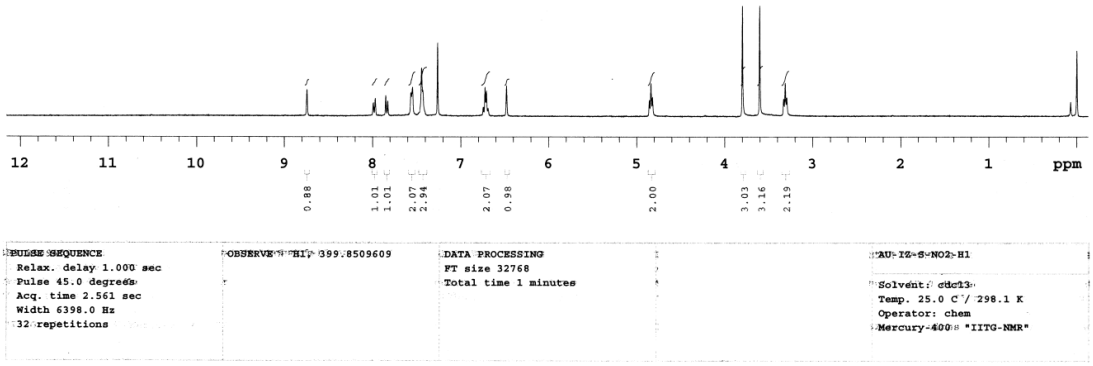


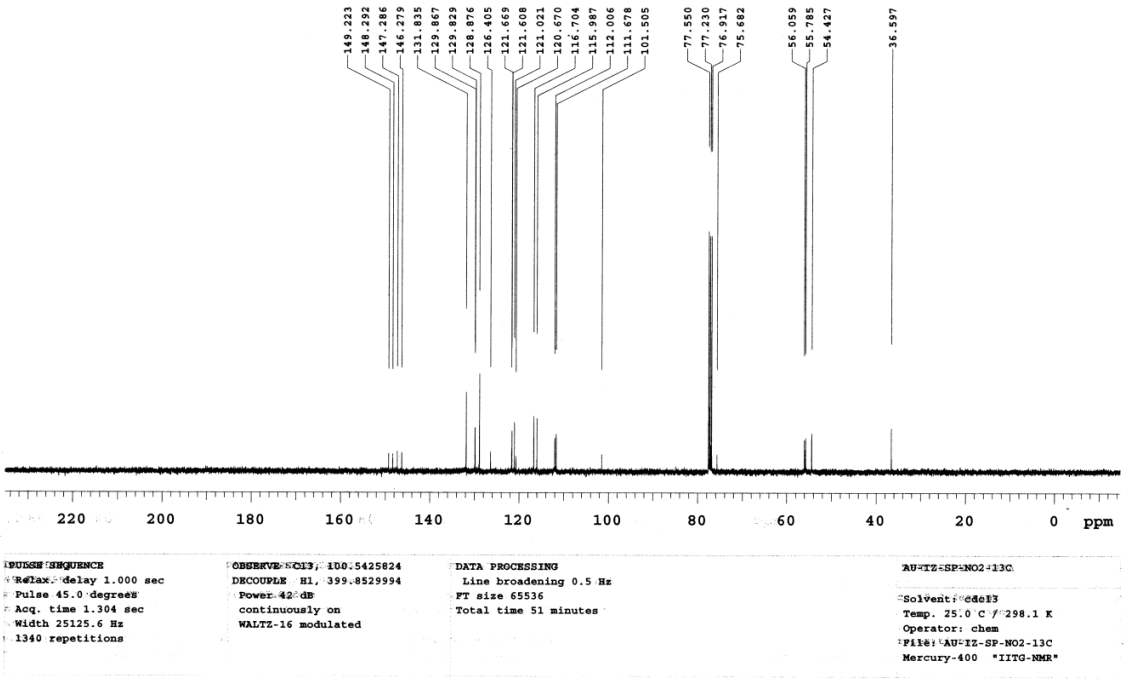




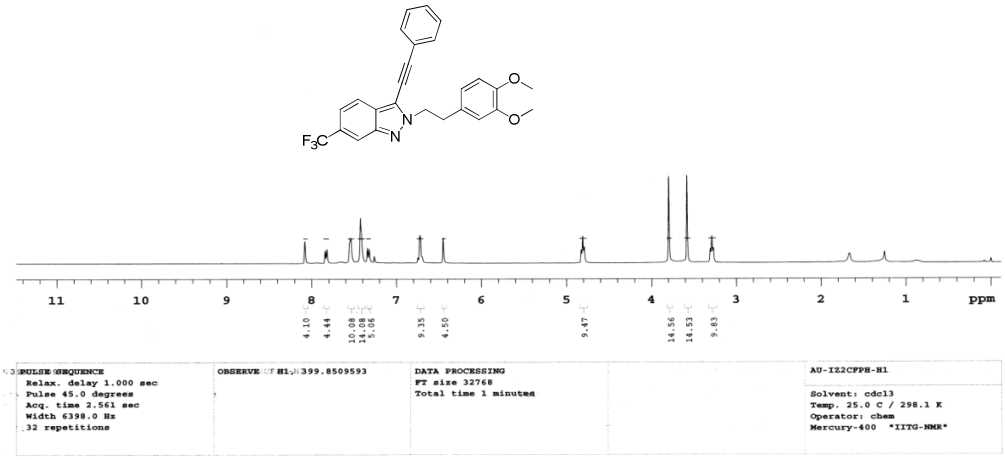
^{1}H and ^{13}C spectra of compound **4b**

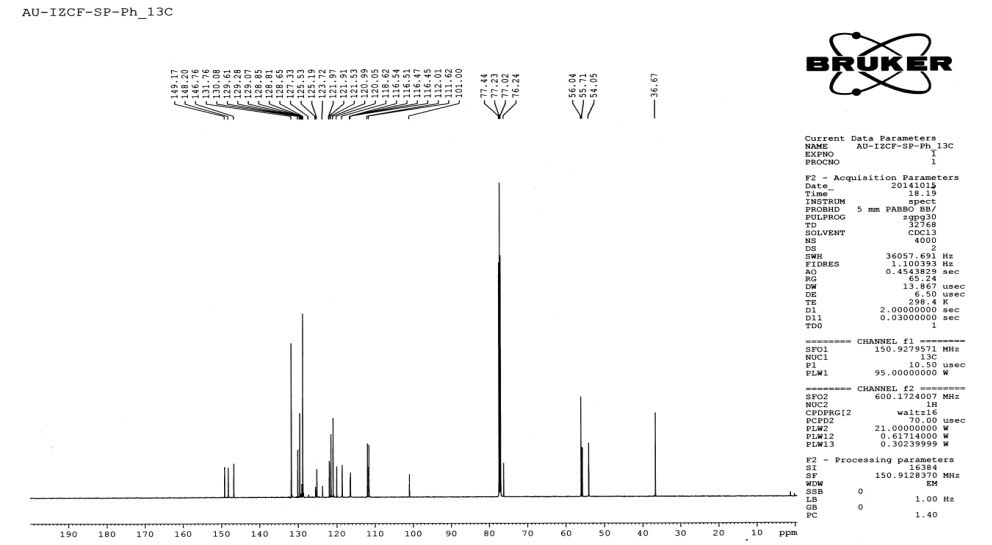


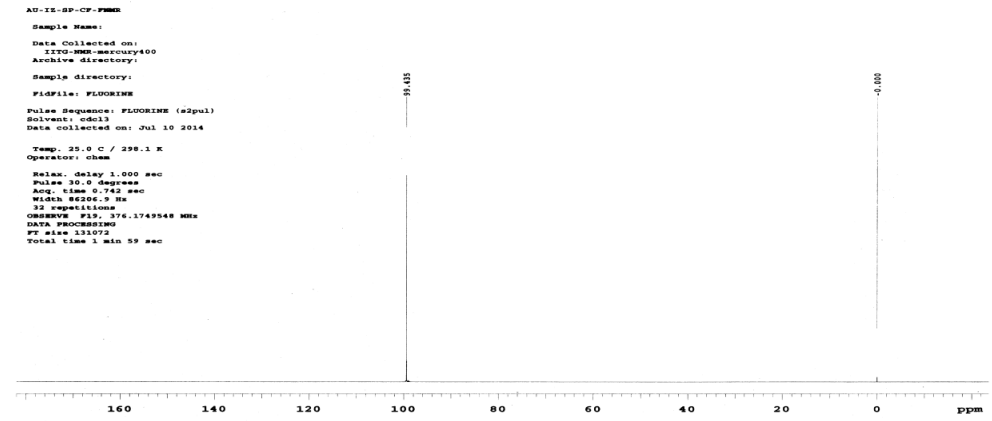




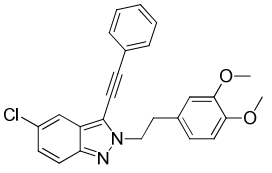
^{1}H and ^{13}C spectra of compound **4c**

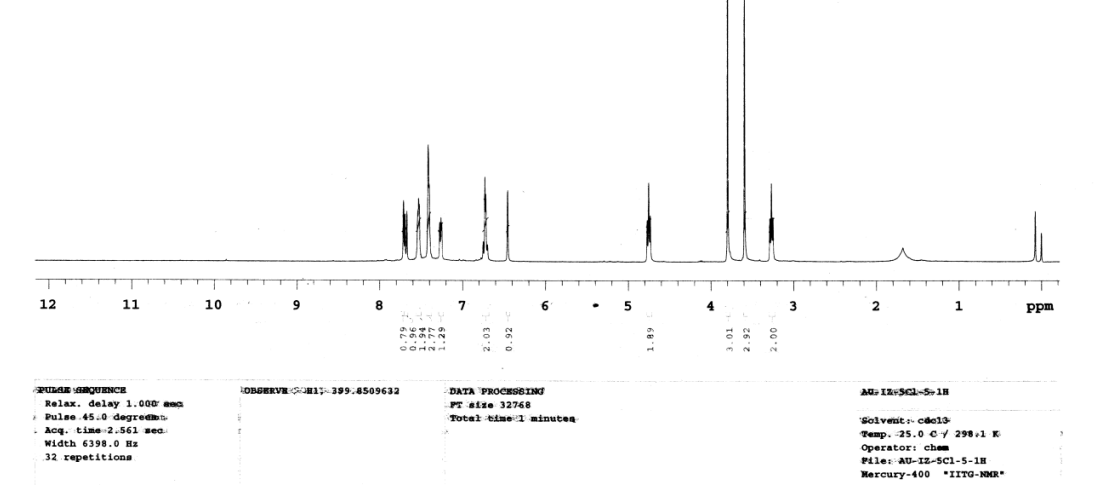


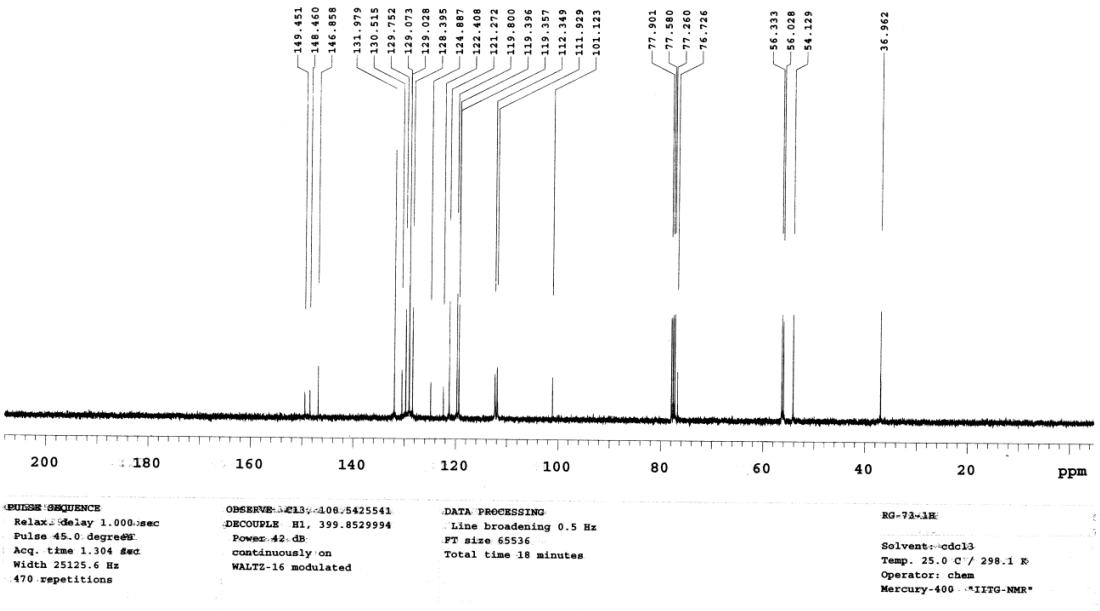




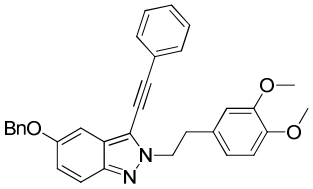
^{1}H and ^{13}C spectra of compound **4d**

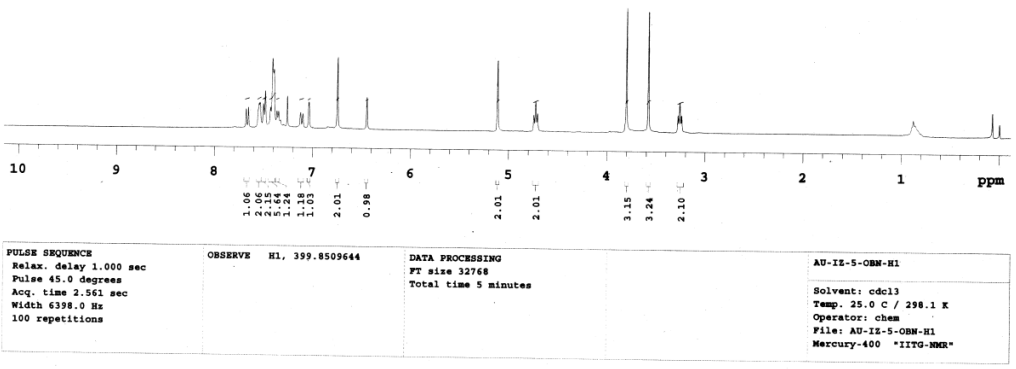


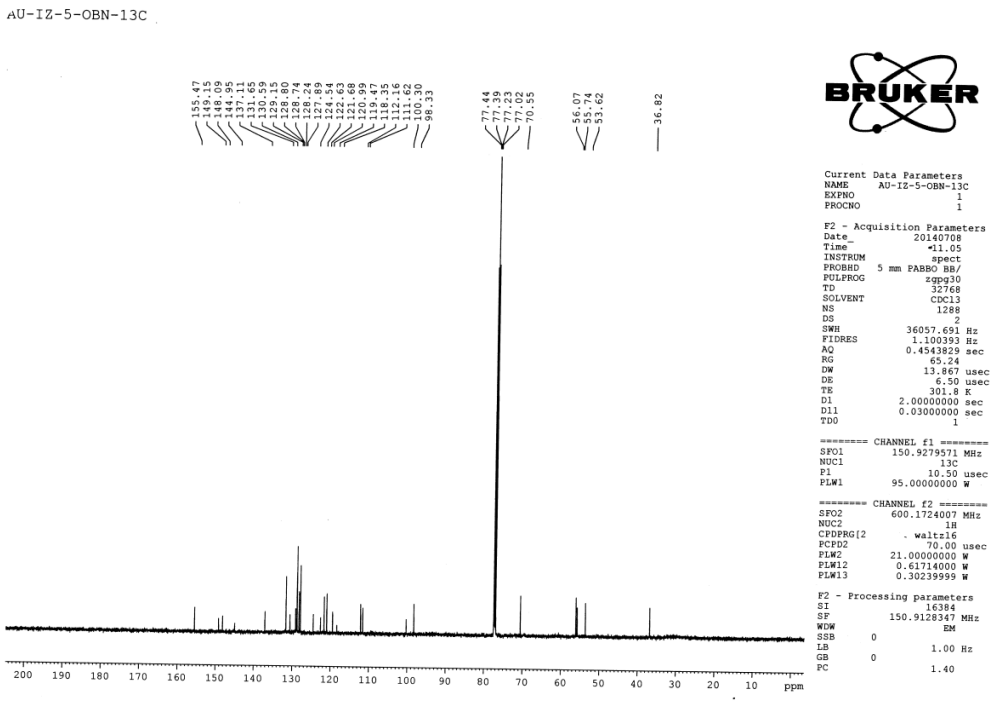




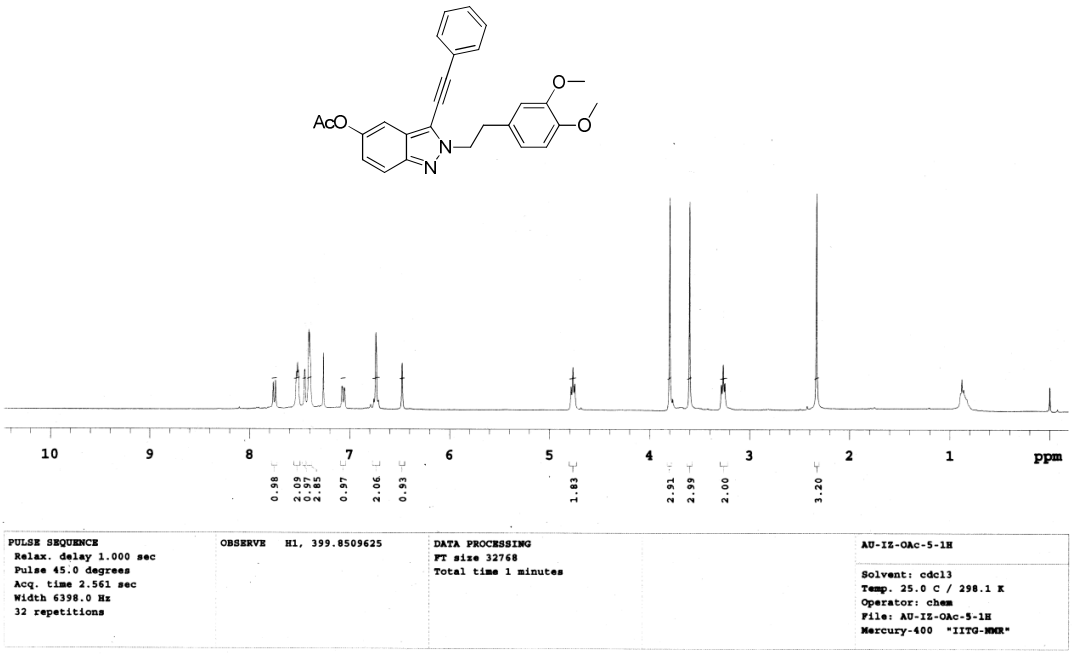
^{1}H and ^{13}C spectra of compound **4e**

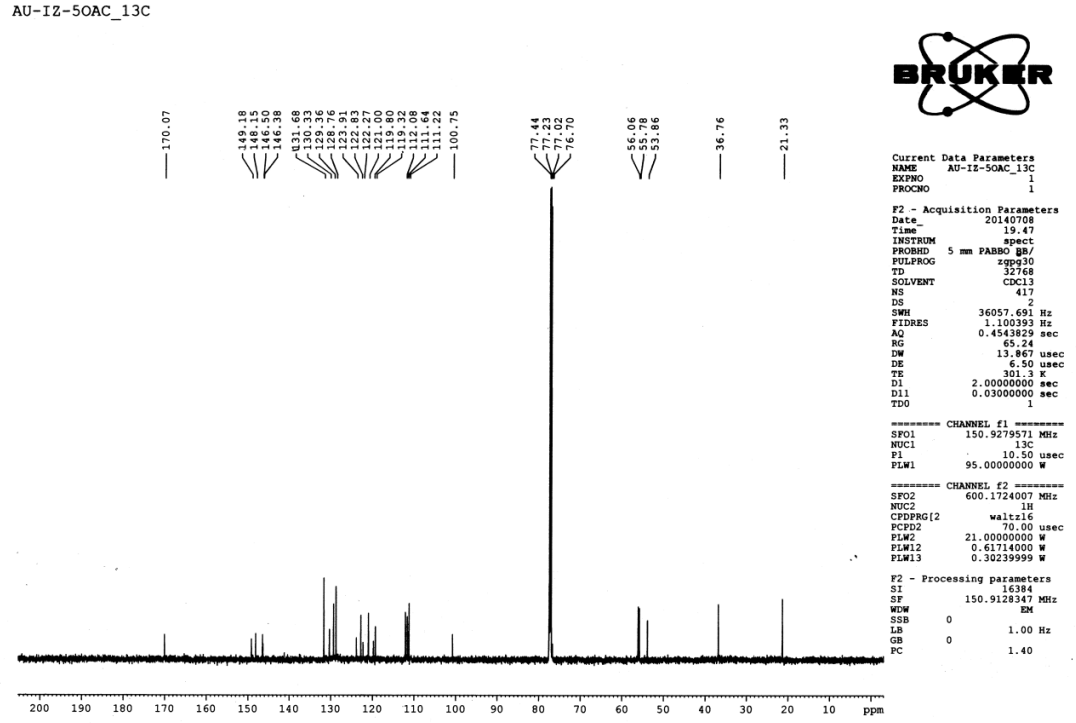




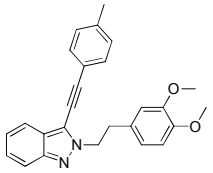


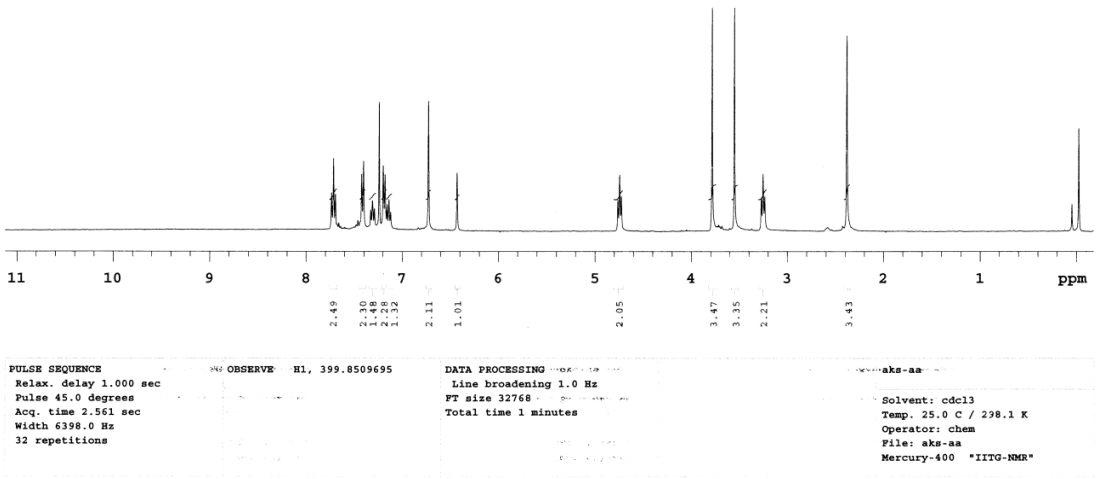
^{1}H and ^{13}C spectra of compound **4f**

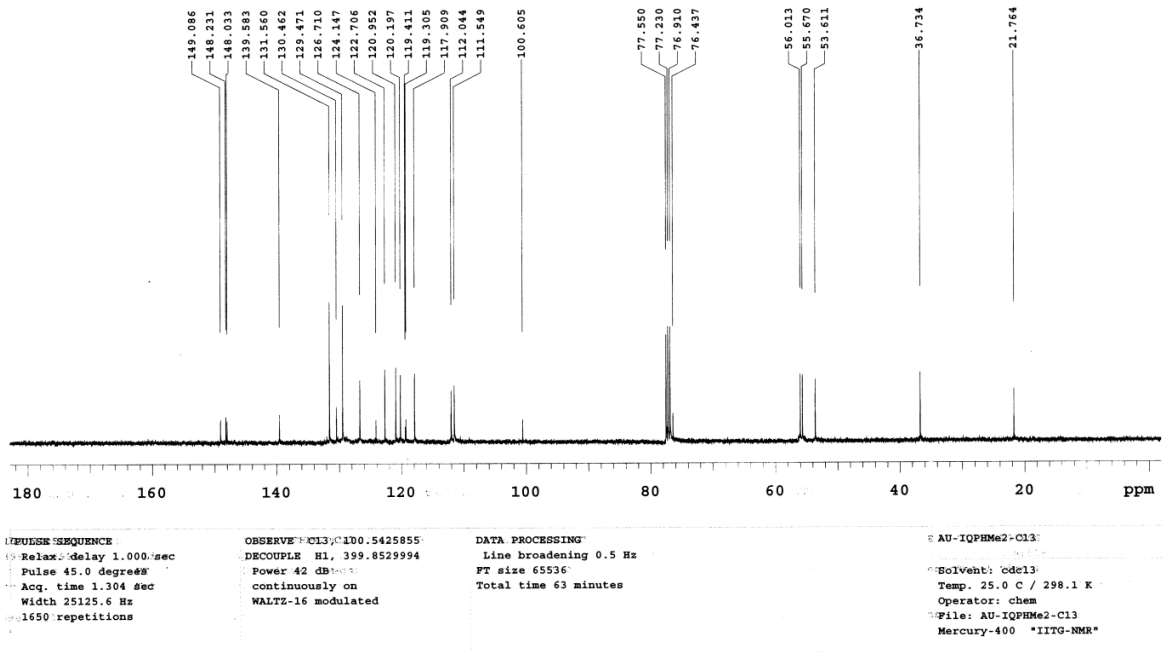




^{1}H and ^{13}C spectra of compound **4g**

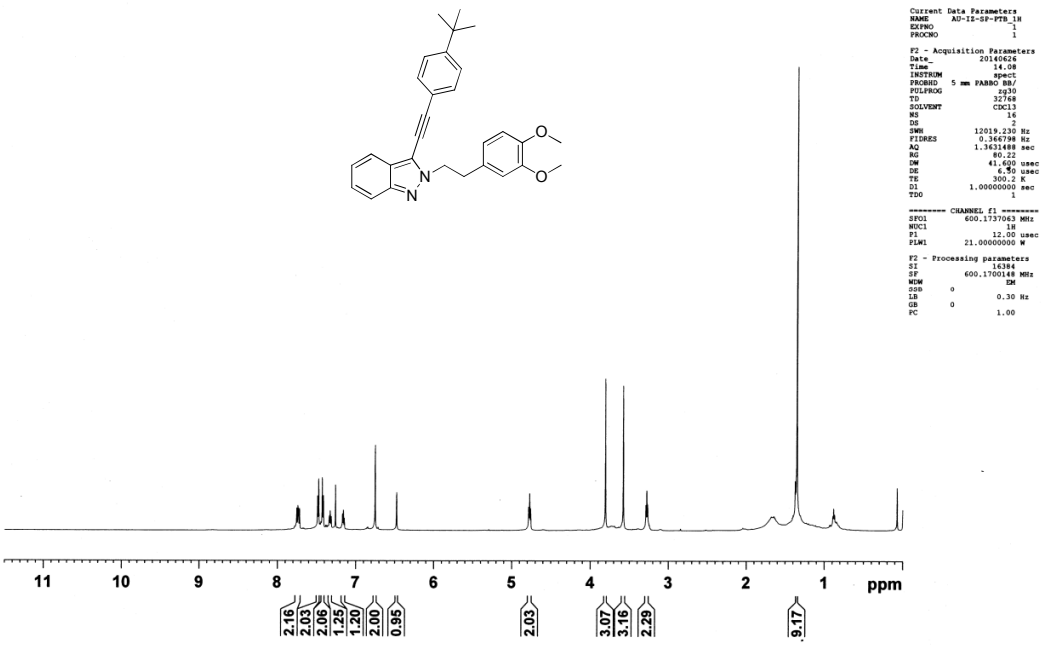




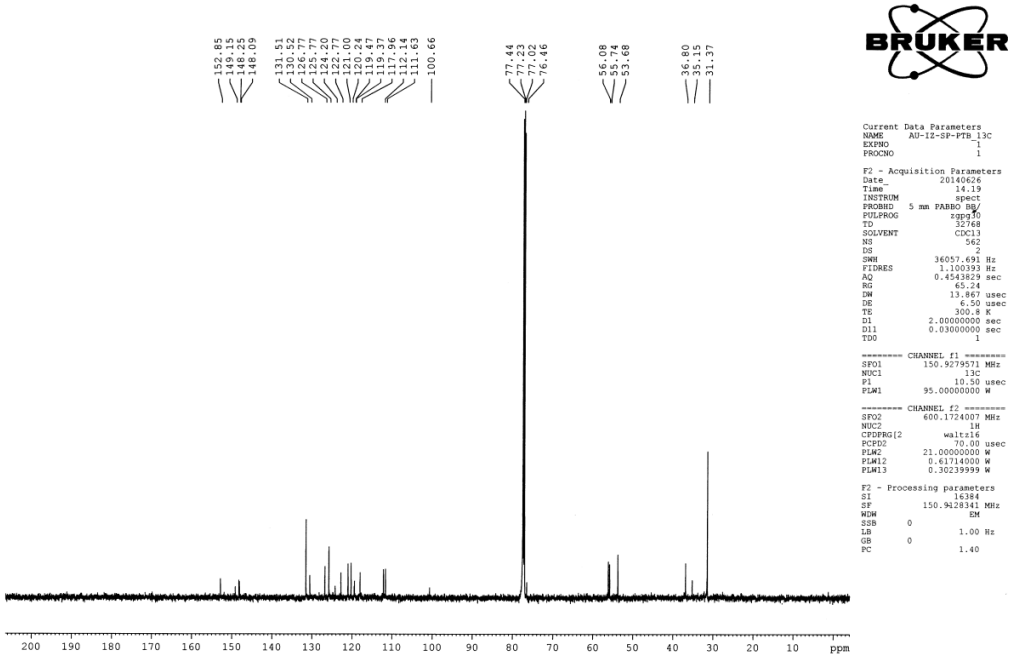


^{1}H and ^{13}C spectra of compound **4h**

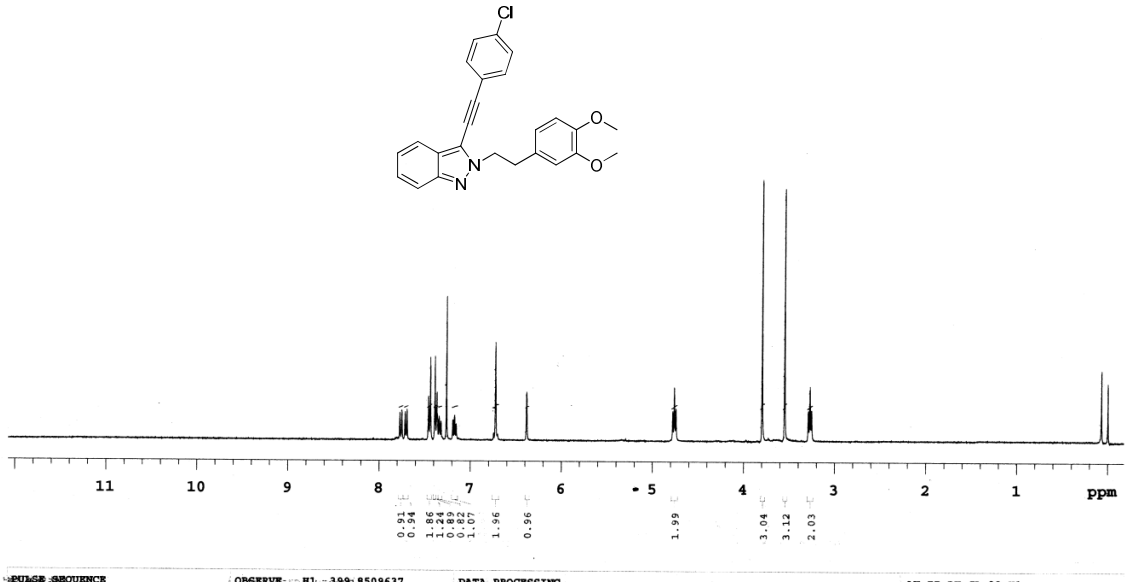
AU-IZ-SP-PTB_1H

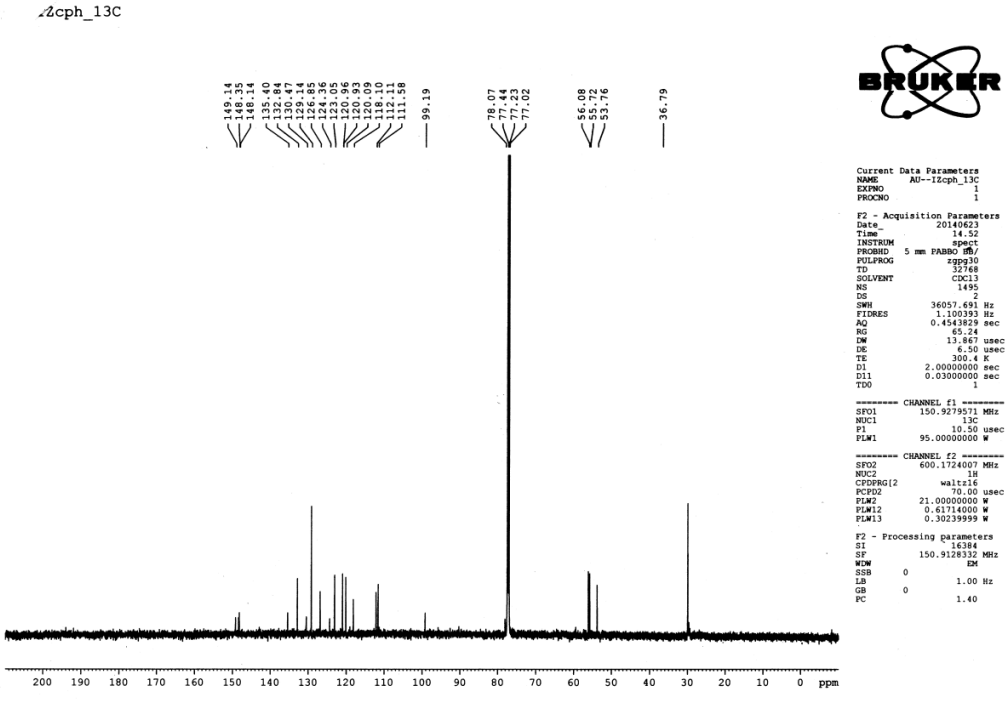


AU-IZ-SP-PTB_13C

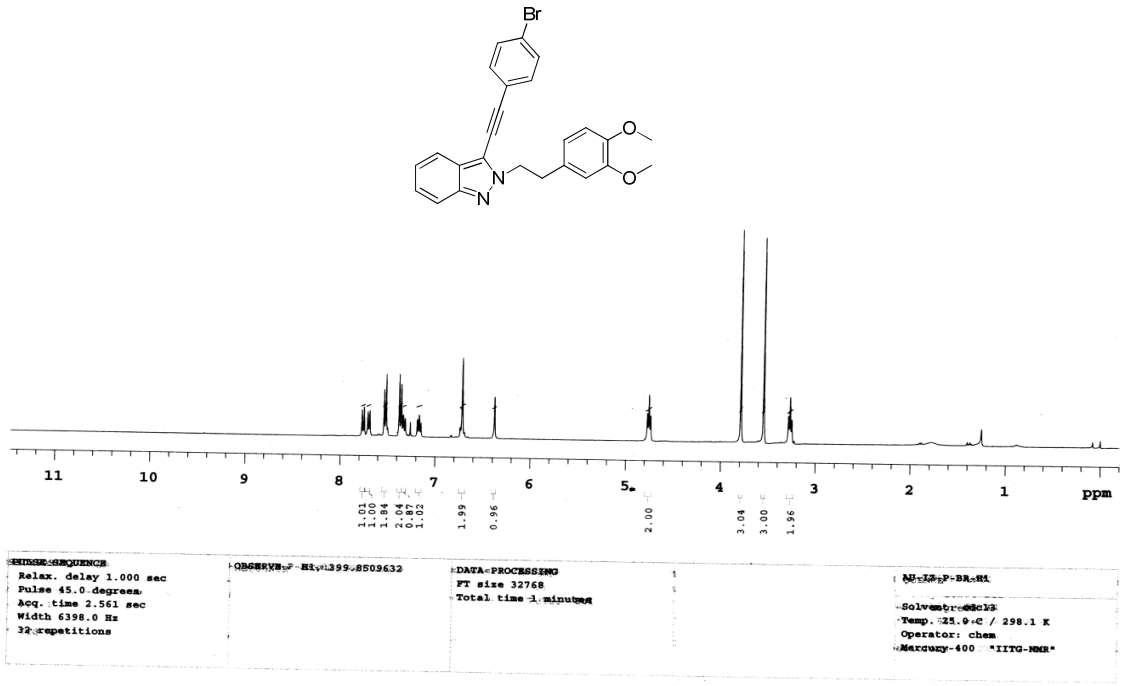


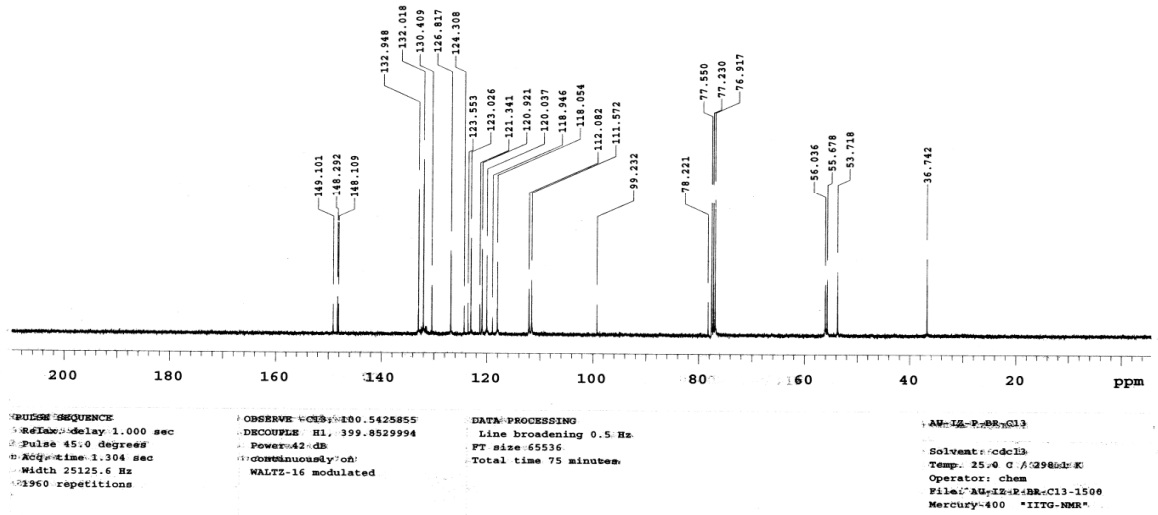
^{1}H and ^{13}C spectra of compound **4i**



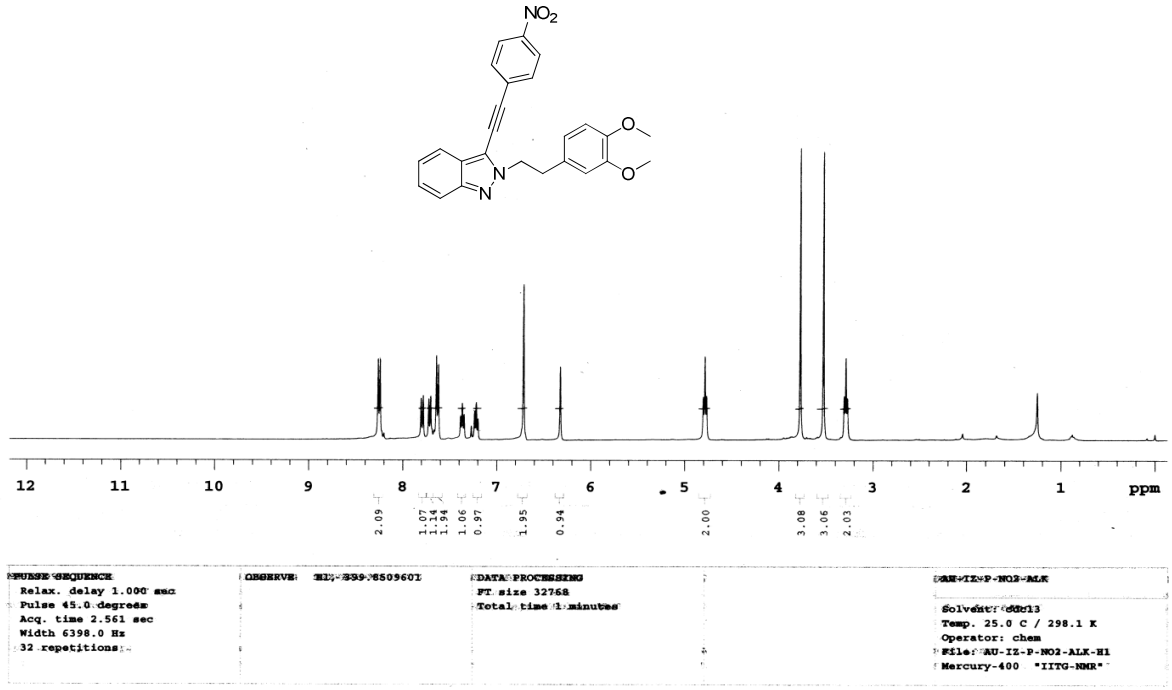


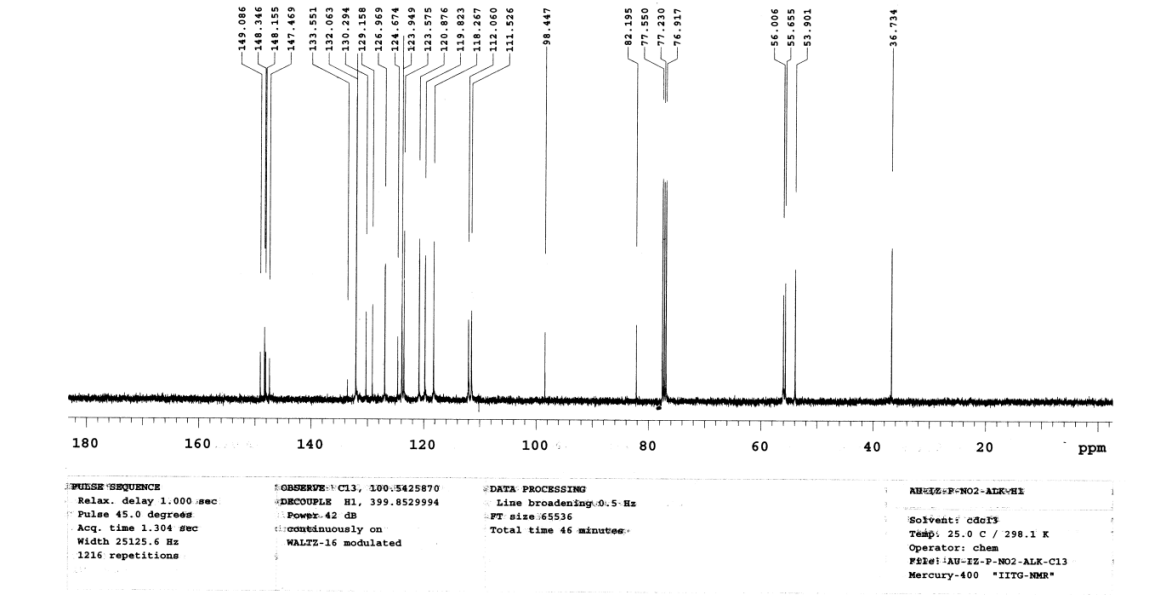
^{1}H and ^{13}C spectra of compound **4j**



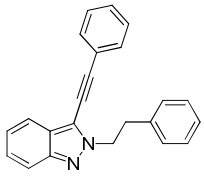


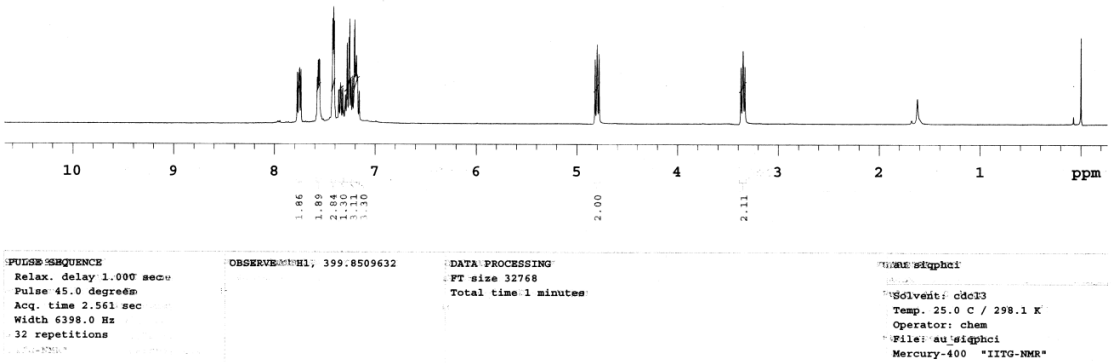
^{1}H and ^{13}C spectra of compound **4k**

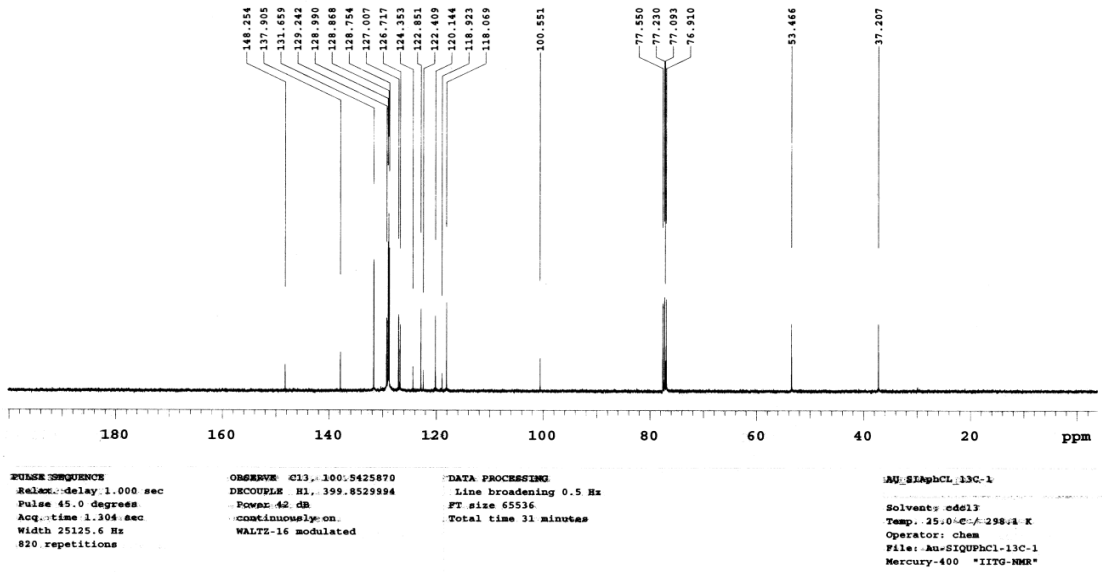




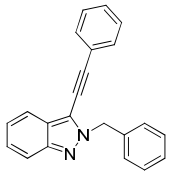
^{1}H and ^{13}C spectra of compound **4l**

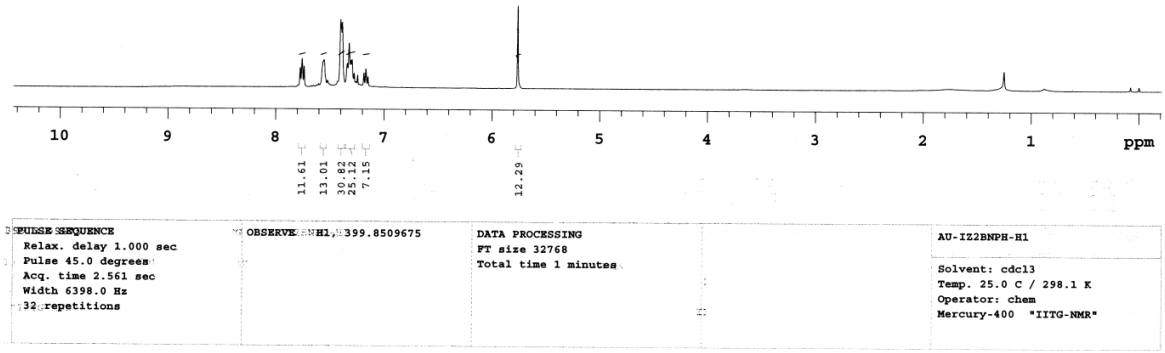


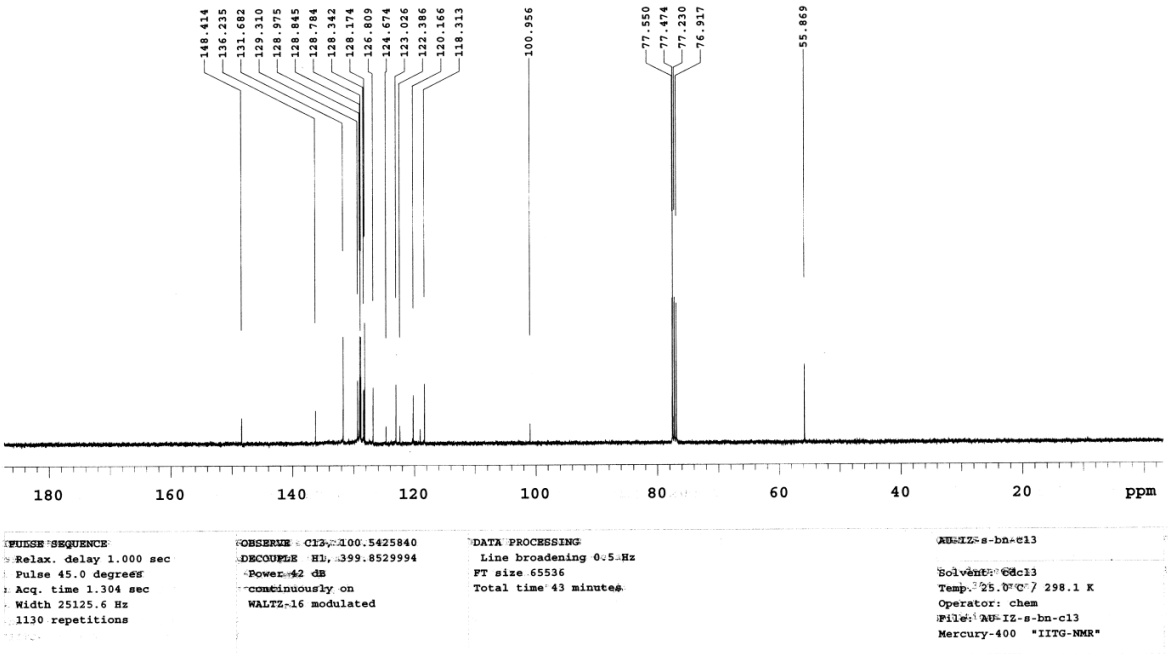




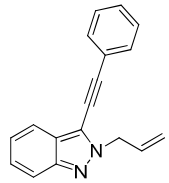
^{1}H and ^{13}C spectra of compound **4m**

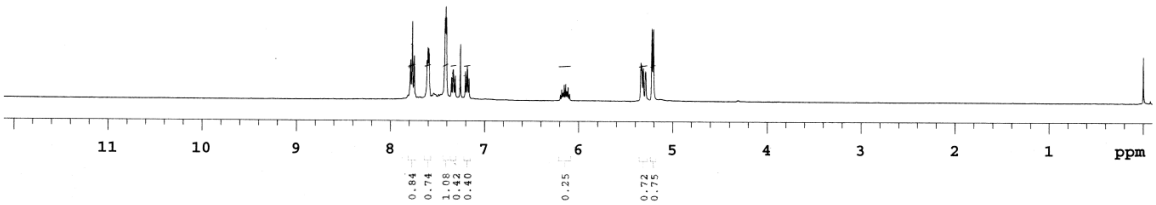






^{1}H and ^{13}C spectra of compound **4n**





PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.561 sec
Width 6398.0 Hz
32 repetitions

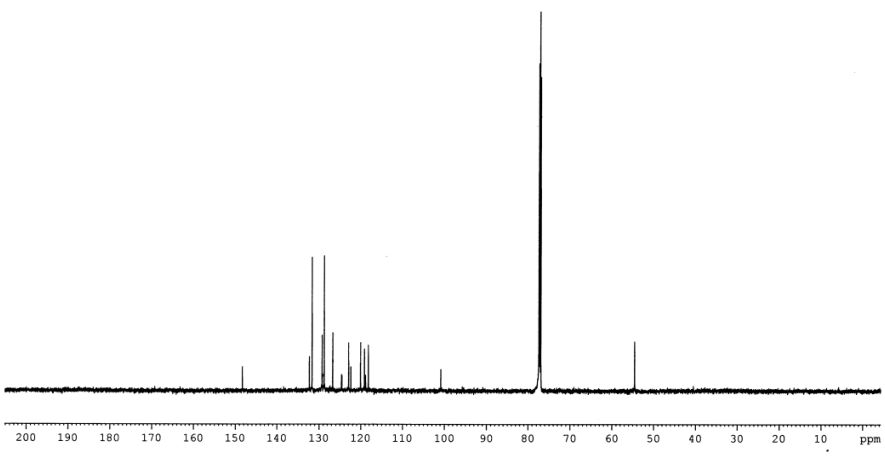
OBSERVE H1, 399.8509636

DATA PROCESSING
FT size 32768
Total time 1 minutes

Au-IZ-AL

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
File: Au-IZ-AL
Mercury-400 "IITG-NMR"

IZ-AL_13C



BRUKER

Current Data Parameters
NAME AU-IZ-AL_13C
EXPNO 1
PROCNO 1

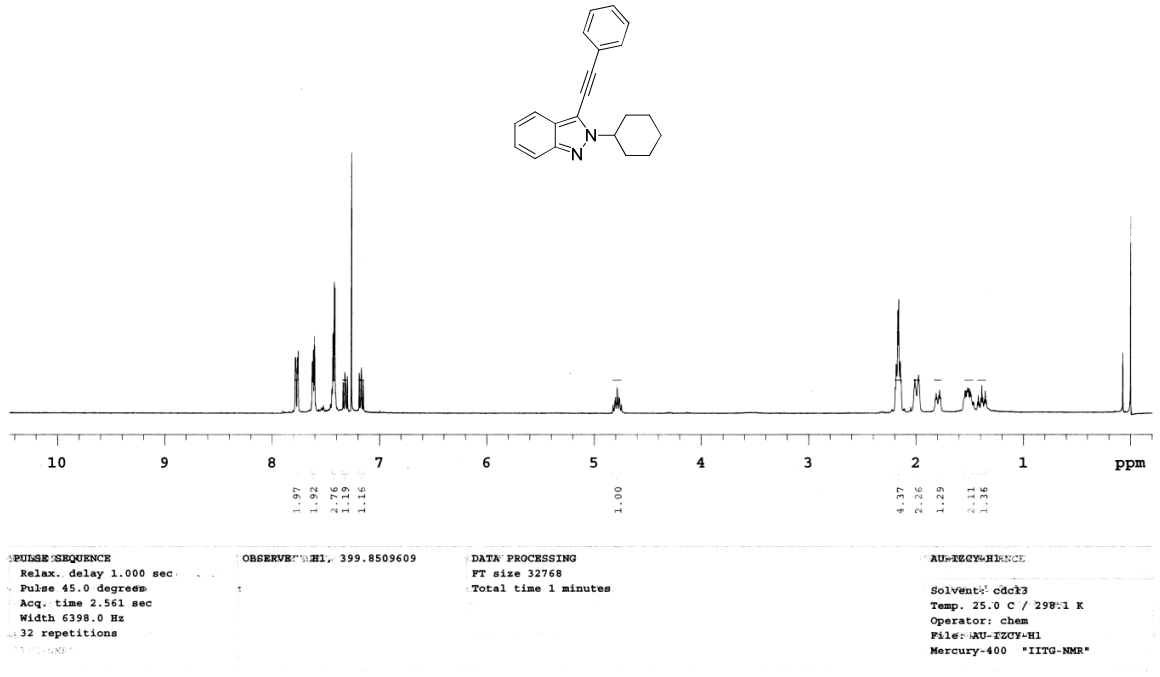
F2 - Acquisition Parameters
Date_ 20140401
Time 16.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 716
DS 2
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4543829 sec
RG 65.24
DW 13.867 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

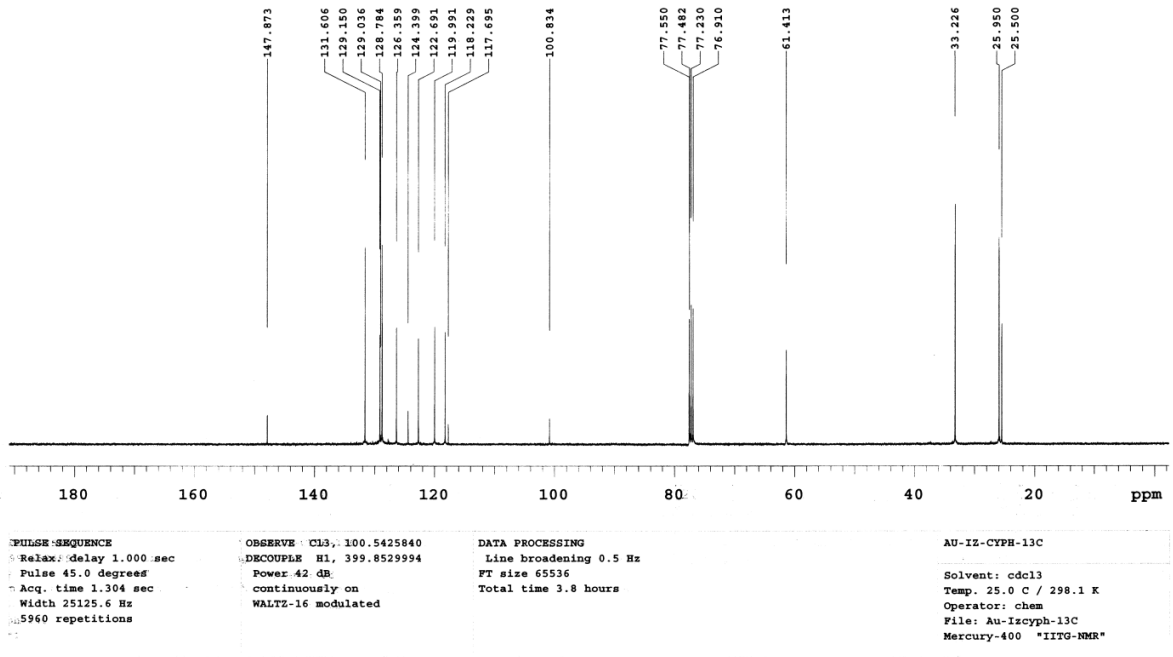
======== CHANNEL f1 ========
SFO1 150.9279571 MHz
NUC1 13C
P1 10.50 usec
PLW1 95.00000000 W

======== CHANNEL f2 ========
SFO2 600.1724007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 21.00000000 W
PLW12 0.61714000 W
PLW13 0.30239999 W

F2 - Processing parameters
SI 16384
SF 150.9128348 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

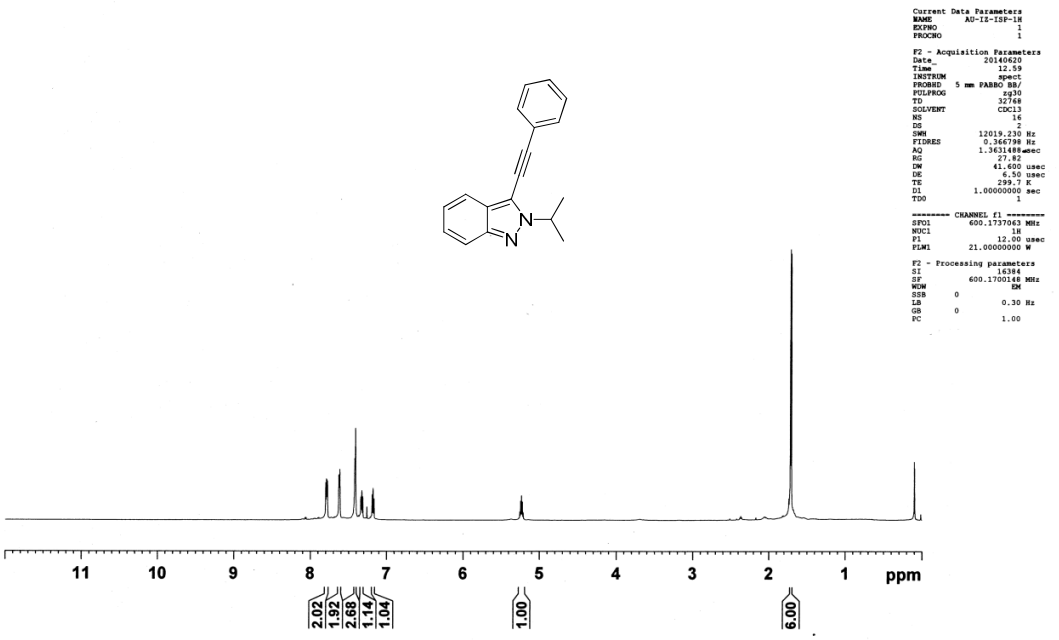
^{1}H and ^{13}C spectra of compound **4o**



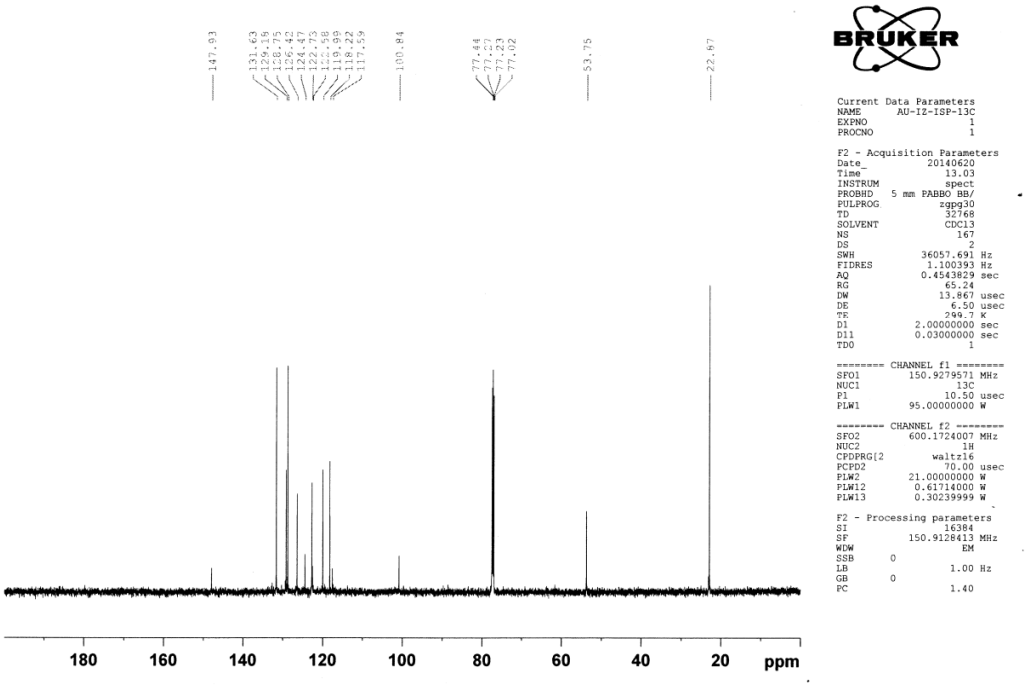


^{1}H and ^{13}C spectra of compound **4p**

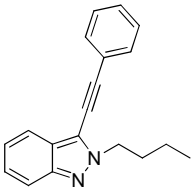
AU-IZ-ISP-1H

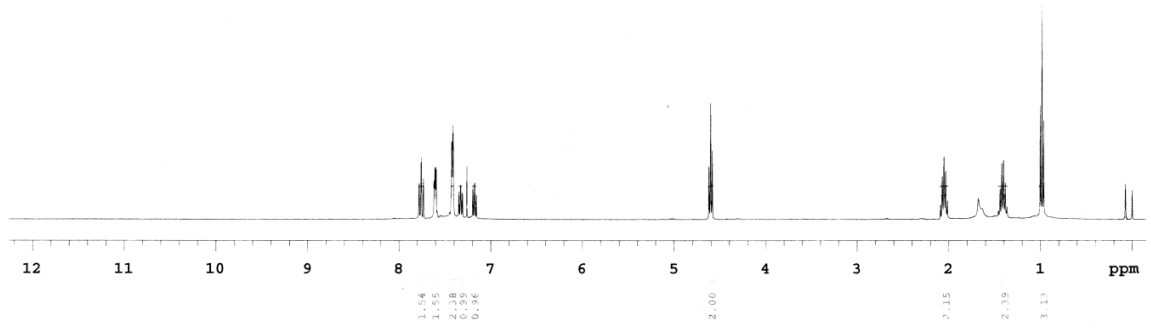


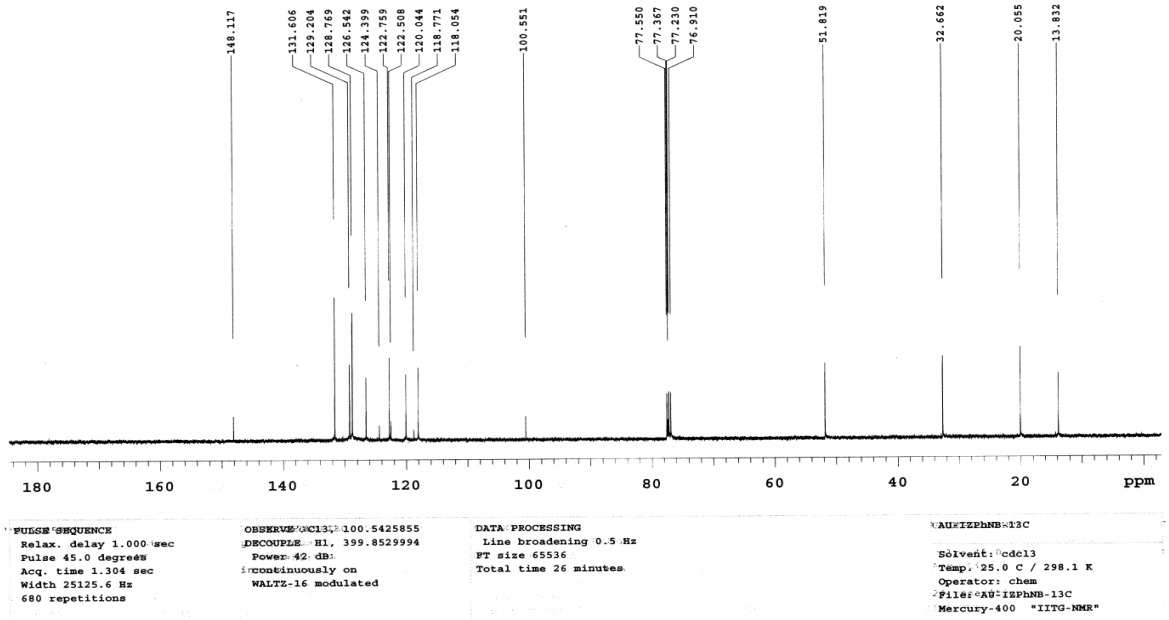
AU-IZ-ISP-13C



^{1}H and ^{13}C spectra of compound **4q**

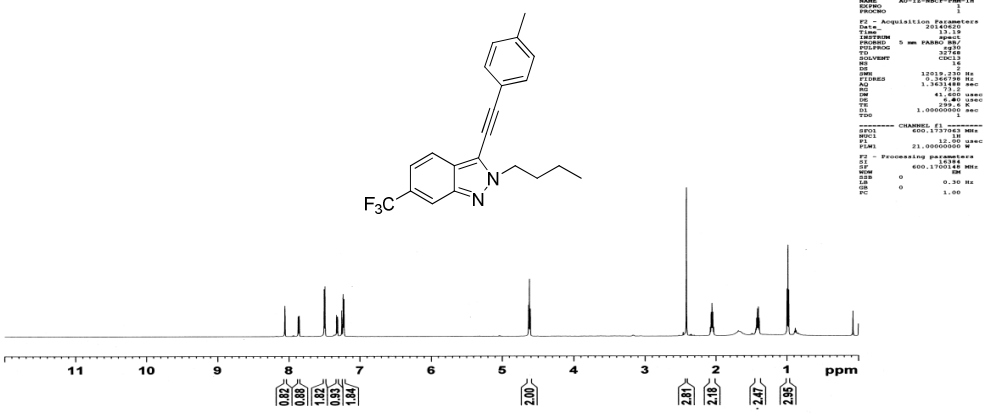




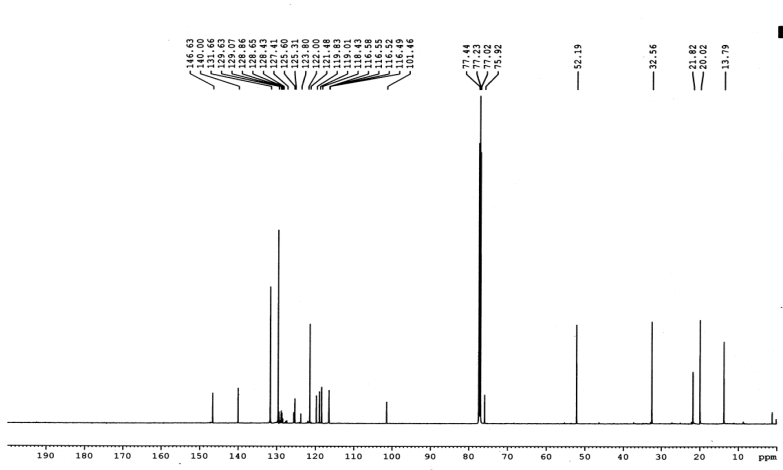


^{1}H, ^{13}C and ^{19}F spectra of compound **4r**

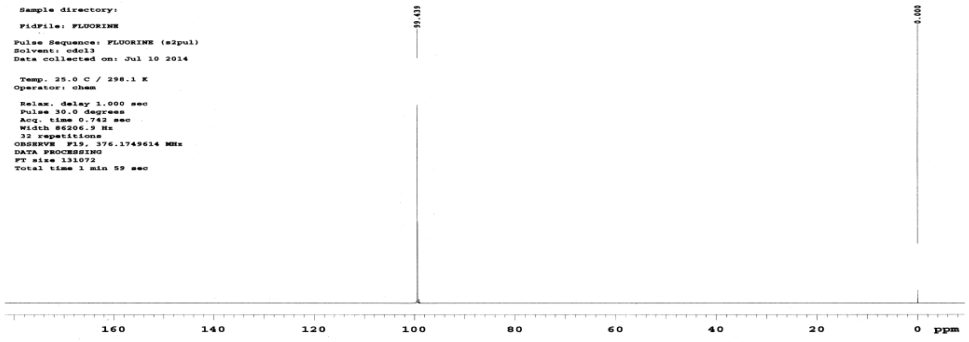
AU-IZ-NBCF-PHM-1H



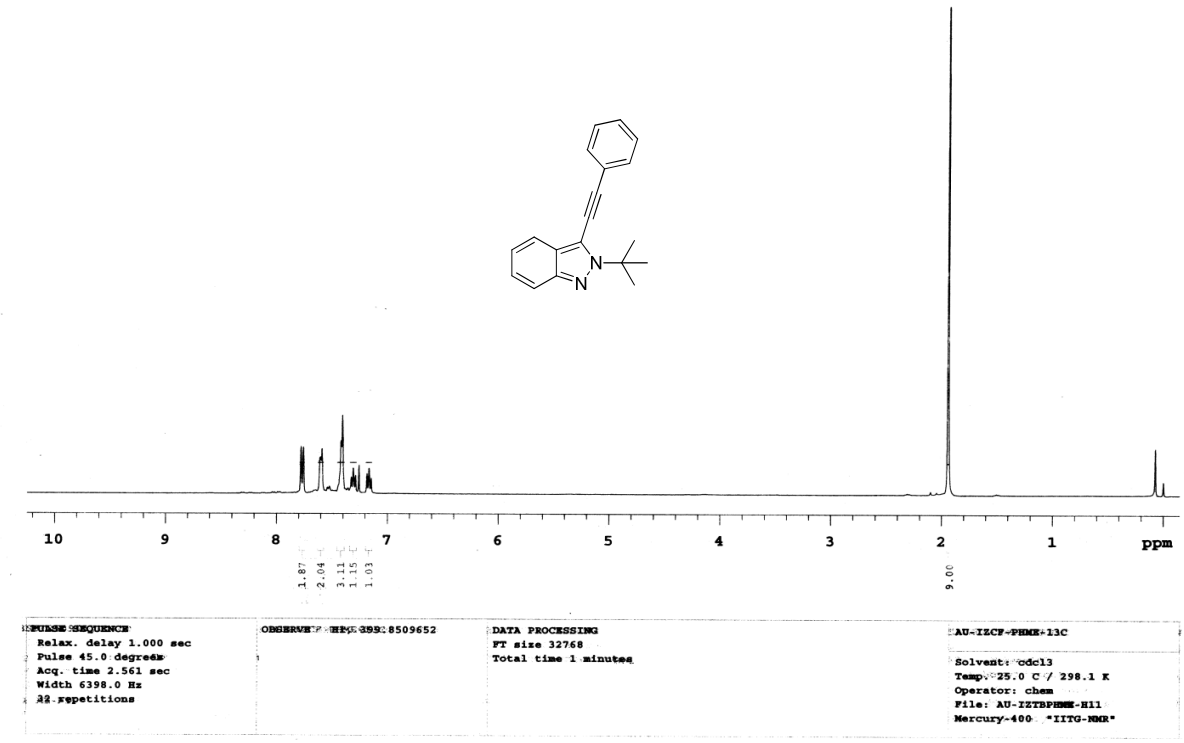
AU-NB-CF3-SP-Ph_13C

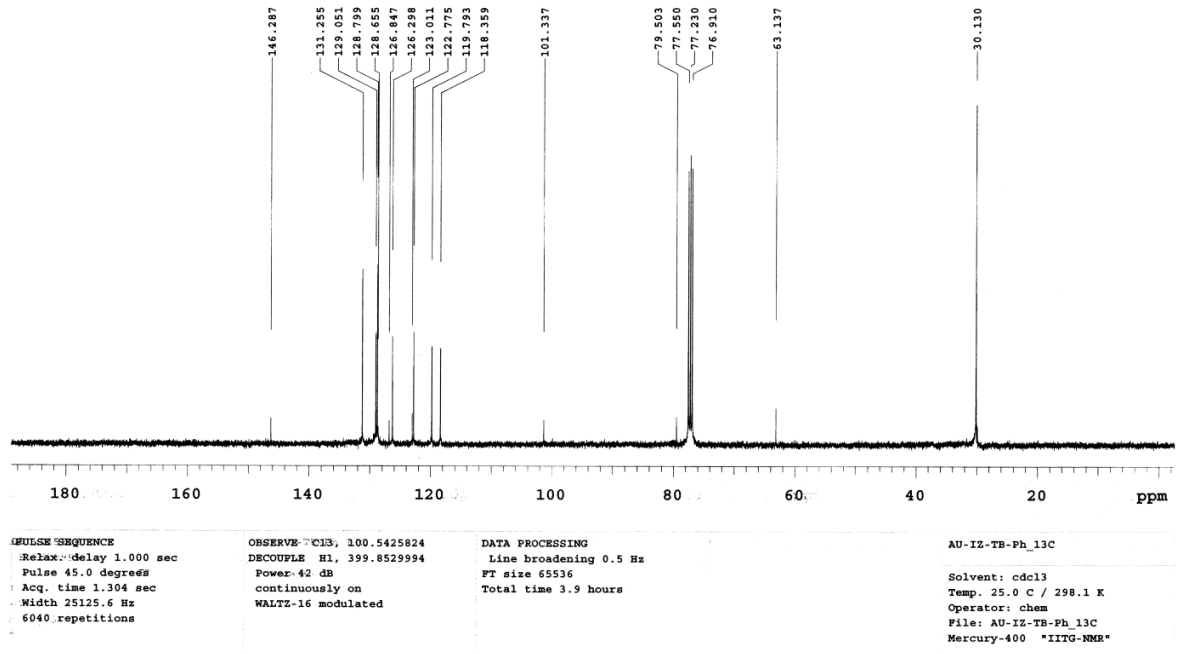


AU-IZ-NB-CF-FMNR

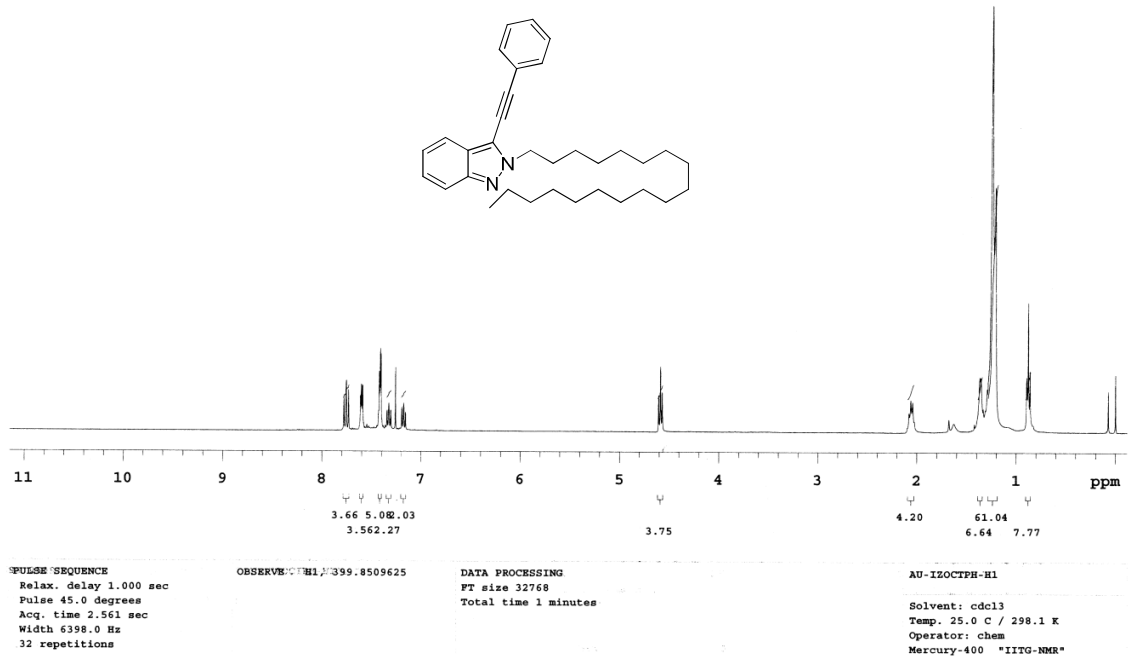


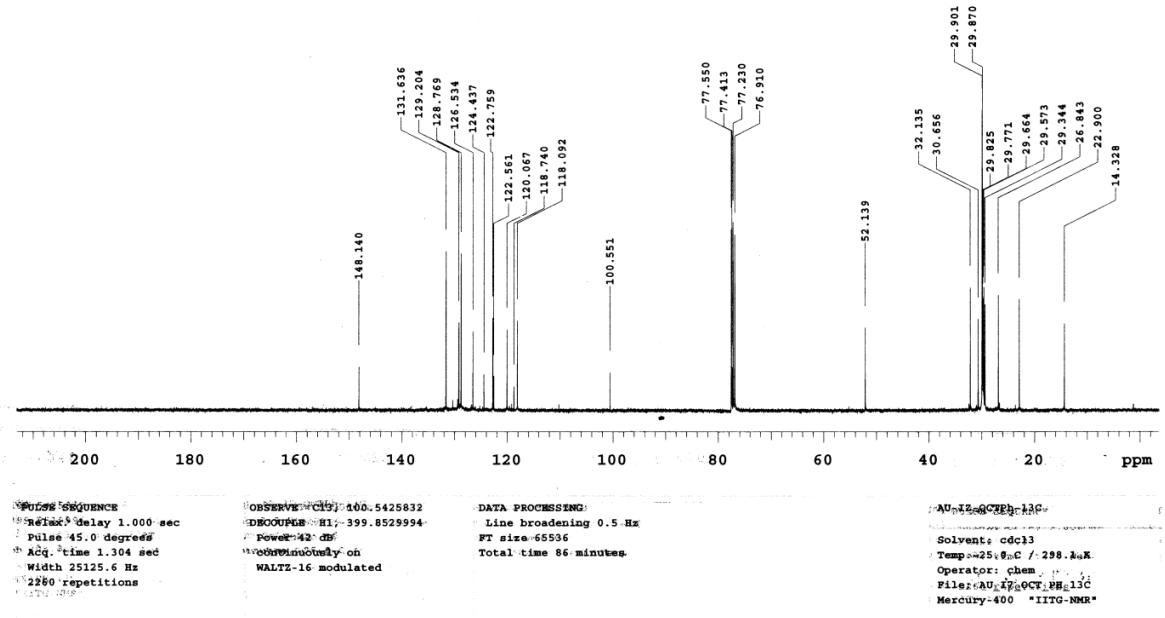
^{1}H and ^{13}C spectra of compound **4s**





^{1}H and ^{13}C spectra of compound **4t**





The crystal parameters of compound **4a**

	4a- CCDC1008821
Formula	$C_{25}H_{22}N_2O_2$
Formula weight	382.45
T/K	296(2)
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
a/Å	5.1346(2)
b/Å	15.0120(4)
c/Å	26.4598(7)
α/º	90.00
β/º	90.00
γ/º	90.00
V/Å^3	2039.54(11)
Z	4
Abs. Coeff./mm^{-1}	0.080
Abs. Correction	Multi-scan
GOF on F^2	1.299
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.0335 *wR2* = 0.0707
R indices [all data]	*R1* = 0.0371 *wR2* = 0.0719

ORTEP diagram of **4a**