Supporting Information

Palladium-Catalyzed Oxidative Alkynylation of Heterocycles with Terminal Alkynes under Air Conditions

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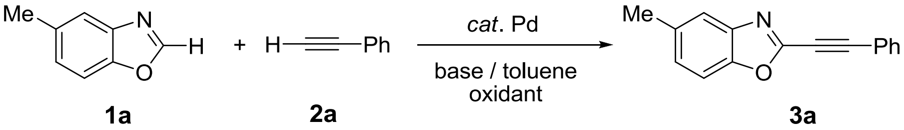
General Methods. Unless otherwise stated, all commercial reagents and solvents were used without additional purification, and atmospheric air was directly used for performing the oxidative alkynylation reaction. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with ceric ammonium molybdate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent. ^{1}H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. Agilent 6980 series GC system with Agilent 5974 network mass selective detector was used to determine GC yields. HP-35MS (Crosslinked 35% PH ME siloxane) was used as capillary column on GC-MS. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI or FAB methods.

Experimental Procedure for the Optimization of the Pd-Catalyzed Oxidative Alkynylation. To an oven dried Schlenk tube were added 5-methylbenzoxazole, palladium catalyst (5 mol %), ligand (11 mol % for a monodentate ligand, 5.5 mol % for a multidentate ligand), and base. The addition of phenylacetylene to the reaction vessel was followed by the addition of an anhydrous solvent (3 mL). The reaction mixture was stirred in a pre-heated oil bath at an indicated temperature for 12 h under Ar (No sealing was used when air was applied) and then cooled to ambient temperature, filtered through a pad of celite washing with dichloromethane (10 mL x 3). The solvents were removed under reduced pressure and the crude yield was measured by NMR using 1,3-benzodioxole as an internal standard. The crude reaction mixture was purified by flash chromatography on silica gel (hexane/EtOAc, 30:1) as an eluent to give the desired product.

Table S1. Optimization of the Pd-Catalyzed Oxidative Alkynylation[a]



entry	catalyst/ligand	oxidant	base	solvent	temp (°C)	yield (%)[b]
1	$Pd(OAc)_2$/2,2'-bipyridine	NBS	LiO-*t*-Bu	toluene	100	N.R.
2	$Pd(OAc)_2$/2,2'-bipyridine	$PhI(OAc)_2$	LiO-*t*-Bu	toluene	100	N.R.
3	$Pd(OAc)_2$/2,2'-bipyridine	benzoquinone	LiO-*t*-Bu	toluene	100	N.R.
4	$Pd(OAc)_2$/2,2'-bipyridine	*tert*-butylperoxide	LiO-*t*-Bu	toluene	100	<5
5	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	30
6	$Pd(OAc)_2$/2,2'-bipyridine	air (1 atm)	LiO-*t*-Bu	toluene	100	18
7	$Pd(OAc)_2$/terpyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	26
8	$Pd(OAc)_2$/4,4'-dimethoxy-2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	23
9	$Pd(OAc)_2$/TMEDA	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	19
10	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiOAc	toluene	100	N.R.
11	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	Li_2CO_3	toluene	100	N.R.
12	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	KO-*t*-Bu	toluene	100	N.R.
13	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	KOAc	toluene	100	N.R.
14	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	chlorobenzene	100	30
15	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	1,4-dioxane	100	N.R.
16	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	DMF	100	N.R.
17	$Pd(OAc)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	DMA	100	N.R.
18	$PdCl_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	<5
19	$Pd(acac)_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	<5
20	$[Pd(C_3H_5)Cl]_2$/2,2'-bipyridine	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	15
21	$PdCl_2(PPh_3)_2$	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	28
22	$PdCl_2(PhCN)_2$	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	25
23	$Pd(PPh_3)_4$	O_2 (1 atm)	LiO-*t*-Bu	toluene	100	38
24	$Pd(PPh_3)_4$	air (1 atm)	LiO-*t*-Bu	toluene	100	50 (0.08 mmol)[e]
25[c]	$Pd(PPh_3)_4$	air (1 atm)	LiO-*t*-Bu	toluene	100	67[f]
26[d]	$Pd(PPh_3)_4$	air (1 atm)	LiO-*t*-Bu	toluene	100	74[f]
27	$Pd_2(dba)_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	<5
28	$Pd(dba)_2$	air (1 atm)	LiO-*t*-Bu	toluene	100	<5

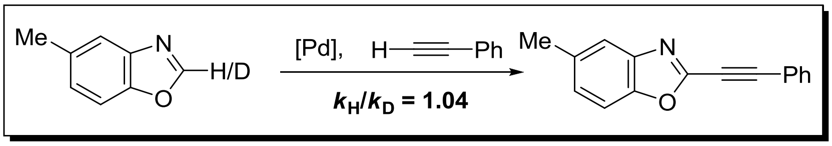
29	$Pd(dba)_2/PPh_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	44
30	$Pd(dba)_2$/P(*o*-Tolyl)$_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	10
31	$Pd(dba)_2/P[(2\text{-}MeO)C_6H_4]_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	46
32	$Pd(dba)_2$/P(2-Furyl)$_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	30
33	$Pd(dba)_2/OPPh_3$	air (1 atm)	LiO-*t*-Bu	toluene	100	20
34	$Pd(PPh_3)_4$	air (1 atm)	LiO-*t*-Bu	toluene	80	10
35	$Pd(PPh_3)_4$	air (1 atm)	LiO-*t*-Bu	xylene	130	<5
36	none	air (1 atm)	LiO-*t*-Bu	toluene	100	N.R.

[a] **1a** (1.5 equiv), **2a** (0.5 mmol), palladium catalyst (5 mol %), ligand (bi- or tri-dentate: 5.5 mol %, monodentate: 11 mol %), base (2 equiv), oxidant (2 equiv, O_2 and air: 1 atm) and solvent (3 mL) for 12 h. [b] NMR yield. N.R. indicates no reaction. [c] **1a** (2 equiv) and base (3 equiv). [d] **1a** (3 equiv) and base (4 equiv). [e] Amount of $OPPh_3$ (measured by GC). [f] Isolated yield.

General Procedure for the Pd-Catalyzed Oxidative Alkynylation of Heterocycles. To an oven dried Schlenk tube were added heterocycle (1.5 mmol), $Pd(PPh_3)_4$ (5 mol %) and LiO-*t*-Bu (2 mmol). The addition of terminal alkyne (0.5 mmol) to the reaction vessel was followed by the addition of anhydrous toluene (3 mL). [The procedure for the slow addition of alkyne: To the mixture of heterocycle, $Pd(PPh_3)_4$ and base in toluene (2 mL) was slowly added by syringe pump over 200 minutes alkyne in toluene (1 mL) under air at 100 ^{o}C.] The reaction mixture was stirred in a pre-heated oil bath at 100 ^{o}C for 12 h without any sealing to use air as an oxidant, and then cooled to ambient temperature. Saturated NH_4Cl (aq) solution (5 mL) was added to the reaction mixture. Organic layer was washed with saturated NH_4Cl (aq) solution (6 mL x 3) and combined water layer was extracted with diethyl ether (6 mL x 2). Combined organic layer was dried using Na_2SO_4 and filtered. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (hexane/EtOAc) to give the desired product.

Experimental Procedure for the KIE Study of the Pd-Catalyzed Oxidative Alkynylation of 5-Methylbenzoxazole Using Deuterated Oxazole. Two sets of reactions were prepared and carried out in a parallel manner, in each case phenylacetylene was allowed to react with 5-methylbenzoxazole and 2-deuterio-5-methylbenzoxazole,[1] respectively. The conversion was measured carefully after designated time (10 min, 20 min, 30 min, and 40 min) by isolation to compare the initial reaction rates.

Table S2. Conversion (%) of the Reaction of 5-Methylbenzoxazole (2-H and 2-D) with Phenylacetylene.



reaction time	conversion (%) from the reaction with 5-methylbenzoxazole	conversion (%) from the reaction with 2-deuterio-5-methylbenzoxazole
0 min	0	0
10 min	11	6
20 min	17	16
30 min	25	21
40 min	31	29

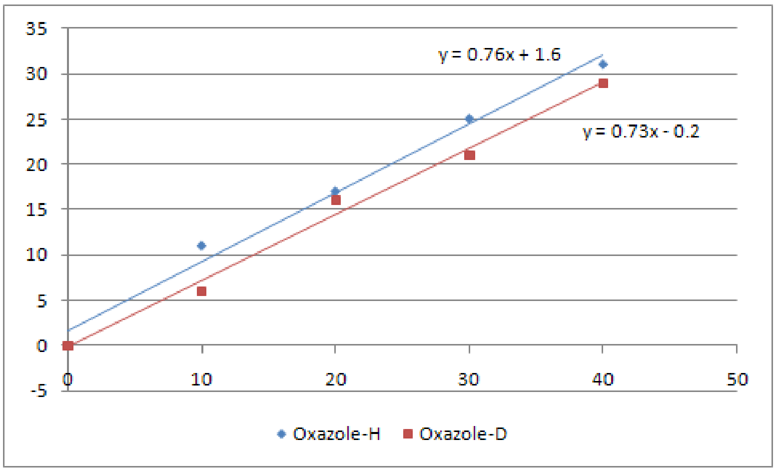


Figure S1. Conversion (%) *versus* Time (min).

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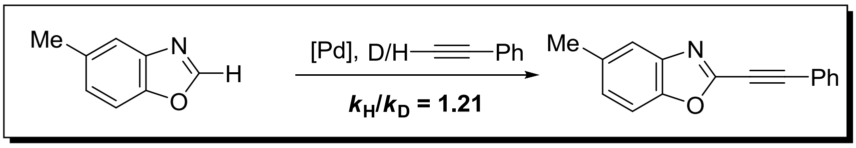
[1] For the synthesis of 2-deuterated oxazoles, see: Crowe, E.; Hossner, F.; Hughes, M. J. *Tetrahedron* **1995**, *51*, 8889.

Experimental Procedure for the KIE Study of the Pd-Catalyzed Oxidative Alkynylation of 5-Methylbenzoxazole Using Deuterated Alkyne. Two sets of reactions were prepared and carried out in a parallel manner, in each case 5-methylbenzoxazole was allowed to react with phenylacetylene and phenylacetylene-*d* respectively. The conversion was measured carefully after designated time (10 min, 20 min, 30 min, and 40 min) by isolation to compare the initial reaction rates.

Table S3. Conversion (%) of the Reaction of 5-Methylbenzoxazole with Phenylacetylene (1-H and 1-D).



reaction time	conversion (%) from the reaction with phenylacetylene	conversion (%) from the reaction with phenylacetylene-*d*
0 min	0	0
10 min	11	11
20 min	17	17
30 min	25	22
40 min	31	26

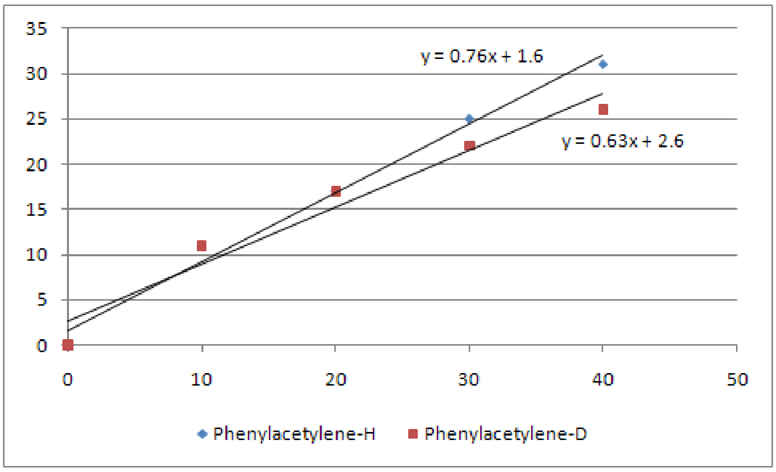


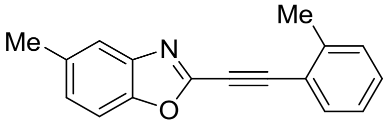
Figure S2. Conversion (%) *versus* Time (min).

Experimental Procedure for the Synthesis of 4-(4-Trifluoromethyl phenyl)oxazole.[2] To an oven dried Schlenk tube were added 2-bromo-4’-(trifluoromethyl)-acetophenone (2 mmol) and formamide (40 mmol). The mixture was stirred in a pre-heated oil bath (130 °C) for 12 h and then cooled to ambient temperature. Water (5 mL) and dichloromethane (5 mL) were added and water layer was extracted with dichloromethane (5 mL x 3). The organic layer was dried using Na_2SO_4 and the solvents were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (hexane:EtOAc, 10/1) as an eluent to give 4-(4-trifluoromethyl phenyl)oxazole in 9% yield.

Experimental Procedure for the Proton and Deuterium Exchange Experiment (Scheme 5). To an oven dried Schlenk tube were added 5-methylbenzoxazole (0.5 mmol), LiO-*t*-Bu (1 mmol), phenylacetylene-*d* (0.5 mmol) and toluene (3 mL). The reaction mixture was stirred in a pre-heated oil bath at 100 °C for 12 h without any sealing, and then cooled to ambient temperature. Saturated NH_4Cl (aq) solution (5 mL) was added to the reaction mixture. Organic layer was washed with saturated NH_4Cl (aq) solution (6 mL x 3) and combined water layer was extracted with diethyl ether (6 mL x 2). Combined organic layer was dried using Na_2SO_4 and filtered. The solvents were removed under reduced pressure and the crude NMR was measured to determine the degree of deuterium incorporation.

Spectroscopic Data for New Compounds

2-(2-Methylphenylethynyl)-5-methylbenzoxazole (Table 2, entry 2):



Light yellow solid (m.p.: 106 ~ 107 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 1H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.39–7.17 (m, 5H), 2.55 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 147.9, 141.6, 141.3, 134.9, 132.8, 130.2, 129.7, 127.4, 125.8, 120.1, 109.9, 92.2, 81.2, 21.4, 20.6; IR (NaCl) ν 3059, 2924, 2359, 2218, 1544, 1456, 1303, 1156, 955, 769, 701, 596 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{13}NO$ $[M]^+$: 247.0097, found: 247.1000.

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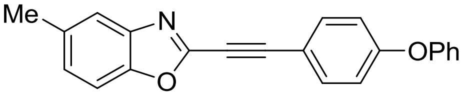
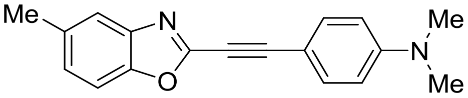
[2] Lafontaine, J. A.; Day, R. F.; Dibrino, J.; Hadcock, J. R.; Hargrove, D. M.; Linhares, M.; Martin, K. A.; Maurer, T. S.; Nardone, N. A.; Tess, D. A.; Dasilva-Jardine, P. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5245.

2-(4-Phenoxyphenylethynyl)-5-methylbenzoxazole (Table 2, entry 4):



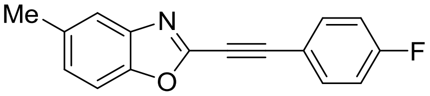
White solid (m.p.: 104 ~ 105 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, J = 8.9 Hz, 2H), 7.50 (m, 1H), 7.37–7.34 (m, 3H), 7.17–7.16 (m, 2H), 7.05–7.03 (m, 2H), 6.96 (d, J = 8.9 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.5, 155.5, 148.5, 147.8, 141.2, 134.8, 134.1, 129.9, 127.3, 124.4, 120.0, 119.9, 117.9, 114.2, 109.8, 93.0, 77.2, 21.3; IR (NaCl) ν 3044, 2359, 2215, 1589, 1542, 1417, 1303, 1244, 1148, 951, 837, 793, 689 cm^{-1}; HRMS (EI) m/z calcd. for $C_{22}H_{15}NO_2$ [M]$^+$: 325.1103, found: 325.1104.

2-(4-Dimethylaminophenylethynyl)-5-methylbenzoxazole (Table 2, entry 5):



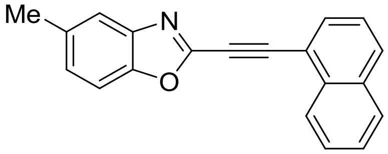
Yellow solid (m.p.: 136 ~ 137 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49–7.47 (m, 3H), 7.35–7.33 (m, 1H), 7.14–7.12 (m, 1H), 6.61–6.59 (m, 2H), 2.96 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.1, 148.6, 148.4, 141.4, 134.5, 133.7, 126.7, 119.7, 111.4, 109.6, 106.0, 95.8, 76.4, 39.8, 21.3; IR (NaCl) ν 2359, 2204, 1699, 1651, 1602, 1557, 1540, 1507, 1457, 1147, 668 cm^{-1}; HRMS (EI) m/z calcd. for $C_{18}H_{16}N_2O$ [M]$^+$: 276.1263, found: 276.1260.

2-(4-Fluorophenylethynyl)-5-methylbenzoxazole (Table 2, entry 8):



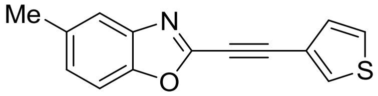
White solid (m.p.: 117 ~ 118 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63–7.59 (m, 2H), 7.50 (m, 1H), 7.38–7.36 (m, 1H), 7.20–7.17 (m, 1H), 7.09–7.05 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.9, 162.4, 148.5, 147.6, 141.2, 135.0, 134.6, 134.5, 127.5, 120.1, 116.4, 116.2, 116.0, 109.9, 92.0, 77.5, 21.4; IR (NaCl) ν 2359, 2222, 1699, 1599, 1499, 1301, 1230, 1150, 951, 834, 744, 594 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{10}FNO$ [M]$^+$: 251.0746, found: 251.0744.

2-(1-Naphthylethynyl)-5-methylbenzoxazole (Table 2, entry 9)



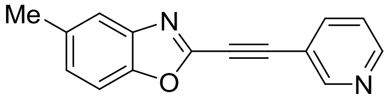
Orange solid (m.p.: 104 ~ 105 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45–8.43 (m, 1H), 7.89–7.86 (m, 3H), 7.62–7.40 (m, 5H), 7.20–7.18 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.8, 141.3, 134.9, 133.2, 132.9, 132.1, 130.8, 128.4, 127.5, 126.8, 125.8, 125.1, 120.1, 117.8, 109.9, 91.6, 82.2, 21.4; IR (NaCl) ν 2922, 2359, 2217, 1542, 1457, 1260, 1151, 949, 795, 773, 668, 595 cm^{-1}; HRMS (EI) m/z calcd. for $C_{20}H_{13}NO$ $[M]^+$: 283.0997, found: 283.0998.

2-(Thiophene-3-ylethynyl)-5-methylbenzoxazole (Table 2, entry 11):



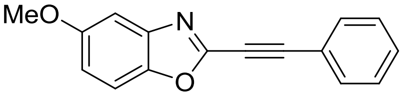
Light yellow solid (m.p.: 93 ~ 94 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.73 (m, 1H), 7.50–7.49 (m, 1H), 7.37–7.18 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 147.7, 141.2, 134.9, 132.4, 129.8, 127.4, 126.0, 120.1, 119.4, 109.8, 88.5, 77.4, 21.4; IR (NaCl) ν 3123, 2359, 2216, 1651, 1558, 1497, 1282, 1186, 1113, 965, 768, 627 cm^{-1}; HRMS (EI) m/z calcd. for $C_{14}H_9NOS$ $[M]^+$: 239.0405, found: 239.0406.

2-(Pyridine-3-ylethynyl)-5-methylbenzoxazole (Table 2, entry 12)



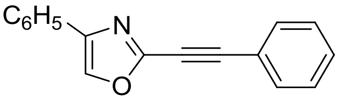
Light yellow solid (m.p.: 114 ~ 115 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86–8.85 (m, 1H), 8.65–8.63 (m, 1H), 7.91–7.89 (m, 1H), 7.52 (m, 1H), 7.41–7.20 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 150.3, 148.6, 147.1, 141.1, 139.2, 135.2, 127.9, 123.2, 120.3, 117.7, 110.0, 89.5, 80.7, 21.4; IR (NaCl) ν 3066, 2920, 2359, 2226, 1773, 1699, 1544, 1409, 1304, 1156, 955, 804, 699 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{10}N_2O$ $[M]^+$: 234.0793, found: 234.0789.

2-(Phenylethynyl)-5-methoxybenzoxazole (Scheme 2, **4d**):



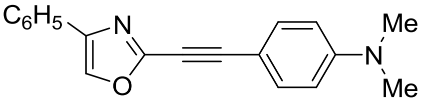
Light red solid (m.p.: 115 ~ 116 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.63 (m, 2H), 7.44–7.39 (m, 4H), 7.19 (d, *J* = 2.5 Hz, 1H), 7.01–6.98 (m, 1H) 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.4, 145.0, 142.0, 132.4, 130.3, 128.6, 120.3, 115.4, 110.8, 102.7, 93.3, 77.6, 56.0; IR (NaCl) ν 2359, 2341, 1699, 1558, 1436, 1273, 1200, 1159, 1024, 806, 668 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{11}NO_2$ [*M*]$^{+}$: 249.0790, found: 249.0787.

2-(Phenylethynyl)-4-phenyloxazole (Scheme 2, **4e**):



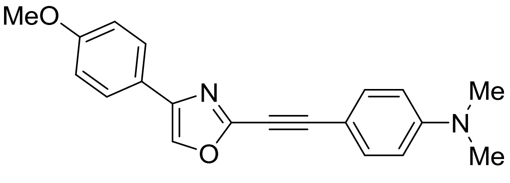
Light yellow solid (m.p.: 117 ~ 118 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.78–7.75 (m, 2H), 7.63–7.61 (m, 2H), 7.43–7.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.0, 134.3, 132.2, 130.2, 130.0, 128.8, 128.5, 125.6, 120.6, 91.7, 77.2; IR (NaCl) ν 3101, 2359, 2341, 2227, 1845, 1717, 1699, 1558, 1521, 1457, 1334, 1161, 1070, 944, 718 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{11}NO$ [*M*]$^{+}$: 245.0841, found: 245.0840.

2-(4-Dimethylaminophenylethynyl)-4-phenyloxazole (Scheme 2, **4f**):



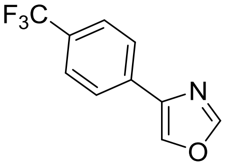
Yellow solid (m.p.: 131 ~ 132 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.78–7.75 (m, 2H), 7.49–7.31 (m, 5H), 6.64–6.61 (m, 2H), 2.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.8, 141.6, 133.7, 133.5, 130.5, 128.7, 128.2, 125.5, 111.5, 106.5, 93.9, 75.6, 39.9; IR (NaCl) ν 2359, 2341, 2211, 1717, 1699, 1612, 1557, 1541, 1151, 817, 668 cm^{-1}; HRMS (EI) m/z calcd. for $C_{19}H_{16}N_2O$ [*M*]$^{+}$: 288.1263, found: 288.1260.

2-(4-Dimethylaminophenylethynyl)-4-(4-methoxyphenyl)oxazole (Scheme 2, **4g**):



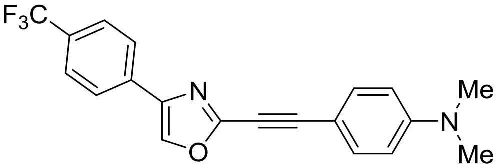
Brown solid (m.p.: 186 ~ 187 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.6, 151.0, 147.7, 141.5, 133.6, 132.7, 126.9, 123.2, 114.2, 111.6, 106.6, 93.7, 77.2, 75.7, 55.3, 40.0; IR (NaCl) ν 2359, 2212, 1699, 1651, 1613, 1557, 1541, 1257, 815 cm^{-1}; HRMS (EI) m/z calcd. for $C_{20}H_{18}N_2O_2$ $[M]^+$: 318.1368, found: 318.1370.

4-(4-Trifluoromethylphenyl)oxazole (Scheme 2, **1h**):



Light yellow solid (m.p.: 57 ~ 58 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 1H), 7.95 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.6, 139.3, 134.8, 134.2, 130.6, 130.3, 130.0, 129.6, 128.6, 128.1, 125.8, 125.7, 125.4, 122.7, 120.0; IR (NaCl) ν 3146, 2359, 1698, 1651, 1558, 1416, 1334, 1169, 1130, 1073, 850, 596 cm^{-1}; HRMS (EI) m/z calcd. for $C_{10}H_6F_3NO$ $[M]^+$: 213.0401, found: 213.0403.

2-(4-Dimethylaminophenylethynyl)-4-(4-trifluoromethylphenyl)oxazole (Scheme 2, **4h**):

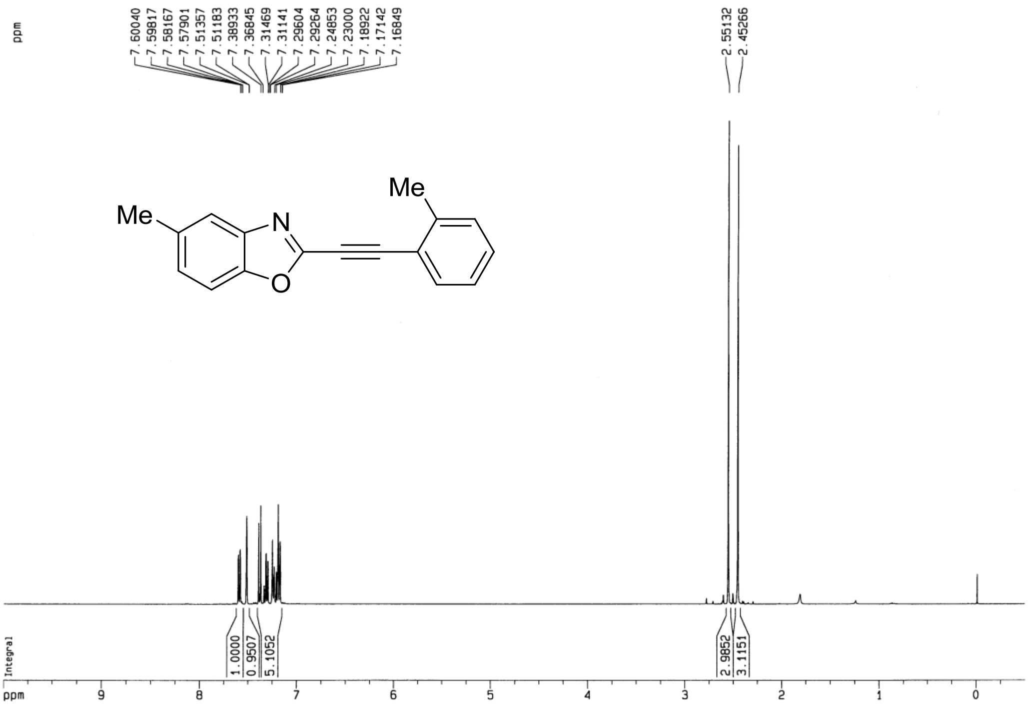


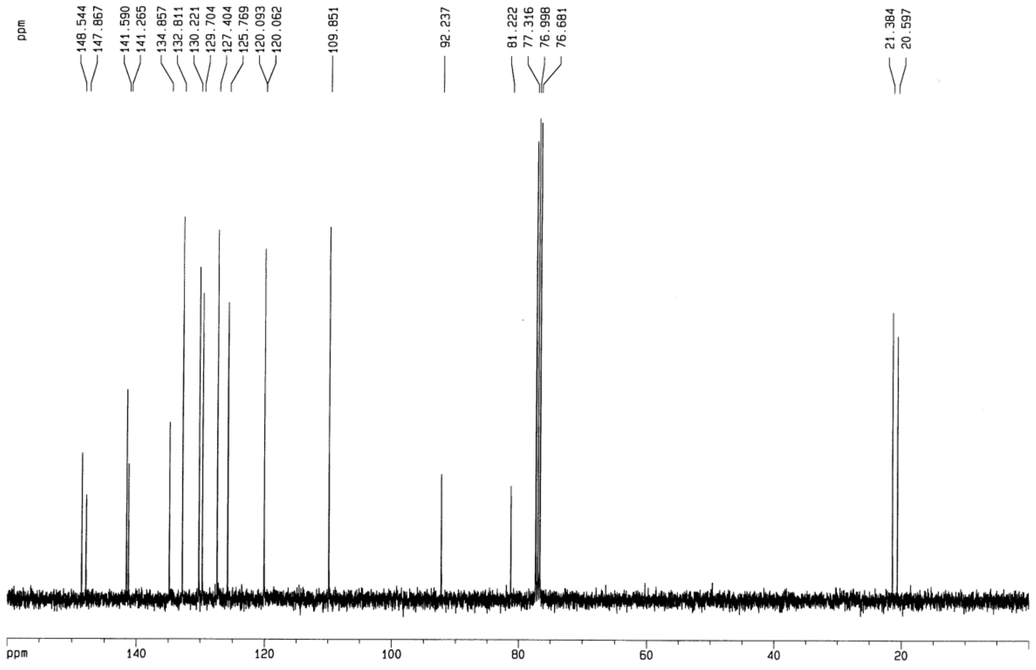
Beige solid (m.p.: 192 ~ 193 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.5, 151.0, 148.1, 140.4, 134.6, 133.9, 133.6, 130.5, 130.2, 129.8, 129.5, 128.0, 125.7, 125.6, 125.3, 122.6, 119.9, 111.5, 103.2, 94.4, 77.1, 75.3, 39.9; IR (NaCl) ν 2359, 2341, 2217, 1699, 1558, 1521, 1331, 1154, 950, 818, 668 cm^{-1}; HRMS (EI) m/z calcd. for $C_{20}H_{15}F_3N_2O$ $[M]^+$: 356.1136, found: 356.1136.

Appendix I

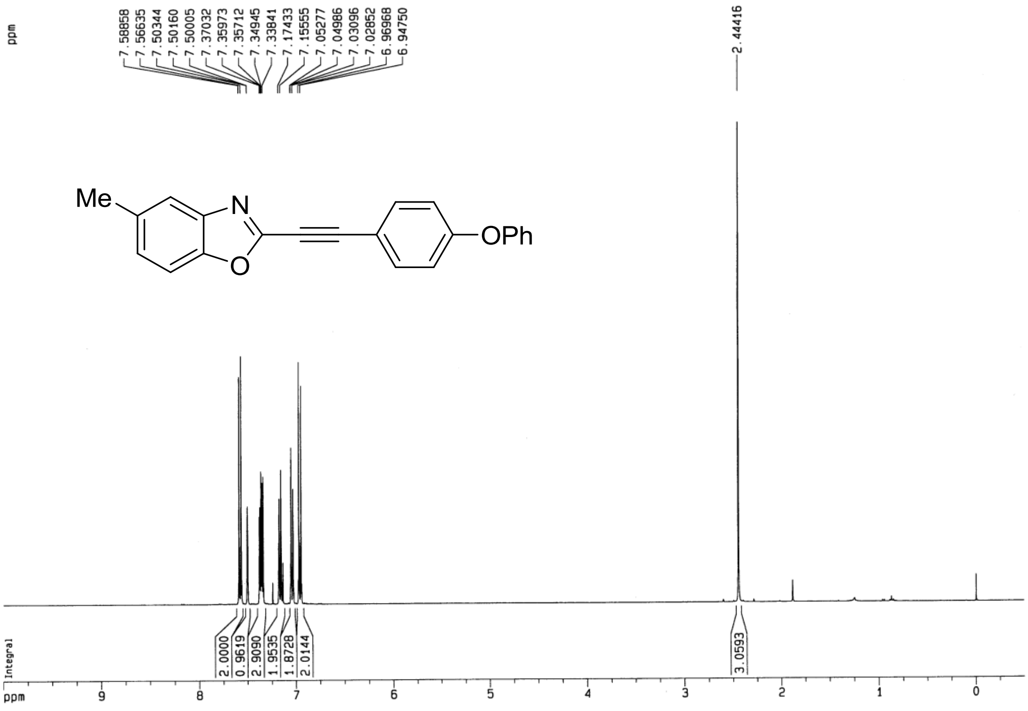
Spectral Copies of ^{1}H and ^{13}C NMR of New Compounds Obtained in This Study

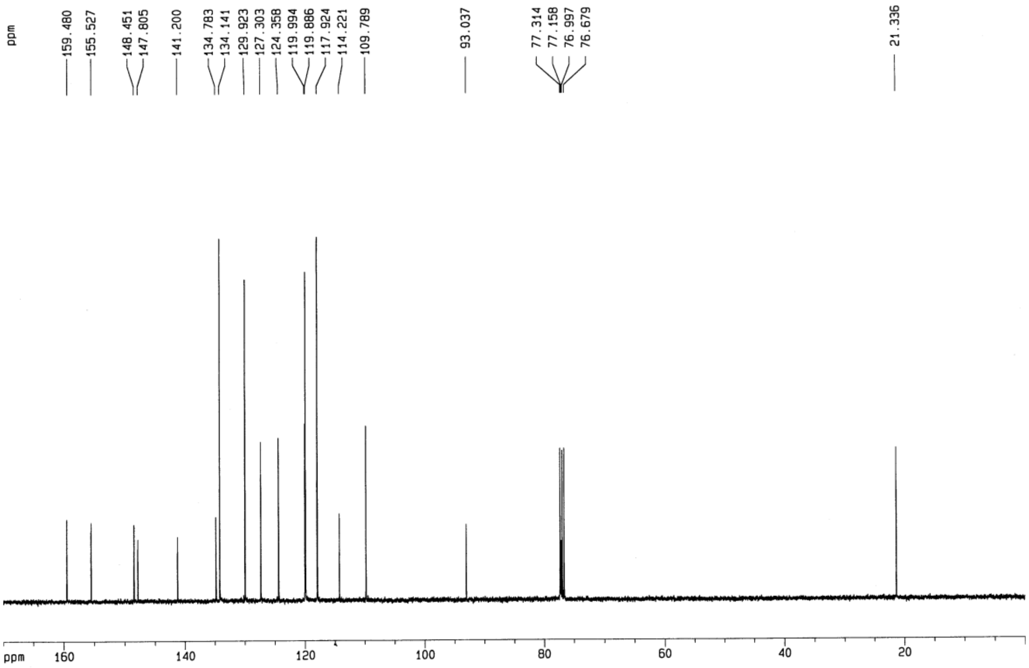
2-(2-Methylphenylethynyl)-5-methylbenzoxazole (Table 2, entry 2):



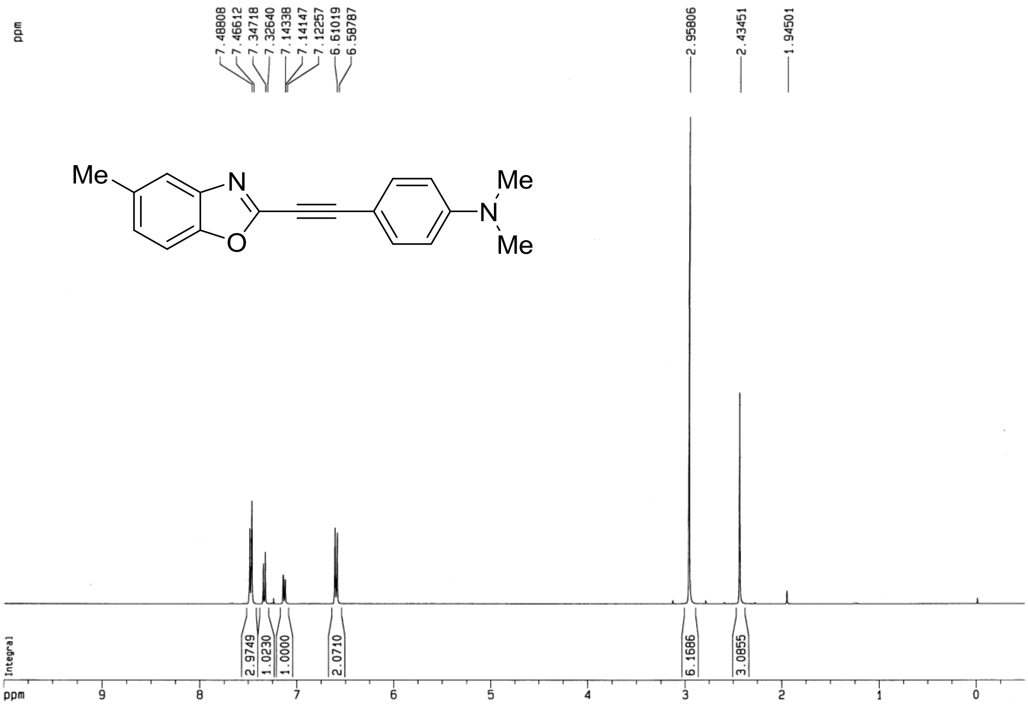


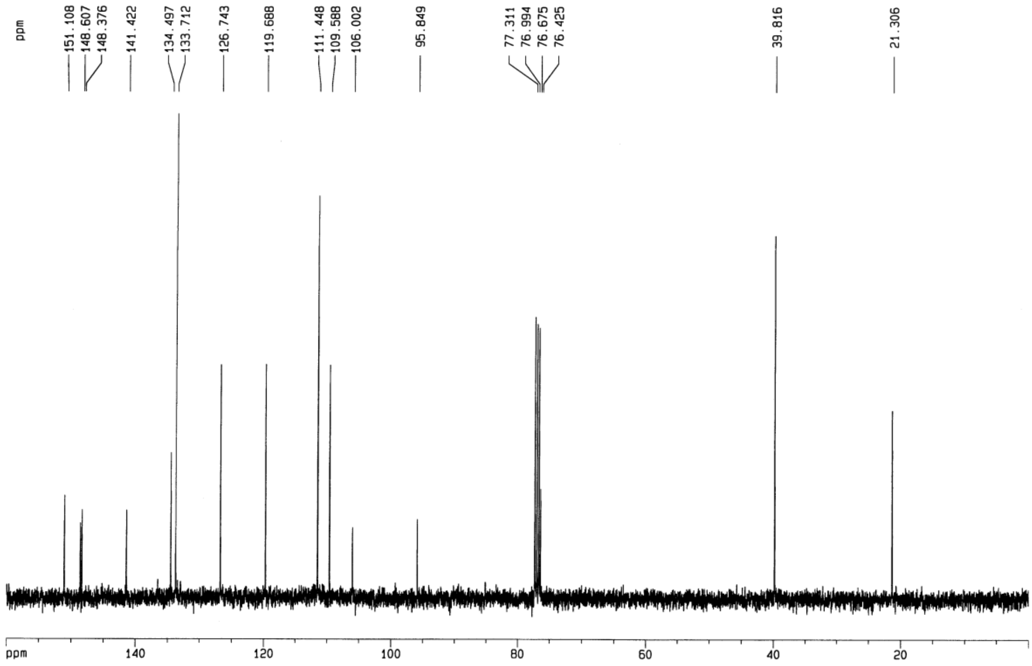
2-(4-Phenoxyphenylethynyl)-5-methylbenzoxazole (Table 2, entry 4):



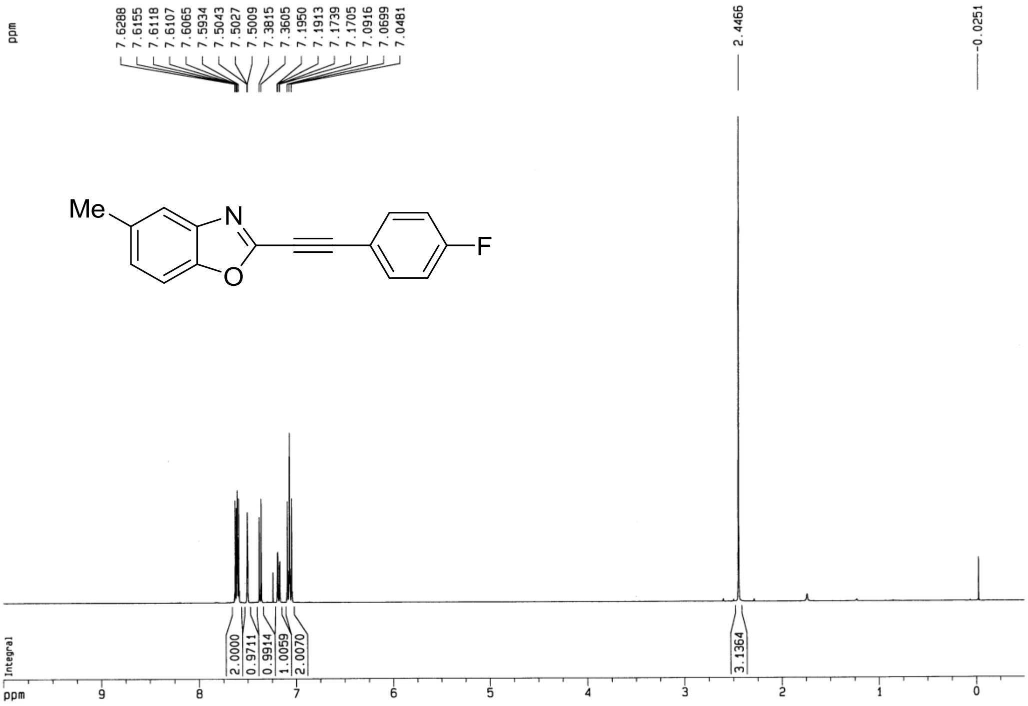


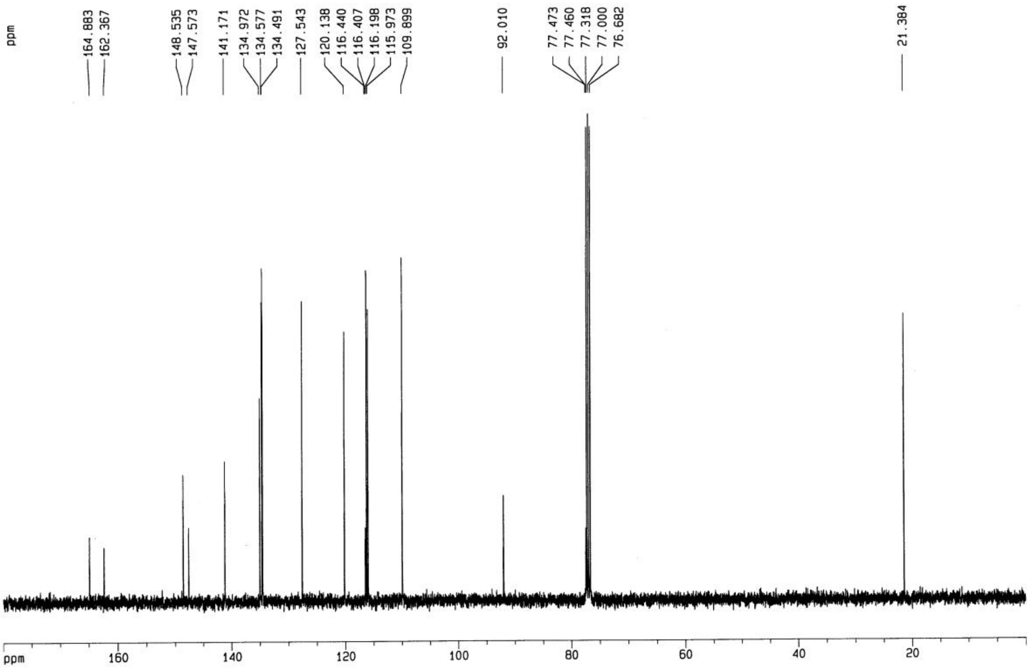
2-(4-Dimethylaminophenylethynyl)-5-methylbenzoxazole (Table 2, entry 5):



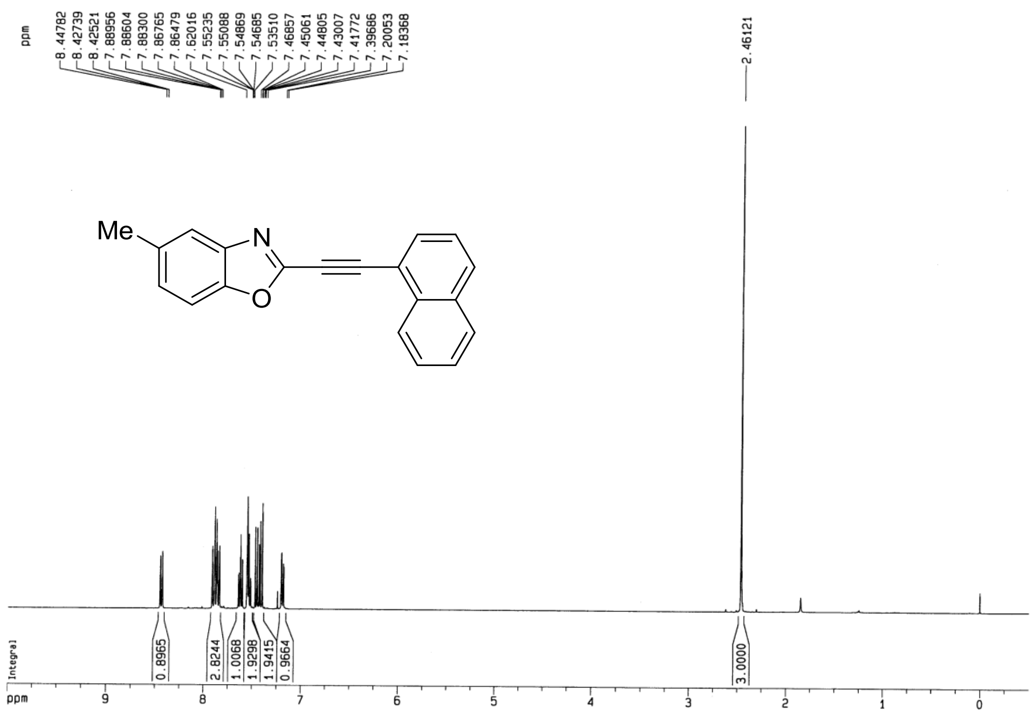


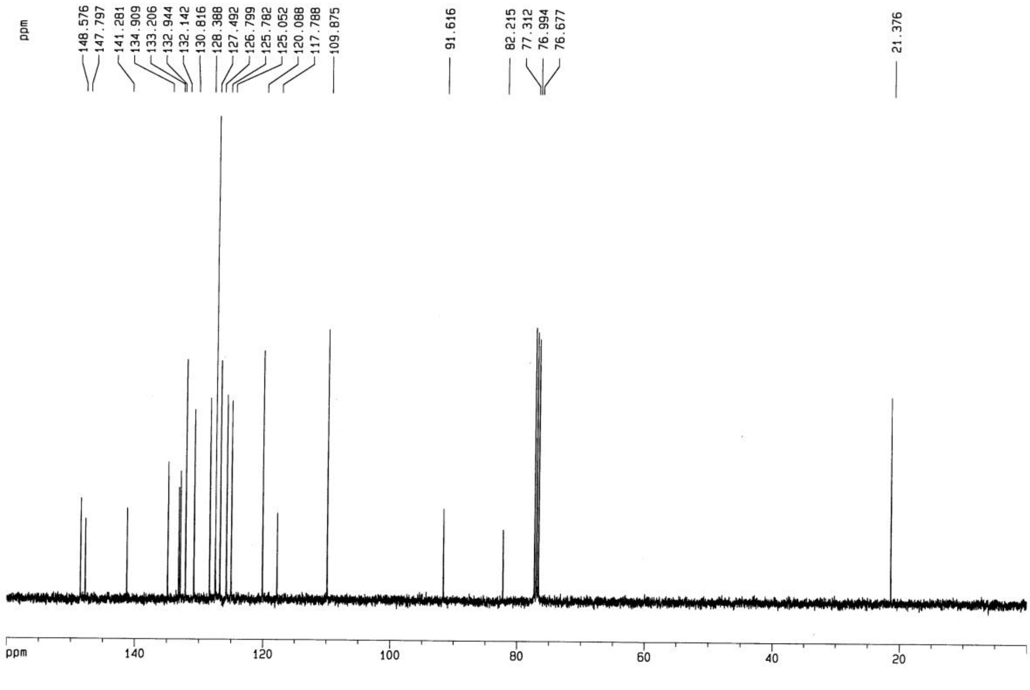
2-(4-Fluorophenylethynyl)-5-methylbenzoxazole (Table 2, entry 8):



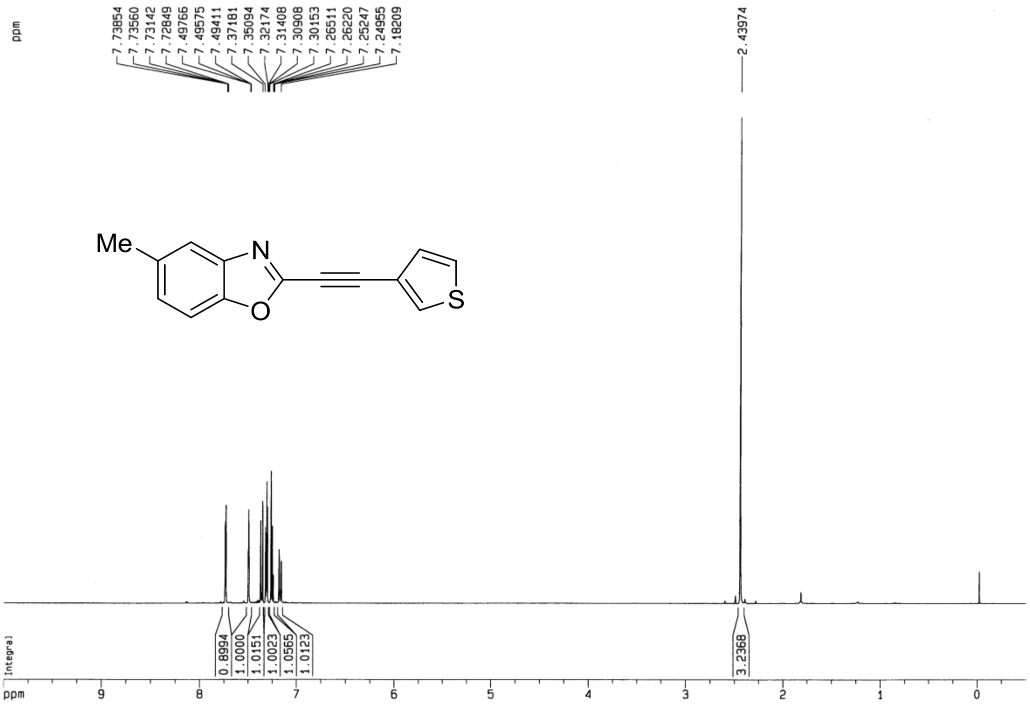


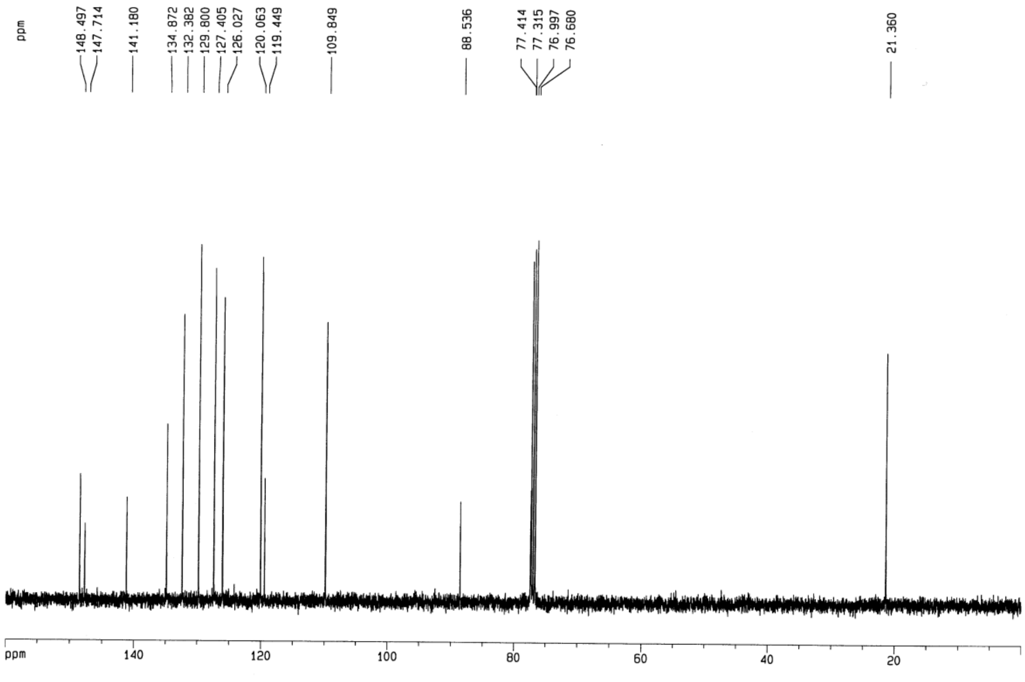
2-(1-Naphthylethynyl)-5-methylbenzoxazole (Table 2, entry 9)



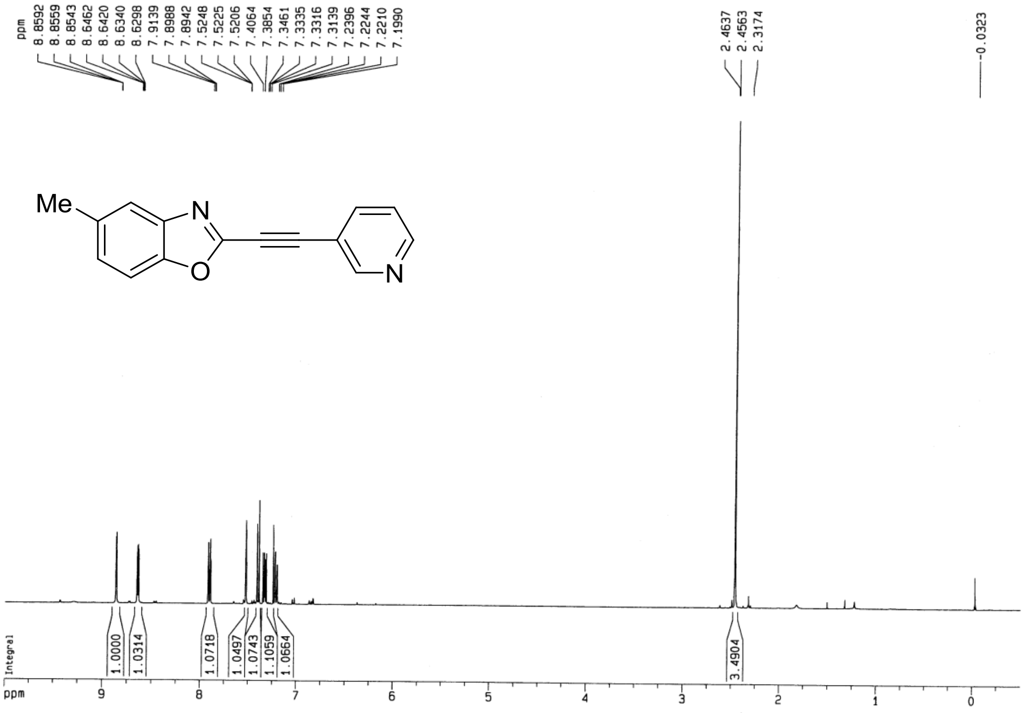


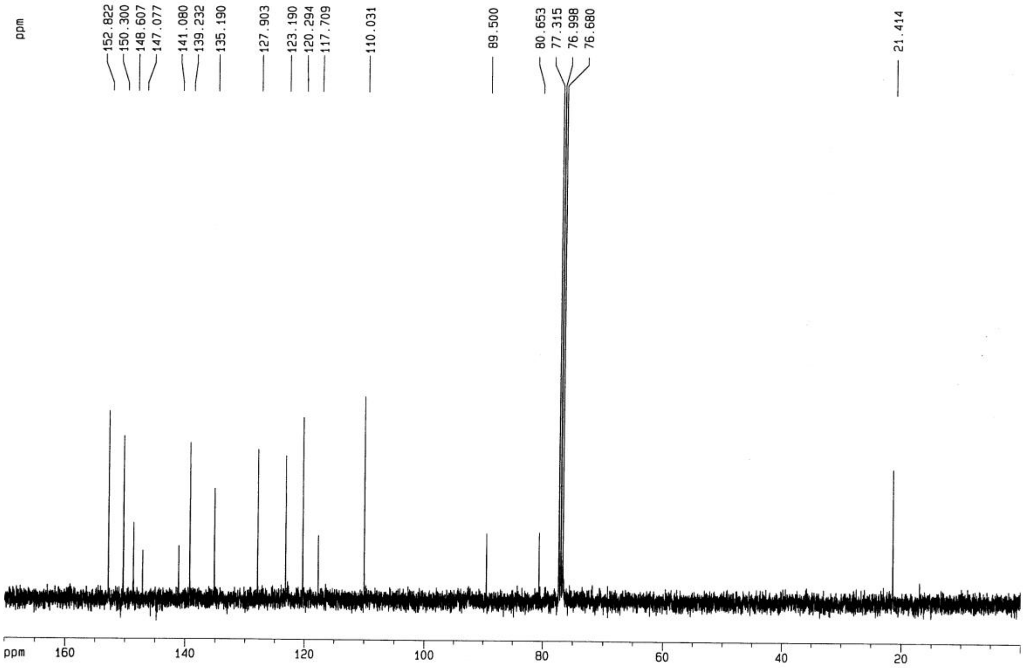
2-(Thiophene-3-ylethynyl)-5-methylbenzoxazole (Table 2, entry 11):



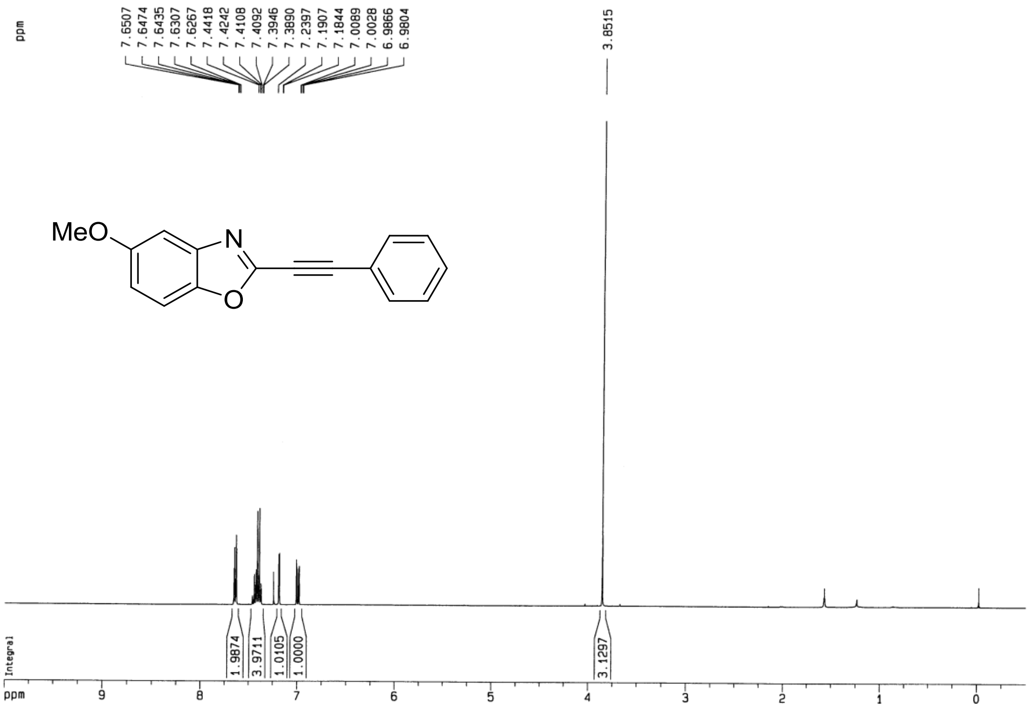


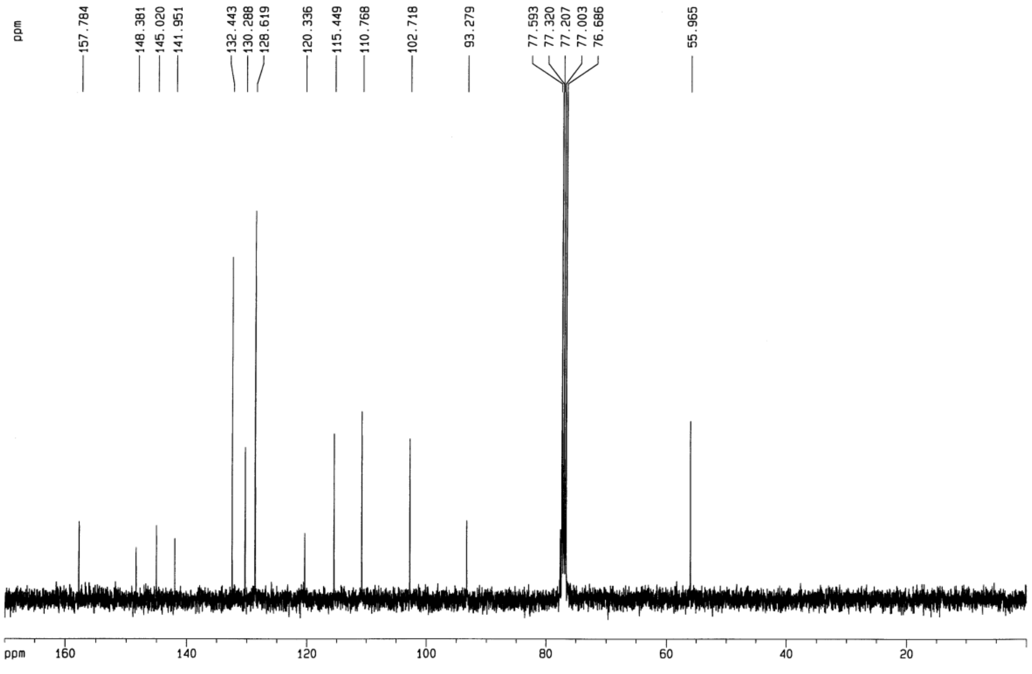
2-(Pyridine-3-ylethynyl)-5-methylbenzoxazole (Table 2, entry 12)



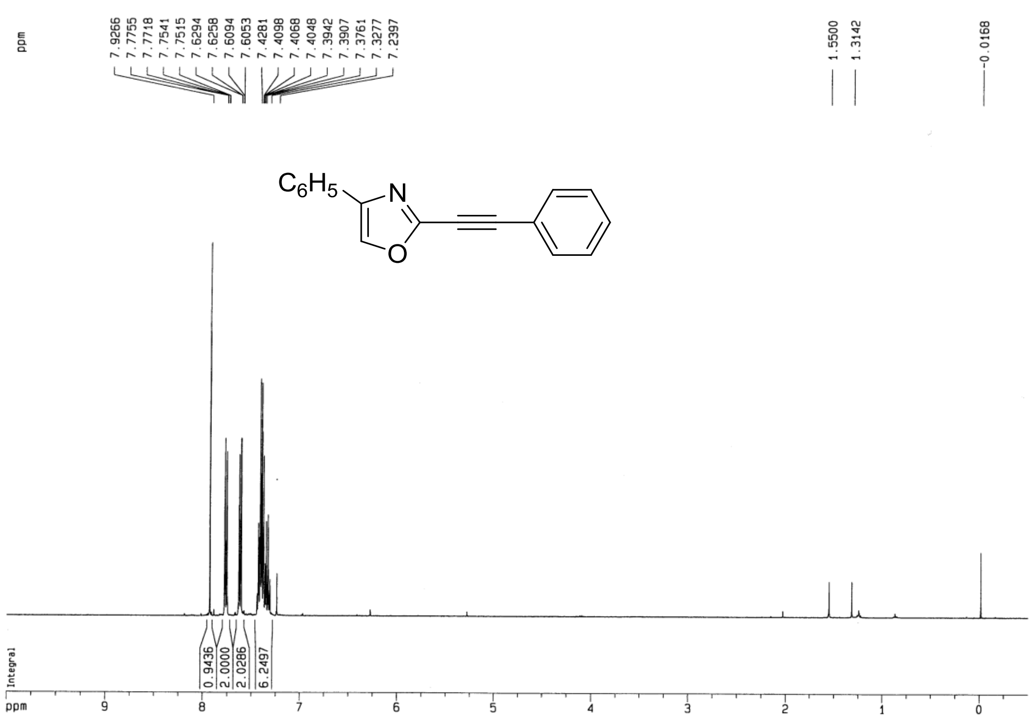


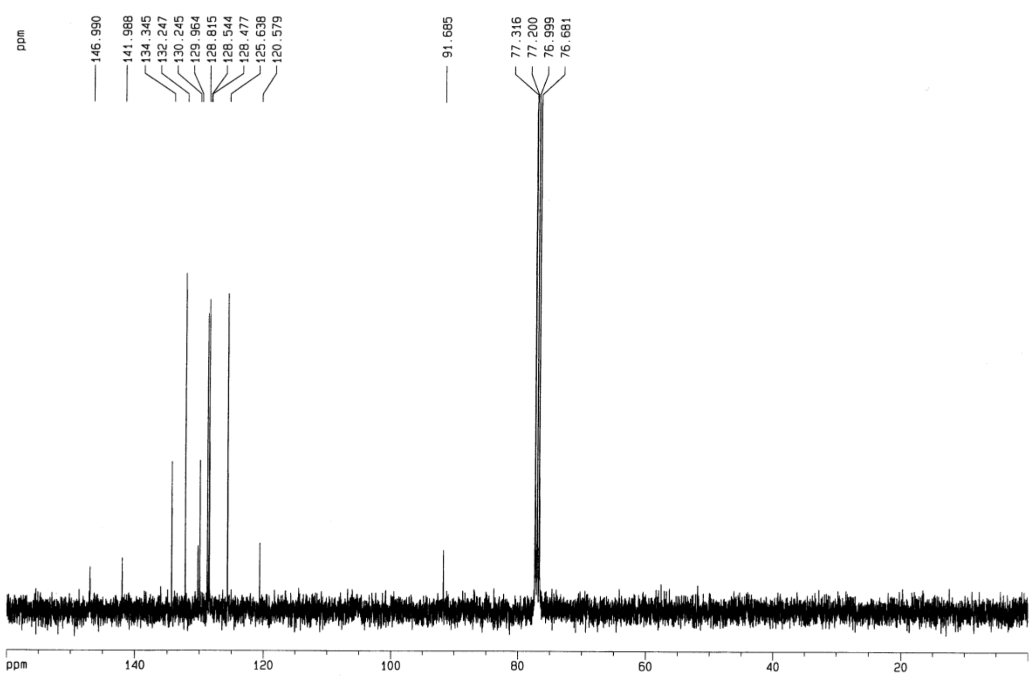
2-(Phenylethynyl)-5-methoxybenzoxazole (Scheme 2, **4d**):



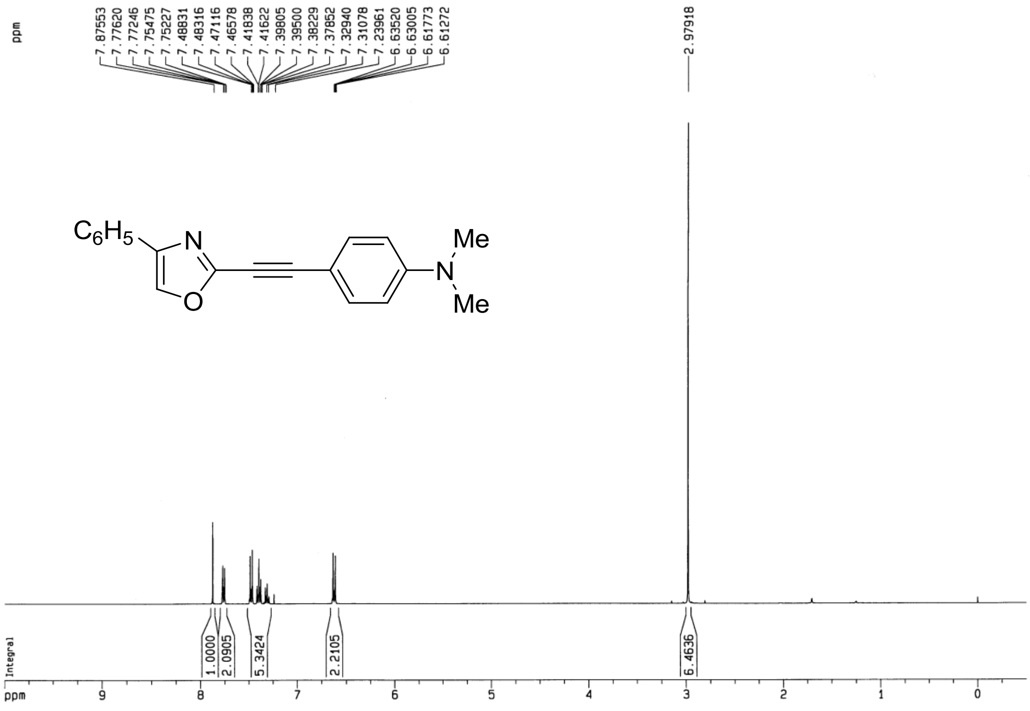


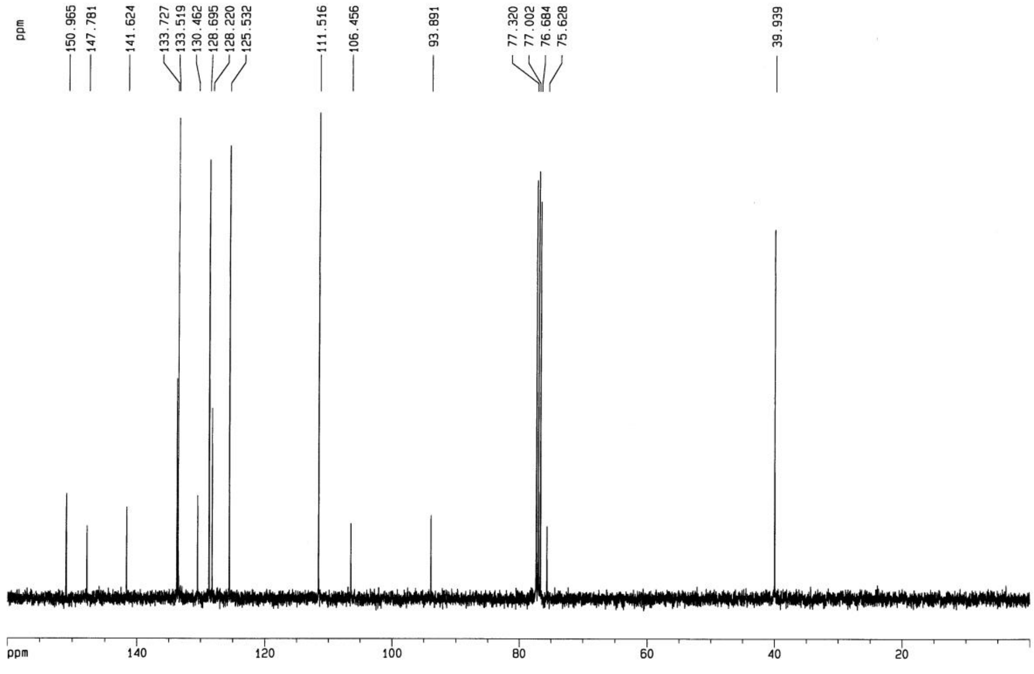
2-(Phenylethynyl)-4-phenyloxazole (Scheme 2, **4e**):



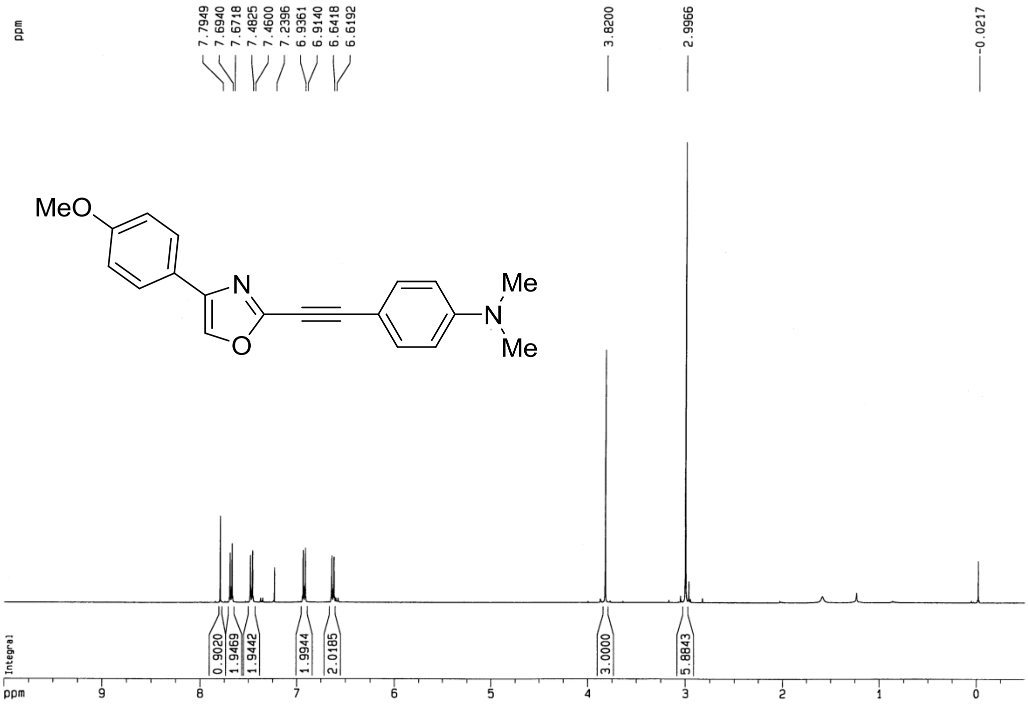


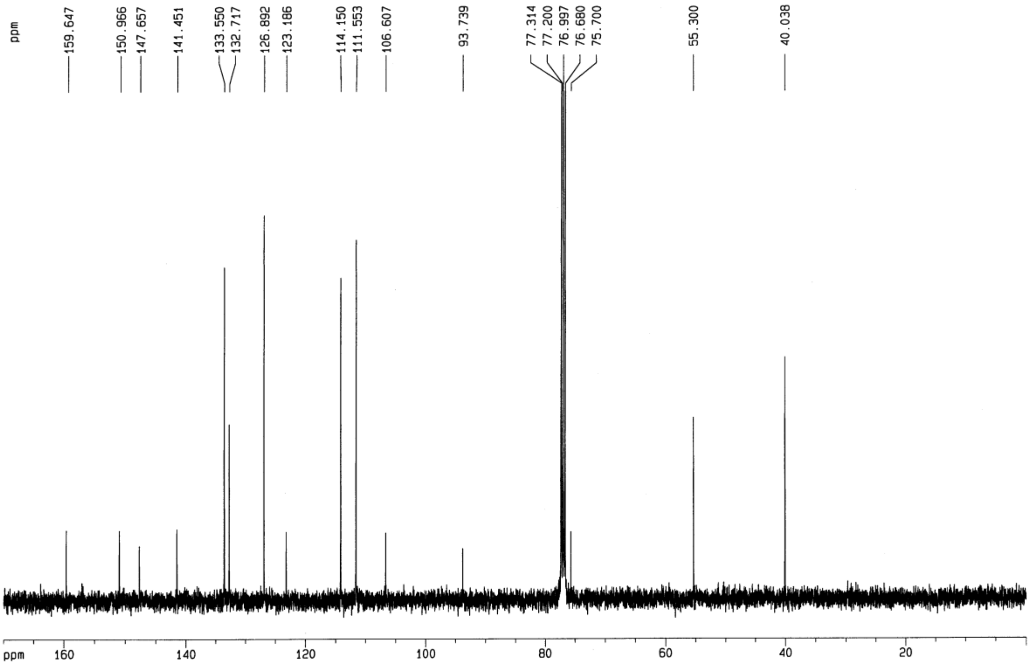
2-(4-Dimethylaminophenylethynyl)-4-phenyloxazole (Scheme 2, **4f**):



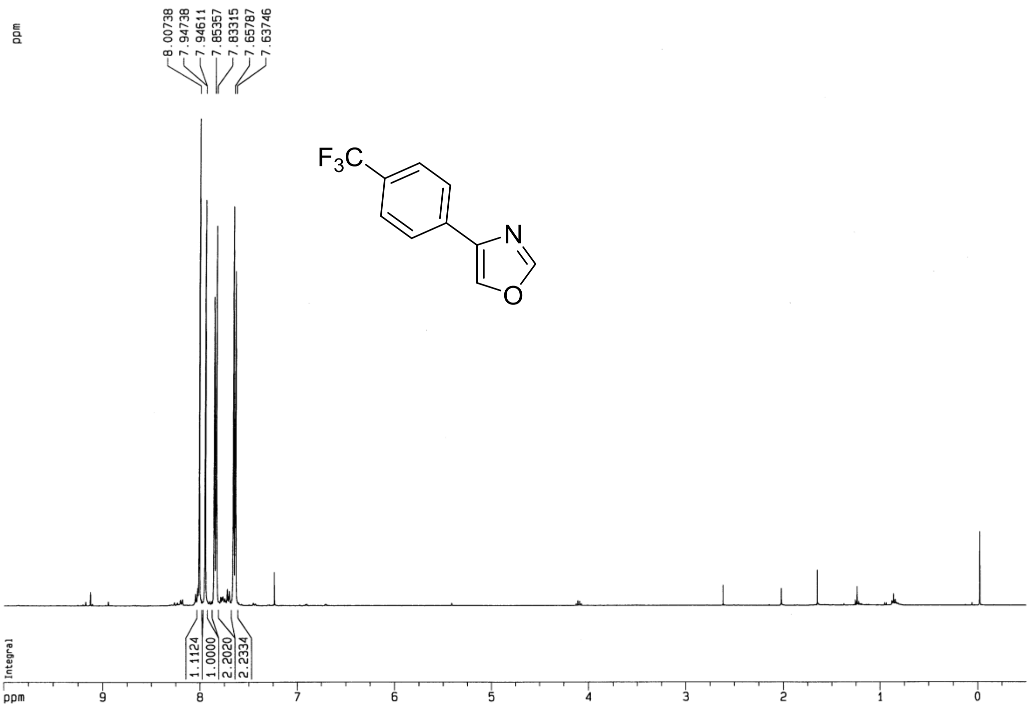


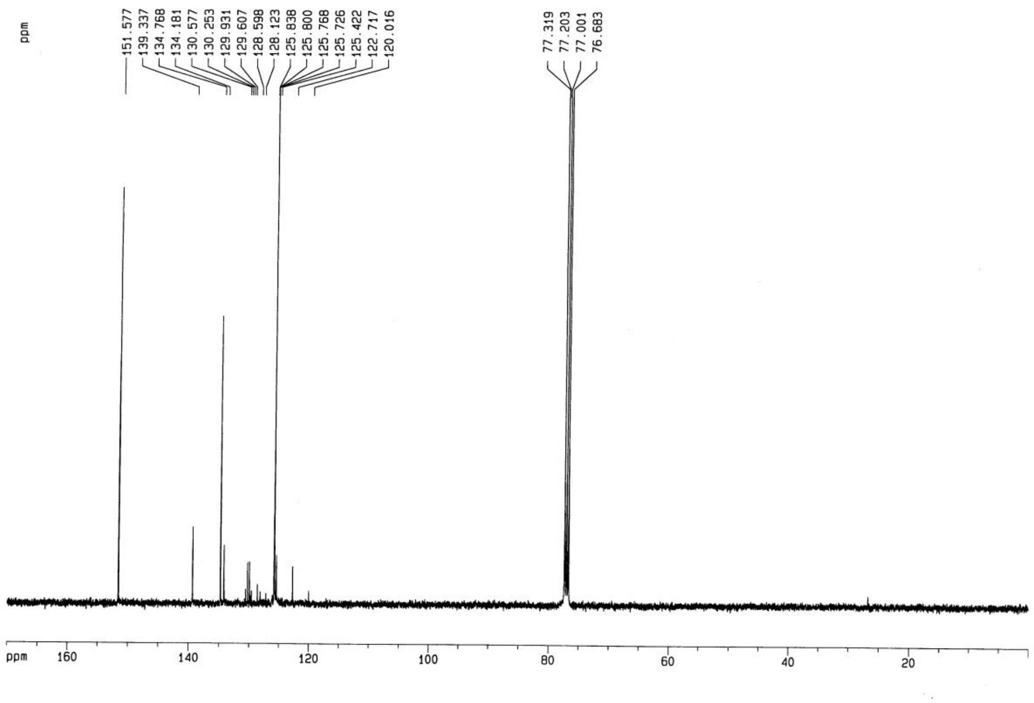
2-(4-Dimethylaminophenylethynyl)-4-(4-methoxyphenyl)oxazole (Scheme 2, **4g**):





4-(4-Trifluoromethylphenyl)oxazole (Scheme 2, **1h**):





2-(4-Dimethylaminophenylethynyl)-4-(4-trifluoromethylphenyl)oxazole (Scheme 2, **4h**):