Electronic Supplementary Information (ESI)

Facile solar photo-thermochemical syntheses of 4-bromo-2,5-disubstituted oxazoles from N-arylethylamides

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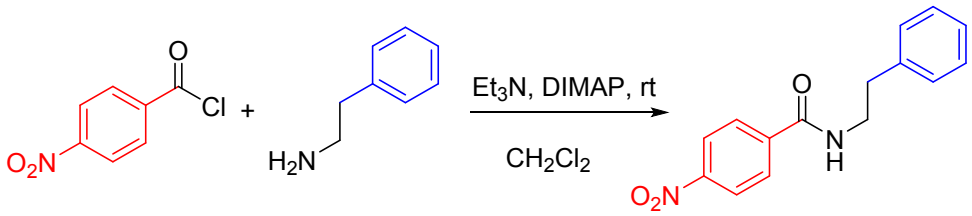
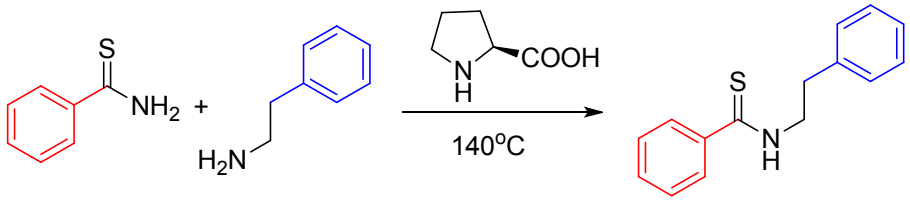
I. Experimental procedure for preparation of substrates for bromo-oxazole and bromothiazole synthesis

4-Nitro- N-(2-phenylethyl)benzamide



2 mmol of 2-phenylethylamine, 2 mmol of triethylamine and catalytic amount (5 mol%) of DIMAP were dissolved in 10 mL DCM solvent and cooled in ice bath. 2.2 mmol of 4-Nitro benzoyl chloride was added portion wise and allowed to react at room temperature under stirring for 2 hours. After the reaction, 10 mL of water was added under stirring for 5 minutes. The DCM layer was collected, dried over anhydrous Na_2SO_4, and the solvent stripped off under vacuum. Solid white product was obtained from DCM layer through slow crystallization (90% yield).

N-phenethylbenzothioamide



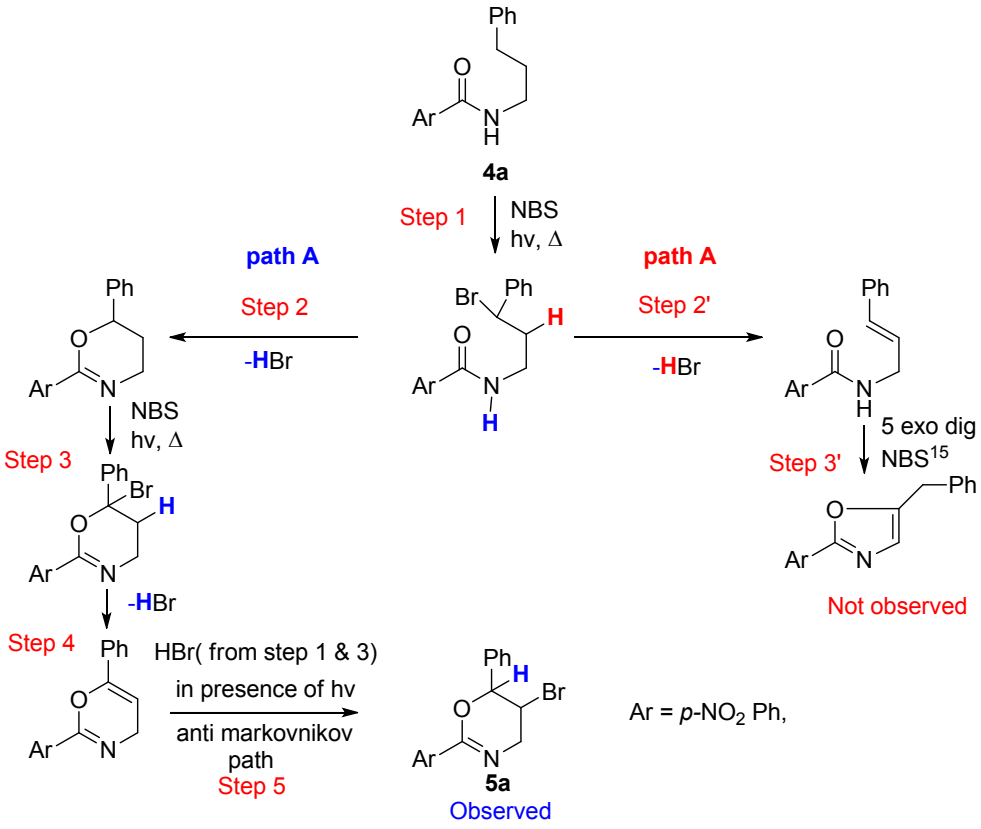
5 mmol each of benzothioamide and 2-phenyl ethyl amine were taken in a 25 mL RB flask and into it was added 0.5 mmol (10 mol %) of L-proline. The contents were heated under neat condition at 140°C for 24 h. The crude mixture was purified on silica gel column using 20% ethyl acetate in hexane yielding the pure substrate in 60% isolated yield.

Table S1. Reaction of N-phenylethyl-4-nitrobenzamide with NBS under different conditions[a]

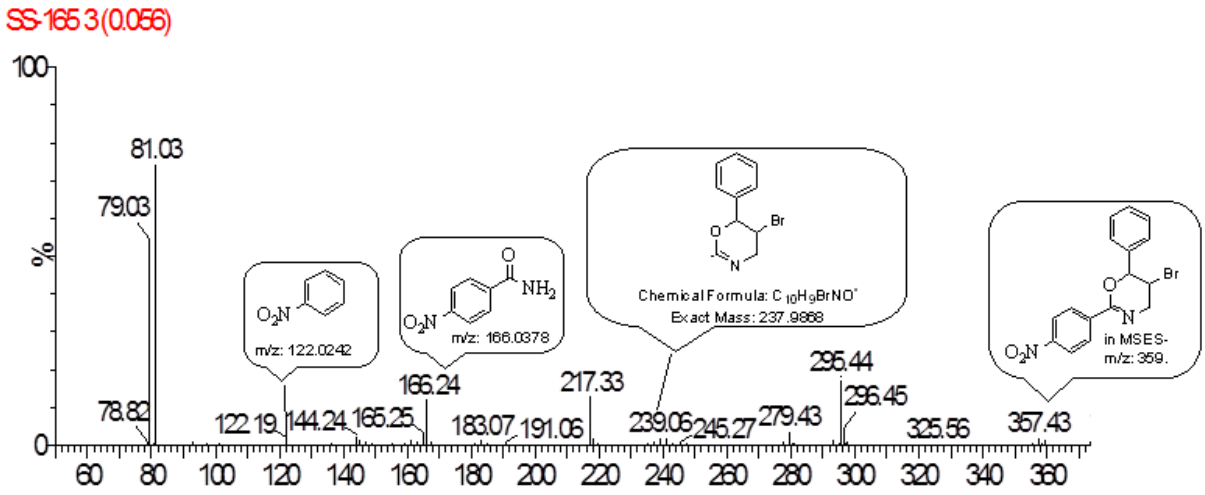
entry	NBS eqv	solvent	light source	heat source	temp. (°C)	time (h)	yields (%)[b] A	B
1	2	CH_3CN	fluoresence light	oil bath	70	8	0	trace
2	2	DMF	"	oil bath	70	8	0	0
3	2	DMSO	"	oil bath	70	8	0	0
4	2	$CHCl_3$	"	oil bath	70	8	trace	25
5	2	CH_2Cl_2	"	oil bath	40	12	0	10
6	2	DCE[c]	"	oil bath	70	8	21	27
7	3	"	"	oil bath	70	6	trace	61
8	3	"	"	-	rt	24	trace	23
9[d]	3	"	"	oil bath	70	6	-	0
10[e]	3	"	no light	oil bath	70	6	-	trace

[a]Reaction conditions: Substrate (0.5mmol), solvent (3 ml); [b]Isolated yields of 2-(4-nitrophenyl)-5-phenyloxazole (A) and 4-bromo-2-(4-nitrophenyl)-5-phenyloxazole (B) ; [c]DCE = 1,2-dichloroethane; [d]Reaction in presence of TEMPO radical scavenger.; [e]Reaction in blackened RB flask to exclude light

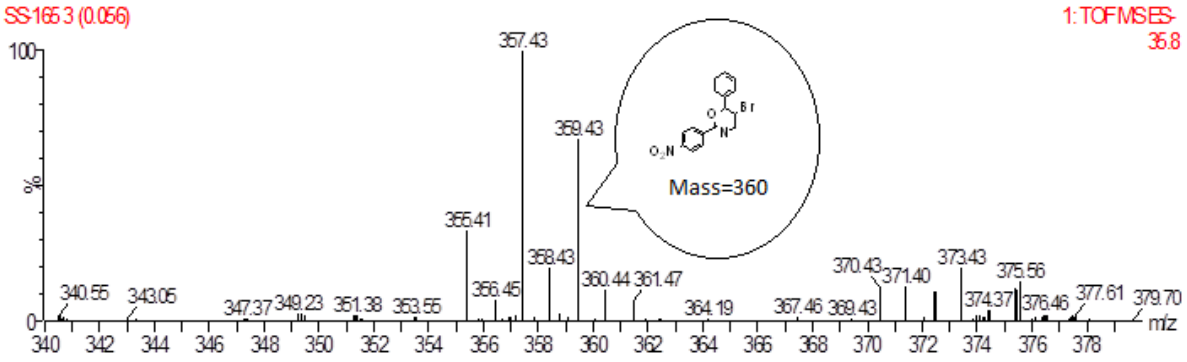
Scheme S1. Inference on mechanism through the experiment with 4-nitro-N-(3-phenylpropyl)benzamide



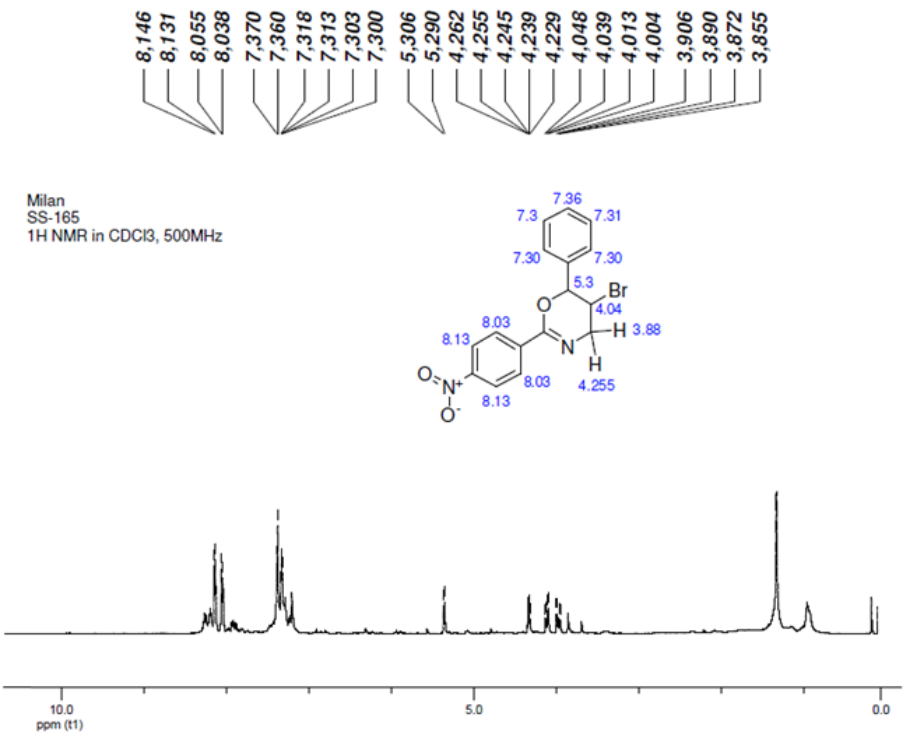
TOF MSES Spectra



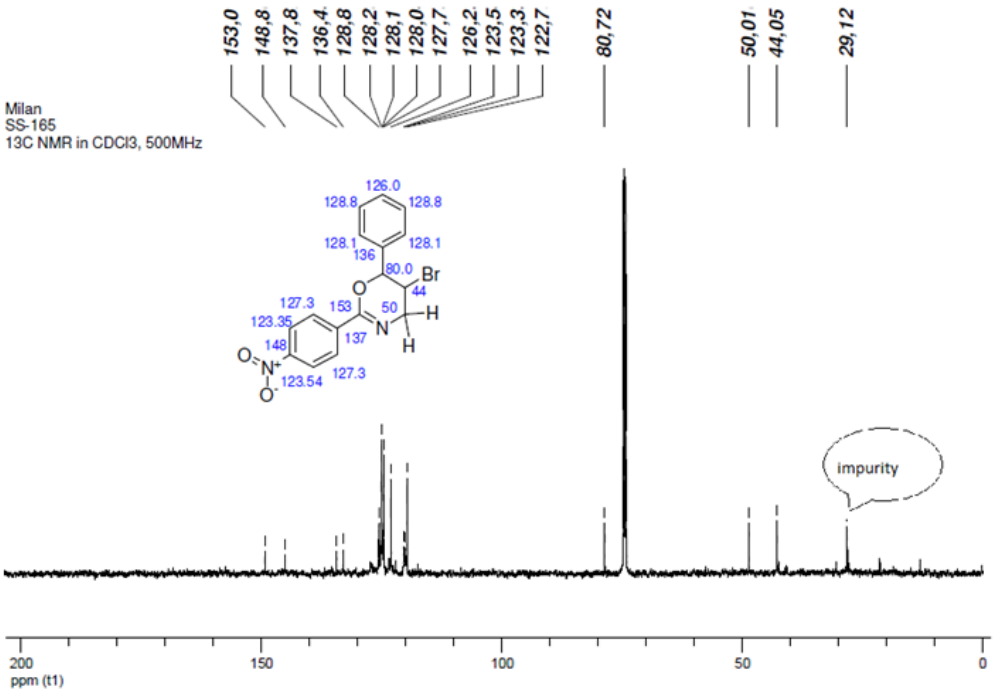
TOF MSES Spectra



^{1}H NMR of 5a



^{13}C NMR of 5a



4-bromo-2-(4-nitrophenyl)-5-phenyloxazole (Table 1, entry 1): (Eluent: 5% EtOAc in Hexane); Yellow solid, crystalline Mp. : 162-165^{o}C ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8, 2H), 8.28 (d, J = 9.0, 2H), 8.046 (m, 2H), 7.527 (m, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 157.3, 148.4, 147.3, 131.1, 129.0, 128.4, 126.5, 125.9, 125.2, 123.8, 112.9. IR (in KBr, cm−1) 3429, 2925, 2854, 2363, 1744, 1600, 1519, 1480, 1338, 1260, 1090, 1020, 972, 851,830, 760, 707,682. Anal. (%) Found C, 52.44; H, 2.98 (calcd. for $C_{15}H_9BrN_2O_3$: C, 52.20; H, 2.63). λ_{max} = 357 nm. Crystal structure: Table S2.

4-bromo-5-(4-chlorophenyl)-2-(4-nitrophenyl)oxazole (Table 1, entry 2): (Eluent: 5 % EtOAc in Hexane); yellow solid, amorphous; Mp. : 193-195^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ *8.367* (d, J = 9.0, 2H), 8.259 (d, J = 9.0, 2H), 7.976 (d, J = 8.5Hz, 2H), 7.497 (d, J = 8.5, 2H) .^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 149.0, 146.9, 135.5, 131.5, 129.2, 127.1, 126.8, 124.8, 124.3, 113.8. IR (in KBr, cm−1) 3427, 2369, 1599, 1520, 1480, 1405, 1340, 1282, 1082, 1011, 975, 854,825, 710, 548, 486. Anal. (%) Found: C, 47.45; H, 2.117 (calcd: for $C_{15}H_8BrClN_2O_3$: C, 47.46; H, 2.12). λ_{max} = 370 nm.

4-bromo-5-(4-bromophenyl)-2-phenyloxazole (Table 1, entry 3):

(Eluent: 5% EtOAc in Hexane); White solid, crystaline ; Mp. : 121-124^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.09-8.08 (m, 2H), 7.97(d, J = 8.5Hz, 2H) 7.79 (d, J=8.5 Hz, 2H), 7.60-7.58 (m, 3H), ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.9, 144.9, 132.2, 131.6, 129.3, 127.1, 126.3, 122.5,113.2, 110.9. IR (in KBr, cm−1) 3430, 2365, 1547, 1478, 1447, 1328, 1204, 1077, 1009, 973, 821, 708, 684, 482. HRMS (ESI): Found: 377.9123 (calcd: for $C_{15}H_9Br_2NO$ [M+H]: 377.9129). λ_{max} = 343 nm. Crystal structure: Table S2.

4-bromo-2,5-diphenyloxazole (Table 1, entry 4): (Eluent: 5% EtOAc in Hexane); White solid, amorphous.; Mp. : 102-105^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.092 (m, 2H), 8.029 (d, J = 7.5 Hz, 1H), 7.969(d, *J* =*8.0* Hz, 1H) 7.791 (d, *J* = 8.5 Hz, 1H), 7.598 (m, 5H). ^{13}C NMR (50 MHz, CDCl3) δ 171.1, 137.8, 134.0, 129.9, 129.6, 43.7, 23.9. HRMS (ESI): Found 300.0018 (calcd. for $C_{15}H_{10}BrNO$ [M+H], 300.0024). λ_{max} = 328 nm.

4-bromo-5-(4-chlorophenyl)-2-phenyloxazole (Table 1, entry 5): (Eluent: 5% EtOAc in Hexane); White solid; White solid, amorphous; Mp. : 111-113^{o}C**,** ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08-8.06 (m, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.59- 7.58 (m, 3H).^{13}C NMR (125 MHz, DMSO-d_6) δ 159.8, 144.8, 133.7, 131.6, 129.3, 129.3, 126.8, 126.3, 125.5, 125.3, 113.1. IR (in KBr, cm−1) 3430, 2365, 1549, 1481, 1480, 1448, 1402, 1331, 1277, 1204, 1089, 1012, 973, 826, 770, 706, 685, 481. HRMS (ESI): Found 333.9628 (calcd. for $C_{15}H_9BrClNO$ [M+H] 333.9634). λ_{max} = 333 nm.

4-bromo-5-(4-bromophenyl)-2-(4-chlorophenyl)oxazole (Table 1, entry 6): (Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 157-159^{o}C, ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.11 (d, *J* = 8.6Hz, 2H), 7.99 (d, *J* = 8.6Hz, 2H), 7.80 (d, *J* = 8.6 Hz,2H), 7.67 (d, *J* = 8.6 Hz, 2H).^{13}C NMR (50 MHz, DMSO-d_6) δ 159.6, 145.8, 136.9, 132.8, 130.1, 128.73, 127.7, 126.1, 125.1, 123.2. IR (in KBr, cm−1) 1598, 1477, 1400, 1323, 1261, 1200, 1165, 1081, 1013, 973, 873, 809, 726, 665, 547, 486, 463. HRMS (ESI): Found: 411.8745 (calcd. for $C_{15}H_8Br_2ClNO$ [M+H]: 411.8739). λ_{max} = 331 nm.

4-bromo-2-(4-chlorophenyl)-5-phenyloxazole (Table 1, entry 7): (Eluent: 5% EtOAc in Hexane); White solid,amorphous ; Mp. : 112-114^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92-7.88 (m, .4H), 7.38-7.33 (m,5H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.7, 150.0, 140.2, 136.2, 133.5, 133.4, 133.2, 131.9, 131.0, 130.2, 129.2, 128.5, 116.6. IR (in KBr, cm−1) 1599, 1478, 1404, 1322, 1263, 1197, 1090, 1012, 973, 828, 758, 727, 685, 542. HRMS (ESI): Found: 333.9609 (calcd: for $C_{15}H_9BrClNO$ [M+H] 333.9634). λ_{max} = 320 nm.

4-bromo-2,5-bis(4-chlorophenyl) oxazole (Table 1, entry 8)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 162-164^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.10 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.66-7.64 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.6, 152.5, 145.8, 136.9, 134.5, 130.12, 129.93, 128.72, 127.57, 125.71, 125.04, 121.06, 120.75, 120.47. IR (KBr, cm^{-1}) 1480, 1403, 1324, 1273, 1200, 1090, 1012, 973, 828, 728, 557, 491. HRMS (ESI): Found: 367.9253. (calcd. for $C_{15}H_8BrCl_2NO$ [M+H]: 367.9245). λ_{max} = 315 nm.

4-bromo-5-(4-bromophenyl)-2-(4-fluorophenyl)oxazole (Table 1, entry 9)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 146-149^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17-8.14 (m,2H) , 7.98 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.45-7.42 (t, J = 9.0 Hz,2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.1, 144.9, 133.8. 129.3, 129.0, 128.9 126.9, 125.2, 122.3, 116.6, 116.5. 113.1. IR (KBr, cm^{-1}) 1604, 1489, 1413, 1230, 1205, 1152, 1081, 1010, 973, 843, 815, 735, 697, 663, 626, 574, 520. Anal. (%) Found: C, 45.64; H, 2.24 (calcd. for $C_{15}H_8Br_2FNO$: C, 45.38; H, 2.03). λ_{max} = 327 nm.

4-bromo-2-(4-fluorophenyl)-5-phenyloxazole (Table 1, entry 10)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 110-112^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.14-8.13 (m, 2H), 8.02 (d, J = 6.5 Hz, 2H), 7.59 (t, J = 7.0 Hz,2H), 7.48 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.9, 158.9, 145.8, 132.2, 129.3, 129.2, 129.0, 128.9, 128.8, 127.0, 126.3, 125.2, 122.4, 116.6, 116.4, 112.5. IR (KBr, cm^{-1}) 1603, 1490, 1412, 1327, 1288, 1231, 1153, 1079, 1011, 972, 908, 835, 759, 732, 684, 624, 573, 515, 488. HRMS (ESI): Found 317.9916 (calcd. for $C_{15}H_9BrFNO$ [M+H]: 317.9930). λ_{max} = 329 nm.

4-bromo-5-(4-chlorophenyl)-2-(4-fluorophenyl)oxazole (Table 1, entry 11)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 141-143^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.16-8.13 (m,2H) , 8.04 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.44 (t, J = 9.0 Hz,2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.9, 164.3, 159.1, 146.9, 144.9, 133.8, 129.3, 129.0, 128.9, 126.9, 125.2, 122.3, 116.6, 116.5, 113.1. IR (KBr, cm^{-1}) 1606, 1560, 1491, 1409, 1326, 1285, 1233, 1201, 1155, 1086, 1011, 972, 831, 733, 694, 663, 628, 574, 497. Anal. (%) Found C, 51.11; H, 2.85 (calcd: for $C_{15}H_8BrClFNO$: C, 51.10; H, 2.29). λ_{max} = 329 nm.

4-bromo-5-(4-bromophenyl)-2-(2-fluorophenyl)oxazole(Table 1, entry 12)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 121-123^{o}C ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (t, J = 7.5 Hz, 1H) , 7. 89 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.66-7.62 (q, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 158.1. 156.2, 144.9, 133.5, 133.4, 132.0, 129.3, 126.7, 125.0, 122.4, 117.0, 116.9, IR (KBr, cm^{-1}) 1584, 1473, 1400, 1329, 1281, 1253, 1211, 1112, 1072, 1009, 973, 819, 768, 736, 698, 667, 465. Anal. (%) Found: C, 45.64; H, 1.629 (calcd. for $C_{15}H_8Br_2FNO$: C, 45.38; H, 2.03).

4-bromo-2-(2-fluorophenyl)-5-phenyloxazole (Table 1, entry 13)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 72-75^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (m,1H) , 7.96 (d, J = 8.0Hz, 2H), 7.64 (m, 1H), 7.58-7.55 (t, J = 7.5 Hz,2H). 7.49-7.40 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.1, 158.1, 155.9, 145.7, 133.3,133.2, 129.1, 128.9, 125.9, 124.9, 117.0, 116.85, 113.6, 113.6, 112.2. Anal. (%) Found: C, 56.32; H, 2.72 (calcd for $C_{15}H_9BrFNO$: C, 56.63; H, 2.85).

4-bromo-5-(4-chlorophenyl)-2-(2-fluorophenyl)oxazole(Table 1, entry 14)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 124-126^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.10-8.07 (m,1H) , 7.95 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 3H), 7.45-7.39 (m,2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.2, 158.2, 156.2. 144.8. 133.4. 129.3. 129.1. 126.6. 125.0. 117.1. 112.8. IR (KBr, cm^{-1}) 1584, 1538. 1479. 1465. 1403. 1330. 1252. 1211. 1089. 1013. 975. 822. 768. 736. 697. 668. 548. 509. 468. Anal. (%) Found: C, 50.77; H, 1.98 (calcd. for $C_{15}H_8BrClFNO$: C, 51.10; H, 2.29).

4-bromo-2-(4-methoxyphenyl)-5-phenyloxazole (Table 1, entry 15)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 137-140^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00-7.93 (m,4H) , 7.56-7.46 (m, 3H), 7.12 (s, 2H), 3.85(s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.6, 158.6, 144.8, 142.6, 129.0, 128.7, 127.9, 124.8, 124.5. 118.0, 114.6, 55.4. IR (KBr, cm^{-1}) 1607, 1493, 1395, 1337, 1264, 1211, 1172, 1088, 1053, 1018, 979, 826, 756, 734, 683, 491. HRMS (ESI): Found: 330.0122 (calcd. for $C_{16}H_{12}BrNO_2$ [M+H]: 330.0130).

4-bromo-5-(4-chlorophenyl)-2-(4-methoxyphenyl)oxazole(Table 1, entry 16)

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 145-147^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03-8.00 (m,4H) , 7.64 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.7, 159.9, 144.0, 133.34, 129.1, 128.1, 126.5, 126.2, 125.2, 117.9, 114.6, 112.8, 55.4. IR (KBr, cm^{-1}) 1608, 1492, 1461, 1397, 1335, 1264, 1199, 1173, 1093, 1055, 1018, 975, 826, 734, 685, 497. HRMS (ESI): Found 363.9758 (calcd. for $C_{16}H_{11}BrClNO_2$ [M+H]: 363.9740)

4-bromo-5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole (Table 1, entry 17)

(Eluent: 5% EtOAc in Hexane); White solid, crystaline; , Mp. : 105-108^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.278(d, J = 7.5 Hz, 2H) , 8.04 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.5 Hz,2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.28, 146.6, 129.6, 129.2, 126.9, 126.2, 126.1, 125.4, 112.8. IR (KBr, cm^{-1}) 1566, 1488, 1412, 1324, 1264, 1174, 1108, 1061, 1014, 974, 849, 757, 680, 592, 488. HRMS (ESI): Found 367.9891 (calcd. for $C_{16}H_9BrF_3NO$ [M+H]: 367.9898). λ_{max} = 337 nm. Crystal structure - Table S1.

4-bromo-5-(4-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)oxazole (Table 1, entry 18)

(Eluent: 5% EtOAc in Hexane); White solid, crystaline; Mp. : 138-140^{o}C, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.29 (d, J = 8.5 Hz, 2H) 8.06 (d, J = 8.5 Hz, 2H) 7.95 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.5, 145.8, 134.1, 129.3, 127.1, 126.3, 124.9, 113.4. IR (KBr, cm^{-1}) 1555, 1483,1413,1319, 1173, 1112, 1060, 1010, 973, 848, 828, 745, 707, 536, 490. HRMS (ESI): Found: 401.9498 (calcd. for $C_{16}H_8BrClF_3NO$ [M+H] 401.9508). λ_{max} = 340 nm. Crystal structure obtained- Table S1.

4-bromo-2-methyl-5-phenyloxazole (Table 1, entry 19):

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; ^{1}H NMR (200 MHz, $CDCl_3$) *δ 7.80-7.70* (d, *J* = 7,2.04 H), 7.37-7.28 (m, 3.67H), *4.39* (s, 0.34 H), 2.43 (s, 2.94). ^{13}C NMR (50 MHz, $CDCl_3$) *δ* 160.4, 146.1, 129.2, 128.6, 127.0, 125.5, 125.1, 110.6, 29.7, 14.1.

4-bromo-5-phenyl-2-(trifluoromethyl)oxazole (Table 1, entry 20):

(Eluent: 5% EtOAc in Hexane); red liq. gum ; ^{1}H NMR (500 MHz, CDCl3) *δ* 7.54-7.53 (m, 2H) , 7.37-7.36 (m, 3H), ^{13}C NMR (125 MHz, CDCl3) *δ* 154.3, 153.9, 135.6, 129.1, 128.6, 127.1, 118.8, 113.3. Anal. (%) Found: C, 41.36; H, 2.11 (calcd: for $C_{10}H_5BrF_3NO$: C, 41.13; H, 1.73).

4-bromo-5-phenyl-2-(thiophen-2-yl)oxazole (Table 1, entry 21):

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; Mp. : 110-112^{o}C, ^{1}H NMR (500 MHz, CDCl3) *δ 7.95* (d, *J* = 8.5,2H) , 7.48-7.39 (m, 5H), 7.10-7.095 (m, 1H), ^{13}C NMR (125 MHz, CDCl3) *δ* 155.0, 145.7, 130.9, 129.9, 128.8, 128.6, 128.3, 126.4, 125.2, 116.8, 112.3. HRMS (ESI) **F**ound: 305.9566 (calcd: for $C_{13}H_8BrNOS$ [M+H]: 305.9588)

2-(benzofuran-2-yl)-4-bromo-5-(4-chlorophenyl)oxazole (Table 1, entry 22):

(Eluent: 5% EtOAc in Hexane); White solid, amorphous; ^{1}H NMR (200 MHz, $CDCl_3$) *δ 8.03* (d, *J* = 10,1H) , 7.99-7.36 (m, 8H), ^{13}C NMR (50 MHz, $CDCl_3$) *δ* 152.6, 150.9, 150.2, 136.4, 134.3, 130.0, 129.2, 128.8, 128.0, 126.7, 124.8, 124.4, 123.9, 112.1, 102.5. HRMS (ESI) **F**ound: 373.9538 (calcd: for $C_{13}H_8BrNOS$ [M+H]: 373.9583)

4-bromo-2,5-diphenylthiazole (Table 2, entry 1):

(Eluent: 5% EtOAc in Hexane); Yellow solid, amorphous; ^{1}H NMR (200 MHz, $CDCl_3$) *δ 7.97* (s, 2H) , 7.78-7.67 (d, *J=8Hz*, 2H), 7.51-7.39 (m, 6H), ^{13}C NMR (50 MHz, $CDCl_3$) *δ* 169.0, 145.2, 144.8, 132.0, 131.1, 130.9, 128.9, 126.6, 126.3, 125.8, 125.7, 122.7. HRMS (ESI) **F**ound: 315.9807 (calcd: for $C_{13}H_8BrNOS$ [M+H]: 315.9796)

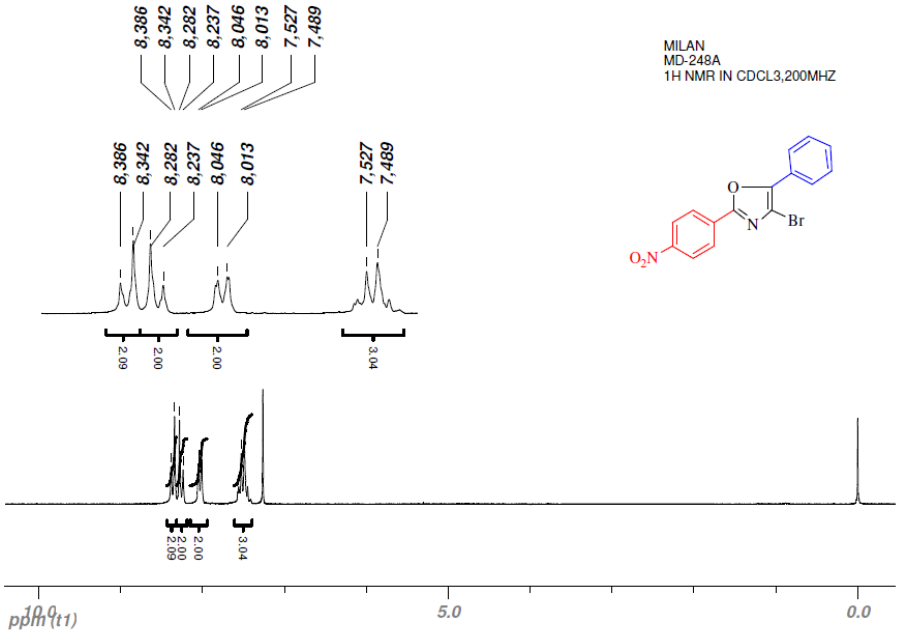
4-bromo-5-(4-chlorophenyl)-2-phenylthiazole (Table 2, entry 2):

(Eluent: 5% EtOAc in Hexane); Yellow solid, amorphous; ^{1}H NMR (200 MHz, $CDCl_3$) *δ 8.05-7.90* (m, 2H) , 7.63-7.39 (m, 7H), ^{13}C NMR (50 MHz, $CDCl_3$) *δ* 166.7, 146.1, 143.8, 130.8, 130.3, 129.2, 129.0, 128.7, 128.3, 127.4, 126.2. HRMS (ESI) Found: 349.8227 (calcd: for $C_{13}H_8BrNOS$ [M+H]: 349.9406)

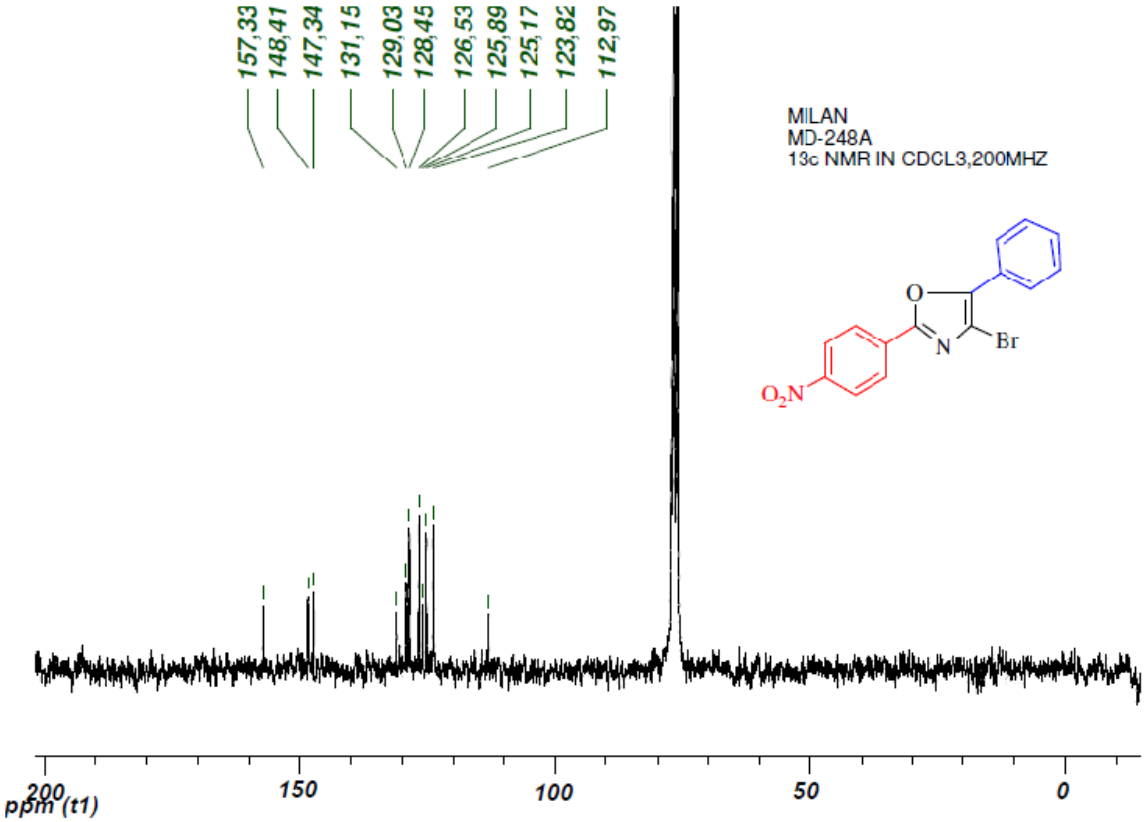
^{1}H and ^{13}C NMR spectra

(entry 1 -22, Table 1 and entry 1,2; table S1)

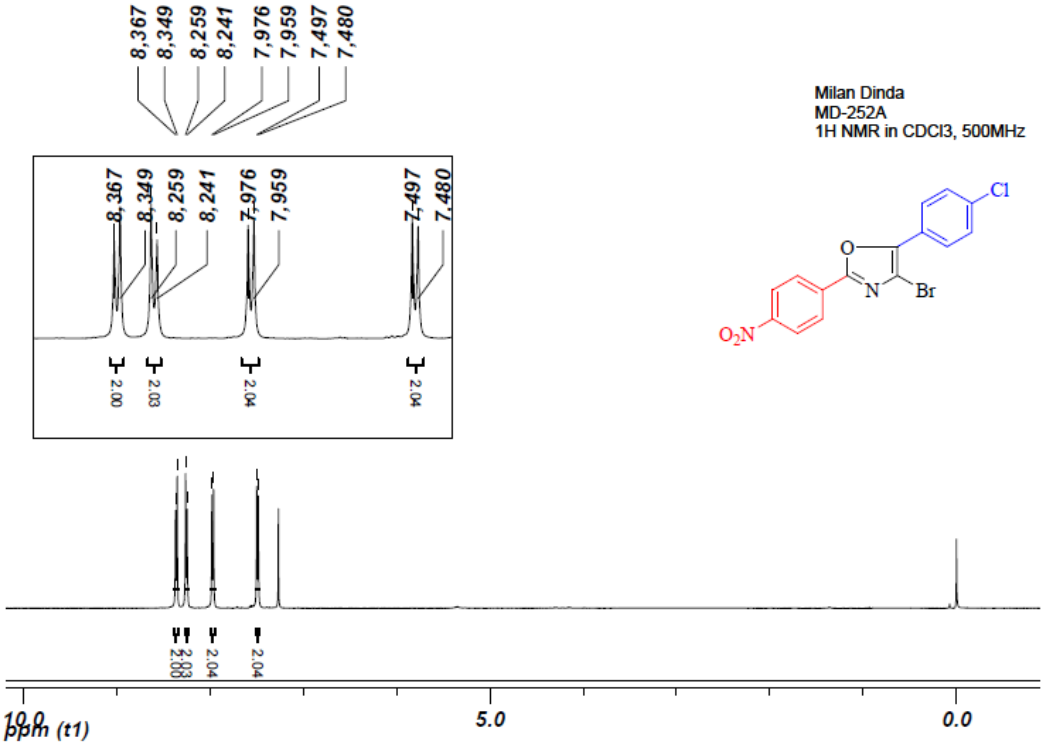
^{1}H NMR (Table 1, entry 1)



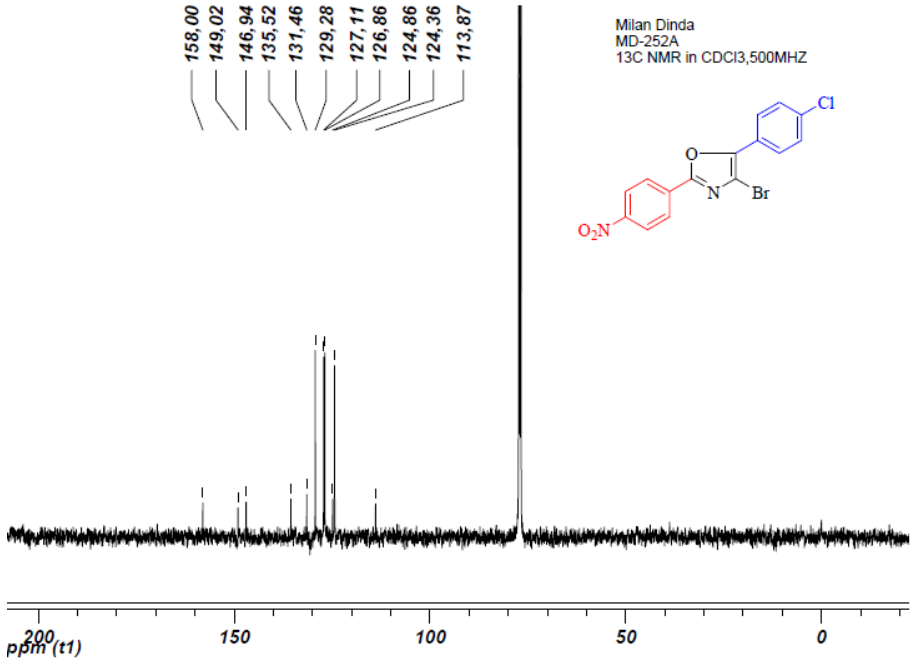
^{13}C NMR of (Table 1, entry 1)



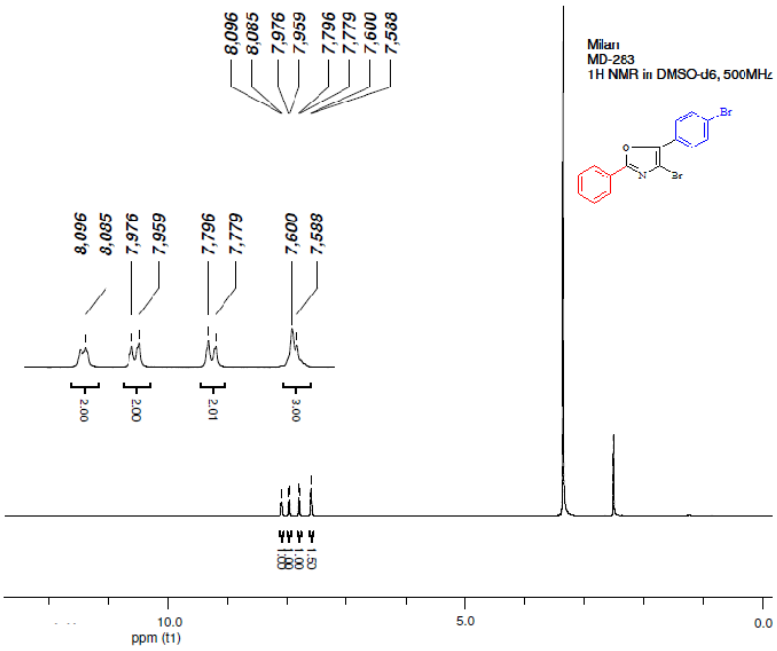
^{1}H NMR (Table 1, entry 2)



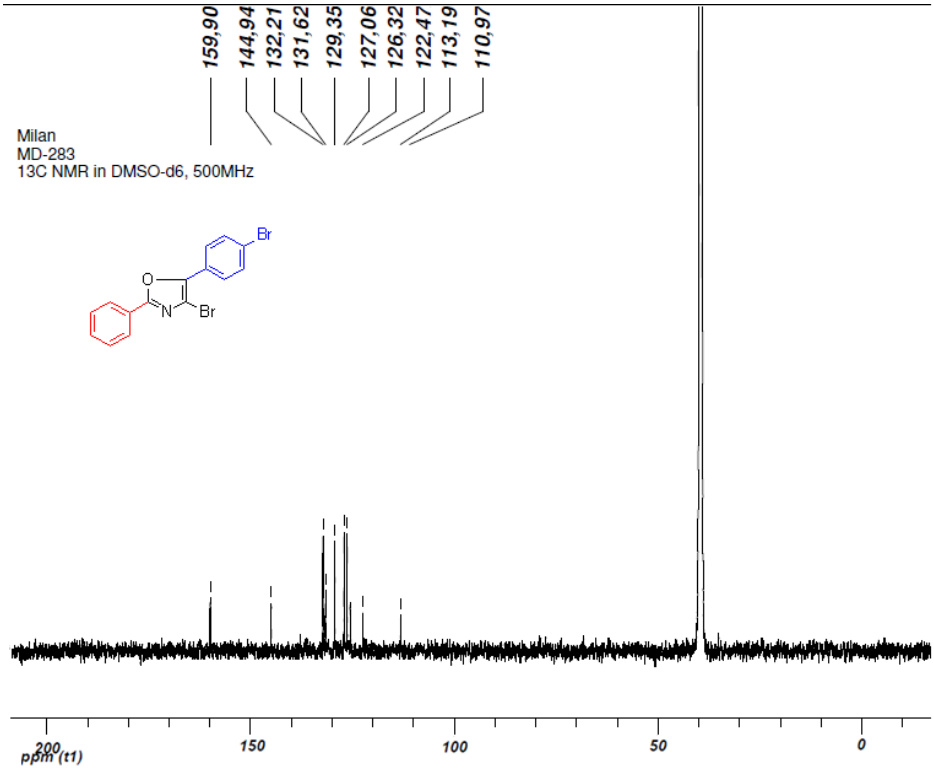
^{13}C NMR (Table 1, entry 2)



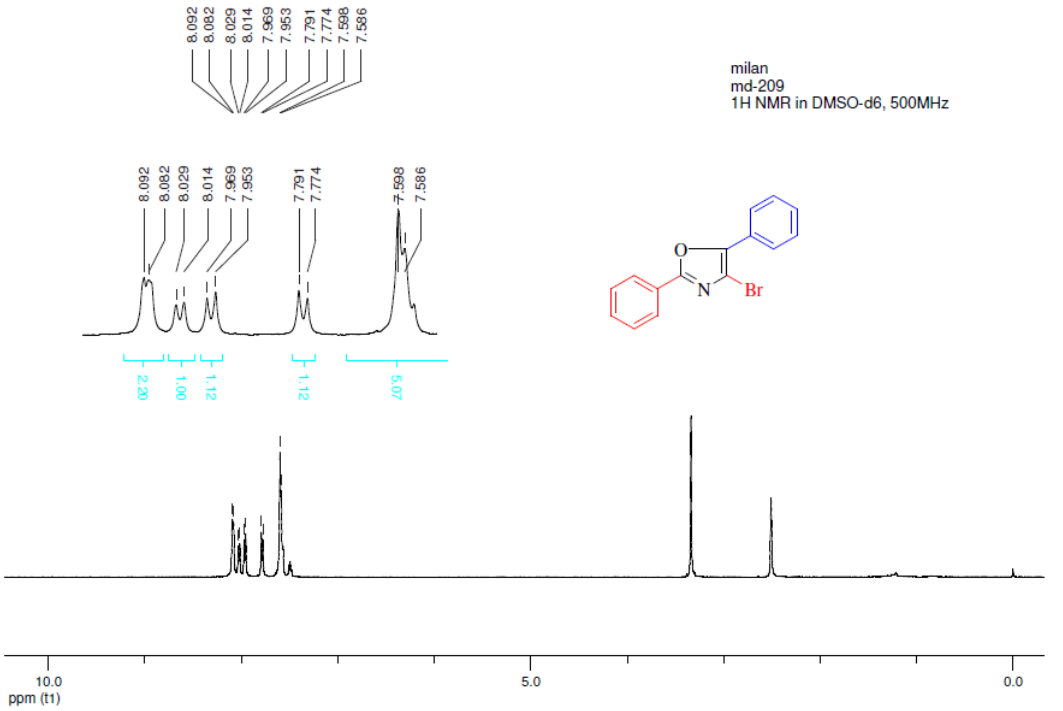
^{1}H NMR of (Table 1, entry 3)



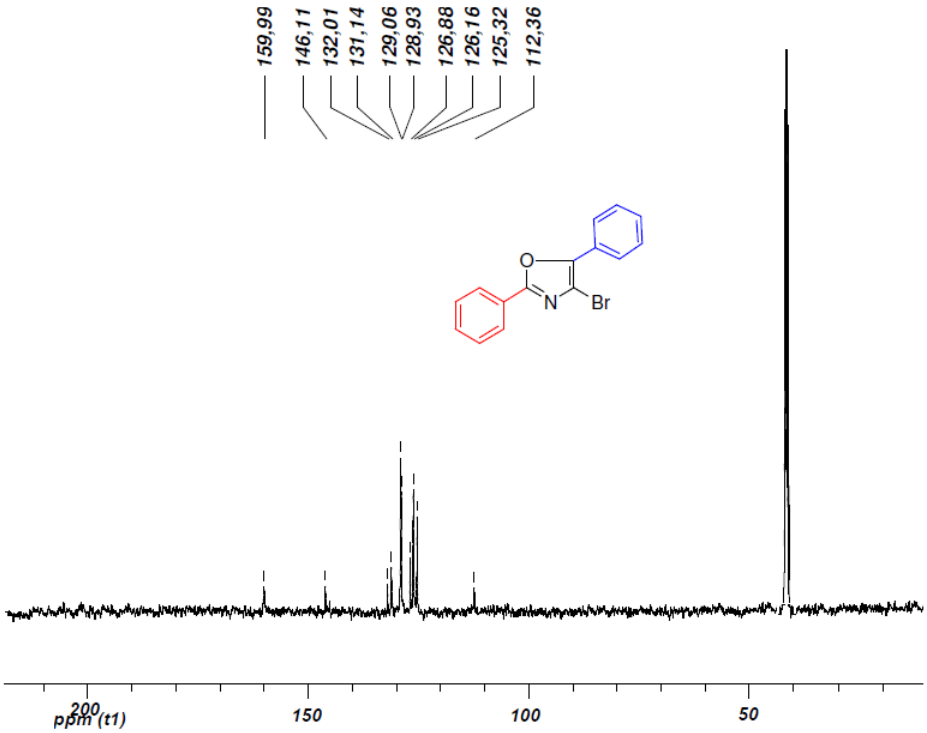
^{13}C NMR (Table 1, entry 3)



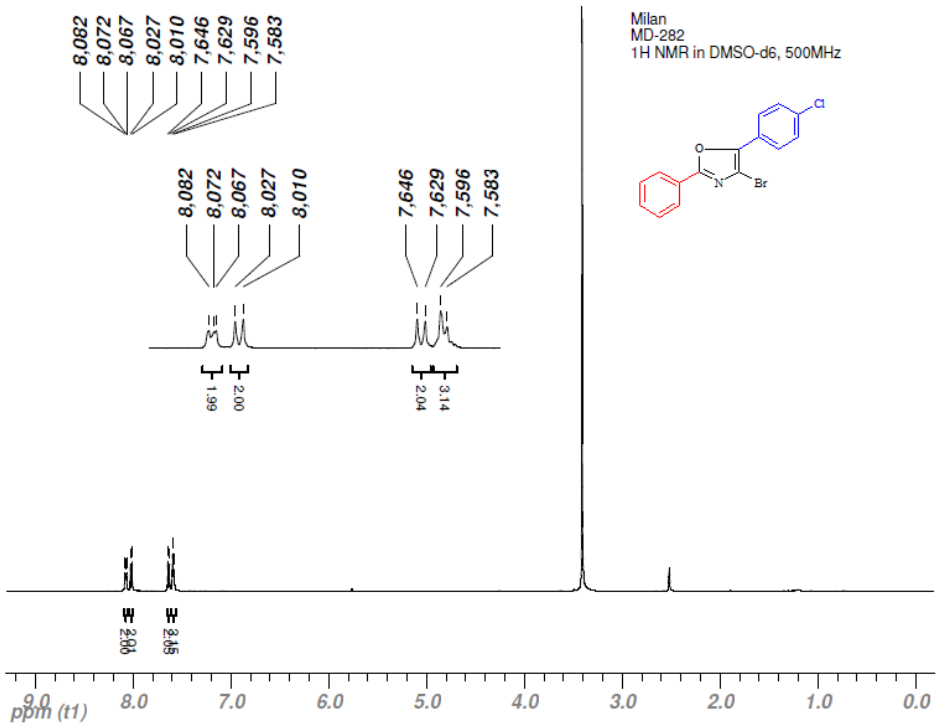
^{1}H NMR (Table 1, entry 4)



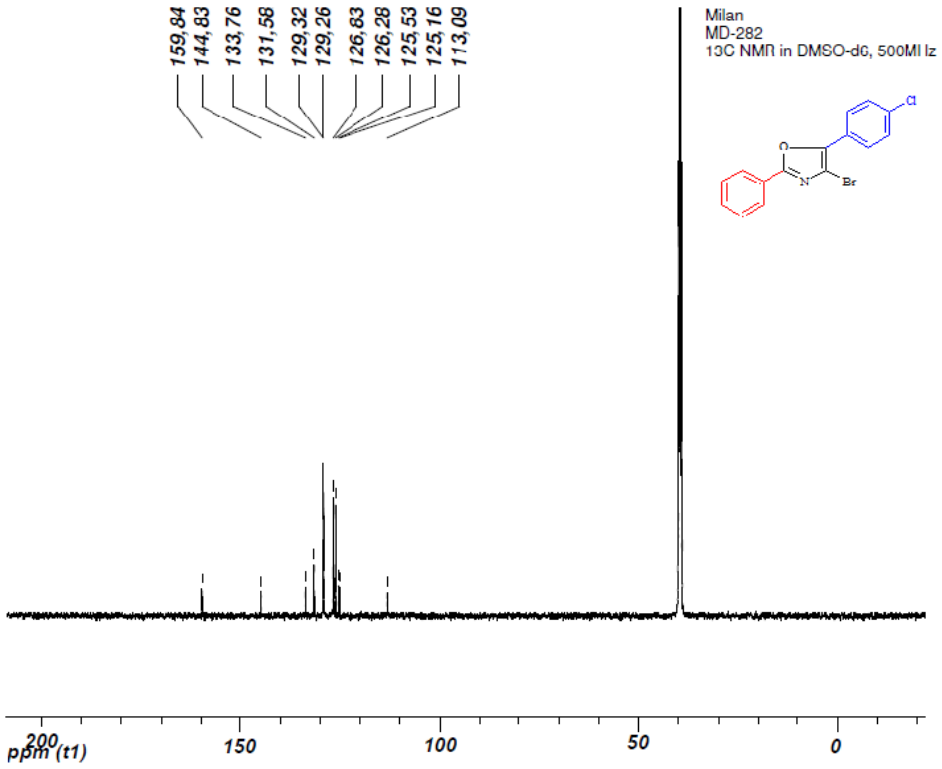
^{13}C NMR (Table 1, entry 4)



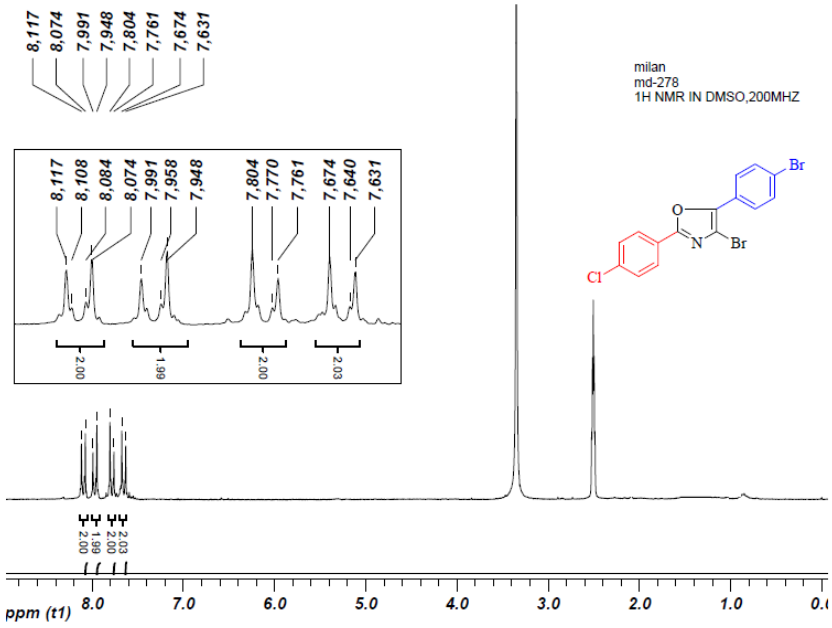
^{1}H NMR (Table 1, entry 5)



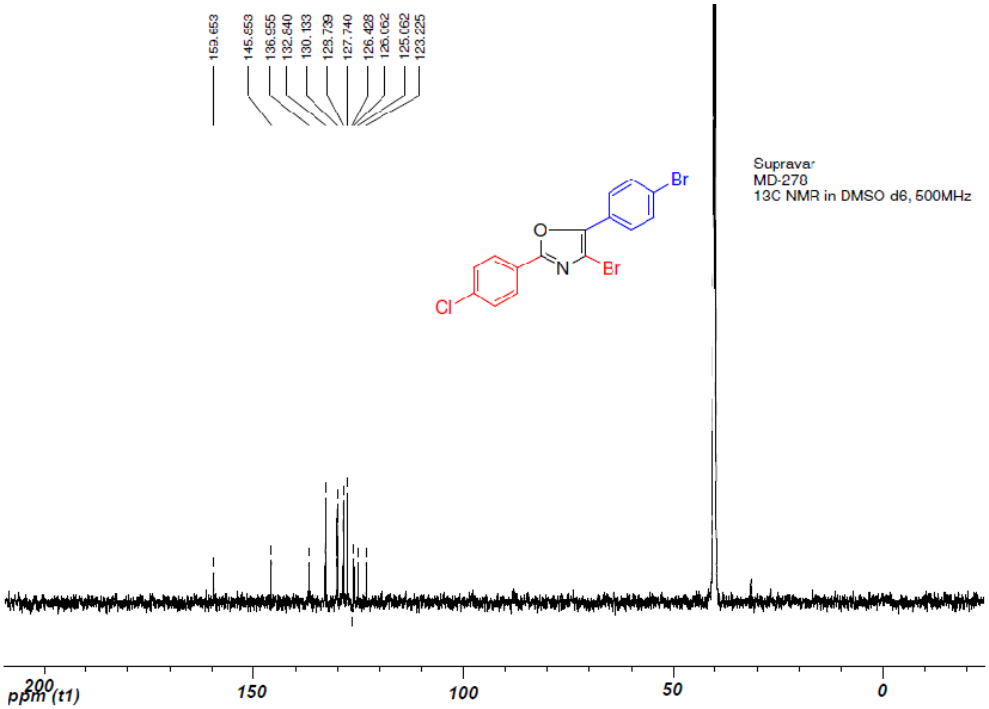
^{13}C NMR (Table 1, entry 5)



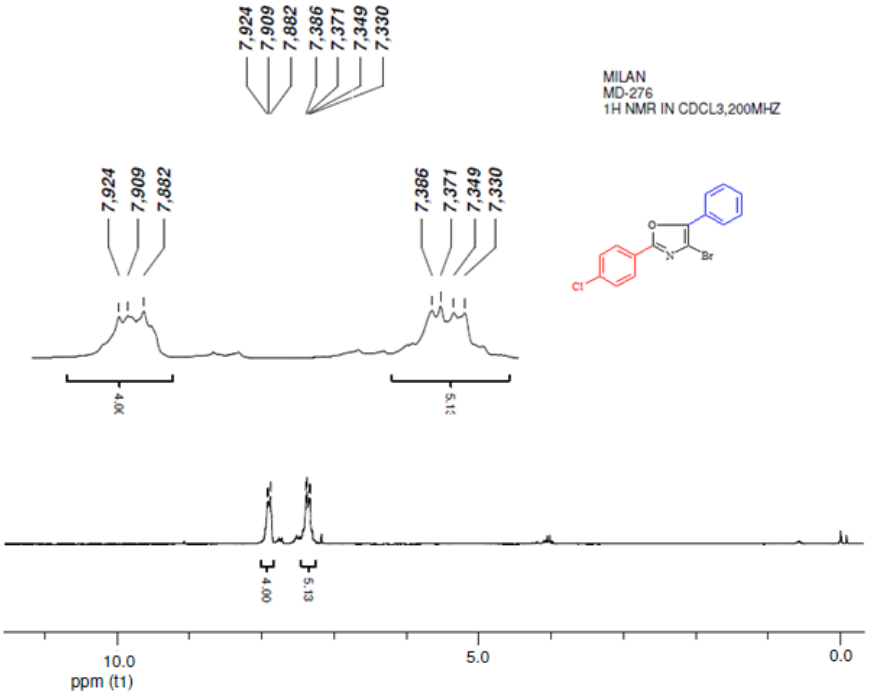
^{1}H NMR (Table 1, entry 6)



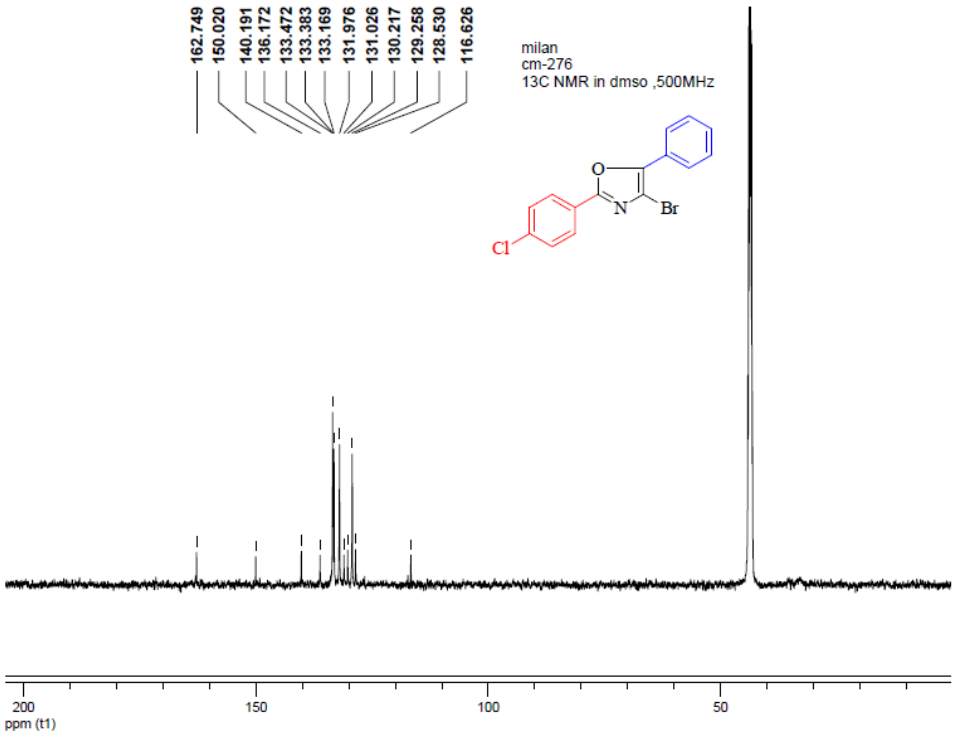
^{13}C NMR (Table 1, entry 6)



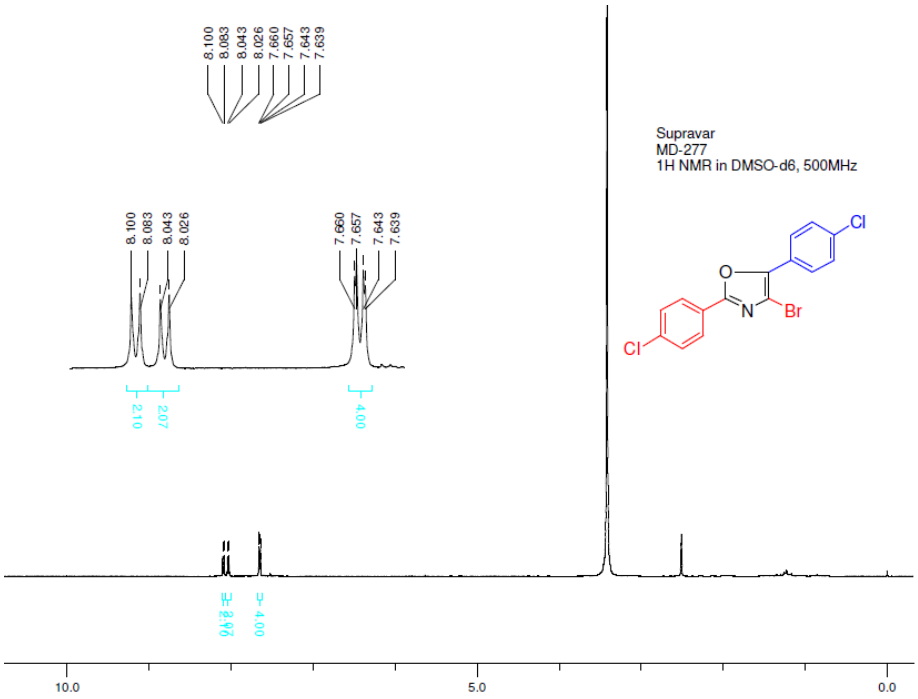
^{1}H NMR (Table 1, entry 7)



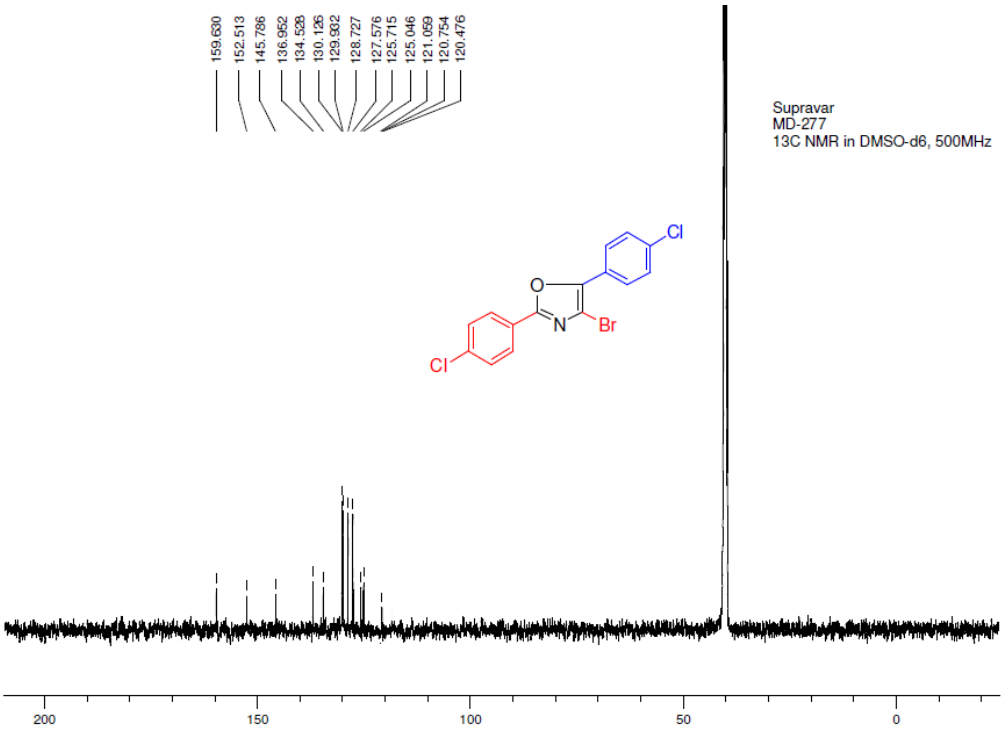
^{13}C NMR (Table 1, entry 7)



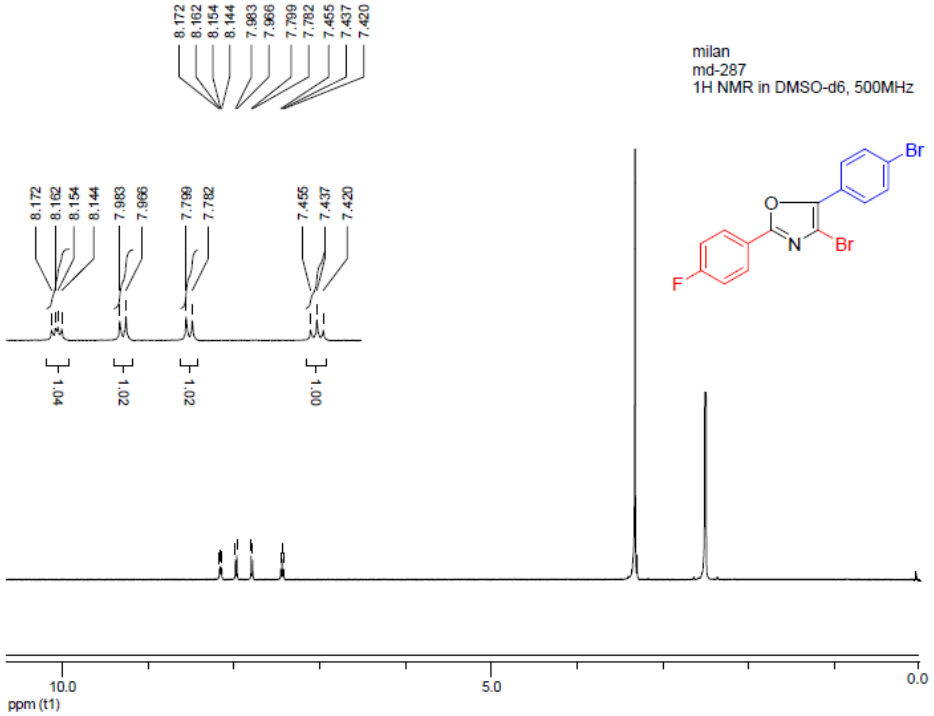
^{1}H NMR (Table 1, entry 8)



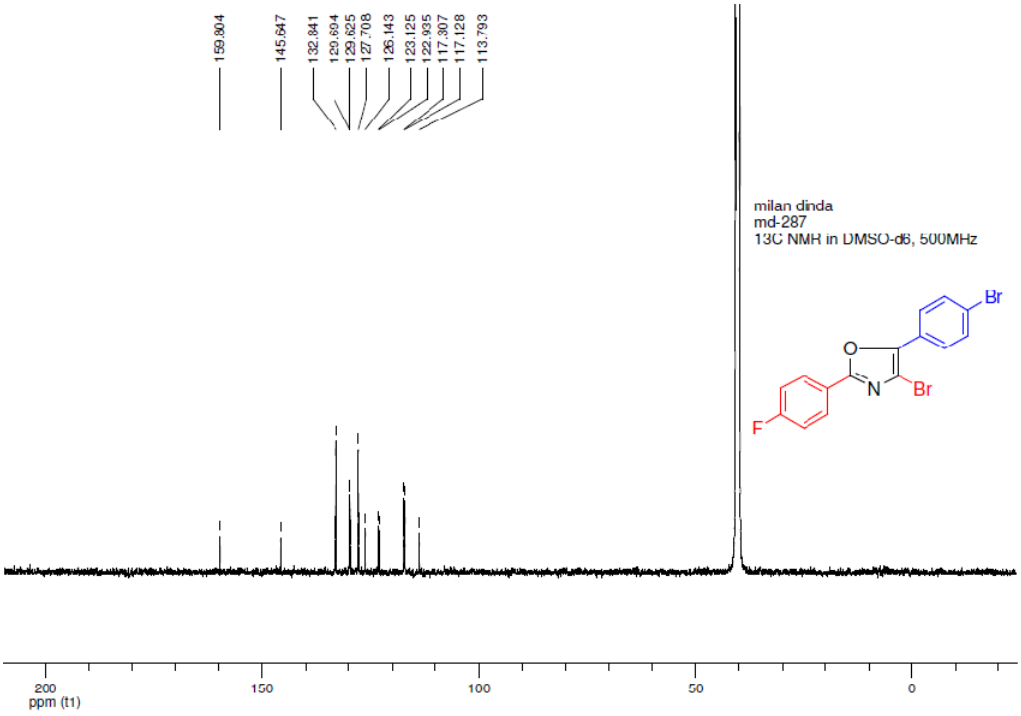
^{13}C NMR (Table 1, entry 8)



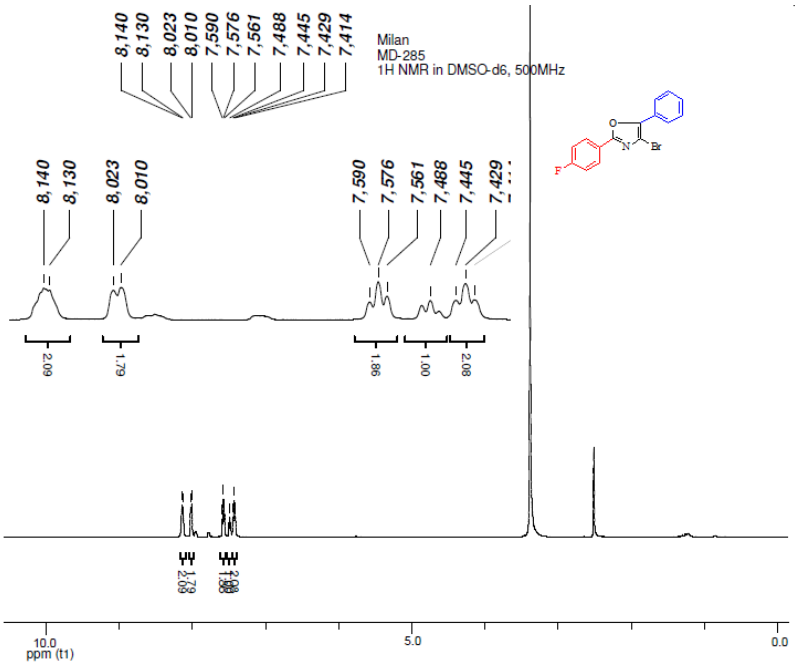
^{1}H NMR (Table 1, entry 9)



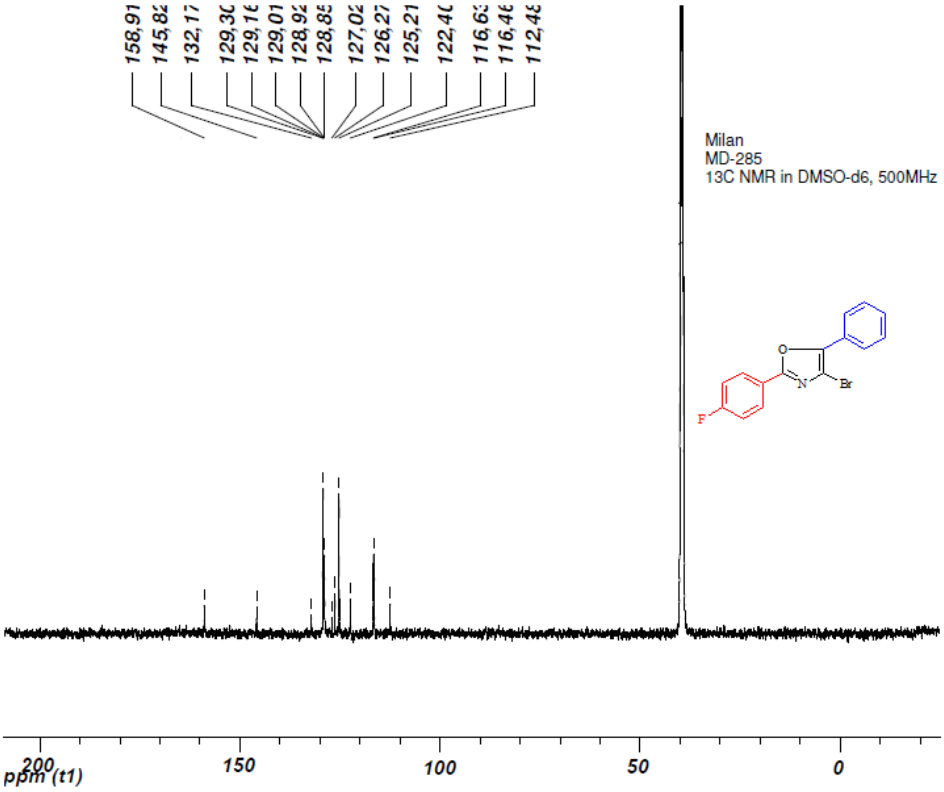
^{13}C NMR (Table 1, entry 9)



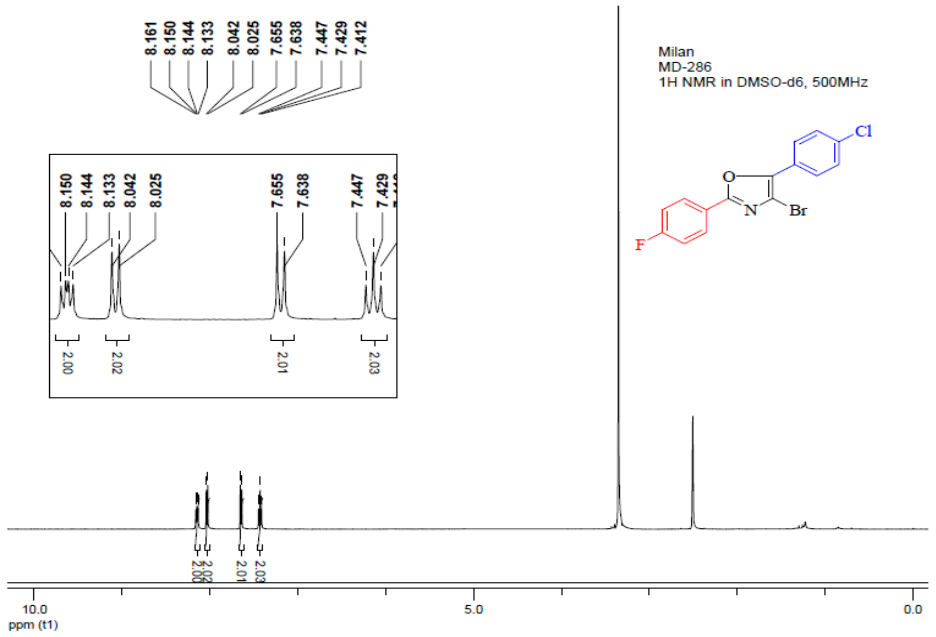
^{1}H NMR (Table 1, entry 10)



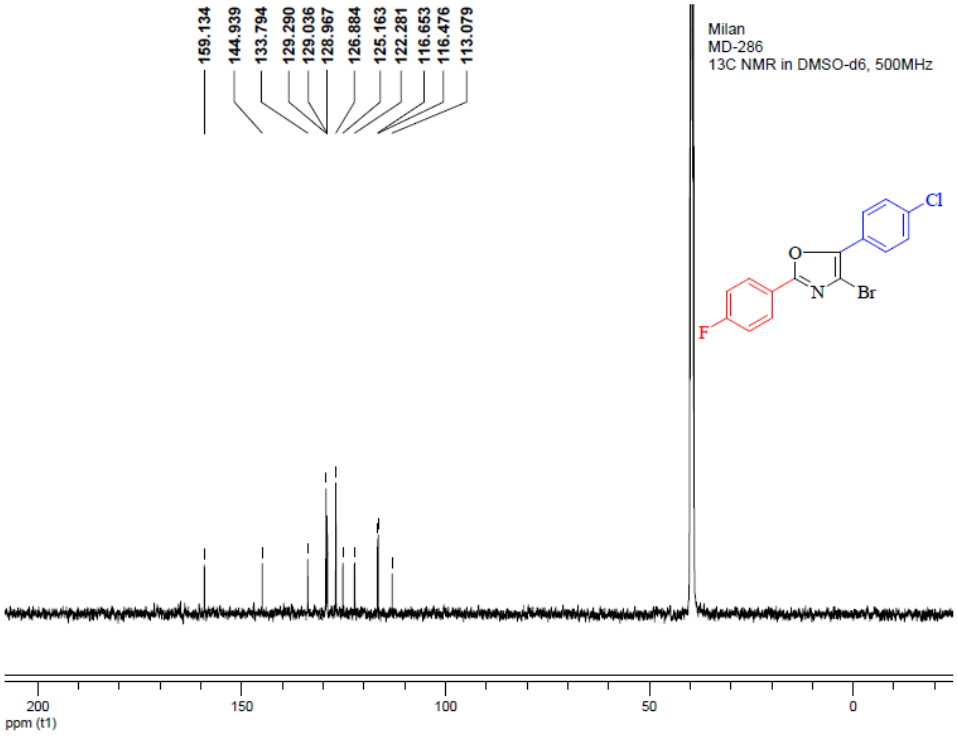
^{13}C NMR (Table 1, entry 10)



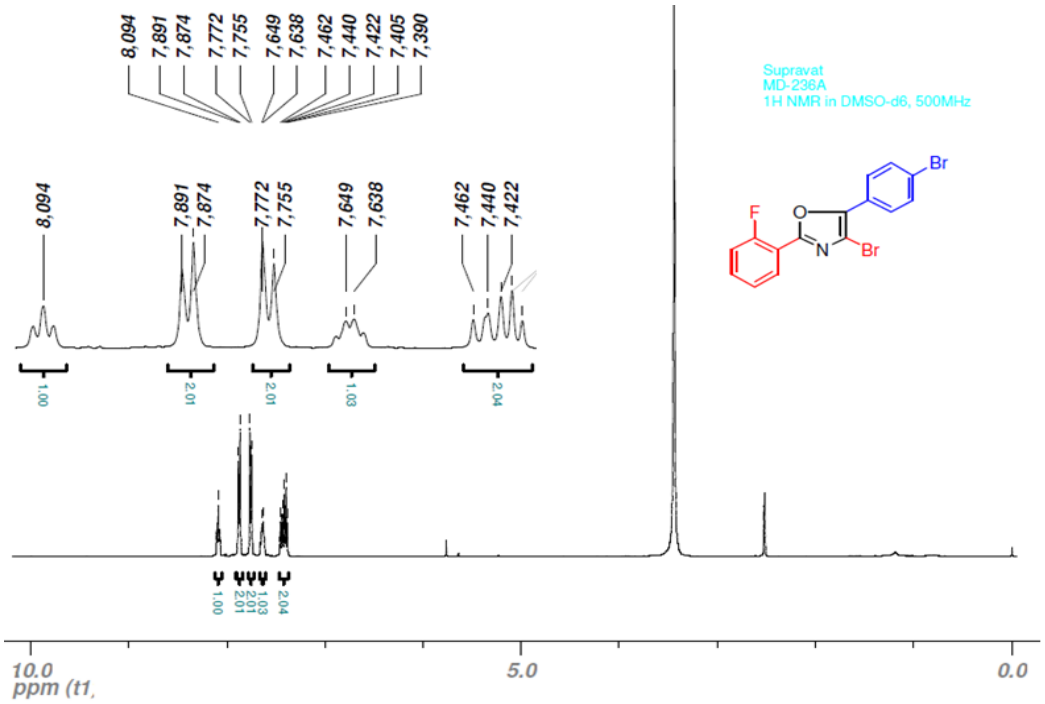
^{1}H NMR (Table 1, entry 11)



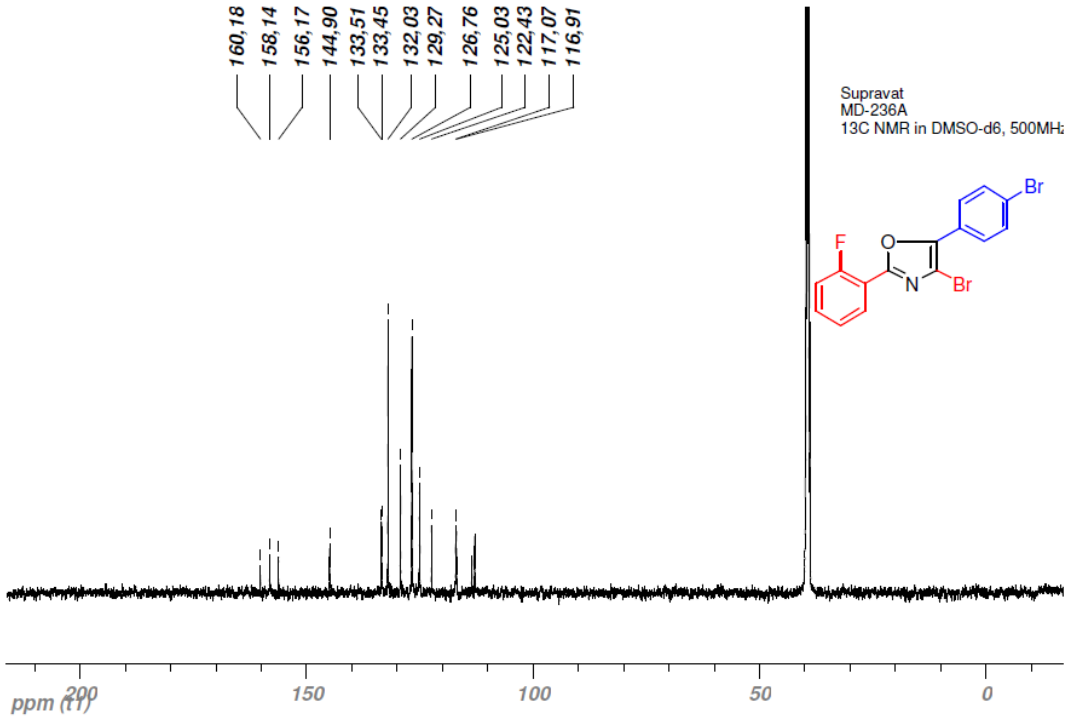
^{13}C NMR (Table 1, entry 11)



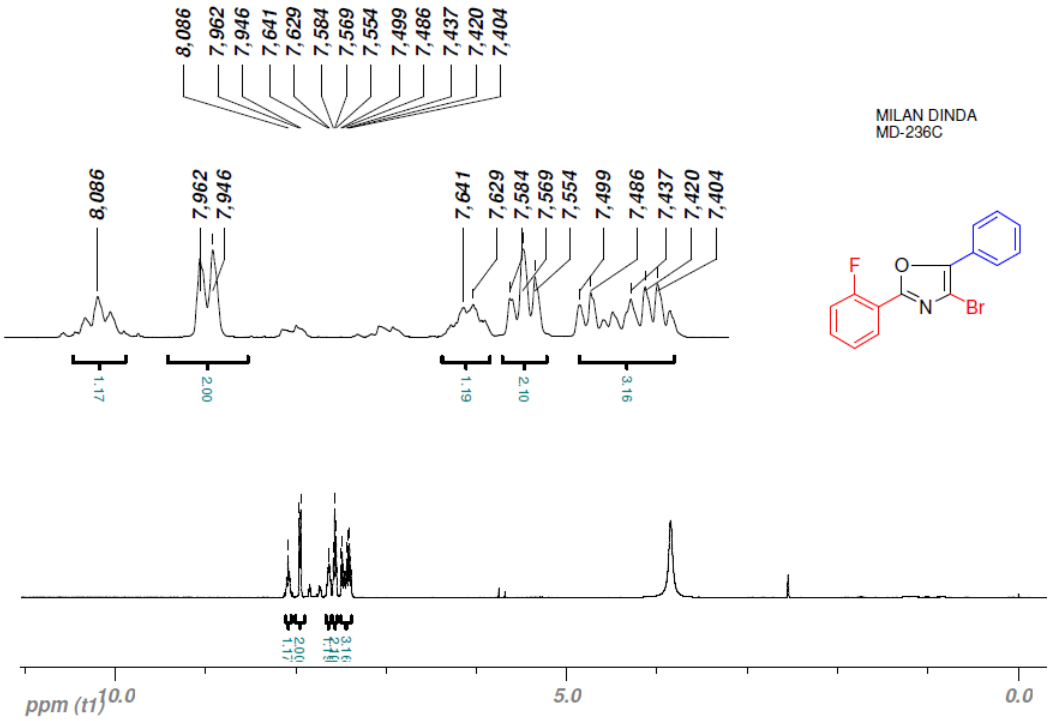
^{1}H NMR (Table 1, entry 12)



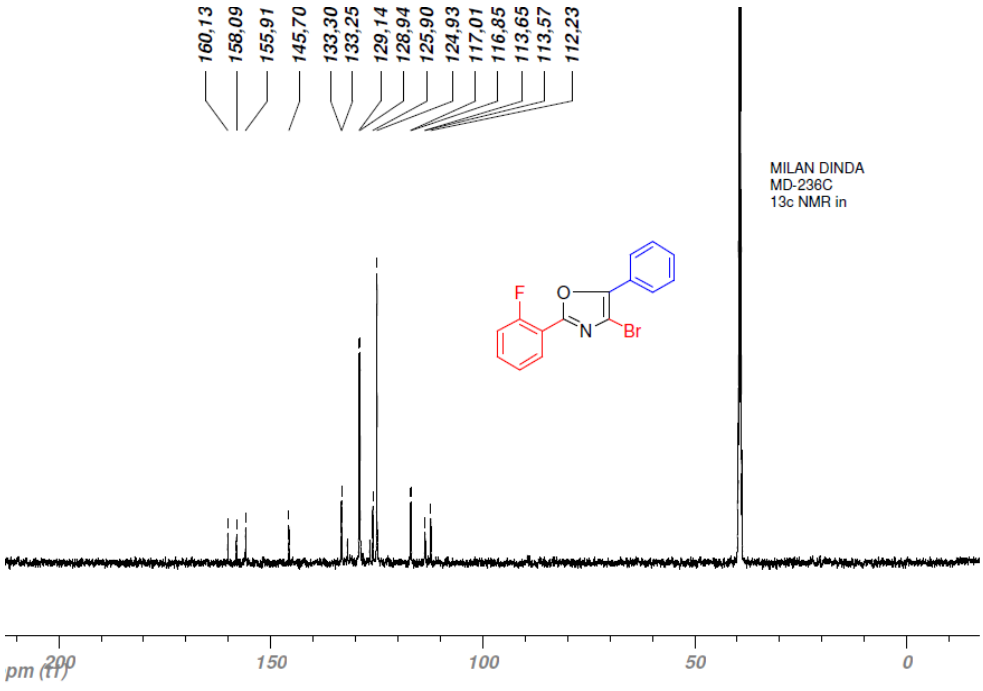
^{13}C NMR (Table 1, entry 12)



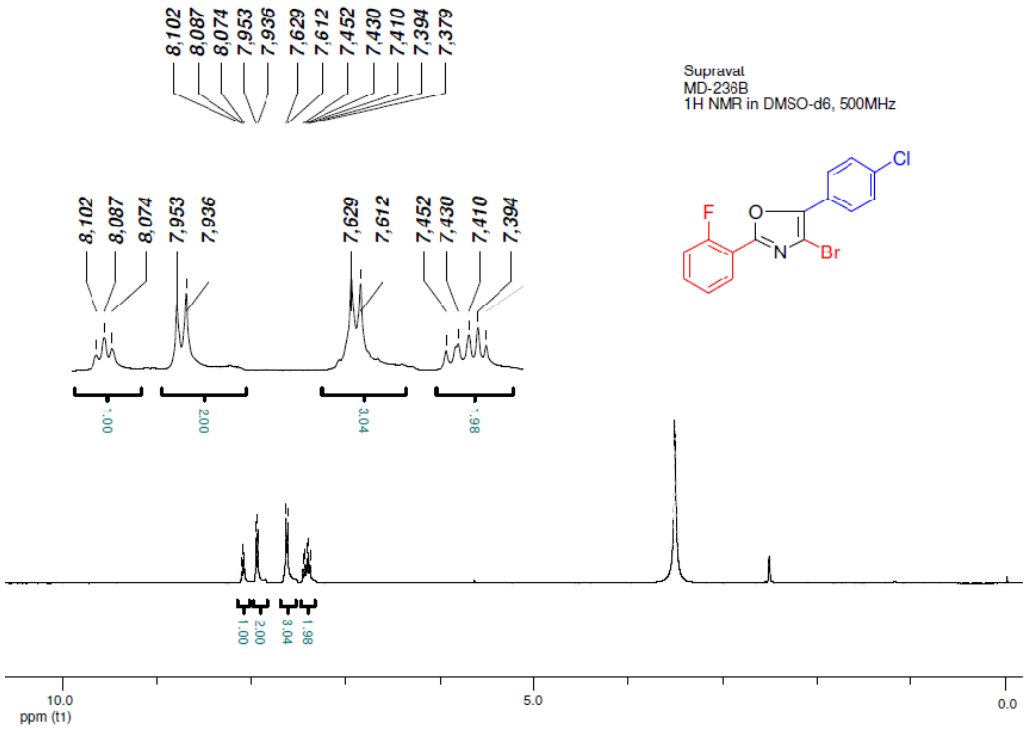
^{1}H NMR (Table 1, entry 13)



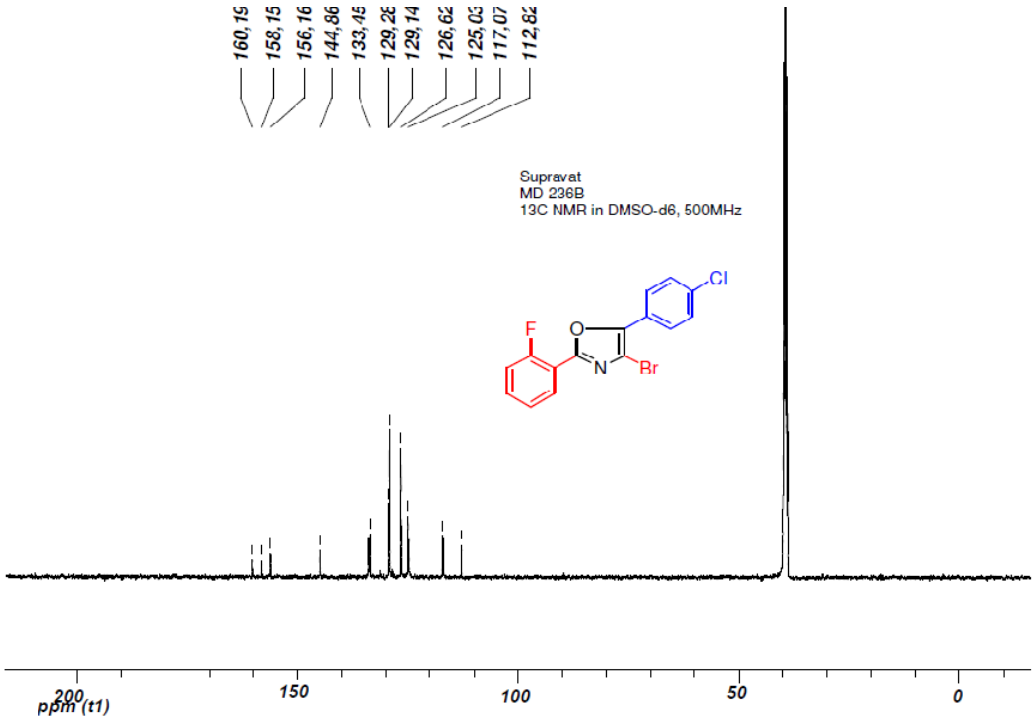
^{13}C NMR (Table 1, entry 13)



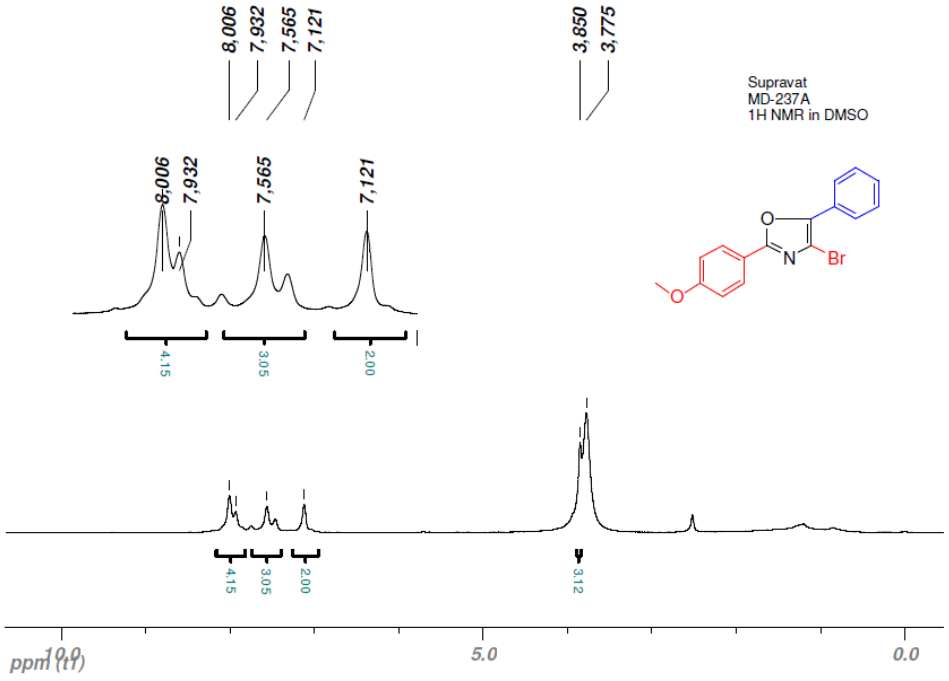
^{1}H NMR (Table 1, entry 14)



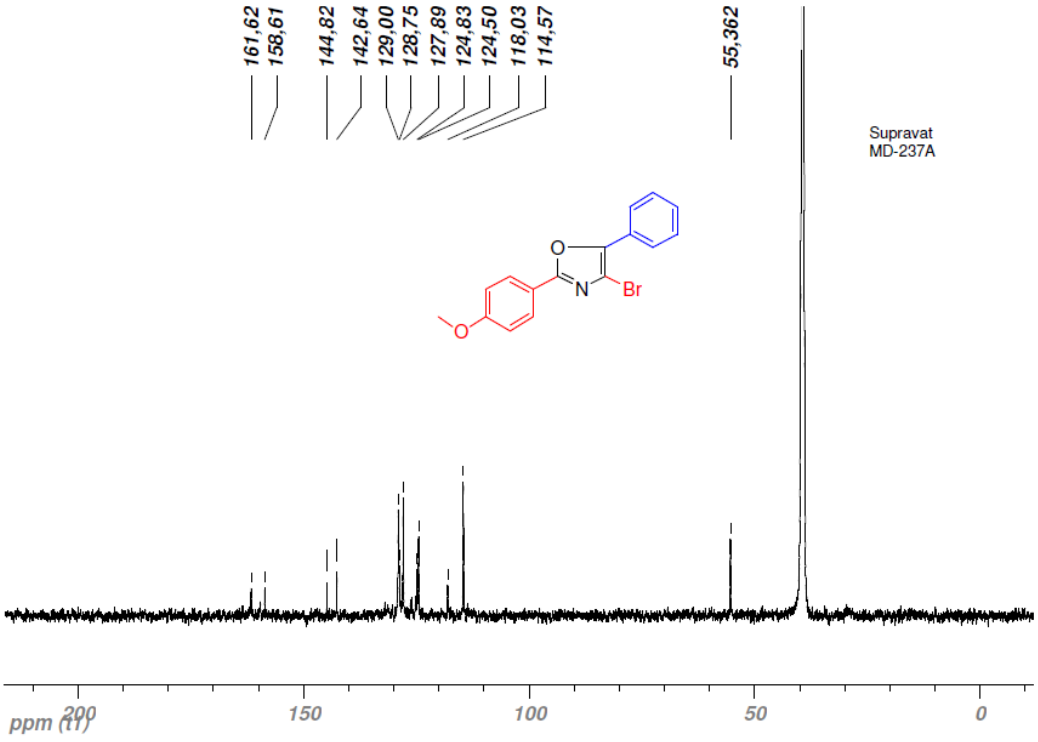
^{13}C NMR (Table 1, entry 14)



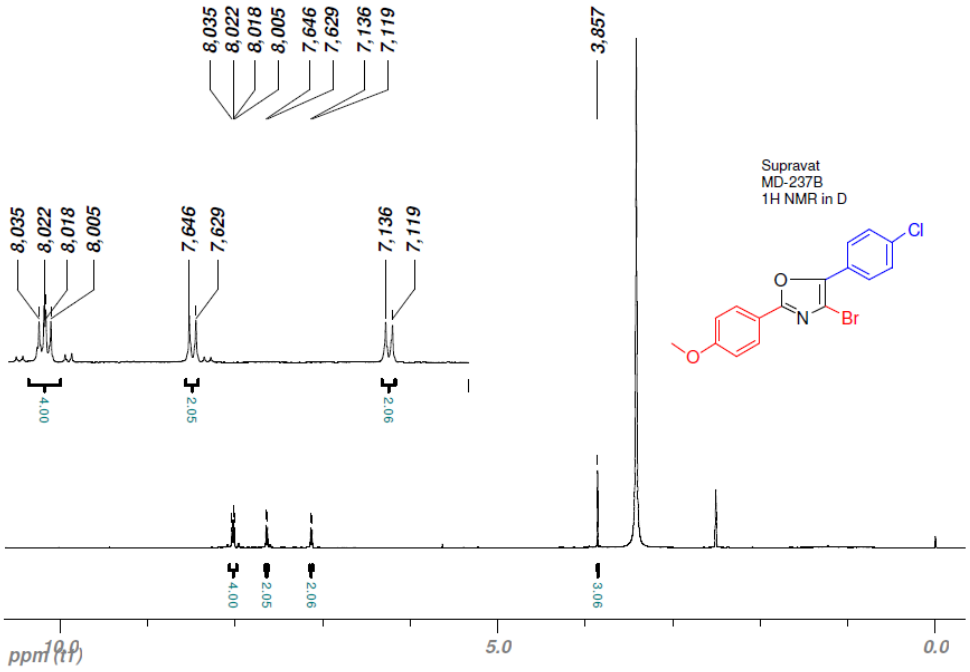
^{1}H NMR (Table 1, entry 15)



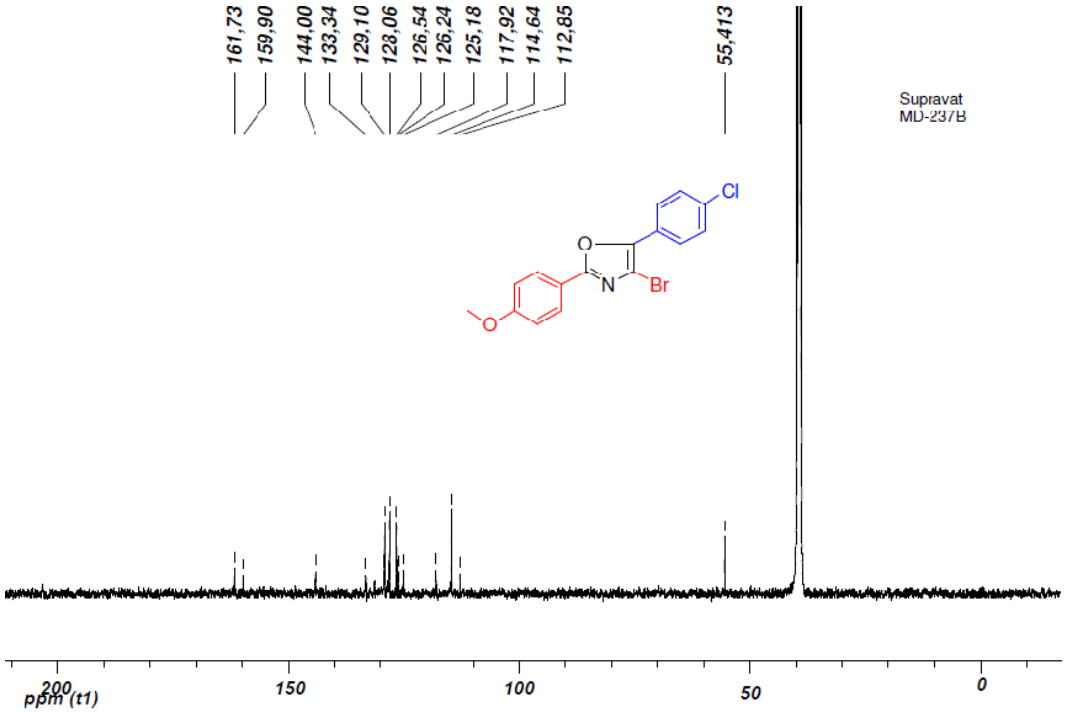
^{13}C NMR (Table 1, entry 15)



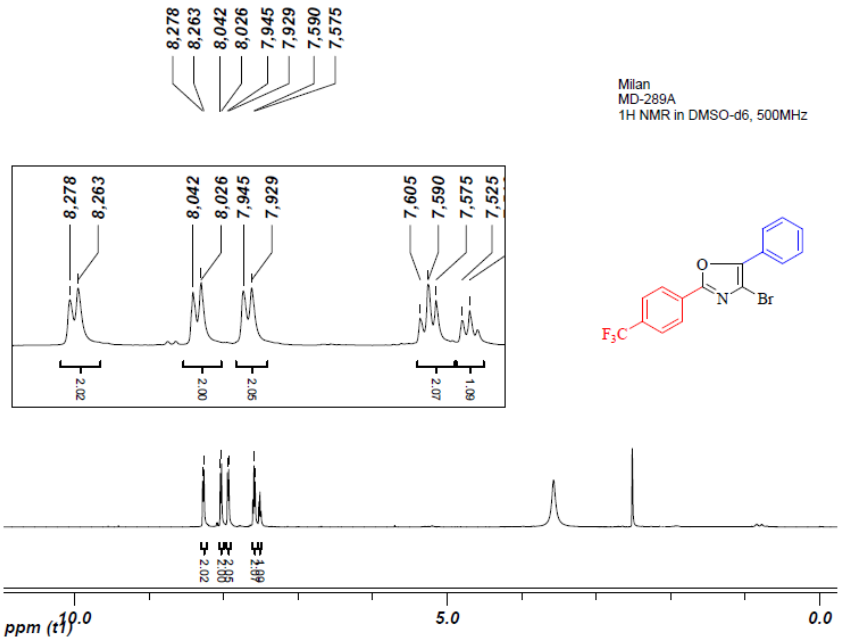
^{1}H NMR (Table 1, entry 16)



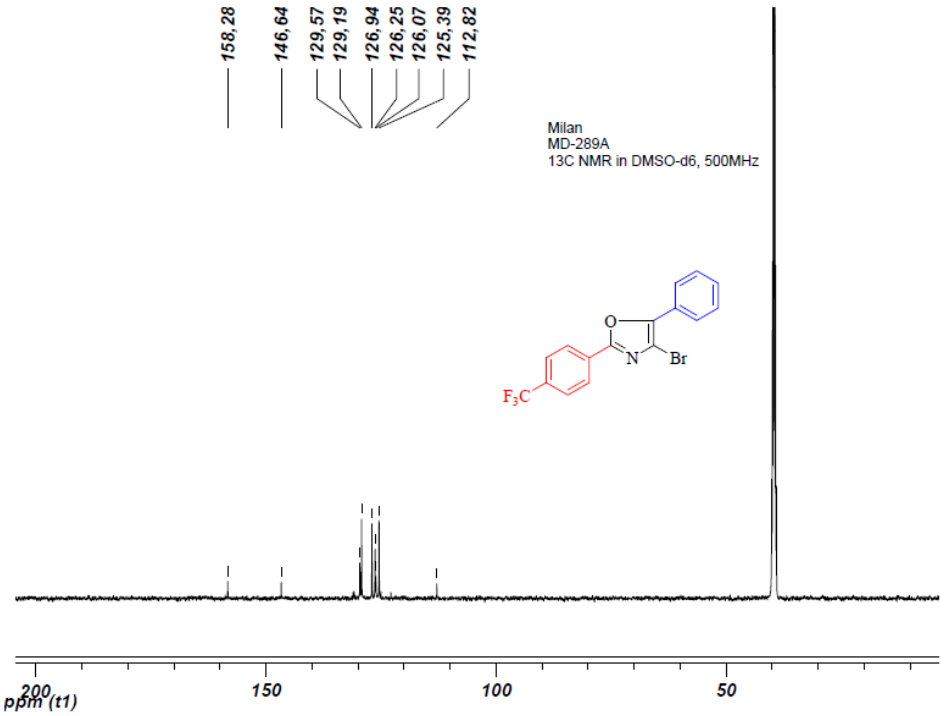
^{13}C NMR (Table 1, entry 16)



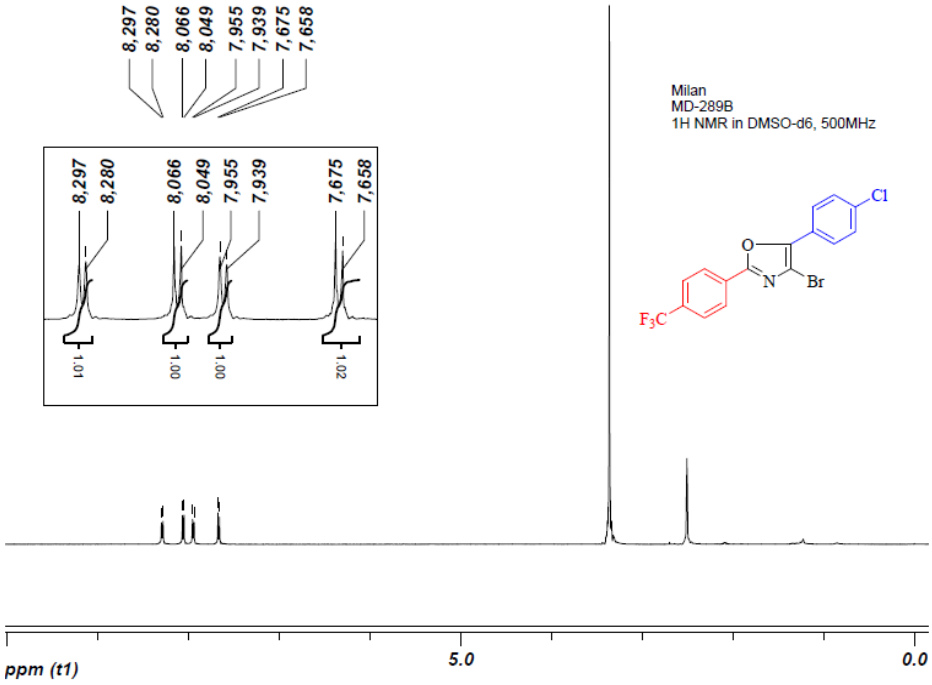
^{1}H NMR (Table 1, entry 17)



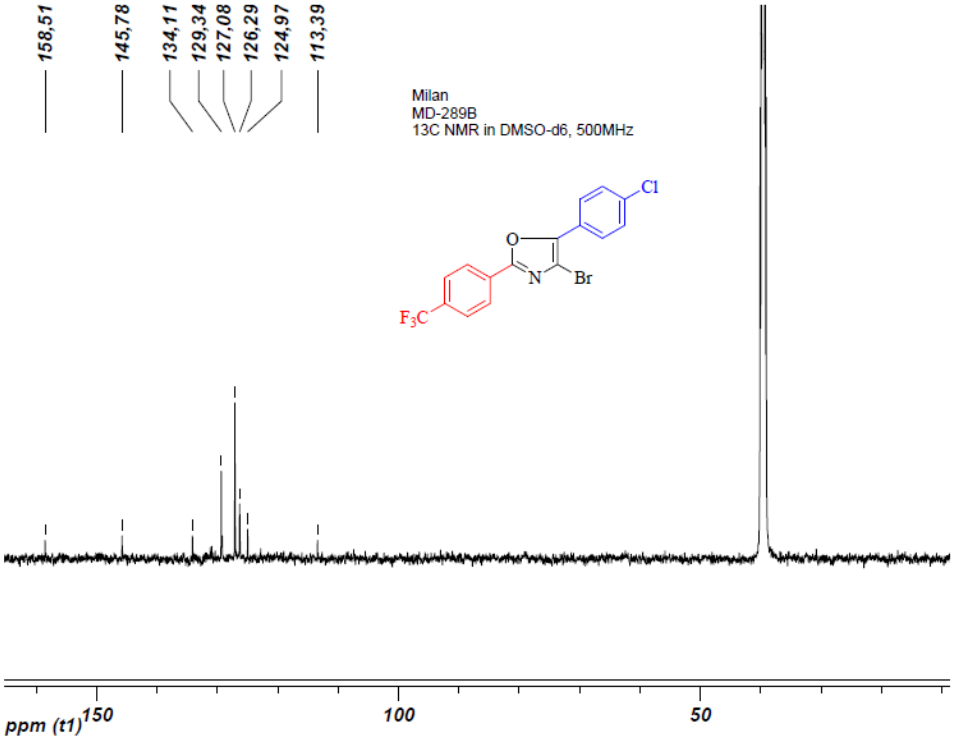
^{13}C NMR (Table 1, entry 17)



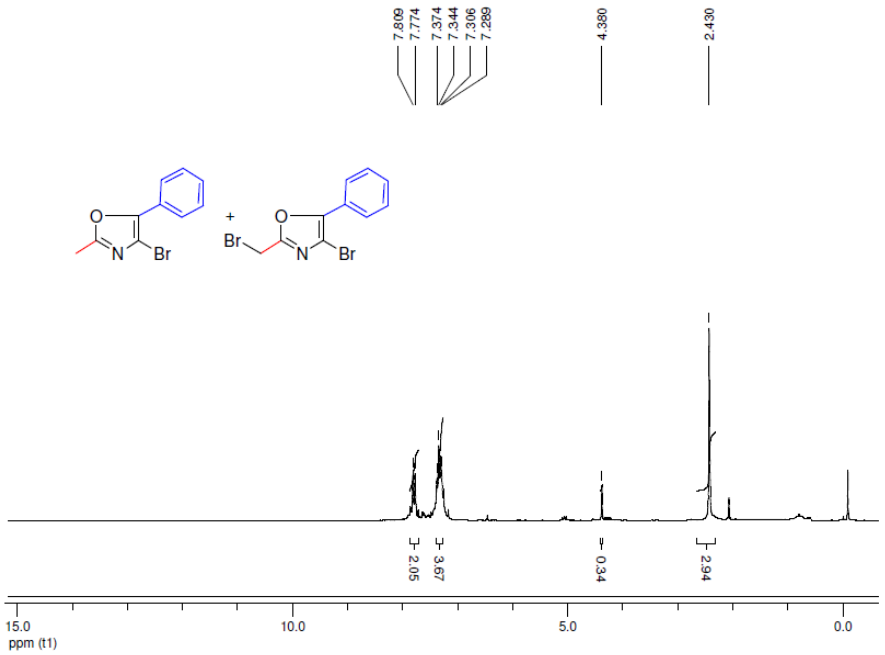
^{1}H NMR (Table 1, entry 18)



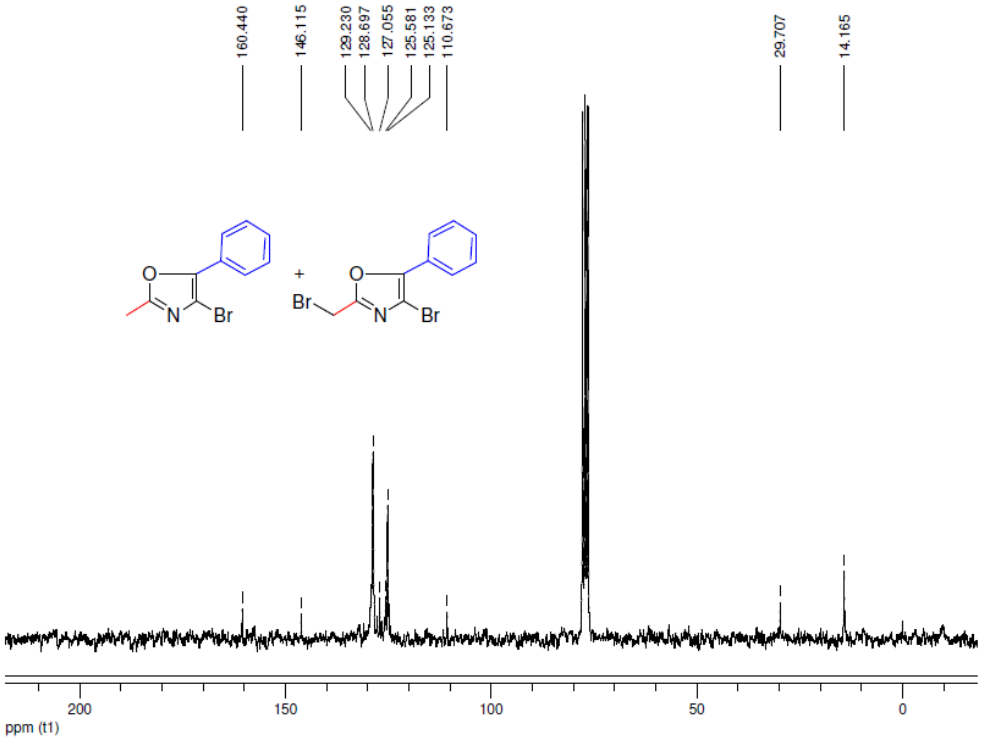
^{13}C NMR (Table 1, entry 18)



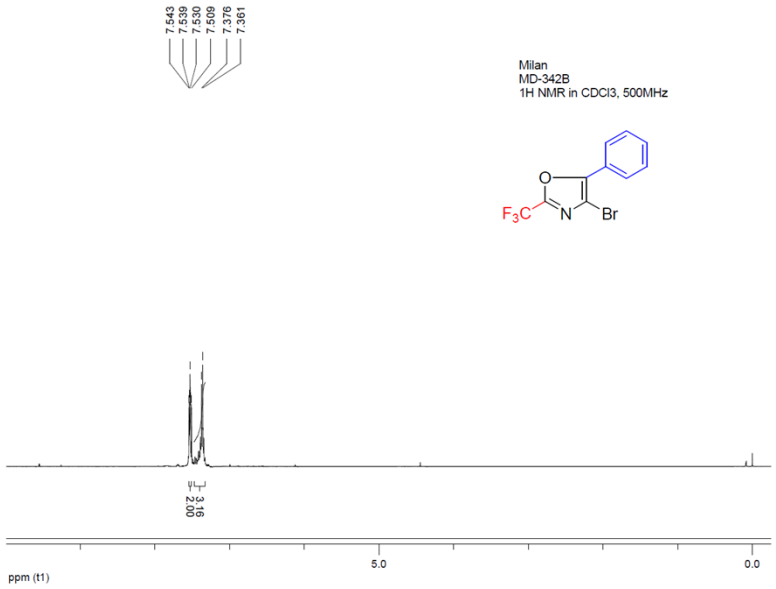
^{1}H NMR (Table 1, entry 19)



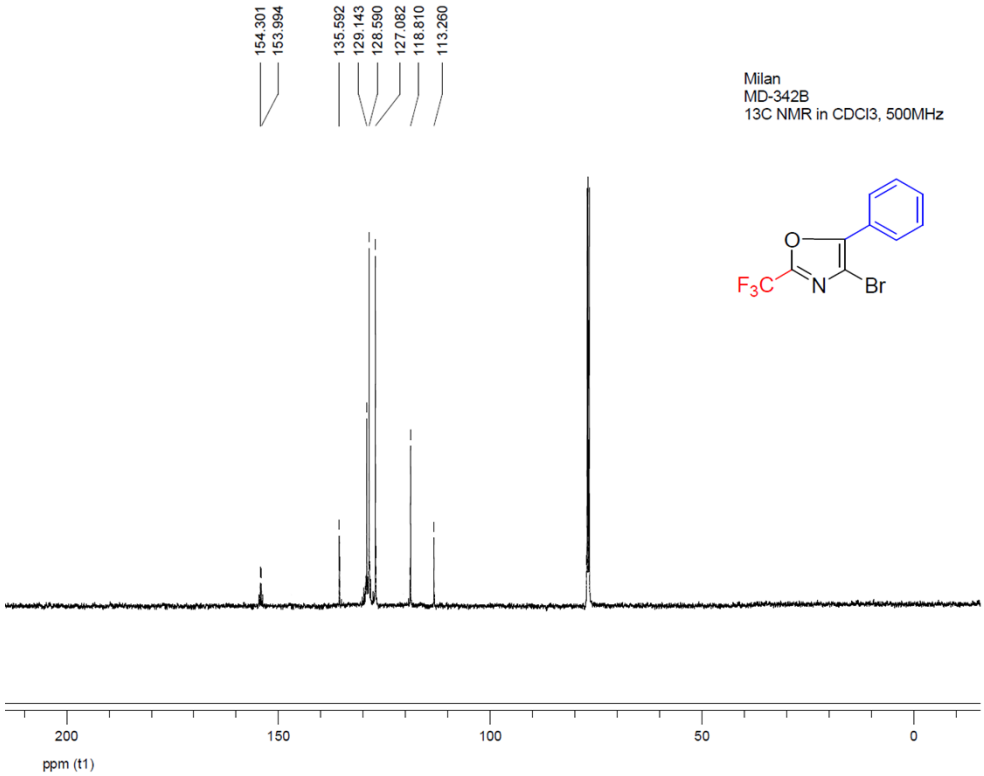
^{13}C NMR (Table 1, entry 19)



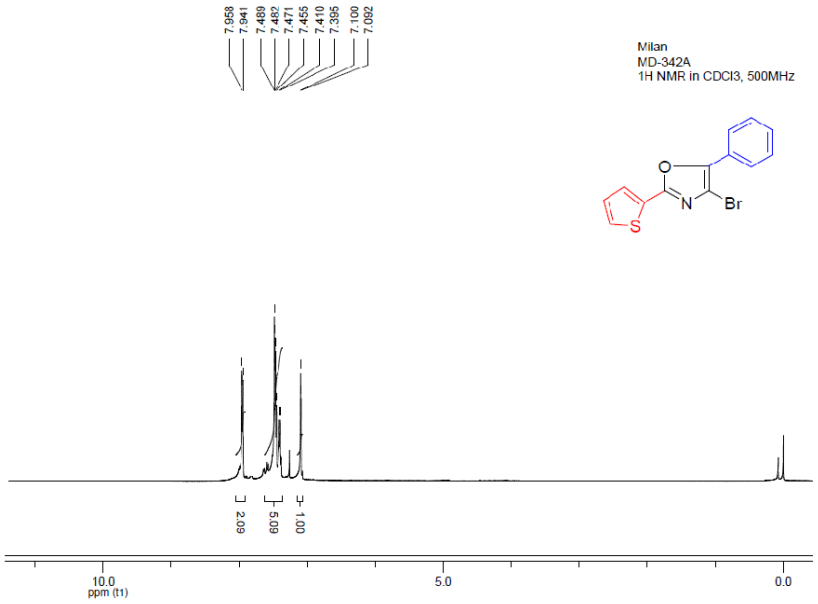
^{1}H NMR (Table 1, entry 20)



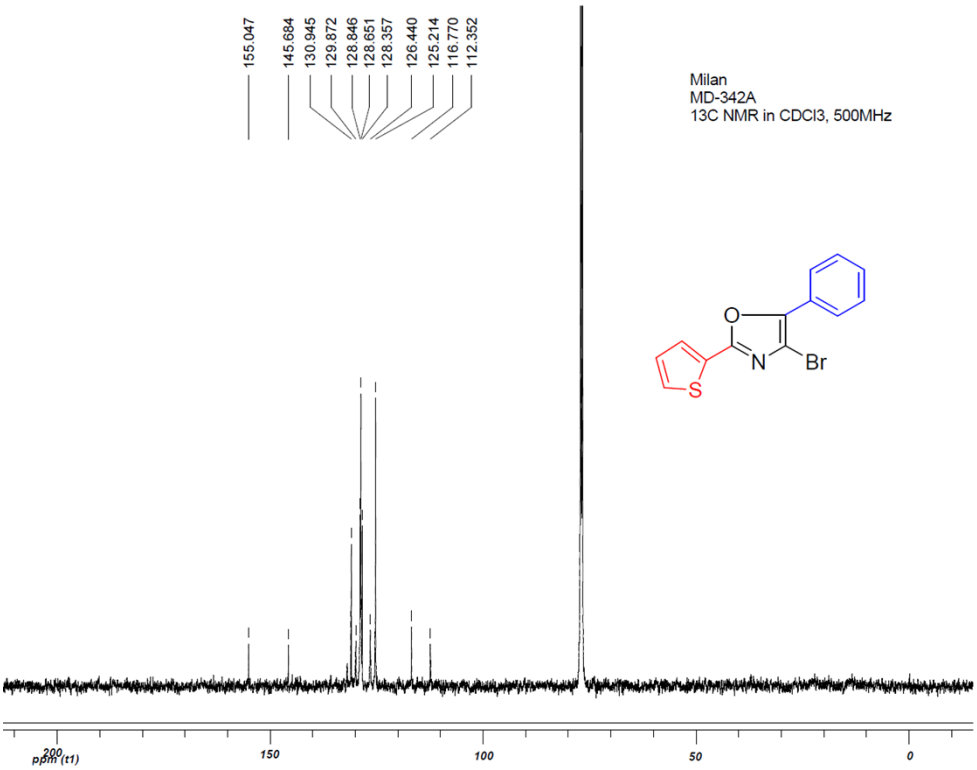
^{13}C NMR (Table 1, entry 20)



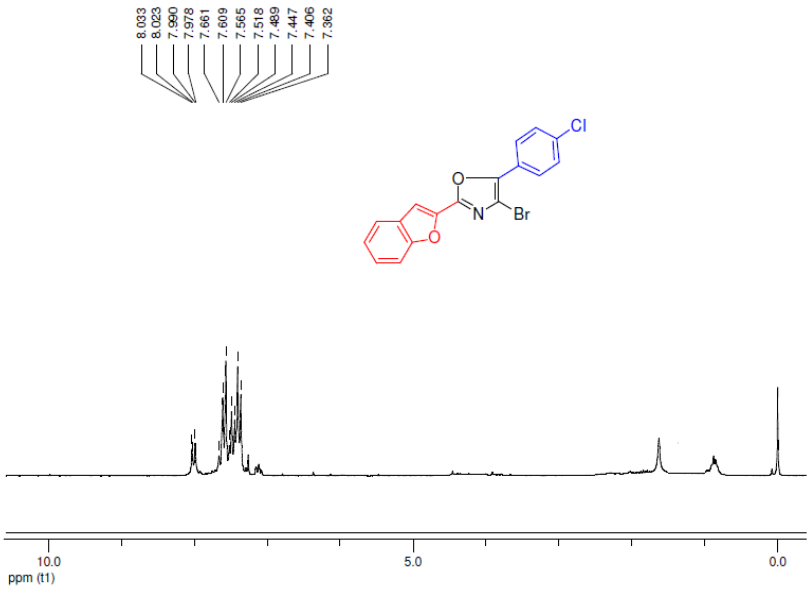
^{1}H NMR (Table 1, entry 21)



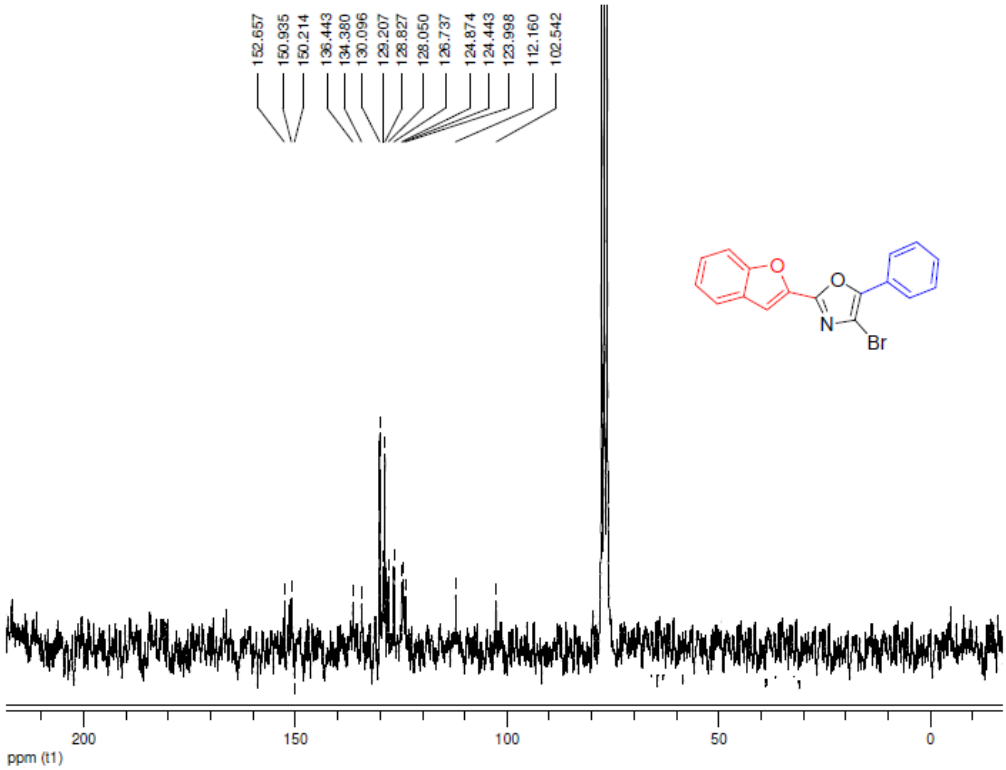
^{13}C NMR (Table 1, entry 21)



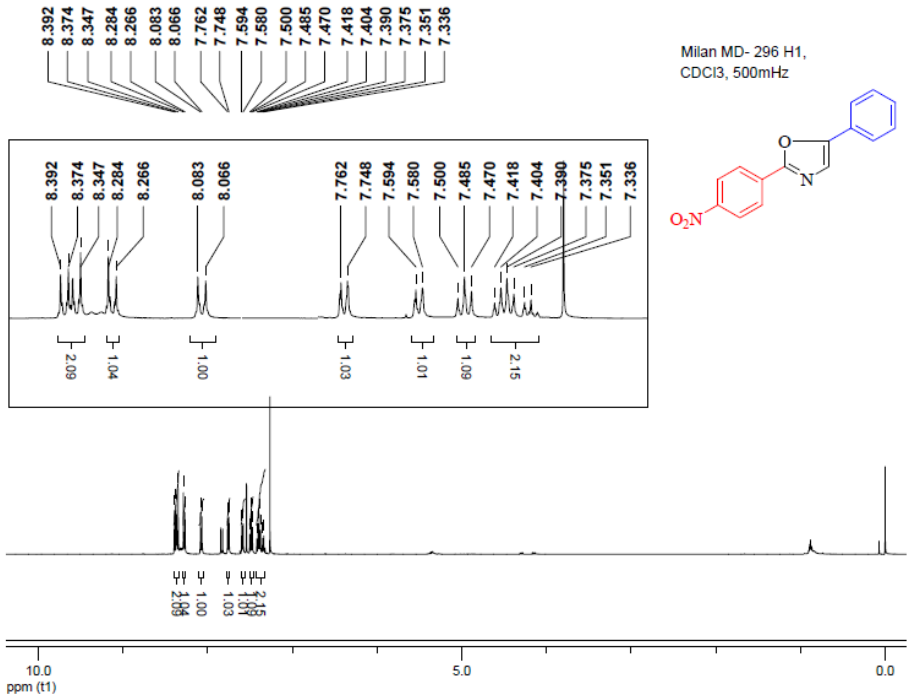
^{1}H NMR (Table 1, entry 22)



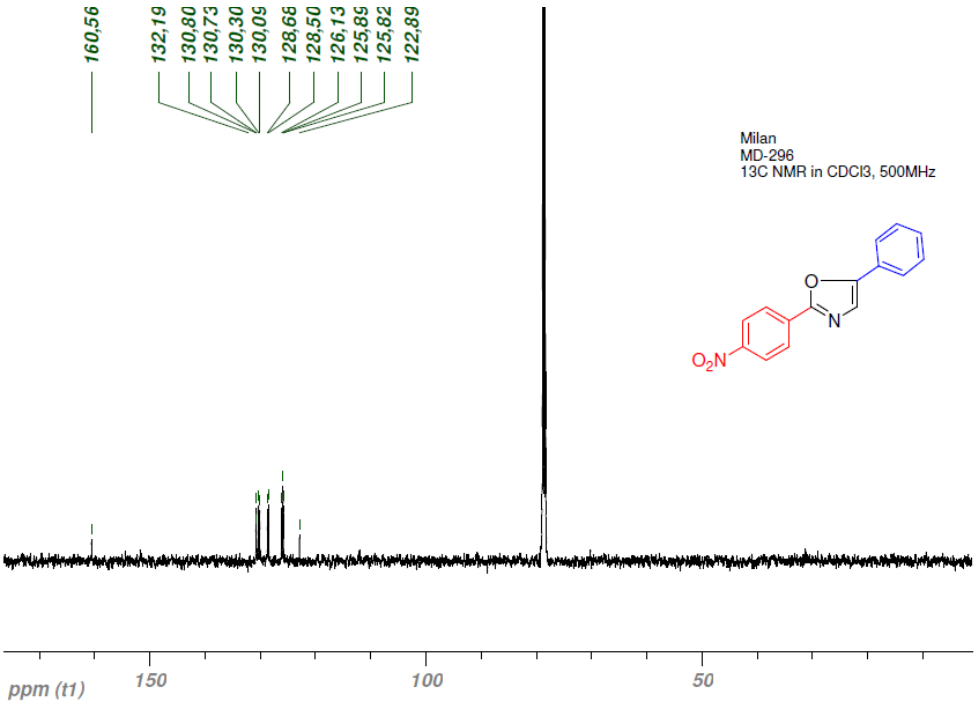
^{13}C NMR (Table 1, entry 22)

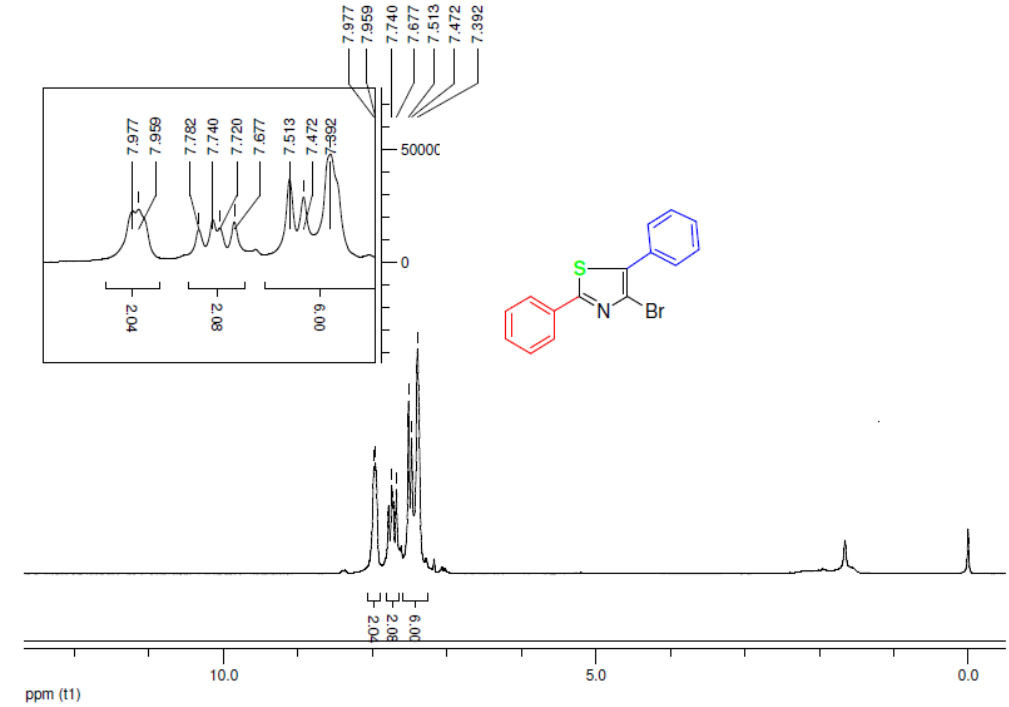


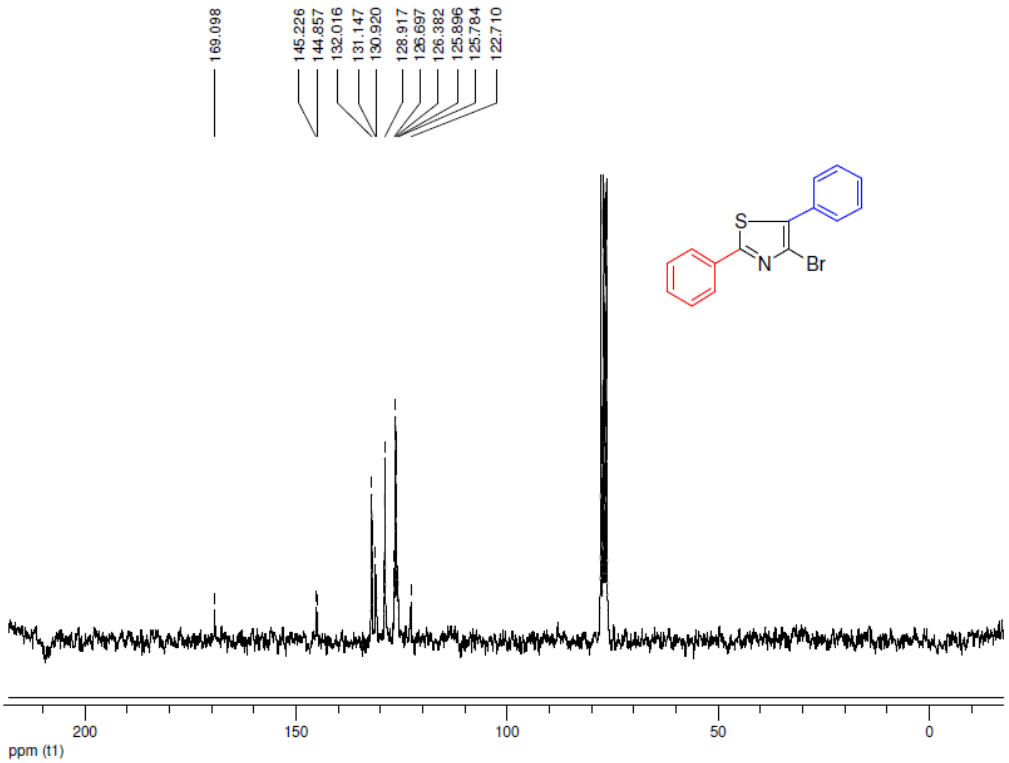
^{1}H NMR (non halo 2,5 disubstituted oxazole)



^{13}C NMR (non halo 2,5 disubstituted oxazole)







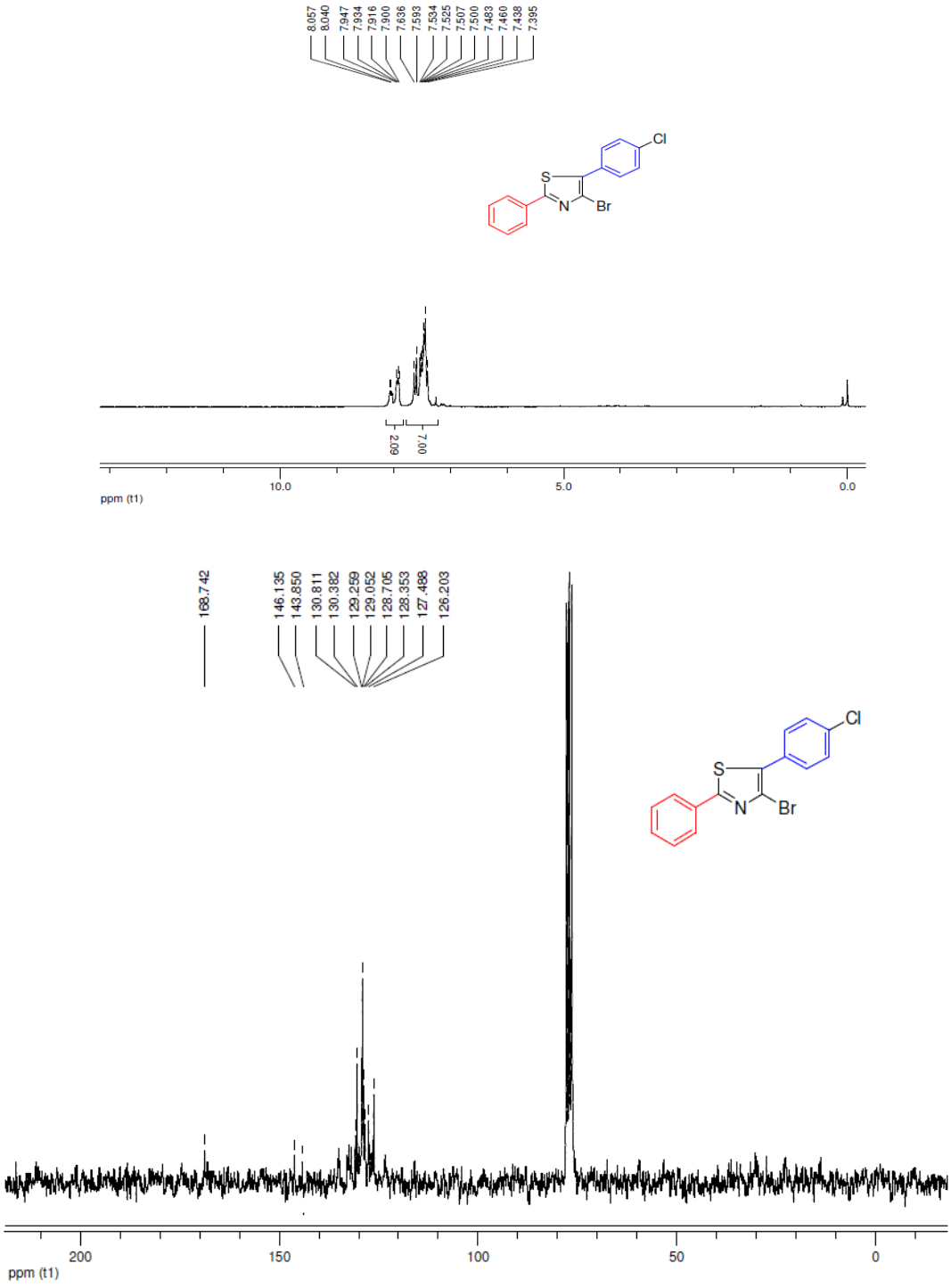
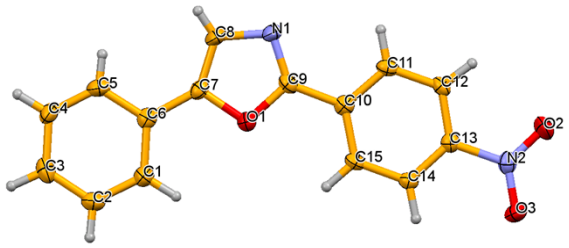


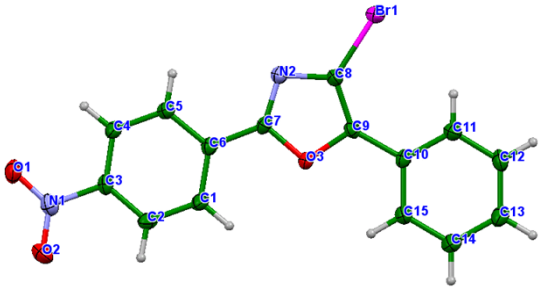
Table S2. Crystal Data and Refinement Parameters for the Organic Compounds synthesized in Table S1 and Table 1

Identification code	Table S1, Entry 6 (A)	Table S1, Entry 6 (B)	Table 1, Entry 3	Table 1, Entry17	Table 1, Entry 18
Chemical formula	$C_{15}H_{10}N_2O_3$	$C_{15}H_9BrN_2O_3$	$C_{30}H_{18}Br_4N_2O_2$	$C_{16}H_9BrF_3NO$	$C_{16}H_8BrClF_3NO$
Formula weight	266.25	345.15	758.10	368.15	402.59
Crystal Colour	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal Size (mm)	0.16 x 0.12 x 0.04	0.14x0.08 x 0.04	0.34 x 0.14 x 0.05	0.22 x 0.10 x 0.04	0.30 x 0.17 x 0.12
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/c$	P-1	$P2_1/c$	C2/c	P-1
a(Å)	5.9087(14)	6.5358(13)	10.3212(17)	25.668(7)	7.538(4)
b(Å)	7.3564(17)	7.8459(16)	12.695(2)	4.4734(12)	8.691(5)
c(Å)	27.796(7)	13.186(3)	20.534(3)	24.653(6)	11.877(7)
α(°)	90	89.524(3)	90	90	80.826(9)
β(°)	93.569(5)	82.760(3)	95.133(3)	91.277(5)	83.217(9)
γ (°)	90	75.013(3)	90	90	73.581(8)
Z	4	2	4	8	2
V(Å^3)	1205.9(5)	647.8(2)	2679.7(7)	2830.0(13)	734.7(7)
Density (Mg/m^3)	1.467	1.770	1.879	1.728	1.820
Absorption Coefficient(mm^{-1})	0.105	3.185	6.039	2.939	3.015
F(000)	552	344	1472	1456	396
Reflections Collected	6319	5434	15215	7522	5850
Independent Reflections	2367	2823	5822	3078	3098
$R_{(int)}$	0.0588	0.0239	0.0392	0.0565	0.0370
Number of parameters	209	190	343	199	208
S(Goodness of Fit) on F^2	1.078	1.092	1.041	1.029	1.126
Final R1/wR2 (I>2σ(I)	0.0665/ 0.1260	0.0392/ 0.0951	0.0476/ 0.1306	0.0612/ 0.1314	0.0430/ 0.1313
Weighted R1/wR2(all data)	0.1150/ 0.1456	0.0480/ 0.0992	0.0629/ 0.1396	0.0983/ 0.1471	0.0452/ 0.1363

$R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

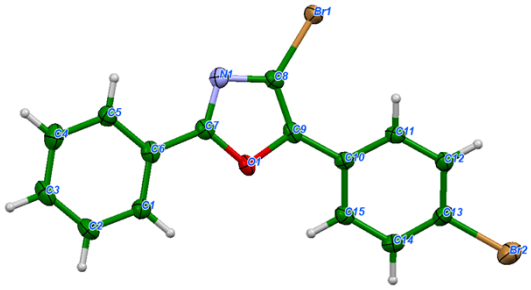
Crystal structures



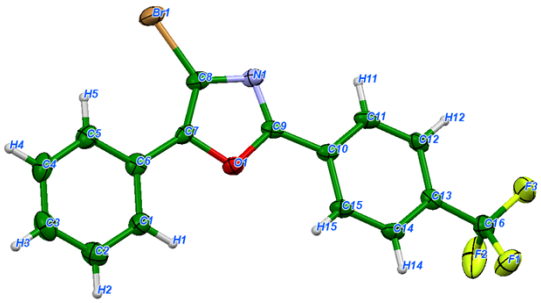


2-(4-nitrophenyl)-5-phenyloxazole (A) **4-bromo-2-(4-nitrophenyl)-5-phenyloxazole (B)**

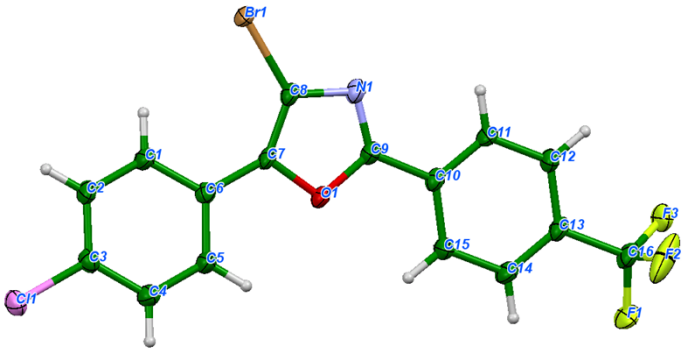
Table S1, entry 6



4-bromo-5-(4-bromophenyl)-2-phenyloxazole (Table 1, entry 3)



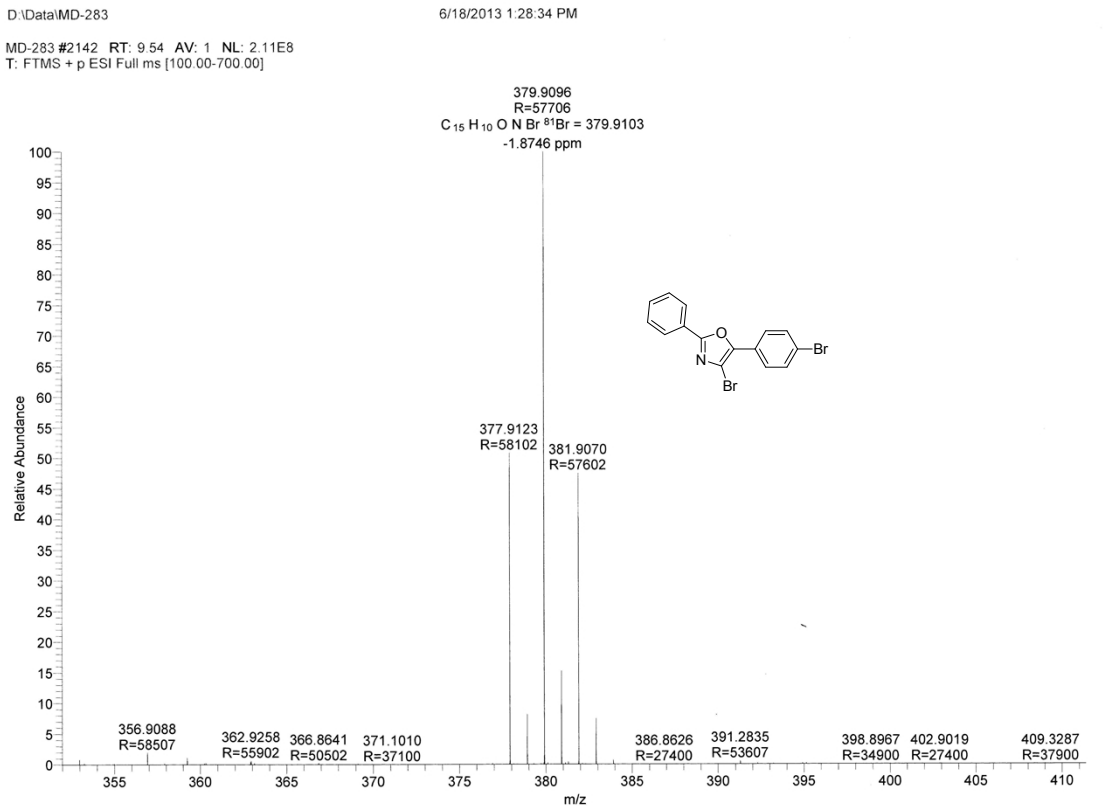
4-bromo-5-(4-chlorophenyl)-2-(4-methoxyphenyl)oxazole (Table 1, entry 17)



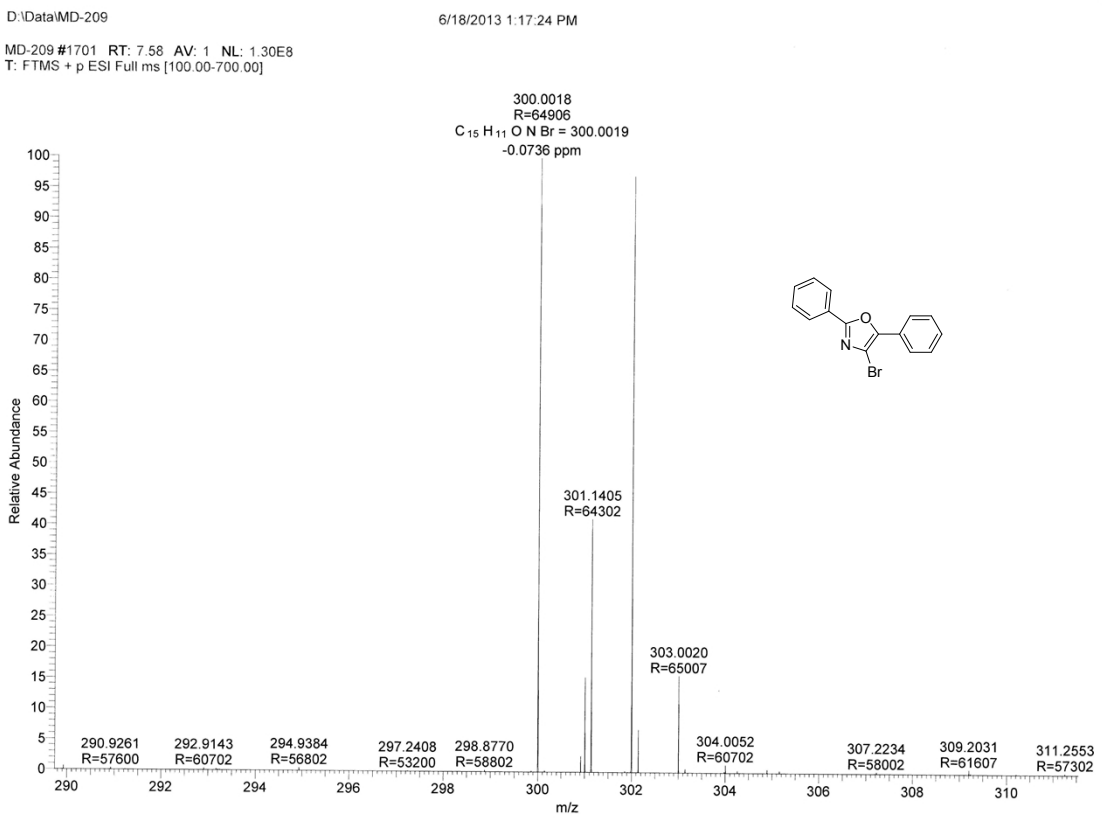
4-bromo-5-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole (Table 1, entry 18)

HRMS data of products at entries 3, 4, 5, 7, 8, 9, 10, 15, 16, 17, 18, 21, 22 of Table 1 and entries 1 and 2 of Table 2

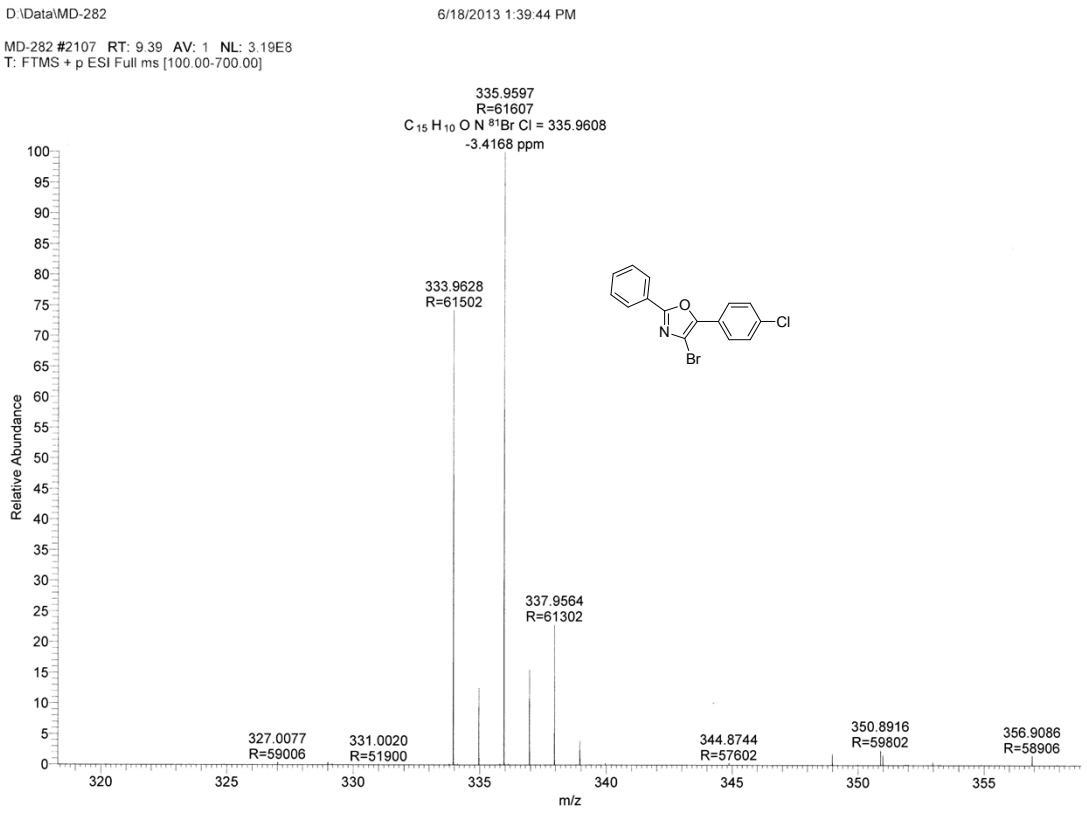
(Table 1, entry 3)



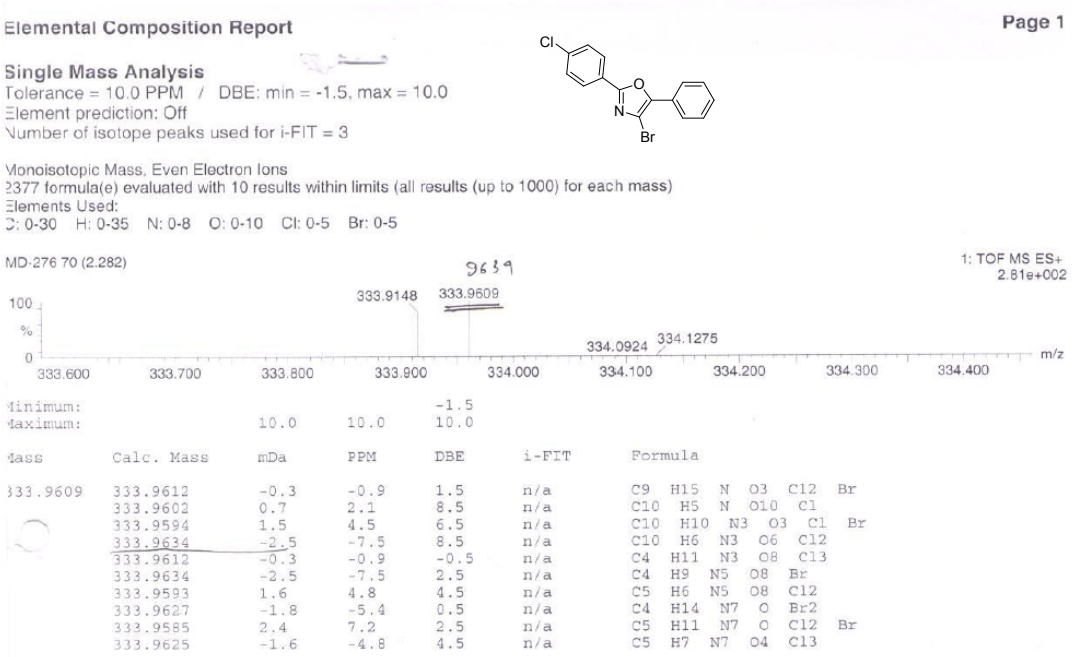
(Table 1, entry 4)



(Table 1, entry 5)



(Table 1, entry 7)



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 10.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2377 formula(e) evaluated with 10 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-35 N: 0-8 O: 0-10 Cl: 0-5 Br: 0-5

MD-276 70 (2.282)

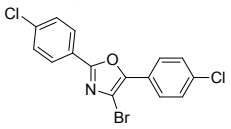
9639

1: TOF MS ES+
2.81e+002

Minimum:				-1.5		
Maximum:		10.0	10.0	10.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
333.9609	333.9612	-0.3	-0.9	1.5	n/a	C9 H15 N O3 C12 Br
	333.9602	0.7	2.1	8.5	n/a	C10 H5 N O10 Cl
	333.9594	1.5	4.5	6.5	n/a	C10 H10 N3 O3 Cl Br
	333.9634	-2.5	-7.5	8.5	n/a	C10 H6 N3 O6 C12
	333.9612	-0.3	-0.9	-0.5	n/a	C4 H11 N3 O8 C13
	333.9634	-2.5	-7.5	2.5	n/a	C4 H9 N5 O8 Br
	333.9593	1.6	4.8	4.5	n/a	C5 H6 N5 O8 C12
	333.9627	-1.8	-5.4	0.5	n/a	C4 H14 N7 O Br2
	333.9585	2.4	7.2	2.5	n/a	C5 H11 N7 O C12 Br
	333.9625	-1.6	-4.8	4.5	n/a	C5 H7 N7 O4 C13

(Table 1, entry 8)

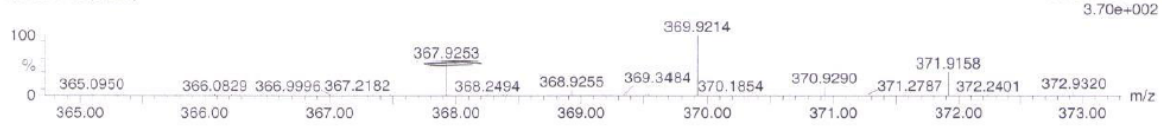
Elemental Composition Report Page 1



Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 10.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

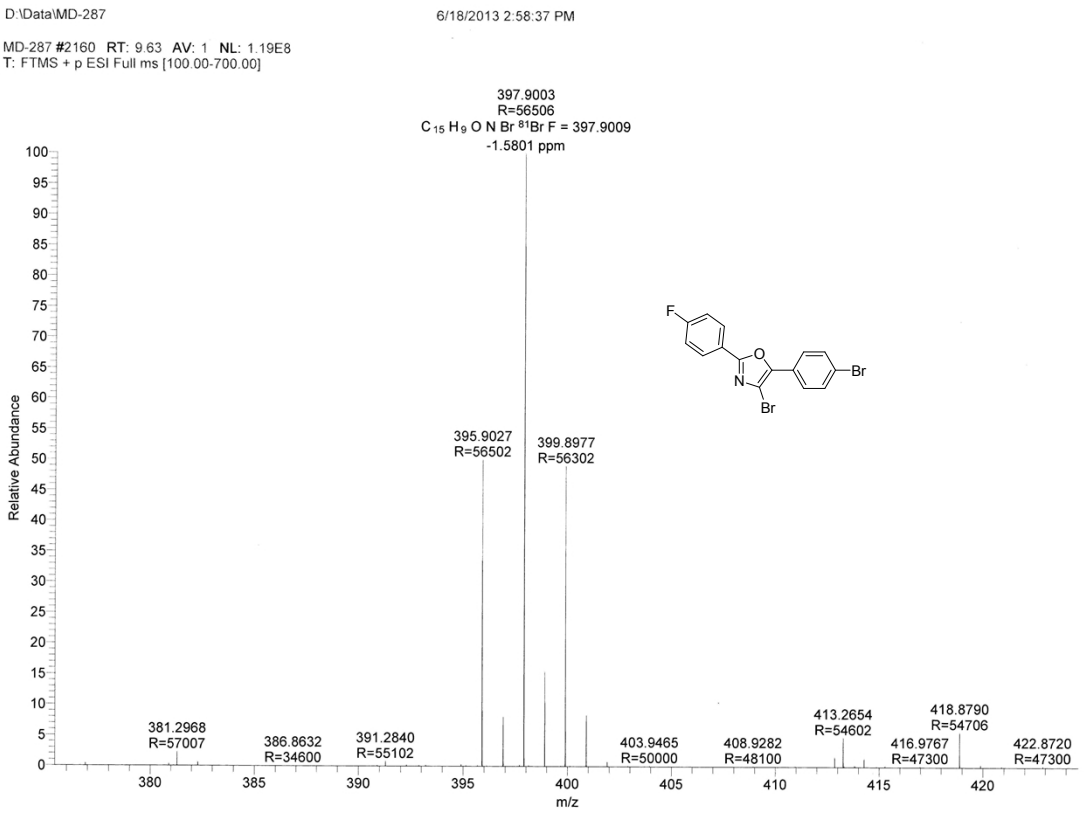
Monoisotopic Mass, Even Electron Ions
3030 formula(e) evaluated with 16 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-35 N: 0-8 O: 0-10 Cl: 0-5 Br: 0-5

MD-277 16 (0.528) 1: TOF MS ES+ 3.70e+002



Minimum:				-1.5		
Maximum:		10.0	10.0	10.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
367.9253	367.9286	-3.3	-9.0	8.5	0.8	C14 H12 N O Br2
	367.9245	0.8	2.2	4.5	1.8	C9 H12 N3 O3 Br2
	367.9223	3.0	8.2	1.5	2.1	C9 H14 N O3 Cl3 Br
	367.9276	-2.3	-6.3	2.5	4.4	C4 H9 N7 O4 Cl2 Br
	367.9254	-0.1	-0.3	-0.5	5.2	C4 H11 N5 O4 Cl5
	367.9264	-1.1	-3.0	-0.5	6.8	C8 H17 N O3 Cl Br2
	367.9285	-3.2	-8.7	6.5	7.2	C9 H8 N3 O6 Cl Br
	367.9276	-2.3	-6.3	8.5	7.6	C10 H6 N5 O2 Cl4
	367.9262	-0.9	-2.4	3.5	7.7	C9 H10 N O6 Cl4
	367.9237	1.6	4.3	0.5	8.9	C4 H13 N7 O Cl Br2
	367.9235	1.8	4.9	4.5	9.3	C5 H6 N7 O4 Cl4
	367.9245	0.8	2.2	2.5	10.3	C4 H8 N5 O8 Cl Br
	367.9222	3.1	8.4	-0.5	11.7	C4 H10 N3 O8 Cl4
	367.9253	0.0	0.0	6.5	23.5	C9 H7 N O10 Br
	367.9244	0.9	2.4	8.5	24.9	C10 H5 N3 O6 Cl3
	367.9226	2.7	7.3	7.5	25.0	C5 H3 N7 O8 Br

(Table 1, entry 9)

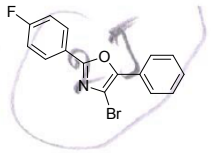


(Table 1, entry 10)

Elemental Composition Report Milan - HRMS

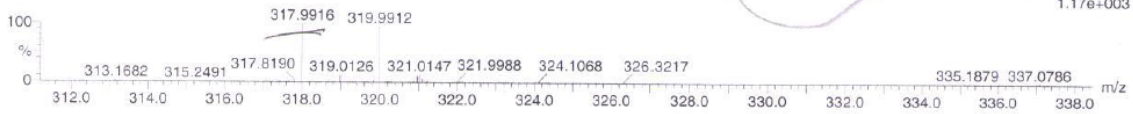
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 10.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2779 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-35 N: 0-8 O: 0-10 F: 0-5 Br: 0-5



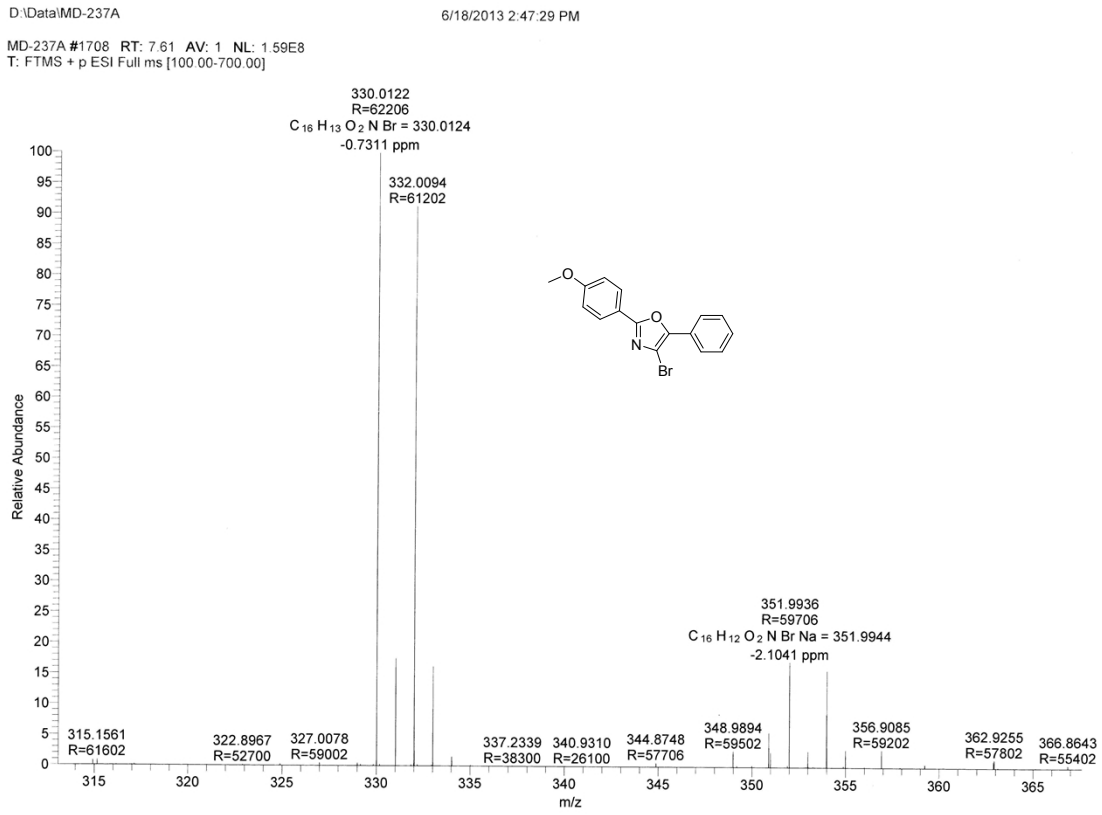
MD-285 55 (1.793)

1: TOF MS ES+
1.17e+003

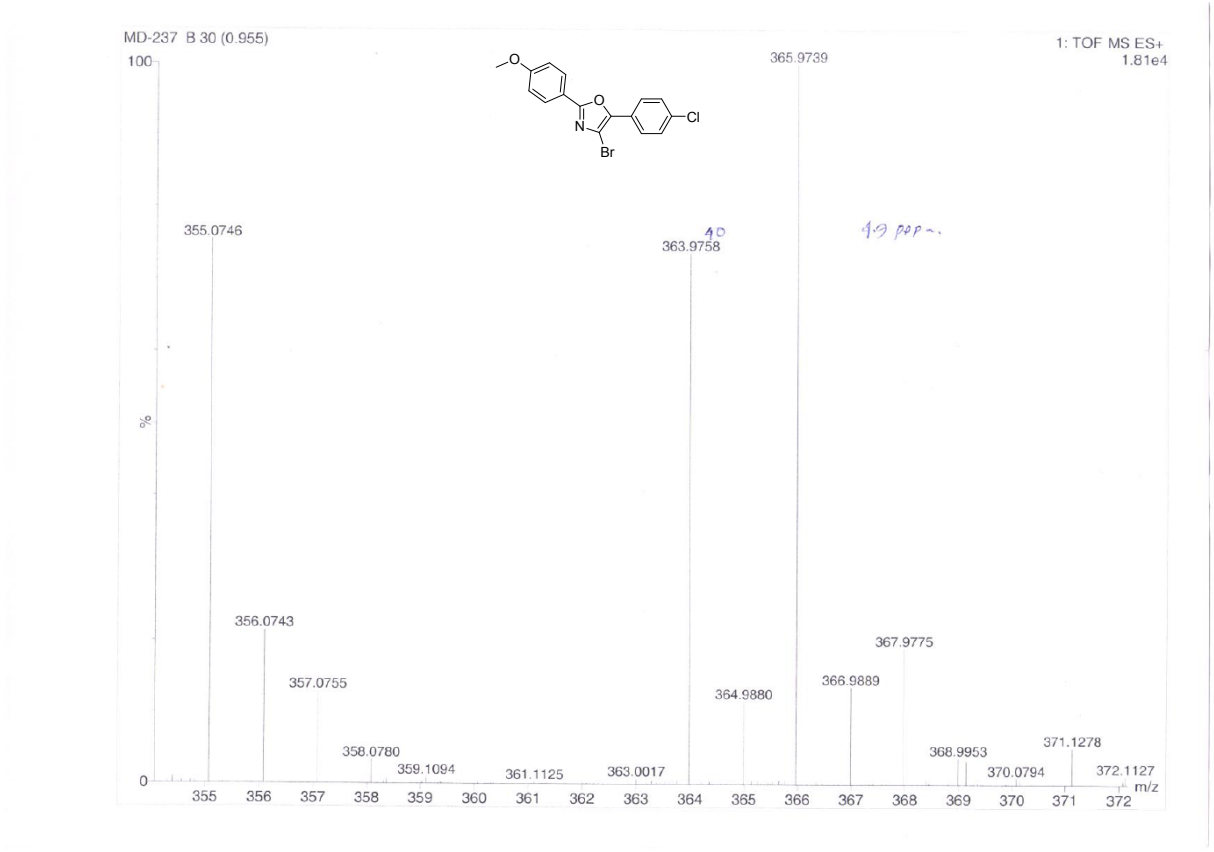


Minimum:				-1.5		
Maximum:		10.0	10.0	10.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
317.9916	317.9914	0.2	0.6	7.5	0.8	C8 H7 N7 F2 Br
	317.9917	-0.1	-0.3	3.5	0.9	C10 H10 N F5 Br
	317.9890	2.6	8.2	6.5	2.2	C10 H10 N3 O3 F Br
	317.9901	1.5	4.7	2.5	2.8	C7 H11 N3 O4 F2 Br
	317.9926	-1.0	-3.1	3.5	4.6	C5 H8 N7 O F3 Br
	317.9941	-2.5	-7.9	6.5	5.0	C12 H11 N O2 F2 Br
	317.9937	-2.1	-6.6	1.5	5.4	C6 H13 N3 O7 Br
	317.9912	0.4	1.3	-1.5	14.6	C4 H12 N3 O5 F3 Br
	317.9937	-2.1	-6.6	-0.5	19.8	C2 H9 N7 O2 F4 Br
	317.9929	-1.3	-4.1	-0.5	139.2	C6 H18 N5 Br2
	317.9897	1.9	6.0	8.5	528.1	C10 H5 N O10 F
	317.9922	-0.6	-1.9	9.5	536.1	C8 H2 N5 O7 F2
	317.9934	-1.8	-5.7	5.5	542.3	C5 H3 N5 O8 F3
	317.9898	1.8	5.7	6.5	544.7	C6 H N5 O5 P5
	317.9884	3.2	10.1	1.5	545.5	C5 H5 N O9 P5
	317.9945	-2.9	-9.1	1.5	559.5	C2 H4 N5 O9 F4
	317.9893	2.3	7.2	1.5	567.1	H3 N7 O10 F3

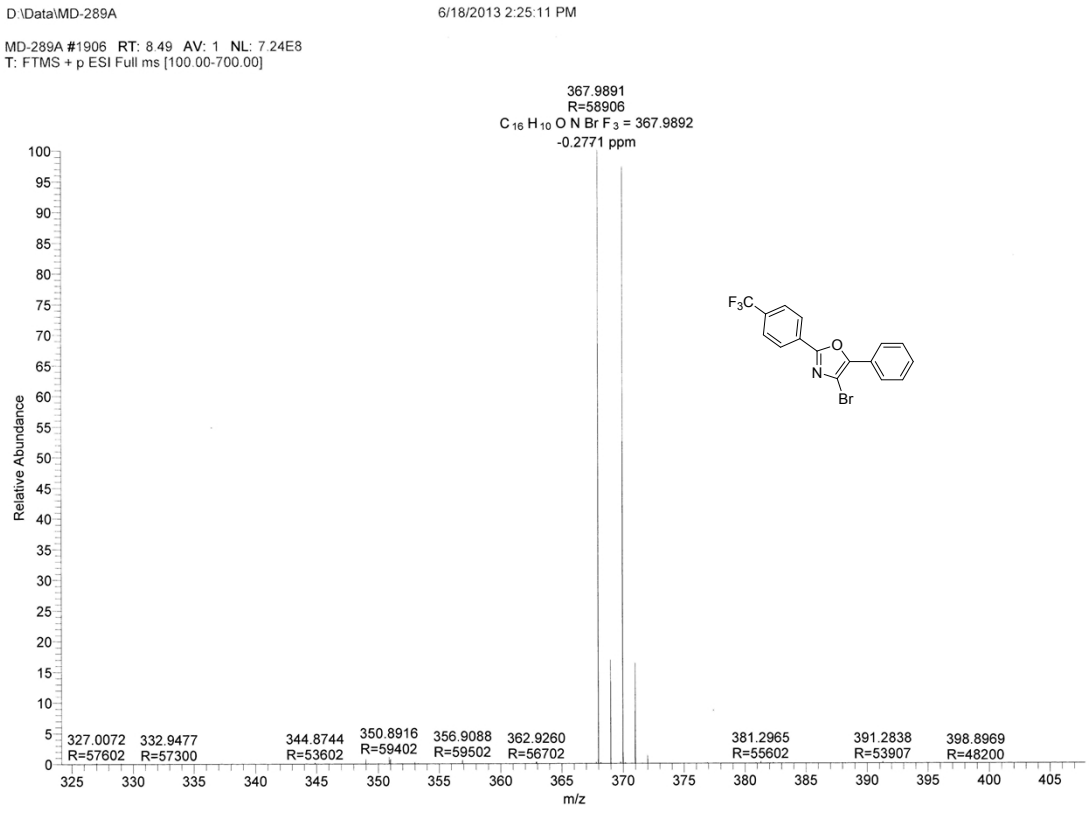
(Table 1, entry 15)



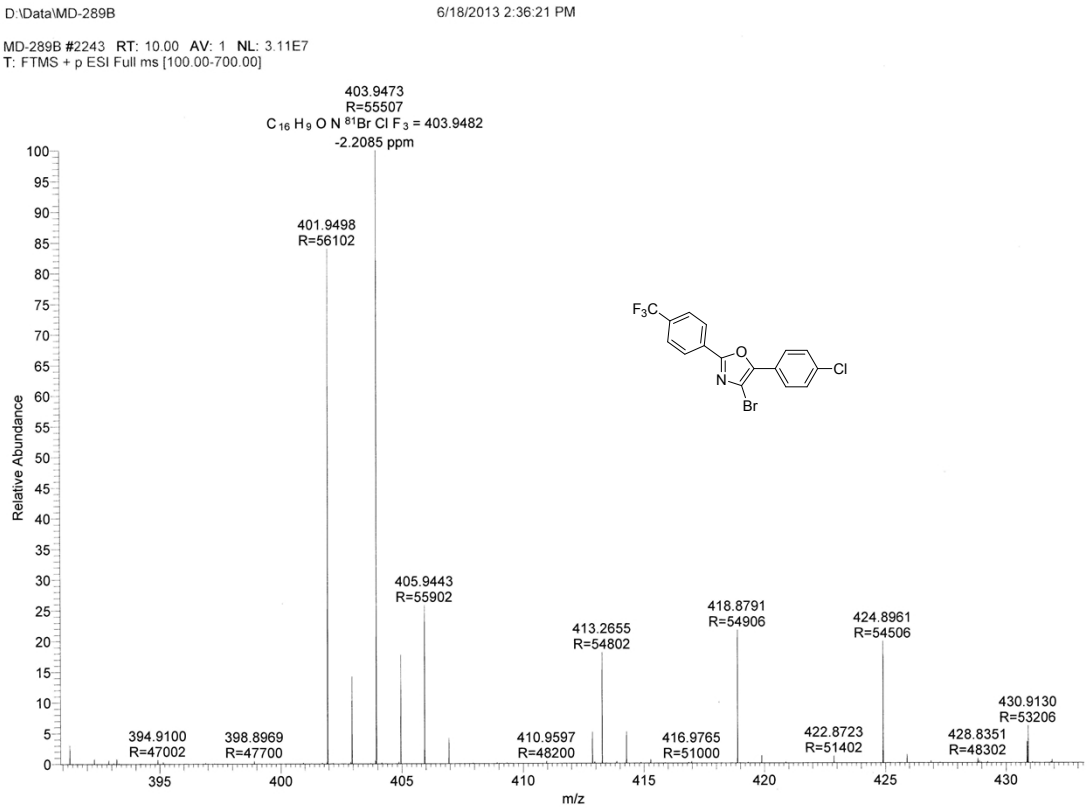
(Table 1, entry 16)



(Table 1, entry 17)

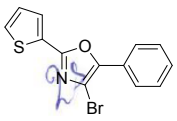


(Table 1, entry 18)



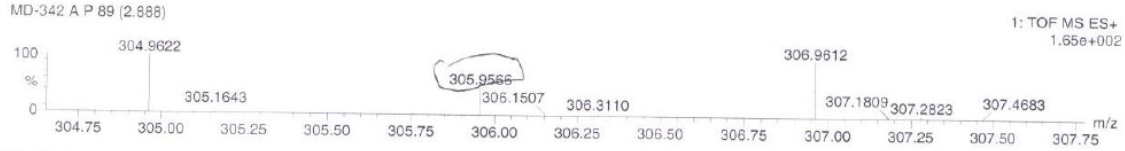
(Table 1, entry 21)

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 10.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



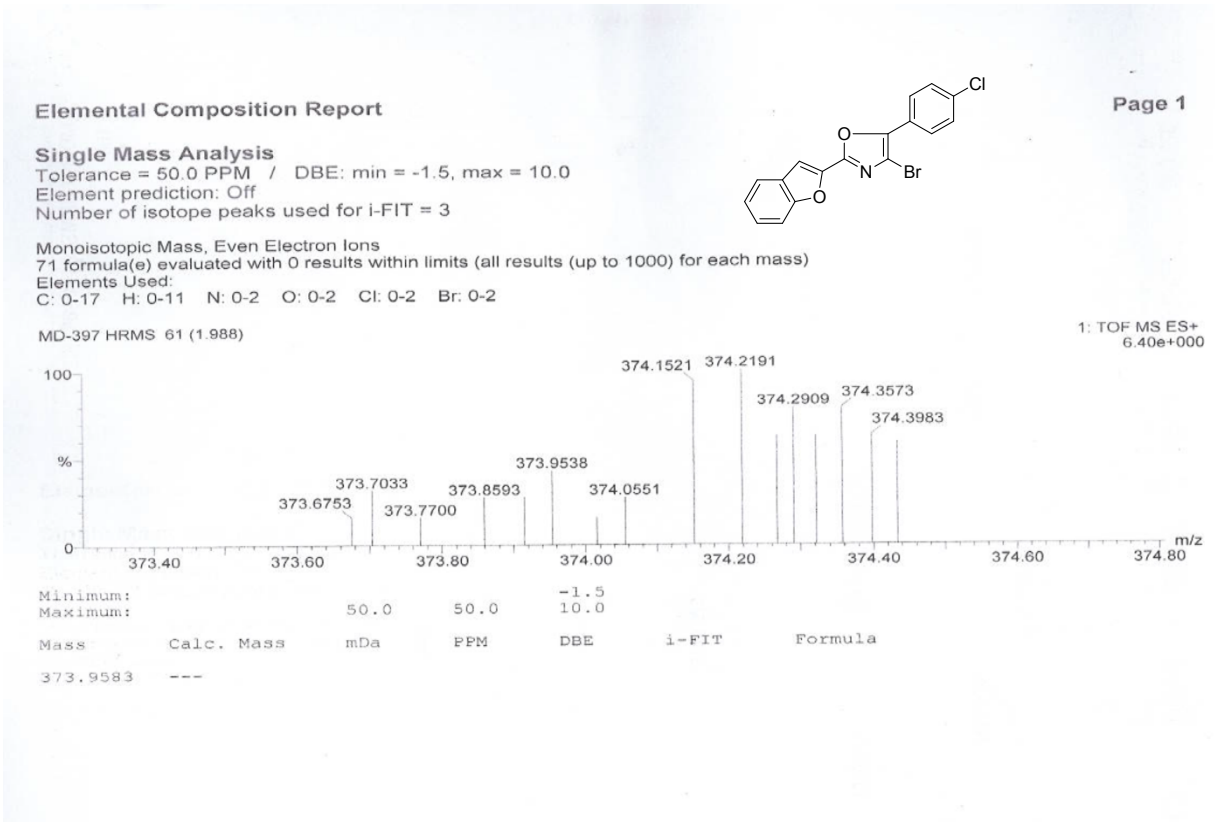
Monoisotopic Mass, Even Electron Ions
93 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-15 H: 0-10 N: 0-3 O: 0-2 S: 0-2 Br: 0-2

MD-342 A P 89 (2.888)

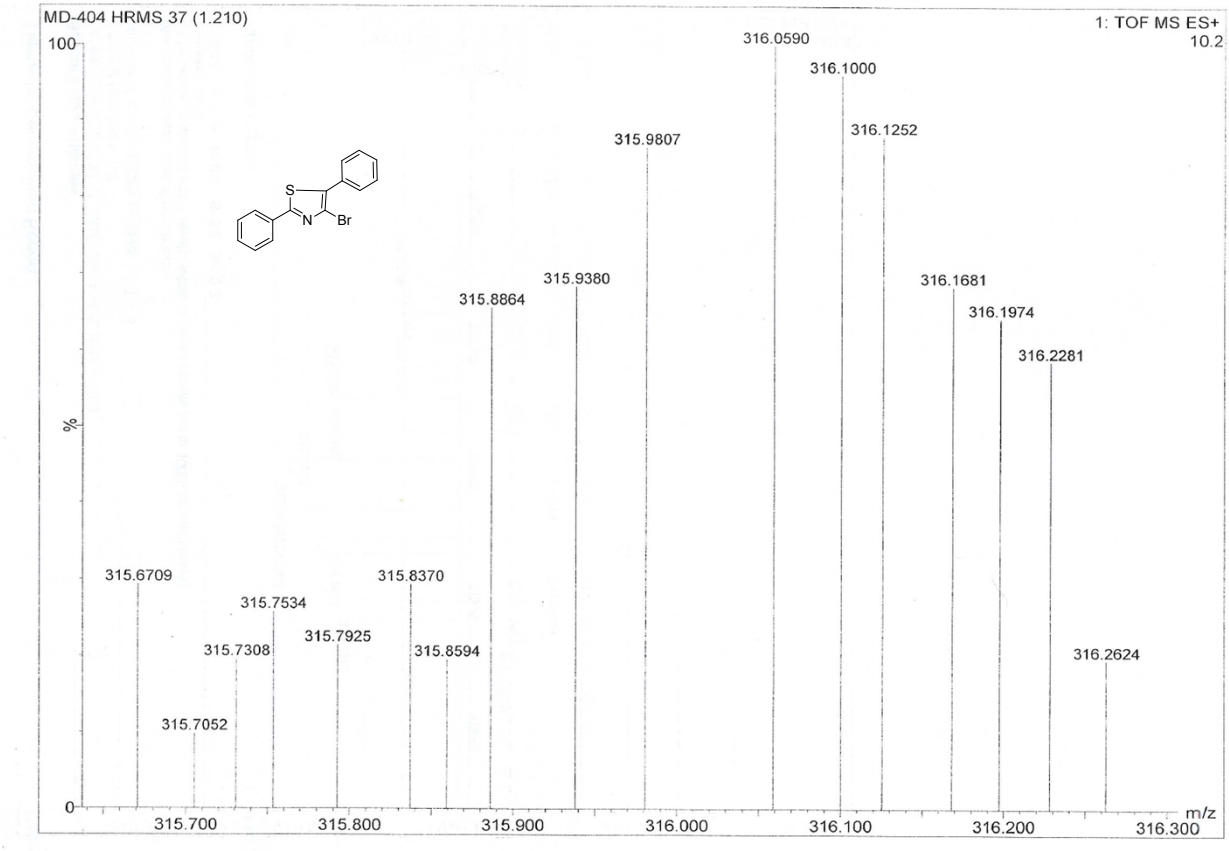


Minimum:				-1.5		
Maximum:		10.0	10.0	10.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
305.9566	305.9588	-2.2	-7.2	9.5	n/a	C13 H9 N O S Br

(Table 1, entry 22)



(Table 2, entry 1)



(Table 2, entry 2)