Supporting Information

Ligand Promoted Palladium-Catalyzed Dehydrogenative Alkenylation of Heteroarenes

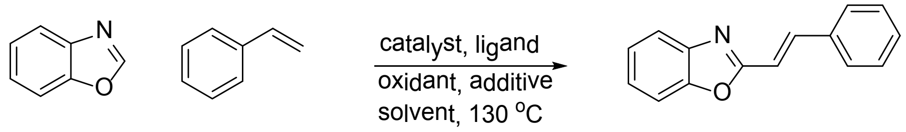
Wei-Chih Lee,[a] Ting-Hsuan Wang[a,b,c] and Tiow-Gan Ong*[a]

[a] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China. Email: tgong@chem.sinica.edu.tw.*
[b] *Department of Engineering and System Science, National Tsing-Hua University, HshiChu, Taiwan, Republic of China.*
[c] *Nano Science and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei, Taiwan, Republic of China.*

General. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk technique or in a glovebox. ^{1}H and ^{13}C NMR spectra were run a Bruker 300 MHz, or 400 MHz spectrometer using the residual proton of the deuterated solvent for reference ($CDCl_3$, ^{1}H NMR: 7.24 ppm. ^{13}C NMR: 77.2 ppm). Chemical shifts are reported in ppm (δ); coupling constants, *J*, are reported in Hz. Standard abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet. Column chromatography was performed using silica gel (spherical, 40-63 m). Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was performed with UV light (254 nm). GC analyses were performed on an Agilent Technologies 7890 GC instrument. High resolution mass spectra were obtained with a JEOL, JMS-700 (EI or FAB+) spectrometer. High resolution MALDI-mass spectra were conducted on an Applied Biosystems 4800 Proteomics Analyzer (Applied Biosystem, Foster City) equipped with an Nd/YAG laser (335nm) operating at a repetition rate of 200 Hz.

Chemicals. All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use. Solvents for chromatography were reagent grade. Toluene was dried over sodium with benzophenone-ketyl intermediate as an indicator. All azoles and styrene derivatives were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification.

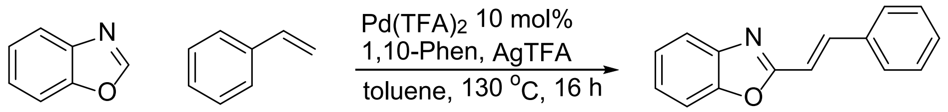
Table S1. Optimization.[a]



entry	catalyst	ligand	oxidant	solvent	Yield (%)[b]
1	$Pd(OAc)_2$ (0.1)	---	AgOAc (2)	NMP	NR
2	$Pd(OAc)_2$ (0.1)	---	BQ (2)	NMP	NR
3	$Pd(OAc)_2$ (0.1)	---	$Cu(OAc)_2$ (1)	NMP	9
4	$Pd(OAc)_2$ (0.1)	---	$Cu(OTf)_2$ (2), Ag_2O (2)	toluene	NR
5	$Pd(OAc)_2$ (0.1)	---	AgTFA (2)	NMP	15
6	$Pd(OAc)_2$ (0.1)	---	AgTFA (2)	toluene	17
7	$Pd(OAc)_2$ (0.1)	---	AgOAc (2)	TFA	NR
8	$Pd(OAc)_2$ (0.1)	---	Ag_2O (2)	TFA	NR
9	$Pd(OAc)_2$ (0.1)	---	$Cu(OAc)_2$ (2)	TFA	NR
10	$Pd(OAc)_2$ (0.1)	PCy_3 (0.2)	$Cu(OAc)_2$ (1)	NMP	14
11	$Pd(OAc)_2$ (0.1)	PPh_3 (0.2)	$Cu(OAc)_2$ (1)	NMP	6
12	$Pd(OAc)_2$ (0.1)	bipy (0.1)	$Cu(OAc)_2$ (1)	NMP	4
13	$Pd(OAc)_2$ (0.1)	---	AgTFA (2), KO^tBu (0.5)	toluene	9
14	$Pd(OAc)_2$ (0.1)	---	AgTFA (2), KO^tBu (1)	toluene	NR
15	$Pd(OAc)_2$ (0.1)	---	AgTFA (2), $AlMe_3$ (0.2)	toluene	23
16	$Pd(OAc)_2$ (0.1)	---	AgTFA (2), IPr (0.1)	toluene	49
17	$Pd(OAc)_2$ (0.1)	PCy_3 (0.1)	AgTFA (2)	toluene	53
18	$Pd(OAc)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2)	toluene	64
19	$Pd(OAc)_2$ (0.1)	PCy_3 (0.2)	AgOAc (2)	toluene	NR
20	$Pd(OAc)_2$ (0.1)	PCy_3 (0.2)	Ag_2CO_3 (2)	toluene	NR
21	$Pd(TFA)_2$ (0.1)	---	$Cu(OAc)_2$ (2)	toluene	NR
22	$Pd(TFA)_2$ (0.1)	---	CuCl (2)	toluene	NR
23	$Pd(TFA)_2$ (0.1)	---	Ag_2CO_3 (2)	toluene	NR
24	$Pd(TFA)_2$ (0.1)	---	AgOAc (2)	toluene	NR
25	$Pd(TFA)_2$ (0.1)	---	$BQ\text{-}Me_2$ (2)	toluene	NR
26	$Pd(TFA)_2$ (0.1)	---	$PhI(OAc)_2$	toluene	NR
27	$Pd(TFA)_2$ (0.1)	---	$K_2S_2O_8$ (2)	toluene	NR
28	$Pd(TFA)_2$ (0.1)	---	AgTFA (2)	toluene	60
29	$Pd(TFA)_2$ (0.1)	---	AgTFA (2) in air	toluene	29
30	$Pd(TFA)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2)	toluene	50
31	$Pd(TFA)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2), NaOTf (1)	toluene	49
32	$Pd(TFA)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2), $Sc(OTf)_3$ (1)	toluene	NR
33	$Pd(TFA)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2), $Cu(OTf)_2$ (1)	toluene	37
34	$Pd(TFA)_2$ (0.1)	PCy_3 (0.2)	AgTFA (2), $AlCl_3$ (0.5)	toluene	NR
35	$Pd(TFA)_2$ (0.1)	pyridine (0.2)	AgTFA (2)	toluene	30
36	$Pd(TFA)_2$ (0.1)	pyridine (0.3)	AgTFA (2)	toluene	30
37	$Pd(TFA)_2$ (0.1)	pyridine (0.5)	AgTFA (2)	toluene	40
38	$Pd(TFA)_2$ (0.1)	pyridine (1)	AgTFA (2)	toluene	68
39	$Pd(TFA)_2$ (0.1)	bipyridine (0.2)	AgTFA (2)	toluene	50
40	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	AgTFA (2)	toluene	87
41	$Pd(TFA)_2$ (0.1)	2,9-Me-1,10-Phen (0.5)	AgTFA (2)	toluene	43
42	$Pd(TFA)_2$ (0.1)	$(CH_2PCy_2)_2$ (0.1)	AgTFA (2)	toluene	38
43	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	AgTFA (2)	xylene	55
44	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	AgTFA (2)	DMF	67
45	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	AgTFA (2)	DMSO	NR
46	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	AgTFA (2)	NMP	73
47	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	air (balloon)	toluene	39
48	$Pd(TFA)_2$ (0.1)	1,10-Phen (0.15)	O_2 (balloon)	toluene	49

[a] Conditions: benzoxazole (0.5 mmol), styrene (2.5 mmol), metal catalyst (0.05 mmol), oxidant, ligand, additive in solvent (1 mL) at 130 °C for 16 hours unless otherwise noted.
[b] Isolated yield.

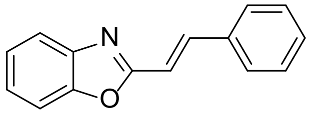
Table S2. Optimization process.



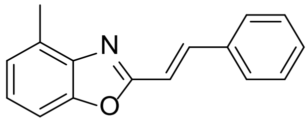
entry	AgTFA (eq)	1,10-Phen (eq)	styrene (eq)	Yield (%)
1	1.5	0.15	5	68
2	2	0.15	5	87
3	2	0.05	5	54
4	2	0.10	5	63
5	2	0.20	5	83
6	2	0.15	2	77
7	2	0.15	3	80
8	2	0.15	4	82

[a] Conditions: benzoxazole (0.5 mmol), styrene (2.5 mmol), Pd(TFA)$_2$ (0.05 mmol), AgTFA, and 1,10-Phen in toluene (1 mL) at 130 °C for 16 hours unless otherwise noted.

General procedure for Pd-catalyzed styrenylation of heteroarenes: To a toluene solution (~1mL) of Pd(TFA)$_2$ (17 mg, 0.05 mmol), 1,10-phenanthroline (14 mg, 0.075 mmol), and benzoxazole (0.5 mmol) was added styrene (2.5 mmol) into the vial. After the vial was screw-capped, the reaction solution was taken outside the glovebox and heated at 130 °C for 16 h. The resulting mixture was filtered through *Celite* and washed with dichloromethane. The filtrate solution was concentrated in *vacuo* to afford crude product. The crude was further purified by flash chromatography using ethyl acetate/hexane (15-25%) as eluent.

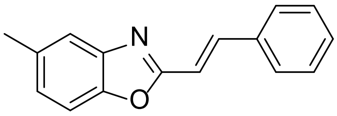


(*E*)-2-styrylbenzo[*d*]oxazole (10aa):[1-3] The reaction was performed according to the above general procedure to give a beige solid (87%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 7.72-7.69 (m, 1H, Ar), 7.57 (d, $^3J_{HH}$ = 4.0 Hz, 2H, Ar), 7.41-7.34 (m, 3H, Ar), 7.33-7.28 (m, 2H, Ar), 7.06 (d, $^3J_{HH}$ = 20.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 162.9, 150.6, 142.4, 139.6, 135.3, 129.9, 129.1, 127.7, 125.3, 124.6, 120.0, 114.1, 110.5. HR-MS (EI): *m/z* calcd. for $C_{15}H_{12}NO$ ($[M+H]^+$) 222.0919, found 222.0915. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[1-3]

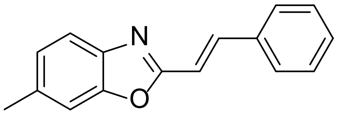


(*E*)-4-methyl-2-styrylbenzo[*d*]oxazole (10ba): The reaction was performed according to the above general procedure to give light yellow oil (86%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.58 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.42-7.33 (m, 4H, Ar), 7.21 (t, $^3J_{HH}$ =

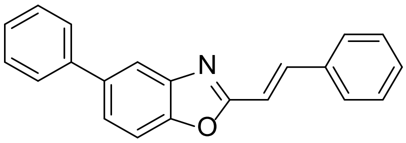
8.0 Hz, 1H, Ar), 7.11 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 2.63 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.1, 150.3, 141.5, 139.0, 135.4, 130.5, 129.7, 129.1, 127.6, 125.1, 125.1, 114.3, 107.7, 16.7. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ($[M+H]^+$) 236.1075, found 236.1032.



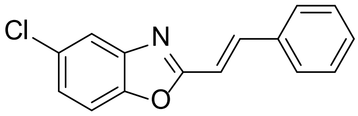
(*E*)-5-methyl-2-styrylbenzo[*d*]oxazole (10ca):[4] The reaction was performed according to the above general procedure to give white needle crystals (79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 7.57 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.48 (s, 1H, Ar), 7.41-7.35 (m, 4H, Ar), 7.12 (d, $^3J_{HH}$ = 7.17 Hz, 1H, Ar), 7.04 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 2.45 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.0, 148.8, 142.5, 139.2, 135.3, 134.4, 129.7, 129.0, 127.6, 126.4, 119.9, 114.2, 109.8, 21.6. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ($[M+H]^+$) 236.1075, found 236.1076. The above ^1H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[4]



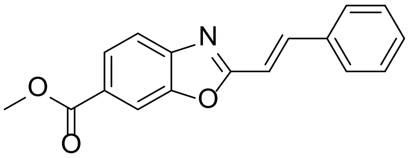
(*E*)-6-methyl-2-styrylbenzo[*d*]oxazole (10da):[5,6] The reaction was performed according to the above general procedure to give a beige solid (87%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 7.57 (t, $^3J_{HH}$ = 12.0 Hz, 3H, Ar), 7.42-7.35 (m, 3H, Ar), 7.31 (s, 1H, Ar), 7.13 (d, $^3J_{HH}$ = 7.12.0 Hz, 1H, Ar), 7.04 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4, 150.8, 140.1, 138.9, 135.8, 135.3, 129.7, 129.0, 127.6, 125.8, 119.3, 114.2, 110.6, 21.9. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ($[M+H]^+$) 236.1075, found 236.1071. The above ^1H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[5-6]



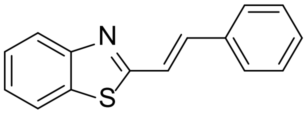
(*E*)-5-phenyl-2-styrylbenzo[*d*]oxazole (10ea):[7] The reaction was performed according to the above general procedure to give a white solid (85%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.81 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.62-7.56 (m, 6H, Ar), 7.47-7.36 (m, 6H, Ar), 7.09 (d, $^3J_{HH}$ = 16.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.6, 150.1, 143.0, 141.2, 139.8, 138.6, 135.3, 130.0, 129.1, 129.0, 127.8, 127.6, 127.4, 125.0, 118.4, 114.0, 110.5. HR-MS (EI): *m/z* calcd. for $C_{21}H_{16}NO$ ($[M+H]^+$) 298.1232, found 298.1231. The above ^1H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[7]



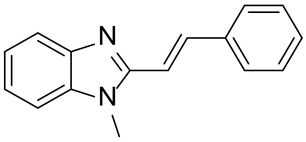
(*E*)-5-chloro-2-styrylbenzo[*d*]oxazole (10fa):[4] The reaction was performed according to the above general procedure to give brown oil (56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.67 (s, 1H, Ar), 7.58 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.44-7.38 (m, 4H, Ar), 7.29 (d, $^3J_{HH}$ = 12.0 Hz, 1H, Ar), 7.04 (d, $^3J_{HH}$ = 16.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.2, 149.1, 143.5, 140.5, 135.0, 130.1, 129.1, 127.8, 125.5, 119.9, 113.6, 111.1. HR-MS (EI): *m/z* calcd. for $C_{15}H_{11}NOCl$ ($[M+H]^+$) 256.0529, found 256.0523. The above ^{1}H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[4]



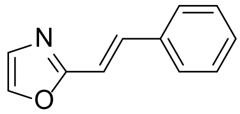
(*E*)-methyl-2-styrylbenzo[*d*]oxazole-6-carboxylate (10ga):[8] The reaction was performed according to the above general procedure to give a light yellow solid (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H, Ar), 8.05 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.85 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.71 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.60 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.43-7.38 (m, 3H, Ar), 7.07 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 3.95 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.7, 165.3, 150.2, 146.2, 141.2, 134.9, 130.2, 129.1, 127.9, 127.2, 126.4, 119.4, 113.5, 112.0, 52.4. HR-MS (EI): *m/z* calcd. for $C_{17}H_{14}NO_3$ ($[M+H]^+$) 280.0974, found 280.0971. The above ^{1}H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[8]



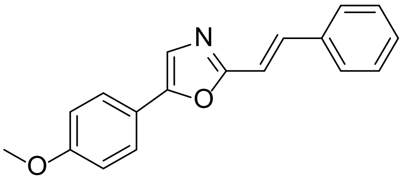
(*E*)-2-styrylbenzo[*d*]thiazole (10ka):[2,9,10] The reaction was performed according to the above general procedure to give light yellow solid (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.59-7.55 (m, 2H, Ar), 7.43-7.35 (m, 7H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 167.2, 154.1, 137.9, 135.6, 134.6, 129.6, 129.2, 127.6, 126.5, 125.6, 123.2, 122.3, 121.7. The above ^{1}H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[2,9,10]



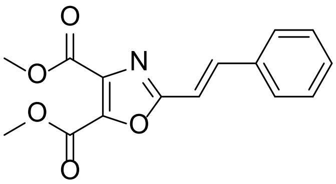
(*E*)-1-methyl-2-styryl-1*H*-benzo[*d*]imidazole (10ma):[10] The reaction was performed according to the above general procedure to give light yellow solid (62%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.77-7.74 (m, 1H, Ar), 7.61 (d, $^3J_{HH}$ =12.0 Hz, 2H, Ar), 7.41-7.37 (m, 2H, Ar), 7.35-7.31 (m, 2H, Ar), 7.27-2.25 (m, 2H, Ar), 7.10 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 3.86 (s, 3H, N-CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 151.2, 142.0, 138.7, 135.5, 135.5, 129.6, 129.0, 127.6, 123.6, 119.4, 112.7, 109.7, 30.4. HR-MS (EI): *m/z* calcd. for $C_{16}H_{15}N_2$ ([M+H]$^+$) 235.1235, found 235.1231. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[10]



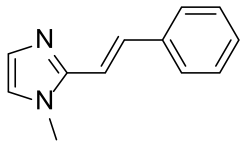
(*E*)-2-styryloxazole (10ha):[2,10] The reaction was performed according to the above general procedure to give light yellow oil (55%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (s, 1H, Ar), 7.53-7.47 (m, 3H, Ar), 7.40-7.32 (m, 3H, Ar), 7.17 (s, 1H, Ar), 6.95 (d, $^3J_{HH}$ = 24.0 Hz, 1H, Ar). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$):δ 161.9, 138.27, 136.3, 135.6, 129.3, 128.9, 128.6, 127.3, 114.0. HR-MS (EI): *m/z* calcd. for $C_{11}H_{10}NO$ ([M+H]$^+$) 172.0762, found 172.0761. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[2,10]



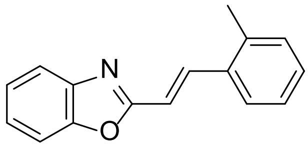
(*E*)-5-(4-methoxyphenyl)-2-styryloxazole (10ia):[2] The reaction was performed according to the above general procedure to give light yellow crystals (72%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ar), 7.55-7.50 (m, 3H, Ar), 7.40-7.32 (m, 3H, Ar), 7.27 (s, 1H, Ar), 6.98-6.94 (m, 3H, Ar), 3.84 (s, 3H, OCH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 160.7, 160.1, 151.2, 135.9, 135.5, 129.2, 129.1, 127.3, 126.0, 122.4, 121.0, 114.6, 114.2, 55.6. HR-MS (MALDI): *m/z* calcd. for $C_{18}H_{15}NO_2$ ([M+H]$^+$) 278.1181, found 278.1193. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[2]



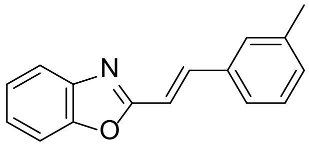
(*E*)-dimethyl 2-styryloxazole-4,5-dicarboxylate (10ja): The reaction was performed according to the above general procedure to give gold needle crystals (58%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.77 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.55-7.53 (m, 2H, Ar), 7.40-7.38 (m, 3H, Ar), 6.94 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 3.98 (s, 6H, OCH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 162.2, 160.8, 157.2, 141.5, 140.9, 137.3, 134.5, 130.3, 129.0, 127.7, 111.9, 52.9. HR-MS (EI): *m/z* calcd. for $C_{15}H_{14}NO_5$ ([M+H]$^+$) 288.0872, found 288.0877.



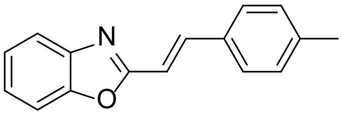
(*E*)-1-methyl-2-styryl-1*H*-imidazole (10na): The reaction was performed according to the above general procedure to give a light brown solid (67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, $^3J_{HH}$ = 18.0 Hz, 1H), 7.55-7.52 (m, 2H, Ar), 7.35-7.33 (m, 3H, Ar), 7.22 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.91 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.83 (d, $^3J_{HH}$ = 18.0 Hz, 1H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 141.9, 134.5, 130. 7, 129.2, 128.1, 122.2, 121.3, 106.8, 34.6. HR-MS (EI): *m/z* calcd. for $C_{13}H_{13}N$ ([M+H]$^+$) 183.1048, found 183.1045.



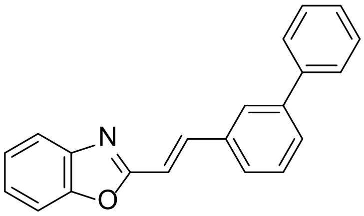
(*E*)-2-(2-methylstyryl)benzo[*d*]oxazole (11ab):[11] The reaction was performed according to the above general procedure to give light yellow oil (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.72-7.70 (m, 1H, Ar), 7.66-7.64 (m, 1H, Ar), 7.54-7.51 (m, 1H, Ar), 7.33-7.31 (m, 2H, Ar), 7.26-7.21 (m, 3H, Ar), 6.99 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 2.51 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.0, 150.5, 142.4, 137.2, 137.1, 134.2, 130.9, 129.7, 126.6, 126.0, 125.3, 124.6, 120.0, 115.0, 110.4, 20.0. HR-MS (FAB): *m/z* calcd. for $C_{16}H_{14}NO$ ([M+H]$^+$) 236.1075, found 236.1078. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[11]



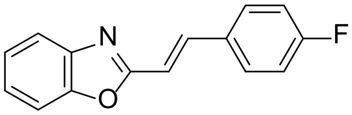
(*E*)-2-(3-methylstyryl)benzo[*d*]oxazole (11ac): The reaction was performed according to the above general procedure to give a golden solid (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.73-7.69 (m, 1H, Ar), 7.52-7.50 (m, 1H, Ar), 7.40-7.38 (m, 2H, Ar), 7.33-7.28 (m, 3H, Ar), 7.19 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.05 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 2.39 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.0, 150.6, 142.4, 139.8, 138.7, 135.3, 130.8, 129.0, 128.4, 125.3, 124.9, 124.6, 112.0, 113.8, 110.4, 21.5. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ([M+H]$^+$) 236.1075, found 236.1078.



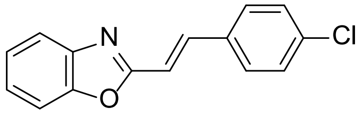
(*E*)-2-(4-methylstyryl)benzo[*d*]oxazole (11ad):[12,13] The reaction was performed according to the above general procedure to give a white solid (87%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.72-7.67 (m, 1H, Ar), 7.52-7.48 (m, 1H, Ar), 7.47 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.33-7.28 (m, 2H, Ar), 7.20 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.01 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 2.37 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 163.2, 150.6, 142.4, 140.3, 139.7, 132.6, 129.9, 127.7, 125.2, 124.6, 120.0, 113.1, 110.5, 21.6. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ([M+H]$^+$) 236.1075, found 236.1066. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[12,13]



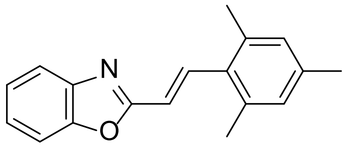
(*E*)-2-(2-([1,1'-biphenyl]-3-yl)vinyl)benzo[*d*]oxazole (11ae): The reaction was performed according to the above general procedure to give a light yellow solid (78%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.72-7.70 (m, 1H, Ar), 7.66-7.65 (m, 3H, Ar), 7.63-7.61(m, 2H, Ar), 7.54-7.51(m, 1H, Ar), 7.47-7.43 (m, 2H, Ar), 7.38 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.34-7.31 (m, 2H, Ar), 7.10 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.0, 150.6, 142.6, 142.4, 140.3, 139.1, 134.3, 129.0, 128.2, 127.9, 127.7, 127.1, 125.3, 124.7, 120.0, 114.0, 110.5. HR-MS (MALDI): *m/z* calcd. for $C_{21}H_{15}NO$ ([M+H]$^+$) 298.1232, found 298.1244.



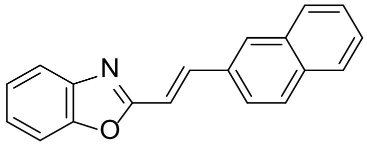
(*E*)-2-(4-fluorostyryl)benzo[*d*]oxazole (11af):[14] The reaction was performed according to the above general procedure to give light yellow crystals (91%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.71-7.69 (m, 1H, Ar), 7.58-7.55 (m, 2H, Ar), 7.52-7.50 (m, 1H, Ar), 7.33-7.31 (m, 2H, Ar), 7.12-7.08 (m, 2H, Ar), 6.98 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.7 (d, $^1J_{CF}$ = 250.0 Hz), 162.6, 150. 5, 142.3, 138.1, 131.5, 129.4, 129.3, 125.3, 124.6, 120.0, 116.1 (d, $^2J_{CF}$ = 20.0 Hz), 113.7, 110.4. HR-MS (EI): *m/z* calcd. for $C_{15}H_{11}NOF$ ([M+H]$^+$) 240.0825, found 240.0823. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[14]



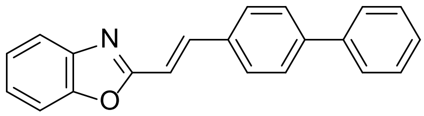
(*E*)-2-(4-chlorostyryl)benzo[*d*]oxazole (11ag):[14] The reaction was performed according to the above general procedure to give colorless crystals (94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.71-7.69 (m, 1H, Ar), 7.52-7.50 (m, 3H, Ar), 7.39-7.31 (m, 4H, Ar), 7.03 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 162.5, 150.5, 142.3, 138.0, 135.7, 133.7, 129.3, 128.7, 125.4, 124.7, 120.1, 114.6, 110.4. HR-MS (MALDI): *m/z* calcd. for $C_{15}H_{10}NOCl$ ([M+H]$^+$) 256.0529, found 256.0540. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[14]



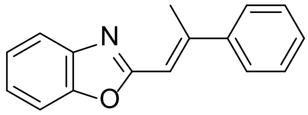
(*E*)-2-(2,4,6-trimethylstyryl)benzo[*d*]oxazole (11ah):[15] The reaction was performed according to the above general procedure to give an off-white crystal (62%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.73-7.69 (m, 1H, Ar), 7.54-7.52 (m, 1H, Ar), 7.35-7.30 (m, 2H, Ar), 6.93 (s, 2H, Ar), 6.70 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 2.42 (s, 6H, CH$_3$), 2.30 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 163.0, 150.6, 142.4, 138.3, 138.2, 136.9, 131.8, 129.5, 125.3, 124.7, 120.1, 119.3, 110.5, 21.4, 21.2. HR-MS (EI): *m/z* calcd. for $C_{18}H_{18}NO$ ([M+H]$^+$) 264.1388, found 264.1383. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[15]



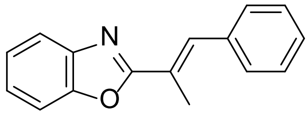
(*E*)-2-(2-(naphthalen-2-yl)vinyl)benzo[*d*]oxazole (11ai): The reaction was performed according to the above general procedure to give a light yellow solid (64%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 (s, 1H, Ar), 7.91 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.88-7.82 (m, 3H, Ar), 7.77-7.71 (m, 2H, Ar), 7.55-7.49 (m, 3H, Ar), 7.34-7.32 (m, 2H, Ar), 7.18 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.0, 150.6, 142.4, 139.6, 134.1, 133.6, 132.8, 129.2, 128.9, 128.6, 127.9, 127.2, 126.8, 125.4, 124.7, 123.3, 120.0, 114.2, 110.5. HR-MS (FAB): *m/z* calcd. for $C_{19}H_{14}NO$ ([M+H]$^+$) 272.1075, found 272.1077.



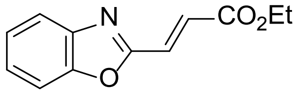
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)benzo[*d*]oxazole (11aj):[16] The reaction was performed according to the above general procedure to give a light yellow solid (75%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.72-7.70 (m, 1H, Ar), 7.66 (m, 3H, Ar), 7.63 (d, $^3J_{HH}$ =8.0 Hz, 2H, Ar), 7.54-7.51 (m, 1H, Ar), 7.47 (t, $^3J_{HH}$ =8.0 Hz, 2H, Ar), 7.38 (d, $^3J_{HH}$ =8.0 Hz, 1H, Ar), 7.34-7.31 (m, 2H, Ar), 7.10 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.0, 150.6, 142.7, 142.4, 140.4, 139.1, 134.3, 129.1, 128.2, 127.9, 127.8, 127.2, 125.4, 124.7, 120.1, 114.0, 110.5. HR-MS (MALDI): *m/z* calcd. for $C_{21}H_{15}NO$ ([M+H]$^+$) 298.1232, found 298.1240. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[16]



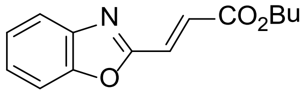
(*E*)-2-(2-phenylprop-1-en-1-yl)benzo[*d*]oxazole (11ak):[17] The reaction was performed according to the above general procedure to give a light yellow solid (67%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.75-7.72 (m, 1H, Ar), 7.60-7.57 (m, 2H, Ar), 7.53-7.50 (m, 1H, Ar), 7.44-7.30 (m, 5H, Ar), 6.78-6.77 (m, 1H, Ar), 2.79 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 163.2, 150.1, 142.6, 129.0, 128.8, 128.3, 127.8, 126.5, 125.1, 124.6, 120.1, 113.0, 110.5, 19.0. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ([M+H]$^+$) 236.1075, found 236.1079. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[17]



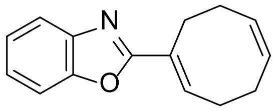
(*E*)-2-(1-phenylprop-1-en-2-yl)benzo[*d*]oxazole (11al):[18] The reaction was performed according to the above general procedure to give white crystals (53%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (s, 1H), 7.75-7.71 (m, 1H, Ar), 7.53-7.48 (m, 3H, Ar), 7.42 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.34-7.29 (m, 3H, Ar), 2.47 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 165.3, 150.7, 142.2, 136.2, 135.1, 129.7, 128.5, 128.2, 125.1, 124.6, 124.4, 119.9, 110.3, 14.9. HR-MS (EI): *m/z* calcd. for $C_{16}H_{14}NO$ ([M+H]$^+$) 236.1075, found 236.1071. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[18]



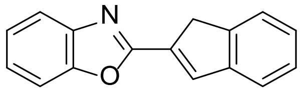
(*E*)-ethyl 3-(benzo[*d*]oxazol-2-yl)acrylate (11am): The reaction was performed according to the above general procedure to give a light yellow solid (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.58-7.53 (m, 2H, Ar), 7.42-7.34 (m, 2H, Ar), 6.99 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 4.32 (q, $^3J_{HH}$ = 20.0 Hz, 2H, CH_2), 1.36 (t, $^3J_{HH}$ =12.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.4, 160.3, 150.7, 142.1, 129.2, 128.3, 126.8, 125.1, 120.9, 110.9, 61.3, 14.3. HR-MS (EI): *m/z* calcd. for $C_{12}H_{12}NO_3$ ($[M+H]^+$) 218.0817, found 218.0818.



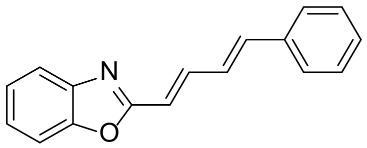
(*E*)-butyl 3-(benzo[*d*]oxazol-2-yl)acrylate (11an): The reaction was performed according to the above general procedure to give white needle crystals (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.52 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.38-7.33 (m, 2H, Ar), 6.97 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 4.22 (t, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 1.67 (qn, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 1.41 (sextet, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 0.93 (t, $^3J_{HH}$ = 8.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.4, 160.3, 150.7, 142.1, 129.2, 128.3, 126.8, 125.1, 120.9, 110.9, 65.2, 30.7, 19.3, 13.8. HR-MS (FAB): *m/z* calcd. for $C_{14}H_{16}NO_3$ ($[M+H]^+$) 246.1130, found 246.1127.



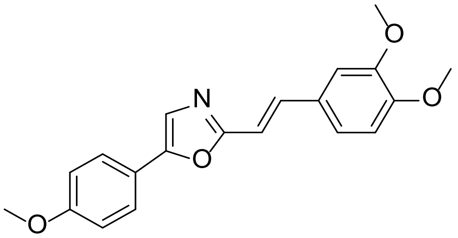
2-((1*E*,5*Z*)-cycloocta-1,5-dien-1-yl)benzo[*d*]oxazole (11ao):[19] The reaction was performed according to the above general procedure to give light yellow crystals (56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.63 (m, 1H, Ar), 7.44-7.40 (m, 1H, Ar), 7.28-7.22 (m, 2H, Ar), 7.07 (t, $^3J_{HH}$ = 6.0 Hz, 1H, CH), 7.57 (t, $^3J_{HH}$ = 6.0 Hz, 2H, CH), 3.09 (t, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.67-2.60 (m, 2H, CH_2), 2.57-2.48 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.4, 150.8, 142.3, 137.3, 129.3, 128.2, 128.1, 124.8, 124.3, 119.9, 110.3, 29.2, 28.4, 27.3, 27.0. HR-MS (EI): *m/z* calcd. for $C_{15}H_{16}NO$ ($[M+H]^+$) 226.1232, found 226.1227. The above ^{1}H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[19]



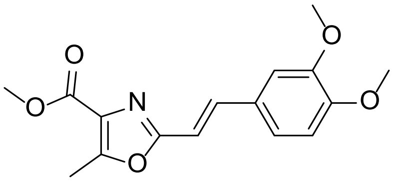
2-(1*H*-inden-2-yl)benzo[*d*]oxazole (11ap):[19] The reaction was performed according to the above general procedure to give dark orange powder (32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H, Ar-CH), 7.74-7.72 (m, 1H, Ar), 7.56-7.52 (m, 3H, Ar), 7.34-7.32 (m, 4H, Ar), 4.02 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.3, 150.8, 144.3, 143.7, 142.5, 136.9, 133.3, 127.3, 125.5, 124.8, 124.4, 123.0, 120.1, 110.6, 38.9. The above ^{1}H and $^{13}C\{^1H\}$ spectral data are consistent with those reported in the literature.[19]



2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzo[*d*]oxazole (11aq): The reaction was performed according to the above general procedure to give a dark yellow solid (55%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75-7.71 (m, 1H, Ar), 7.60 (dd, $^3J_{HH}$ = 16.0 and 12.0 Hz, 1H), 7.54-7.51 (m, 3H, Ar), 7.41-7.31 (m, 5H, Ar), 7.06-6.91 (m, 2H), 6.65 (d, $^3J_{HH}$ = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 163.0, 150.6, 142.5, 139.9, 138.9, 136.5, 129.0, 127.4, 127.3, 125.3, 124.7, 120.0, 117.2, 110.4. HR-MS (EI): *m/z* calcd. for $C_{17}H_{13}NO$ ([M+H]$^+$) 247.0997, found 247.1001.



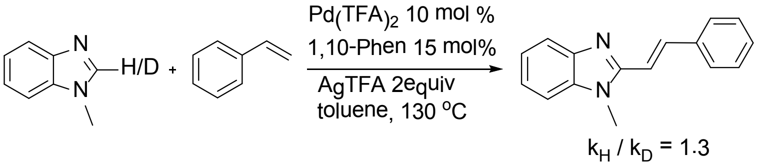
(*E*)-2-(3,4-dimethoxystyryl)-5-(4-methoxyphenyl)oxazole (12):[2,9] The reaction was performed according to the above general procedure to give a light yellow solid (68%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.46 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7,25 (s, 1H), 7.11-7.08 (m, 2H), 6.95 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 6.87 (d, $^3J_{HH}$ = 12.0 Hz, 1H), 6.84 (d, $^3J_{HH}$ = 20.0 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 160.9, 159.9, 150.8, 150.3, 149.4, 135.2, 128.9, 125.8, 122.2, 121.2, 121.0, 114.5, 112.1, 111.4, 109.2, 56.0, 56.0, 55.4. HR-MS (MALDI): *m/z* calcd. for $C_{20}H_{19}NO_4$ ([M+H]$^+$) 338.1392, found 338.1402. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[2,9]



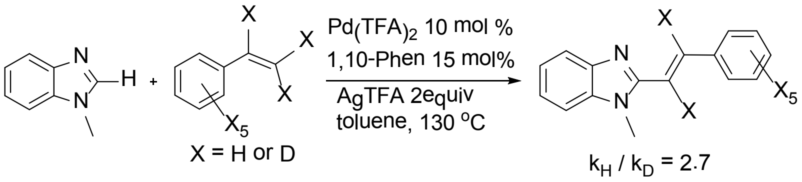
methyl (*E*)-2-(3,4-dimethoxystyryl)-5-methyloxazole-4-carboxylate (13):[20,21] The reaction was performed according to the above general procedure to give a light yellow solid (50%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.07 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.02 (s, 1H), 6.86 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 6.75 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 3.91 (s, 3H, OCH$_3$), 3.90 (s, 3H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 2.65 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 162.4, 159.4, 155.5, 150.2, 149.0, 136.6, 128.1, 128.0, 121.0, 111.0, 110.7, 108.9, 55.7, 55.6, 51.6, 11.7. The above ^{1}H and ^{13}C{^{1}H} spectral data are consistent with those reported in the literature.[20,21]

Kinetic Isotope Effect (KIE) Experiments

(a) Intermolecular competition reactions between N-methylbenzimidazole and its deuterated derivative with styrene: To perform the KIE experiments, the target coupling product **10na** was prepared as the standard for GC-MS analysis to afford the calibration curve involving product concentration and peak area. The deuterated N-methylbenzimidazole was prepared according to the procedure in our recent report.[22] The intermolecular competition reactions between N-methylbenzimidazole and its deuterated derivative with styrene were examined in two separated vials. The reaction was carried out according to the general procedure under the same conditions. After cooling down, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate**.** The filtrate was concentrated under reduced pressure. The resulting crude mixture was subjected and analyzed by GC. The GC yield of the product **10na** was obtained according to the calibration curve. The ratio of the two product yields represents the KIE value ($k_H/k_D = 1.3$).



(b) Intermolecular competition reactions between styrene and d_8-styrene with N-methylbenzimidazole: To perform the KIE experiments, the target coupling product **10na** was prepared as the standard for GC-MS analysis to afford the calibration curve involving product concentration and peak area. The d_8-styrene was purchased from Aldrich and was directly used in the reaction. The intermolecular competition reactions between styrene and d_8-styrene with N-methylbenzimidazole were examined in two separated vials. The reaction was carried out according to the general procedure. After cooling down, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The resulting crude mixture was subjected and analyzed by GC. The GC yield of the product **10na** was obtained according to the calibration curve. The ratio of the two product yields represents the KIE value ($k_H/k_D = 2.7$).



Reference

1. Chen, Y. -X.; Qian, L.-F.; Zhang, W.; Han, B. *Angew. Chem., Int. Ed.* **2008,** *47*, 9330.

2. Besselievre, F.; Piguel, S.; Mahuteau-Betzer, F.; Grierson, DS. *Org. Lett.* **2008**, *10*, 4029.

3. Yoo, W.-J.; Yuan, H.; Miyamura, H.; Kobayashi, S. *Adv. Synth. Catal.* **2011**, *353,* 3085.

4. Park, H. J.; Park, M. S.; Lee, T. H.; Park, K. H. *J. Heterocycl. Chem.* **2013**, *50*, 663.

5. Viirre, R. D.; Evindar, G.; Batey, R. A. *J. Org. Chem.* **2008**, *73*, 3452.

6. Peng, J.-S.; Zong, C. -J.; Ye, M.; Chen, T. -G.; Gao, D. -W.; Wang, Y. -F.; Chen, C. -X. *Org Biomol Chem*, **2011**, *9*, 1225.

7. Oda, T.; Imada, T.; Naito, K.; Tamura, T.; Furuya, S., Bicyclic derivative, process for producing the same, and use. U.S. patent, US20050101647, May, 12, 2005.

8. CIBA Ltd. *Chem.Abstr.* **1966**, *65*, 2396d.

9. Yang, Z. -Y.; Chen, X.; Wang, S. -Z.; Liu, J. -D.; Xie, K.; Wang, A. -W.; Tan, Z. *J. Org. Chem.* **2012**, *77*, 7086.

10. Vabre, R.; Chevot, F.; Piguel, S.; Legraverend, M. *J. Org. Chem.* **2011**, *76*, 9542.

11. Dryanska, V.; Ivanov, C. *Tetrahedron Lett.* **1975**, *16*, 3519.

12. Houpis, I. N.; Molina, A.; Lynch, J.; Reamer, R. A.; Volante, R. P.; Reider, P. J. *J. Org. Chem.* **1993**, *58*, 3176.

13. Rose, U. *J. Heterocycl. Chem.* **1992**, *29*, 551.

14. Shao, J. -G.; Zhong, Q.; Liao, H. -P.; Liu, C. -Q.; Zhou, J. -F. *Org. Prep. Proced. Int.* **1992**, *24*, 520.

15. Sun, J.; Yan, C. -G.; Han, Y. *Synth. Commun.* **2001**, *31*, 151.

16. Postowskii et al. *J. Gen. Chem. USSR (Engl. Transl.),* **1962**, *32*, 2617.

17. Rupnicki, L.; Saxena, A.; Hon, W. L. *J. Am. Chem. Soc.* **2009**, *131*, 10386.

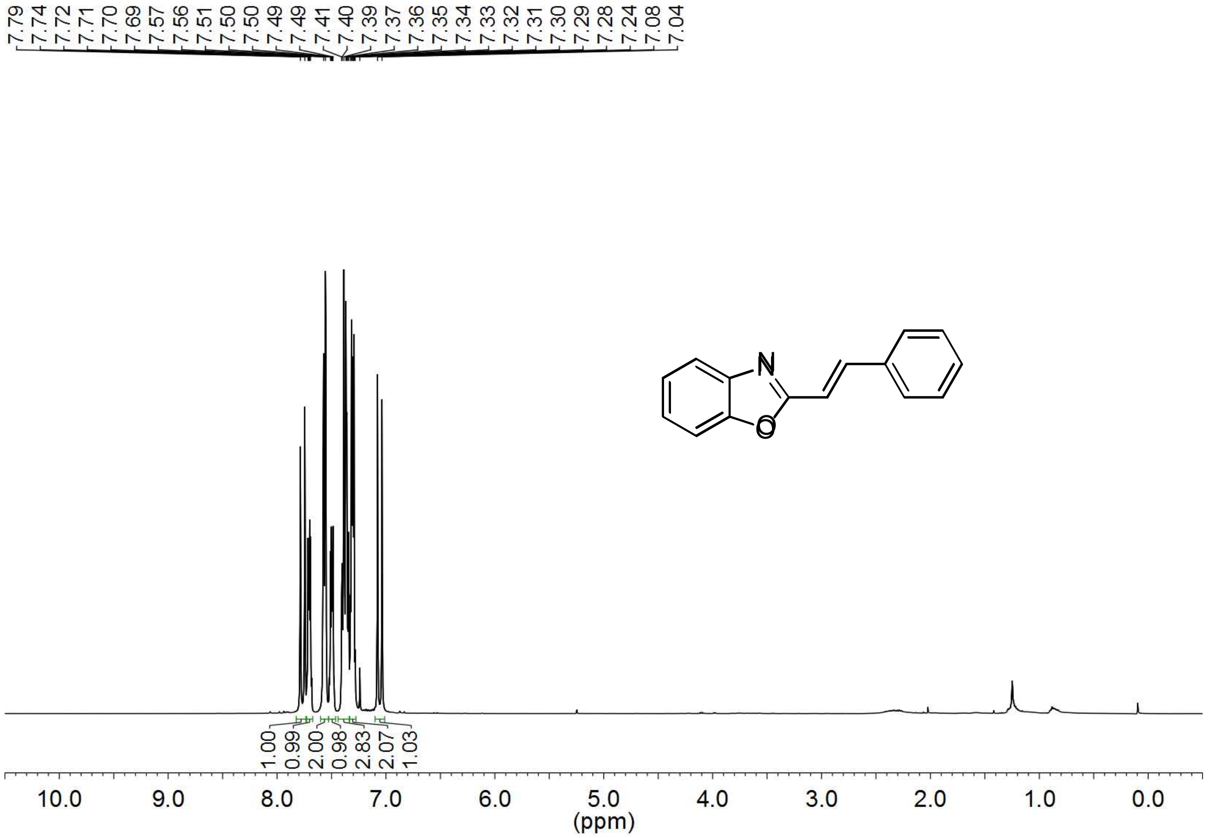
18. Dryanska, V.; Ivanov, C. *Chem.Abstr.* **1974**, *80*, 95800z.

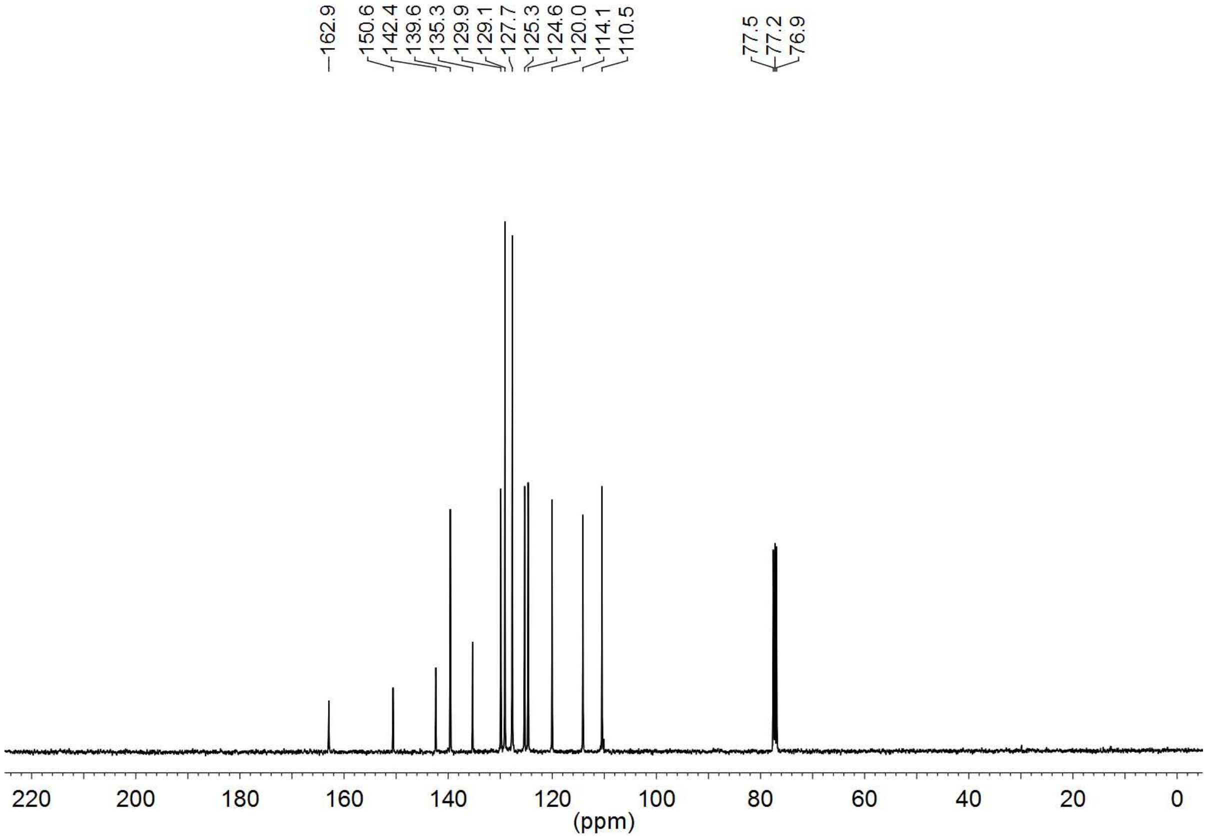
19. Bhumgara, S. K.; Seshadri, S. *Indian J. Chem., Sect B.* **1985**, *24*, 703.

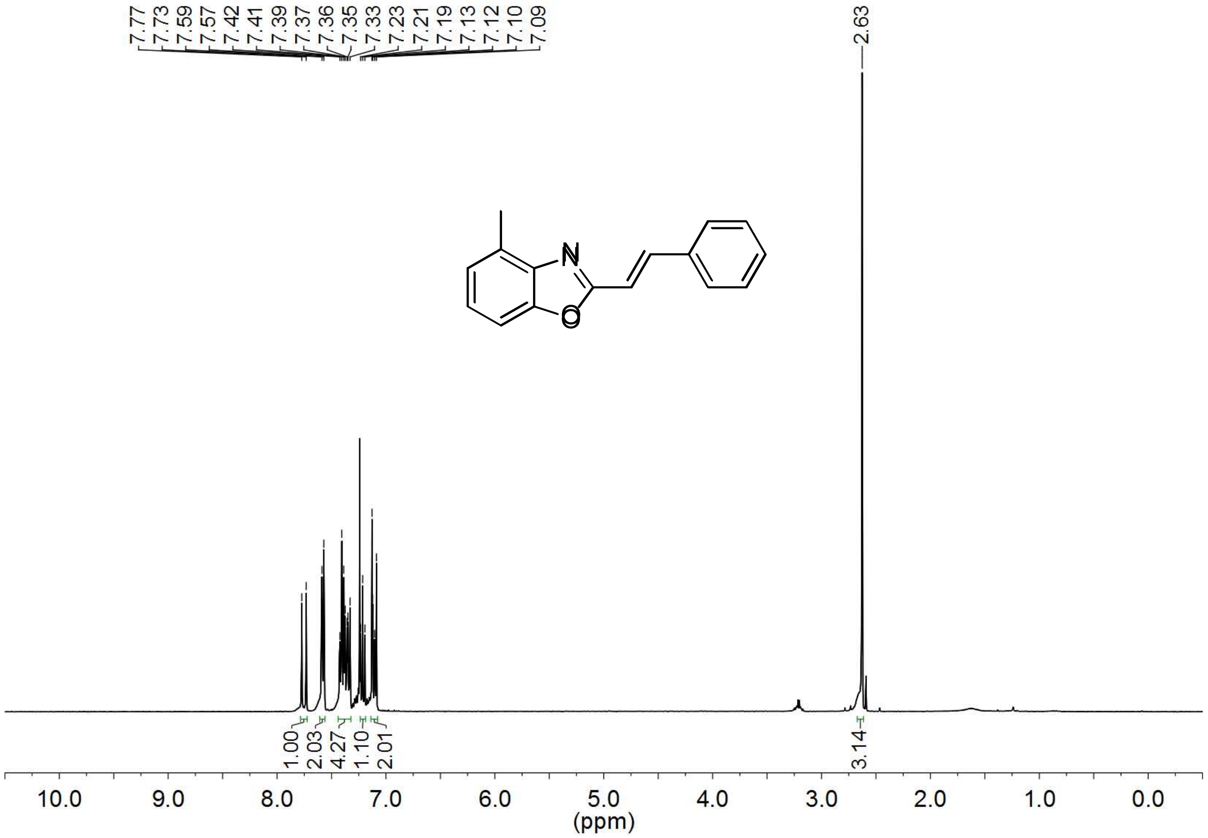
20. Linder, J.; Blake, A. J.; Moody, C. J. *Org. Biomol. Chem.* **2008**, *6*, 3908-3916.

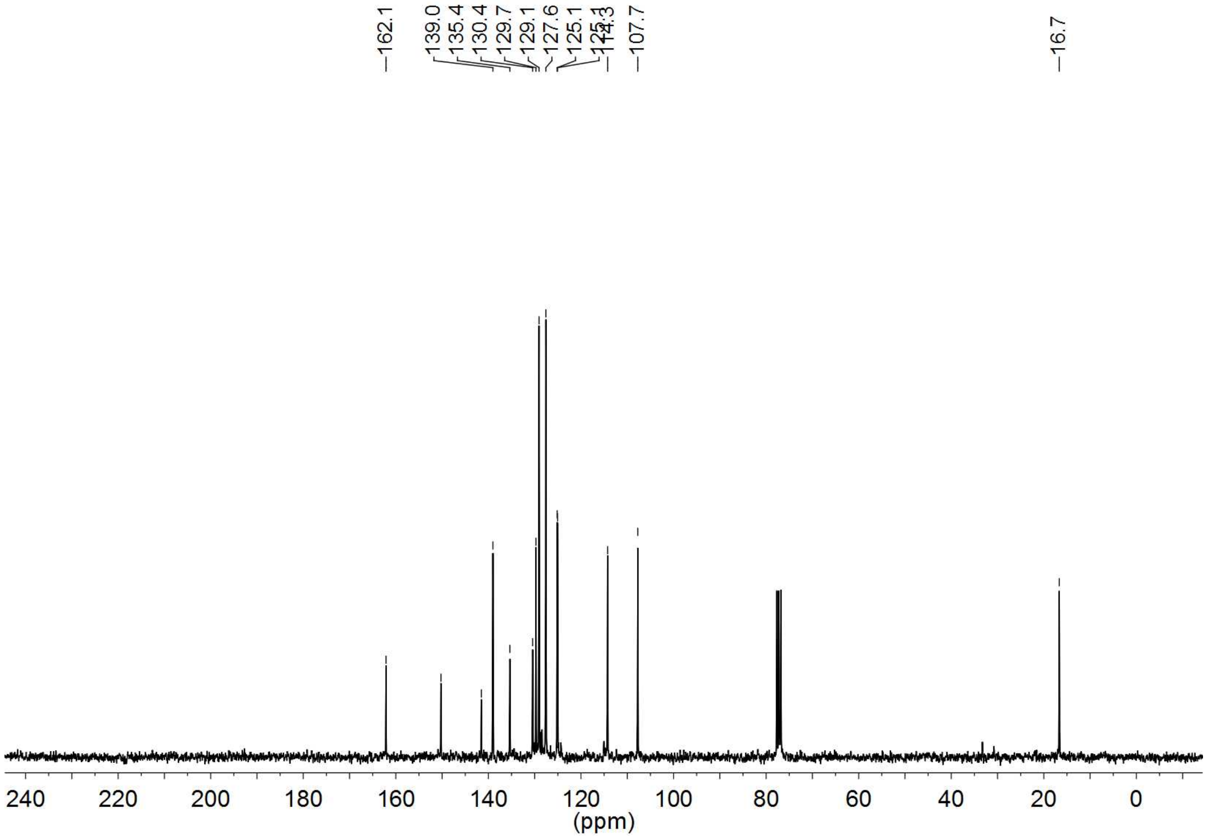
21. LingKui, M.; Kamada, Y.; Muto, K.; Yamaguchi, J.; Itami, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 10048.

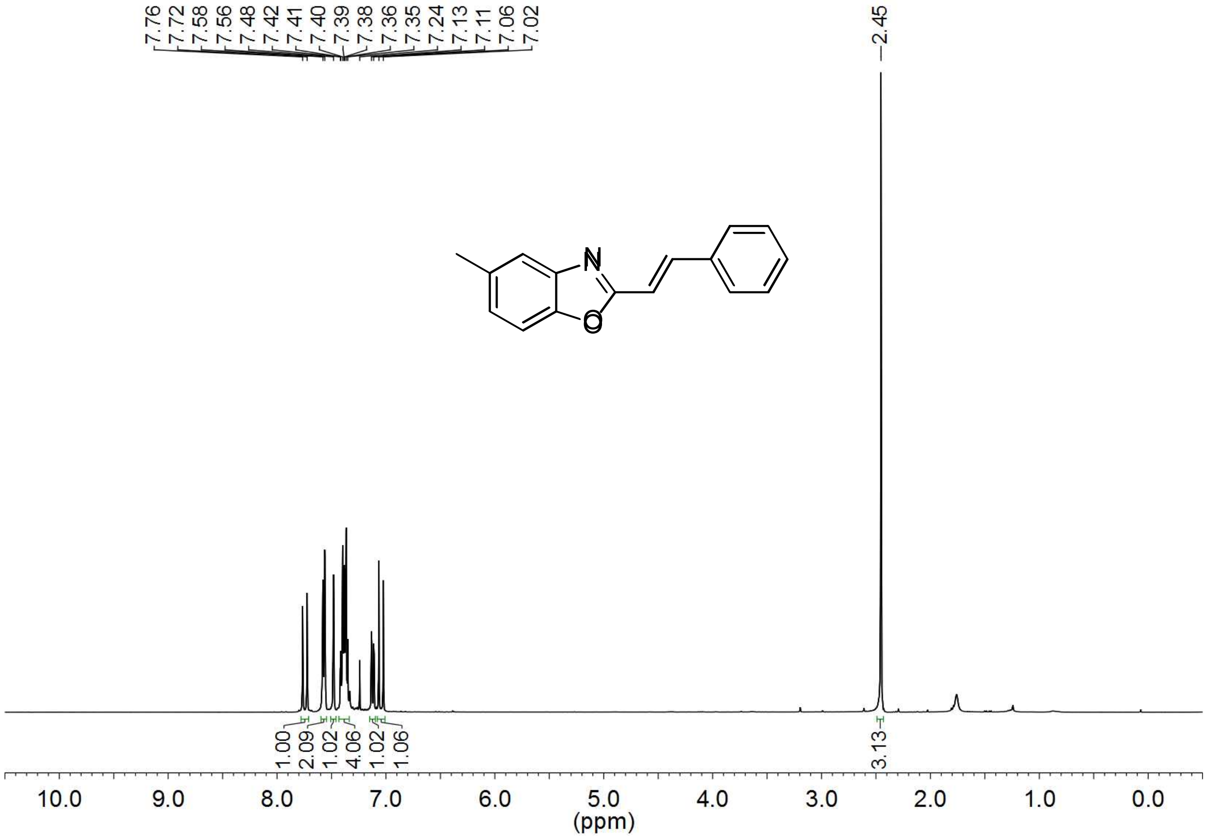
22. Lee, W.-C.; Wang, C.-H.; Lin, Y.-H.; Shih, W.-C.; Ong, T.-G. *Org. Lett.* **2013**, *15*, 5358-5361.

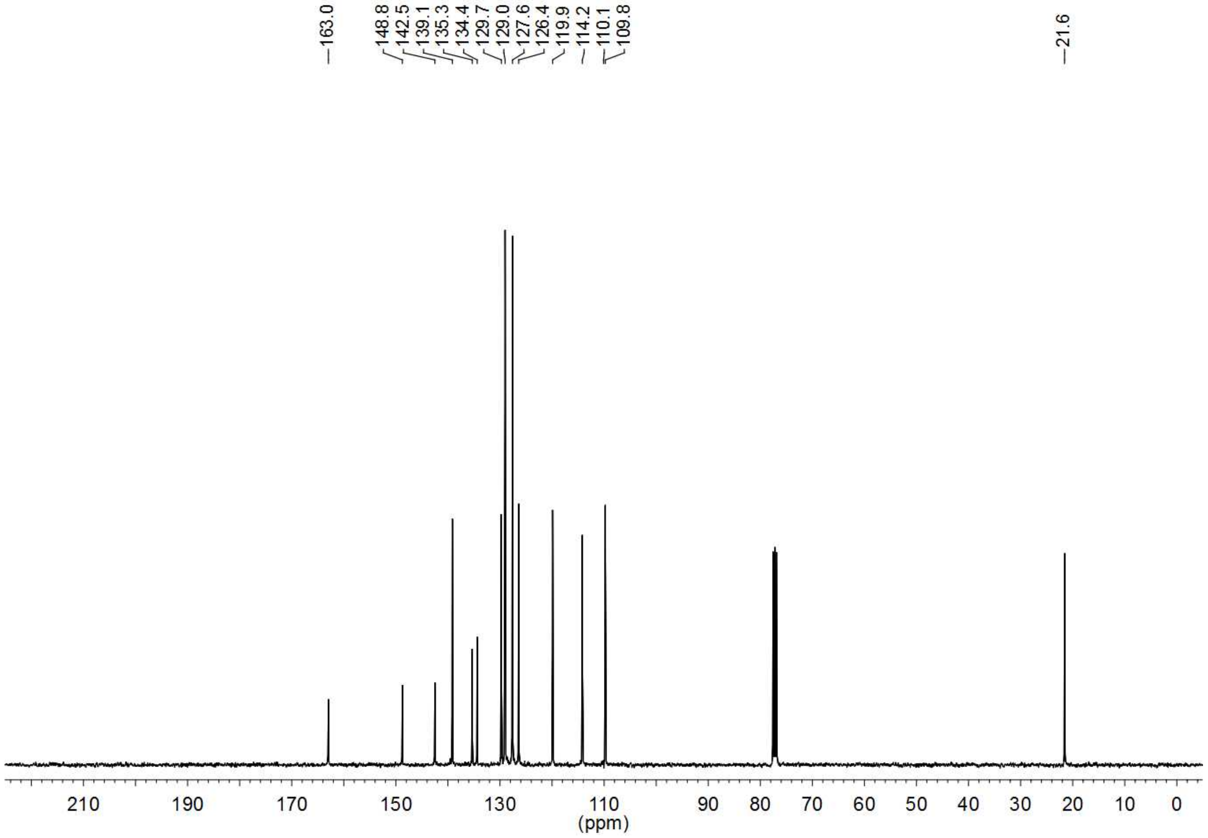

7.79
7.74
7.72
7.71
7.70
7.69
7.57
7.56
7.51
7.50
7.50
7.49
7.49
7.41
7.40
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.24
7.08
7.04
N
O
1.00
0.99
2.00
0.98
2.83
2.07
1.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

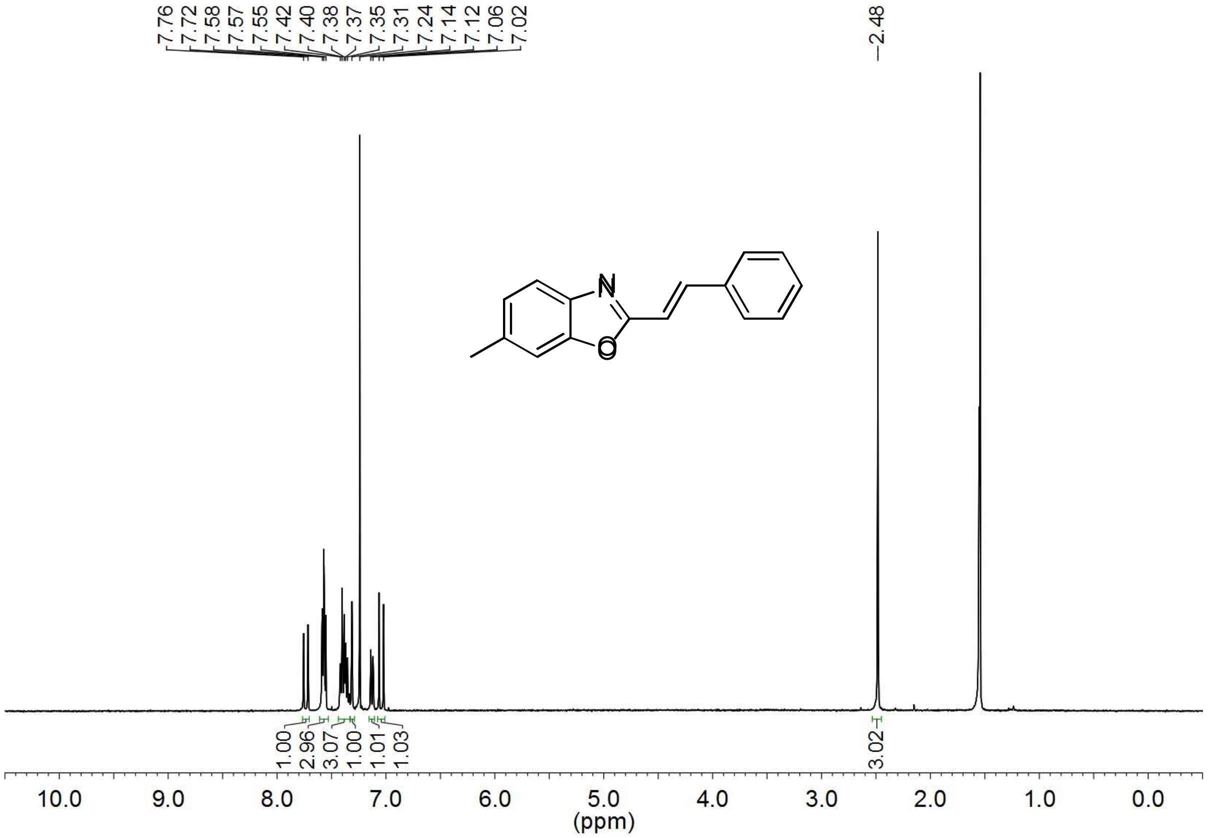

162.9
150.6
142.4
139.6
135.3
129.9
129.1
127.7
125.3
124.6
120.0
114.1
110.5
77.5
77.2
76.9
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

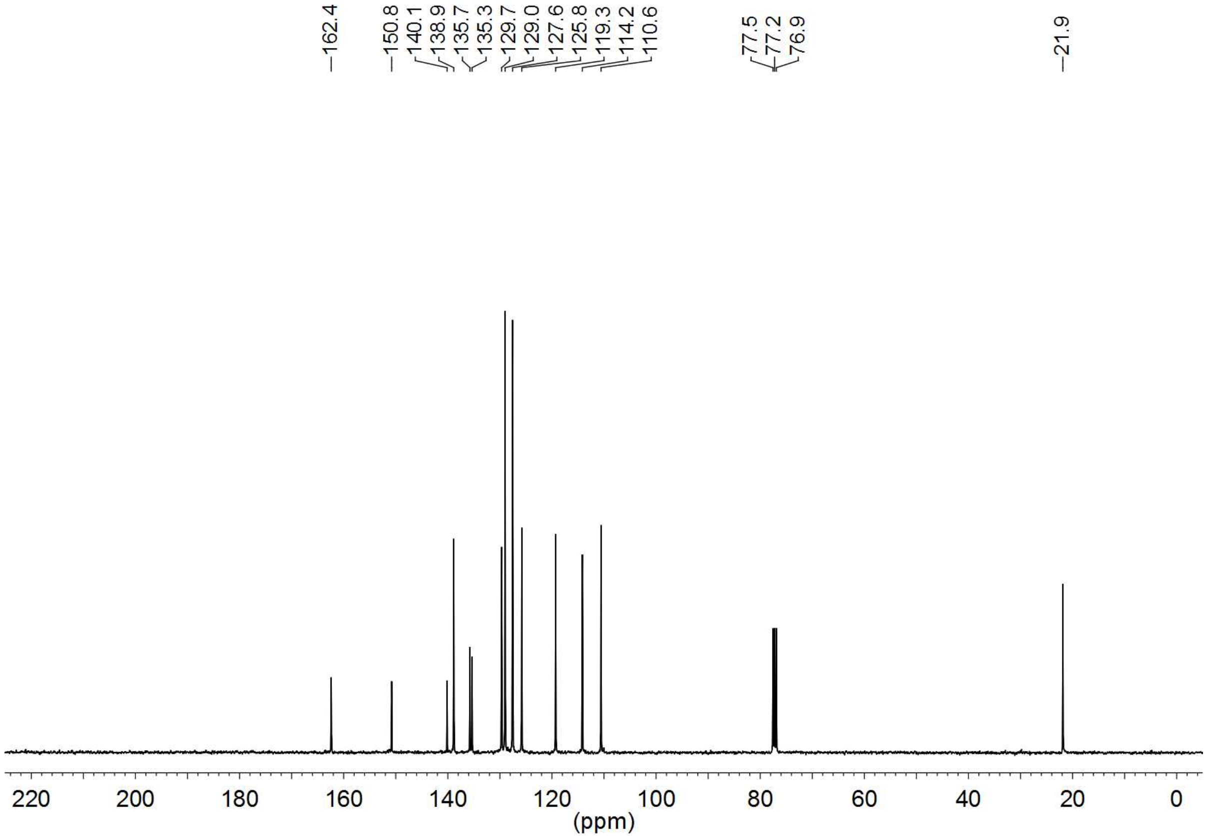

7.77
7.73
7.59
7.57
7.42
7.41
7.39
7.37
7.36
7.35
7.33
7.23
7.21
7.19
7.13
7.12
7.10
7.09
2.63
N
O
1.00
2.03
4.27
1.10
2.01
3.14
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

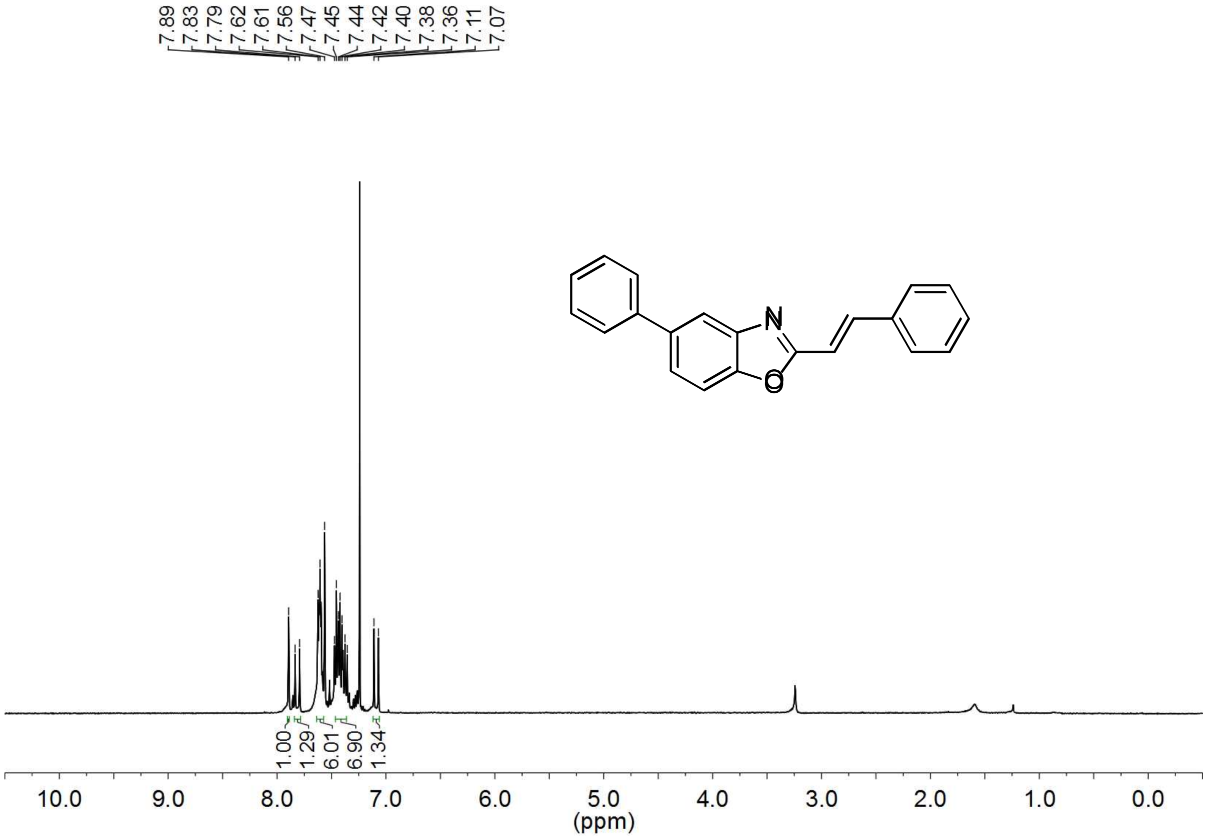

162.1
139.0
135.4
130.4
129.7
129.1
127.6
125.1
125.1
114.3
107.7
16.7
240
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

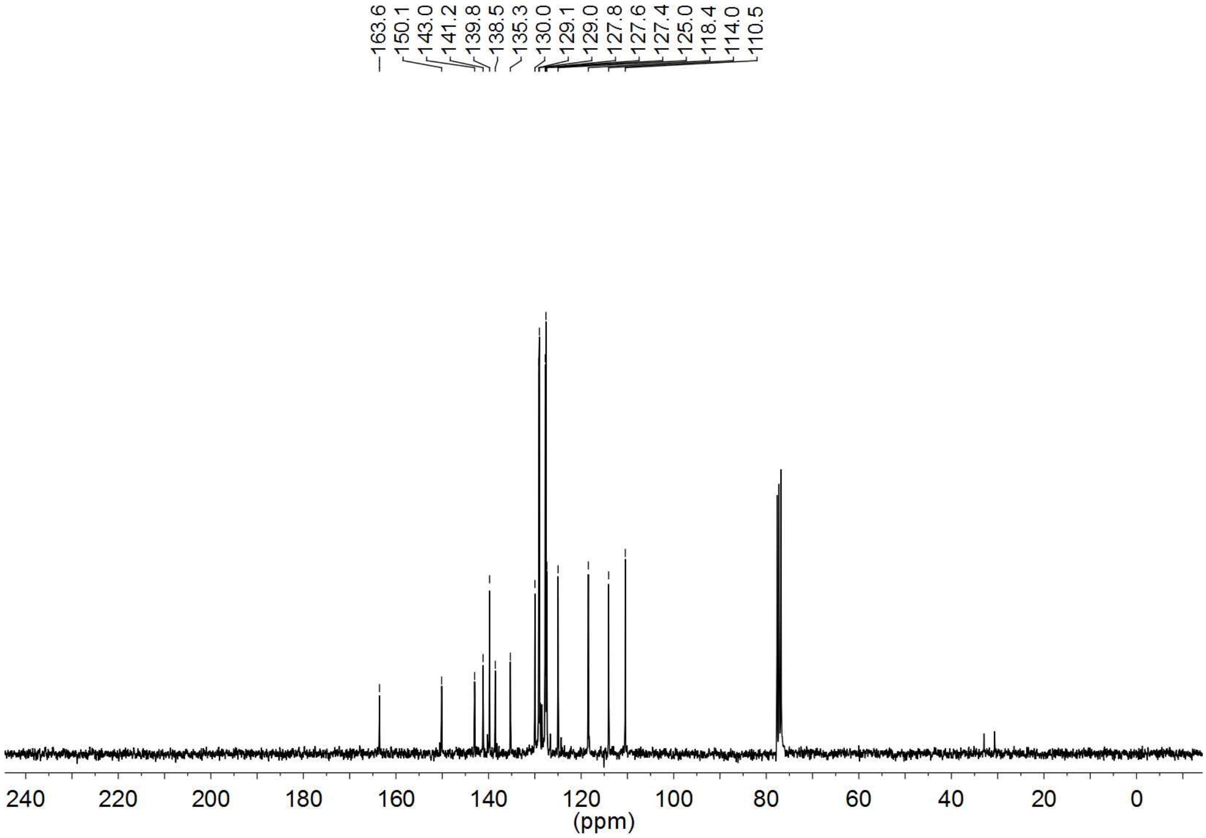

7.76
7.72
7.58
7.56
7.48
7.42
7.41
7.40
7.39
7.38
7.36
7.35
7.24
7.13
7.11
7.06
7.02
2.45
N
O
1.00
2.09
1.02
4.06
1.02
1.06
3.13
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

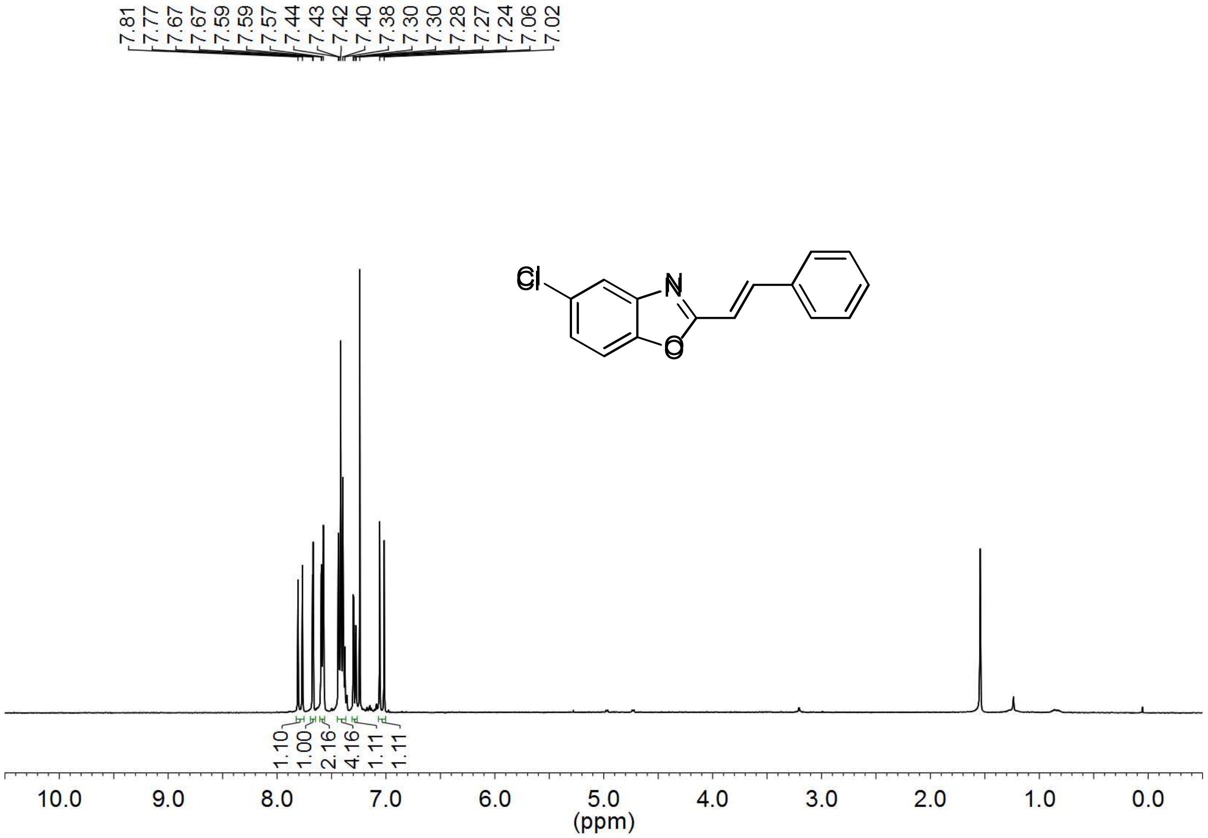

163.0
148.8
142.5
139.1
135.3
134.4
129.7
129.0
127.6
126.4
119.9
114.2
110.1
109.8
21.6
210
190
170
150
130
110
(ppm)
90
80
70
60
50
40
30
20
10
0

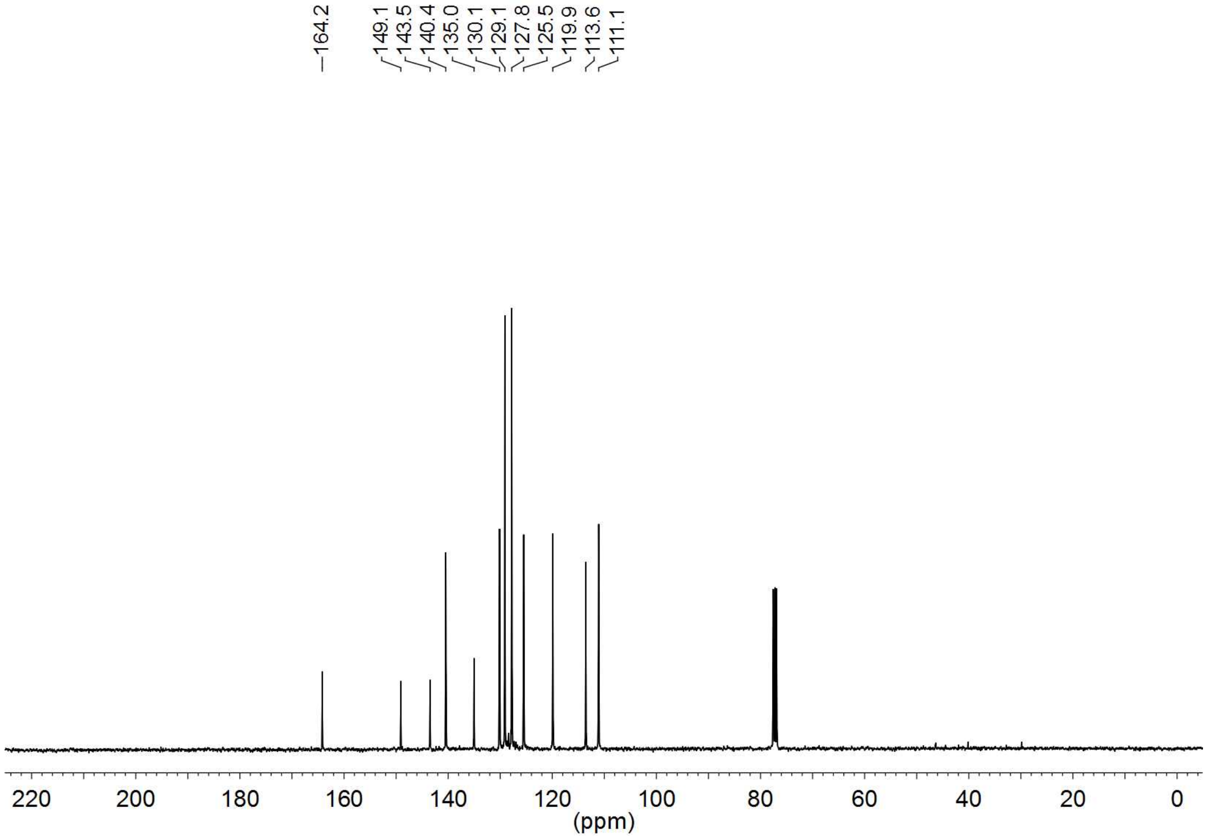

7.76
7.72
7.58
7.57
7.55
7.42
7.40
7.38
7.37
7.35
7.31
7.24
7.14
7.12
7.06
7.02
2.48
N
O
1.00
2.96
3.07
1.00
1.01
1.03
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

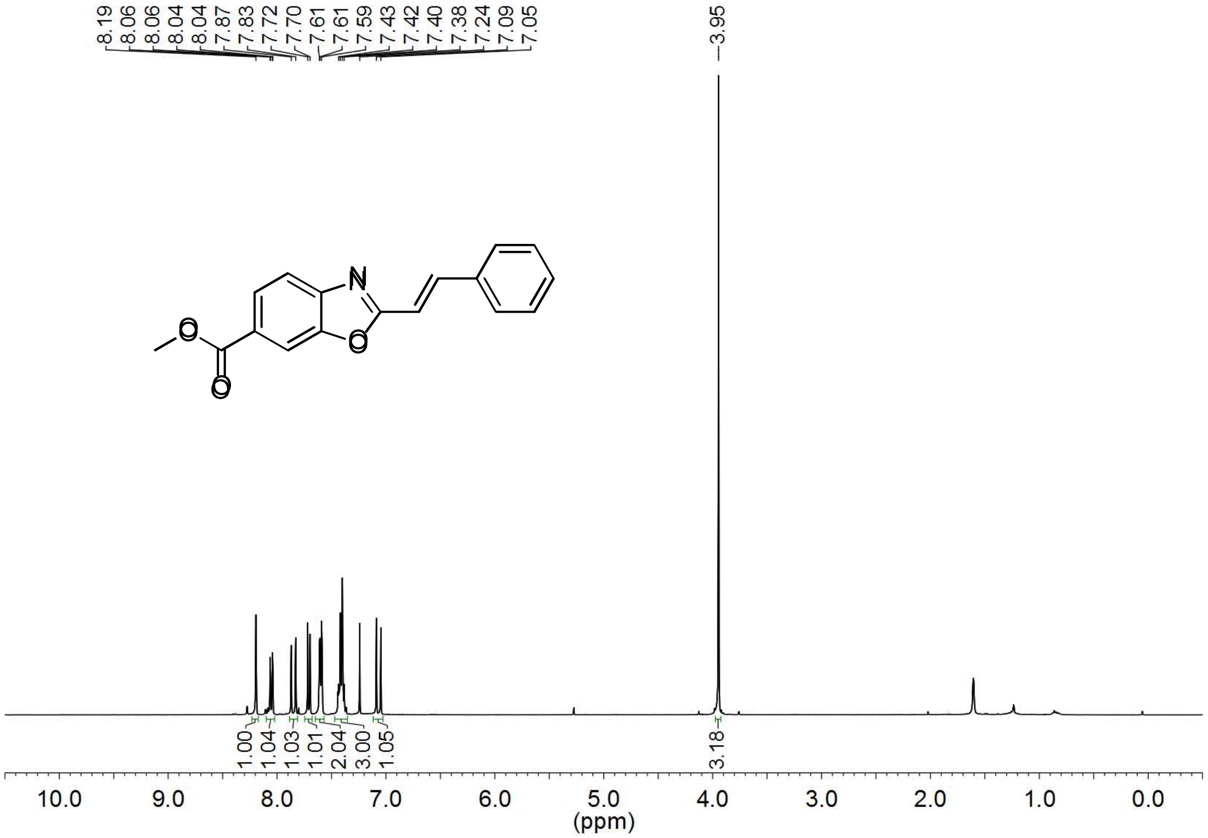

162.4
150.8
140.1
138.9
135.7
135.3
129.7
129.0
127.6
125.8
119.3
114.2
110.6
77.5
77.2
76.9
21.9
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

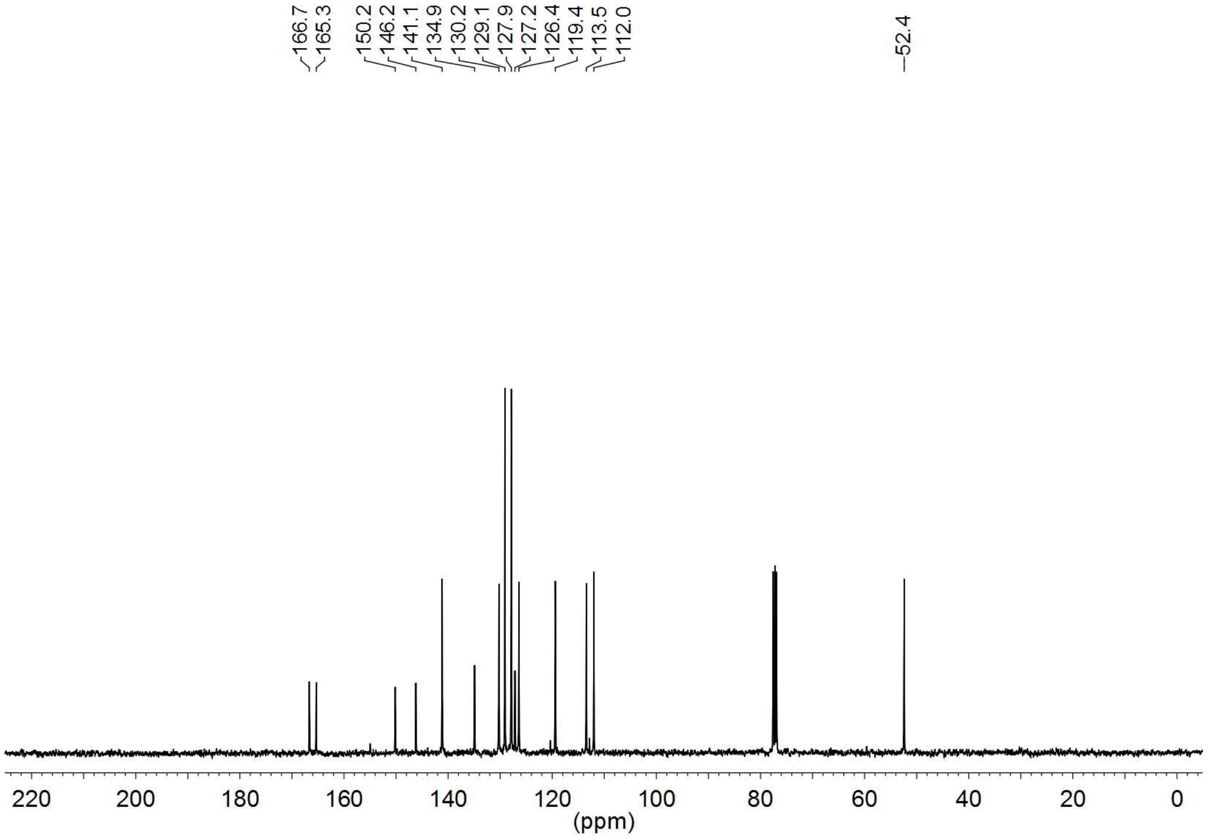

7.89
7.83
7.79
7.62
7.61
7.56
7.47
7.45
7.44
7.42
7.40
7.38
7.36
7.11
7.07
N
O
1.00
1.29
6.01
6.90
1.34
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

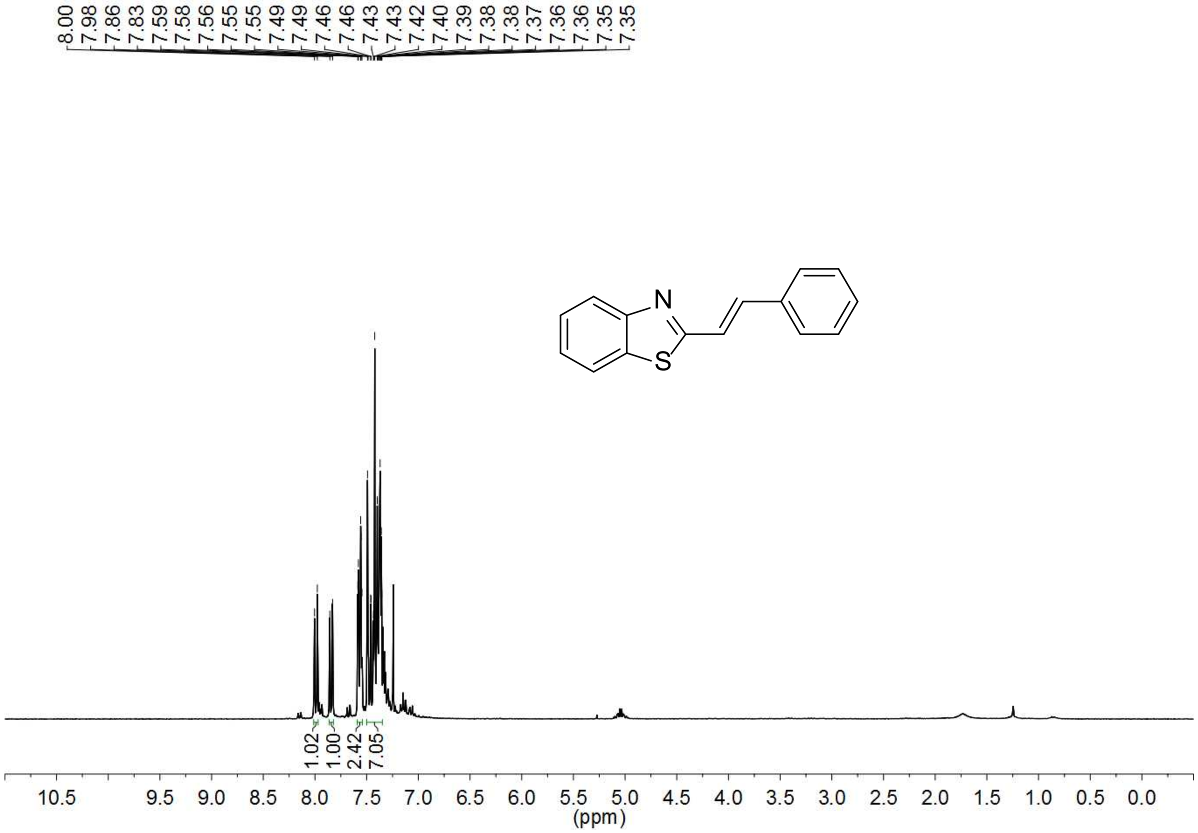

163.6
150.1
143.0
141.2
139.8
138.5
135.3
130.0
129.1
129.0
127.8
127.6
127.4
125.0
118.4
114.0
110.5
240
220
200
180
160
140
120
(ppm)
100
80
60
40
20
0

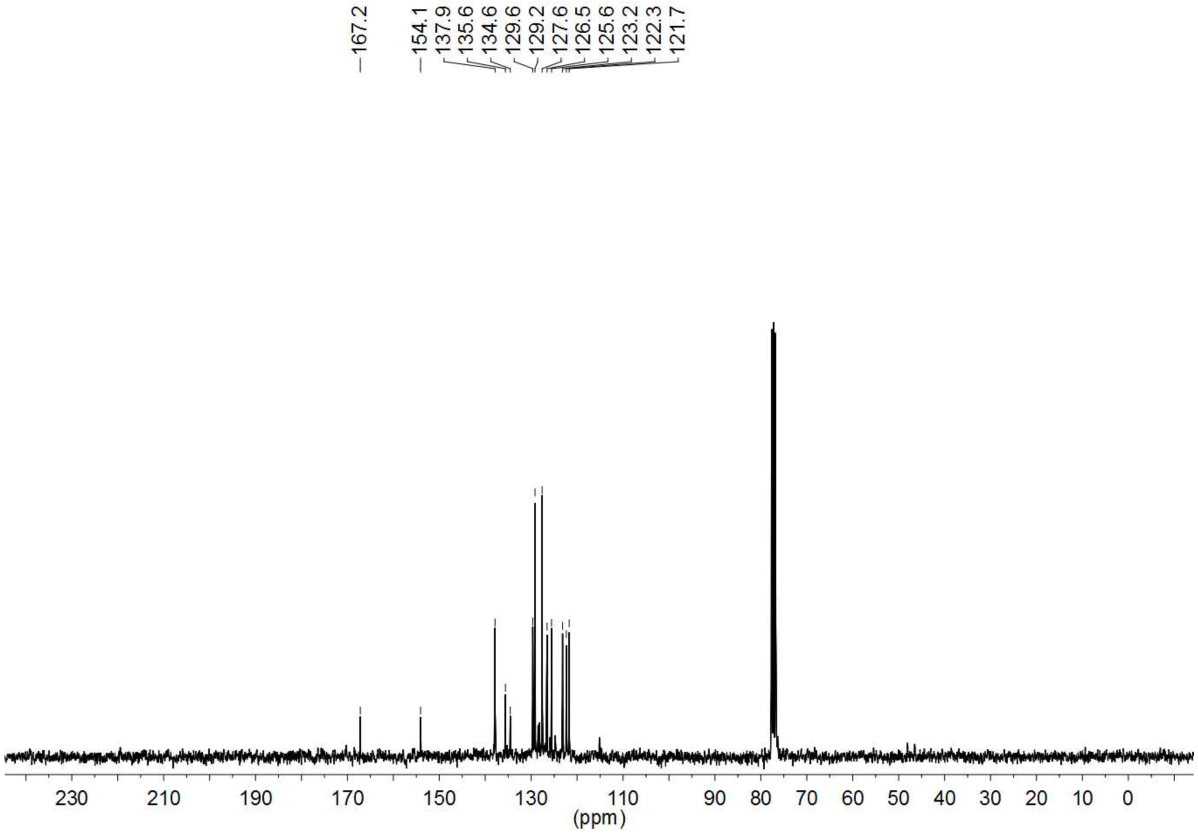

7.81
7.77
7.67
7.67
7.59
7.59
7.57
7.44
7.43
7.42
7.40
7.38
7.30
7.30
7.28
7.27
7.24
7.06
7.02
Cl
N
O
1.10
1.00
2.16
4.16
1.11
1.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

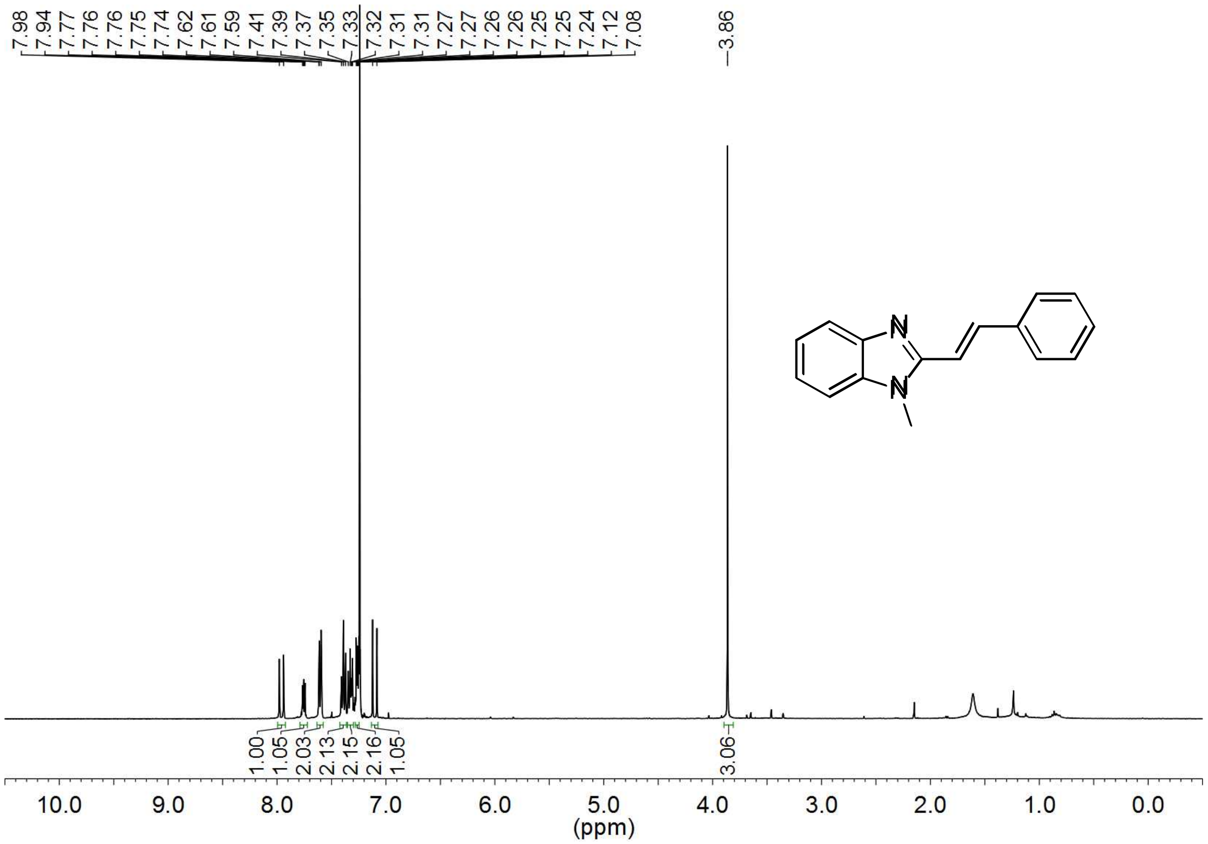

164.2
149.1
143.5
140.4
135.0
130.1
129.1
127.8
125.5
119.9
113.6
111.1
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

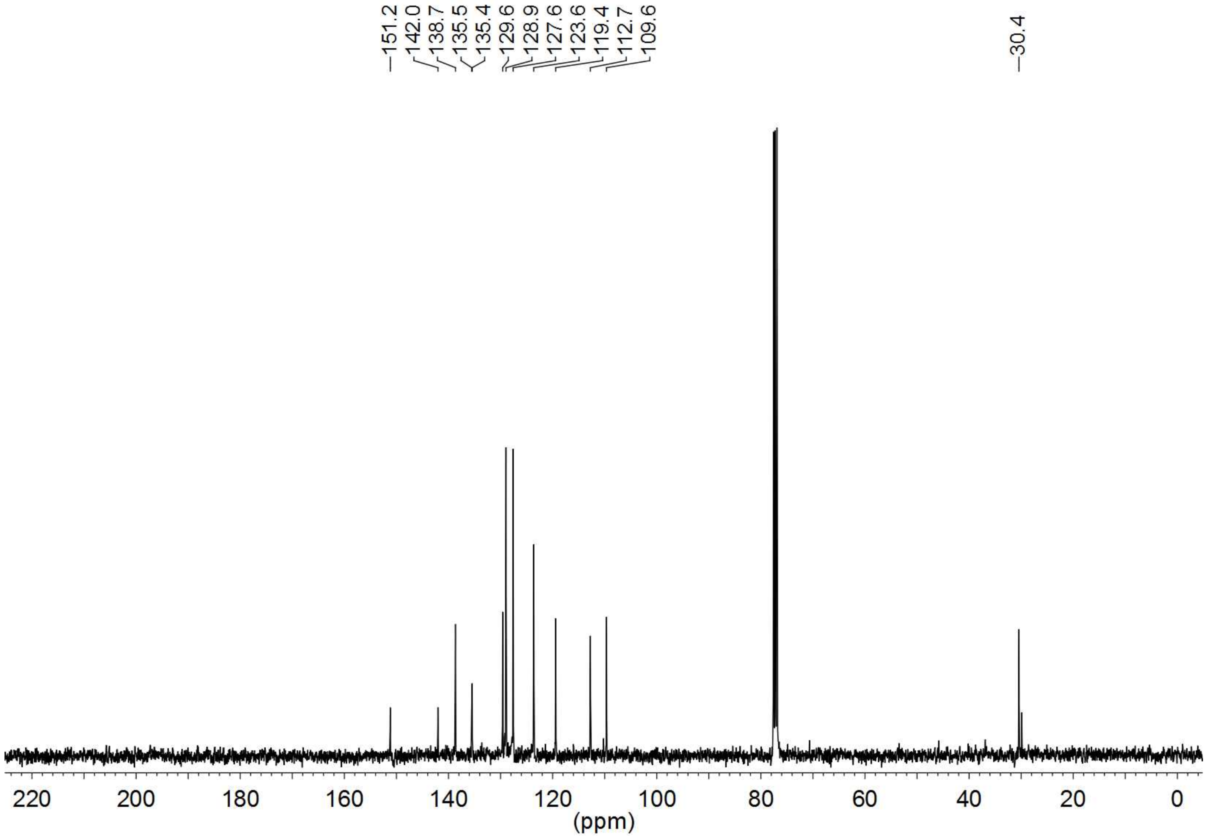

8.19
8.06
8.06
8.04
8.04
7.87
7.83
7.72
7.70
7.61
7.61
7.59
7.43
7.42
7.40
7.38
7.24
7.09
7.05
3.95
N
O
O
O
1.00
1.04
1.03
1.01
2.04
3.00
1.05
3.18
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

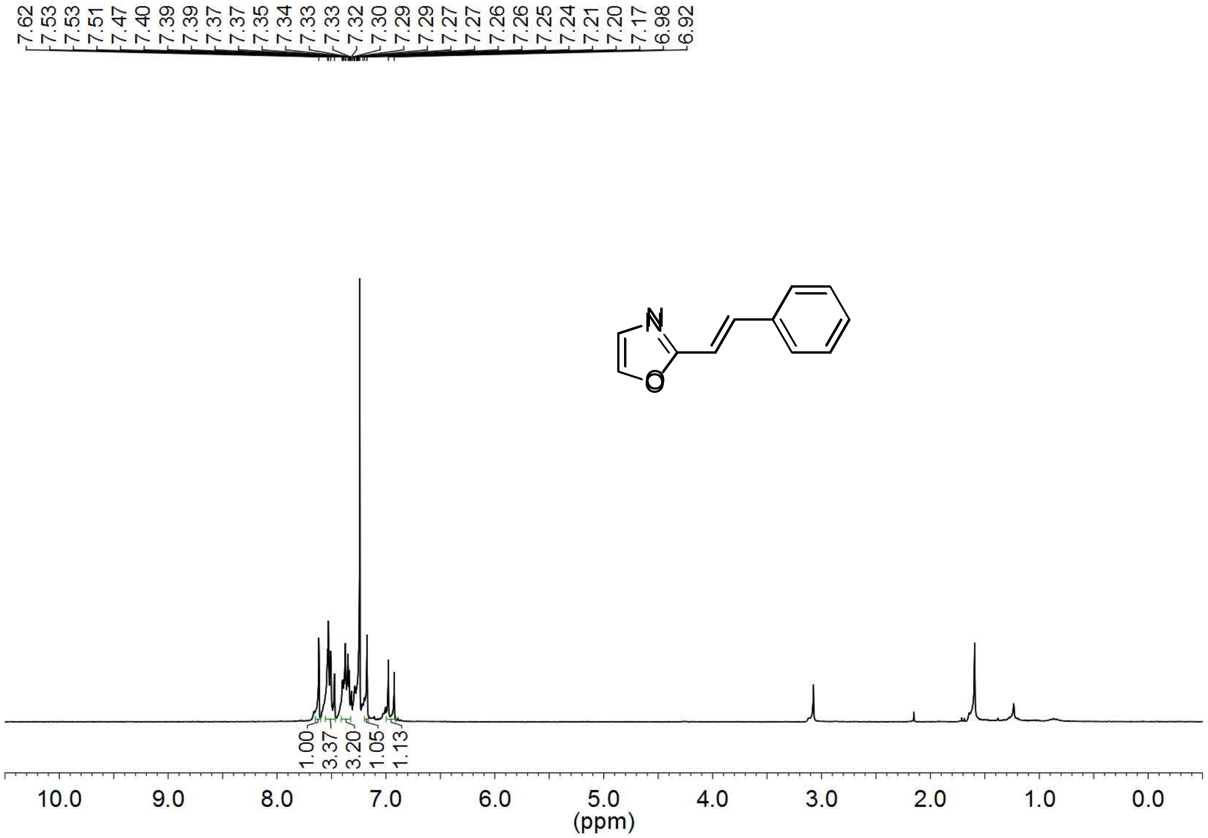

166.7
165.3
150.2
146.2
141.1
134.9
130.2
129.1
127.9
127.2
126.4
119.4
113.5
112.0
52.4
220
200
180
160
140
120
100
(ppm)
80
60
40
20
0

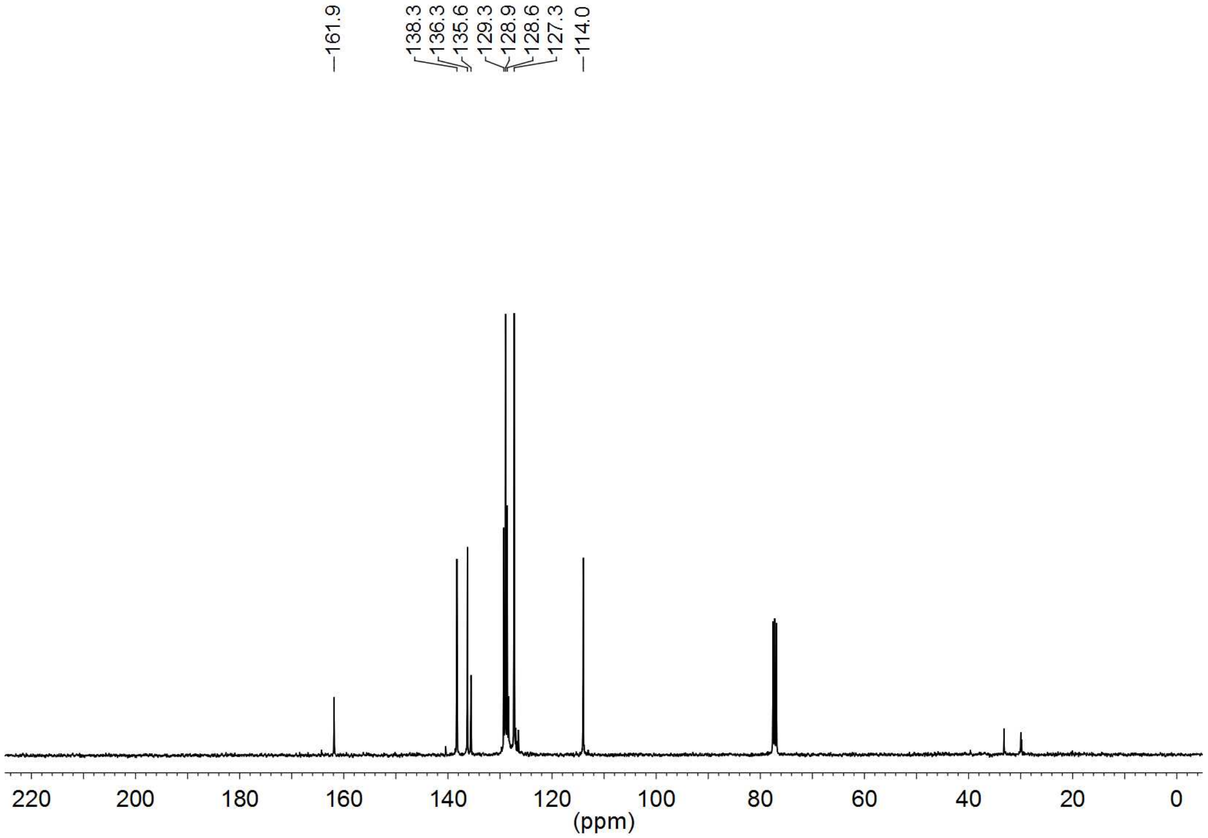

8.00
7.98
7.86
7.83
7.59
7.58
7.56
7.55
7.55
7.49
7.49
7.46
7.46
7.43
7.43
7.42
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
N
S
1.02
1.00
2.42
7.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

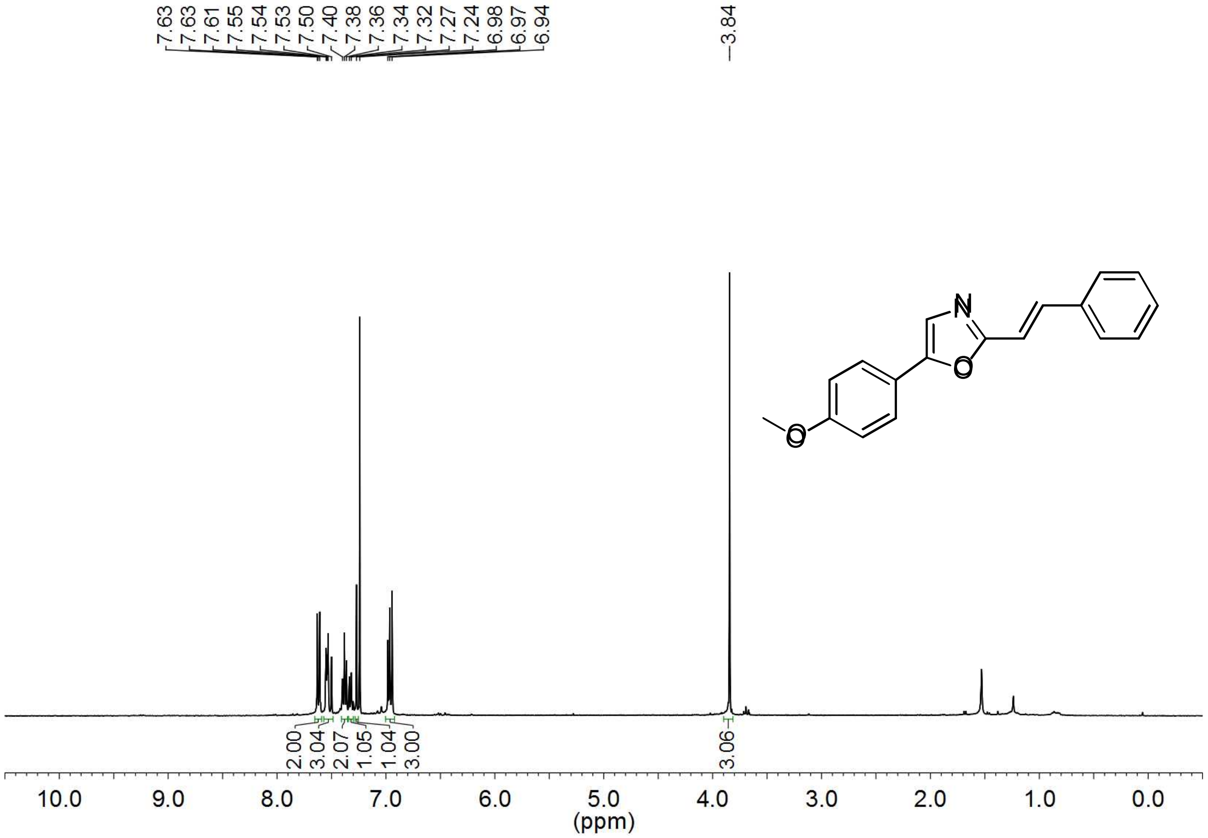

167.2
154.1
137.9
135.6
134.6
129.6
129.2
127.6
126.5
125.6
123.2
122.3
121.7
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

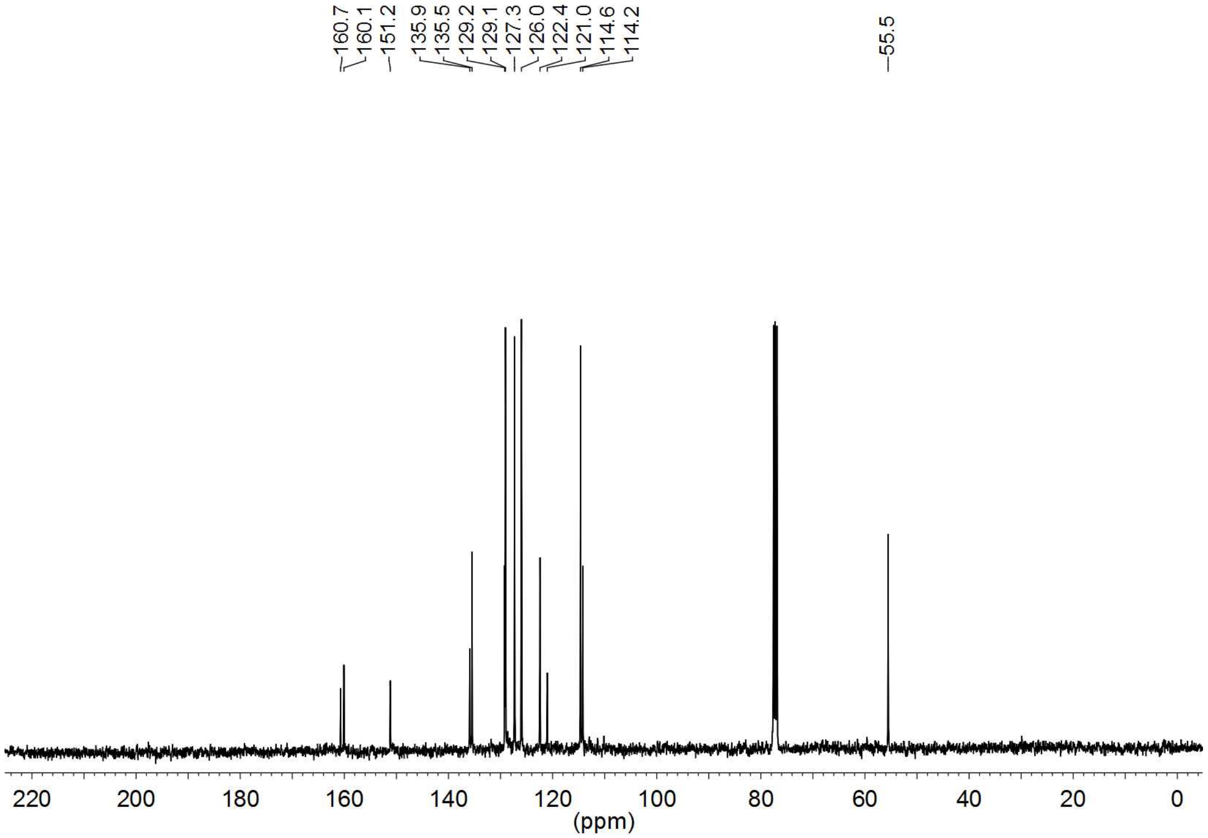

7.98
7.94
7.77
7.76
7.76
7.75
7.74
7.62
7.61
7.59
7.41
7.39
7.37
7.35
7.33
7.32
7.31
7.31
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.12
7.08
3.86
N
N
1.00
1.05
2.03
2.13
2.15
2.16
1.05
3.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

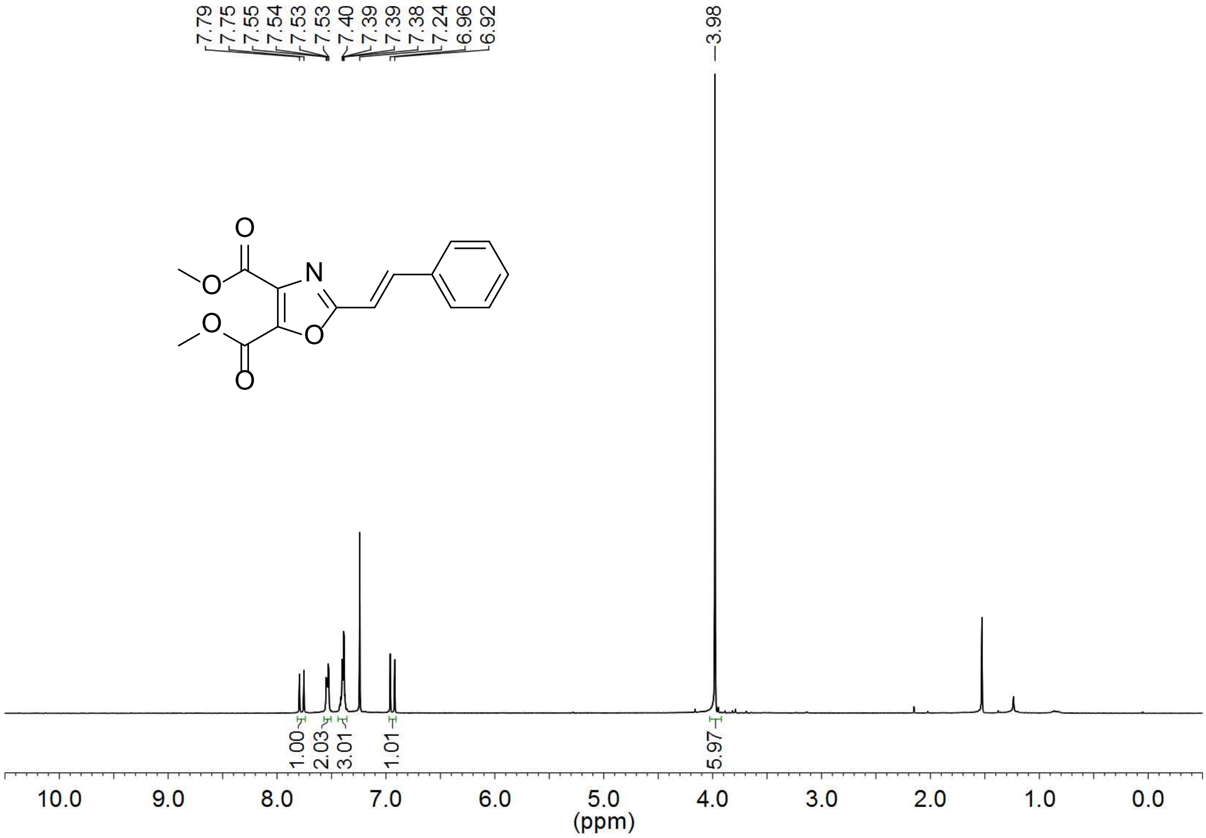

151.2
142.0
138.7
135.5
135.4
129.6
128.9
127.6
123.6
119.4
112.7
109.6
30.4
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

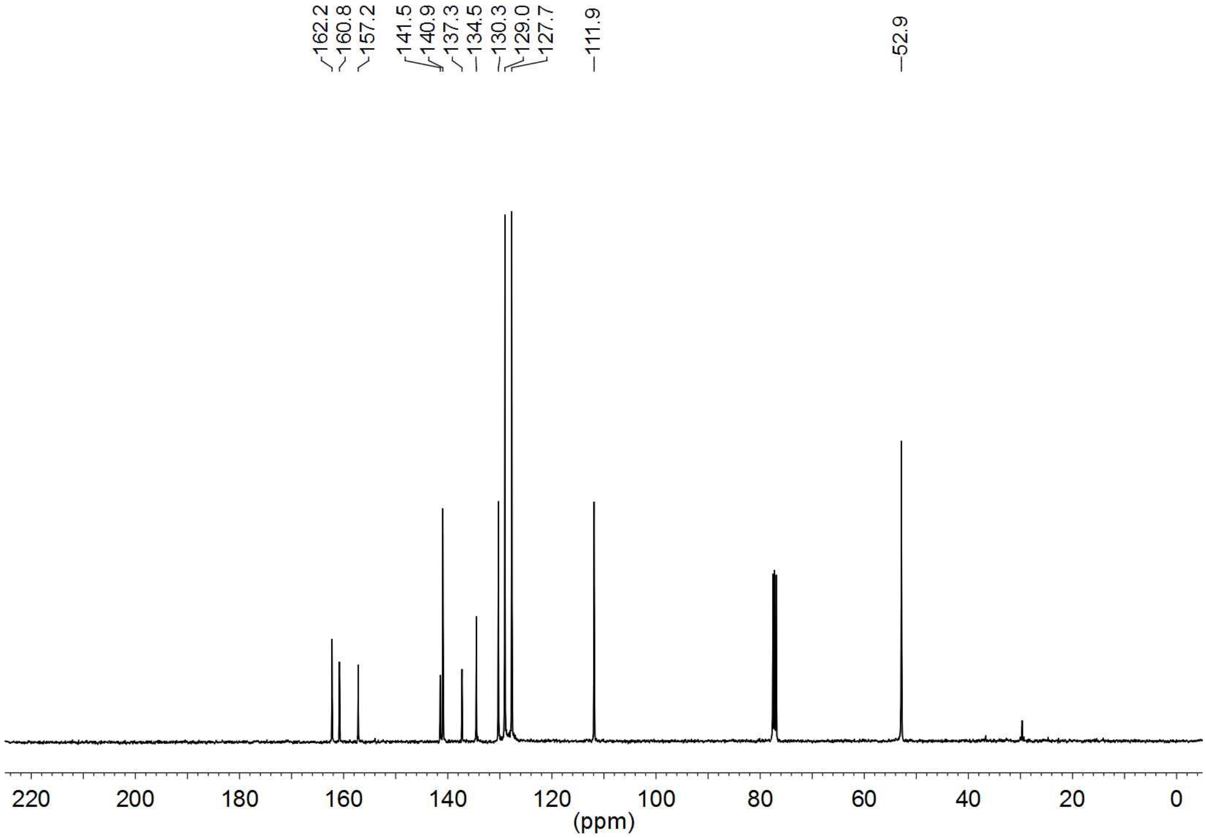

7.62
7.53
7.53
7.51
7.47
7.40
7.39
7.39
7.37
7.37
7.35
7.34
7.33
7.33
7.32
7.30
7.29
7.29
7.27
7.27
7.26
7.26
7.25
7.24
7.21
7.20
7.17
6.98
6.92
N
O
1.00
3.37
3.20
1.05
1.13
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

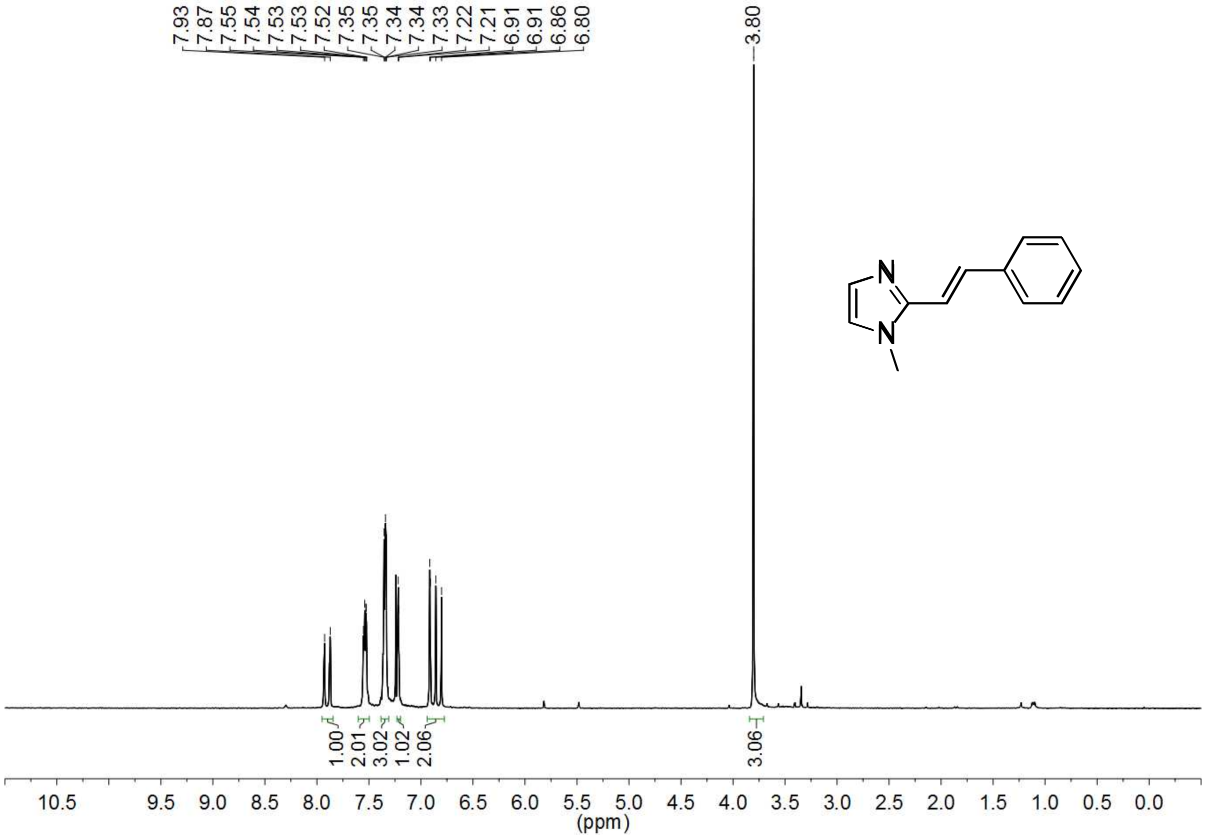

161.9
138.3
136.3
135.6
129.3
128.9
128.6
127.3
114.0
220
200
180
160
140
120
100
(ppm)
80
60
40
20
0

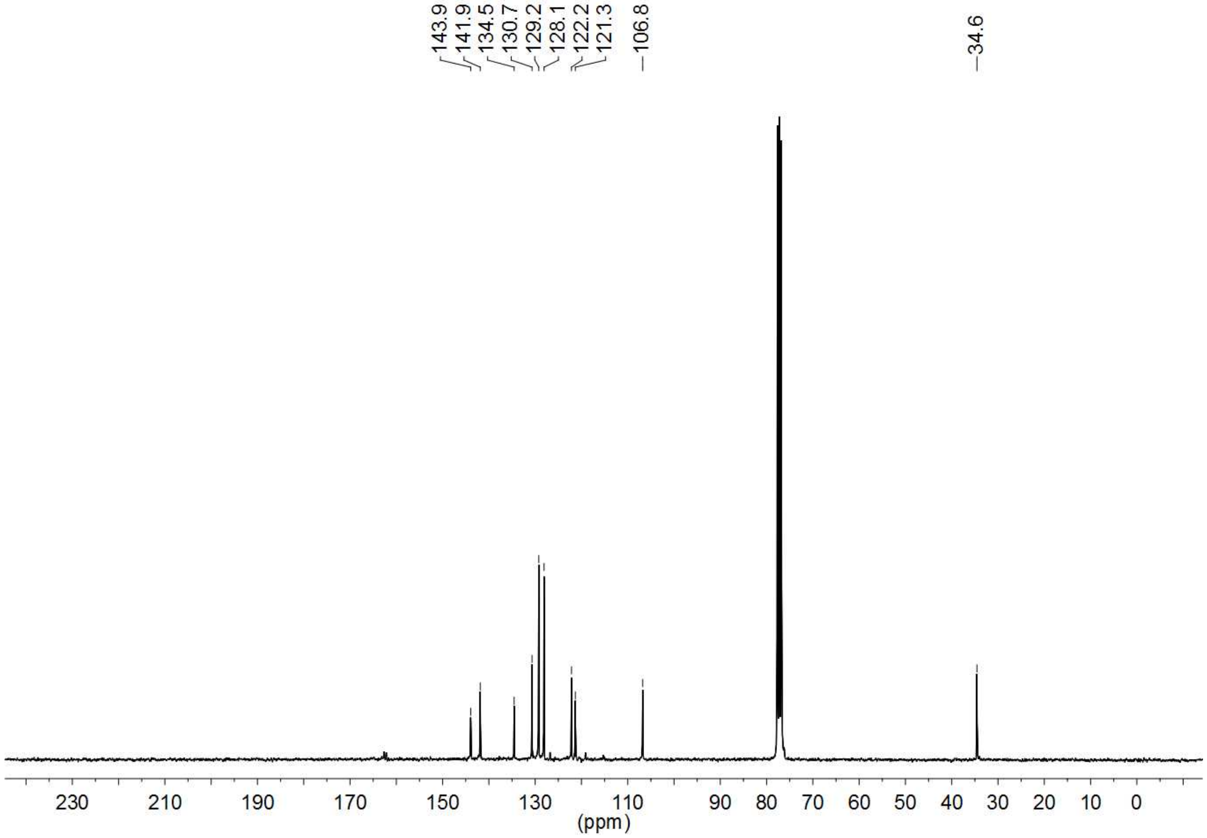

7.63
7.63
7.61
7.55
7.54
7.53
7.50
7.40
7.38
7.36
7.34
7.32
7.27
7.24
6.98
6.97
6.94
3.84
N
O
O
2.00
3.04
2.07
1.05
1.04
3.00
3.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

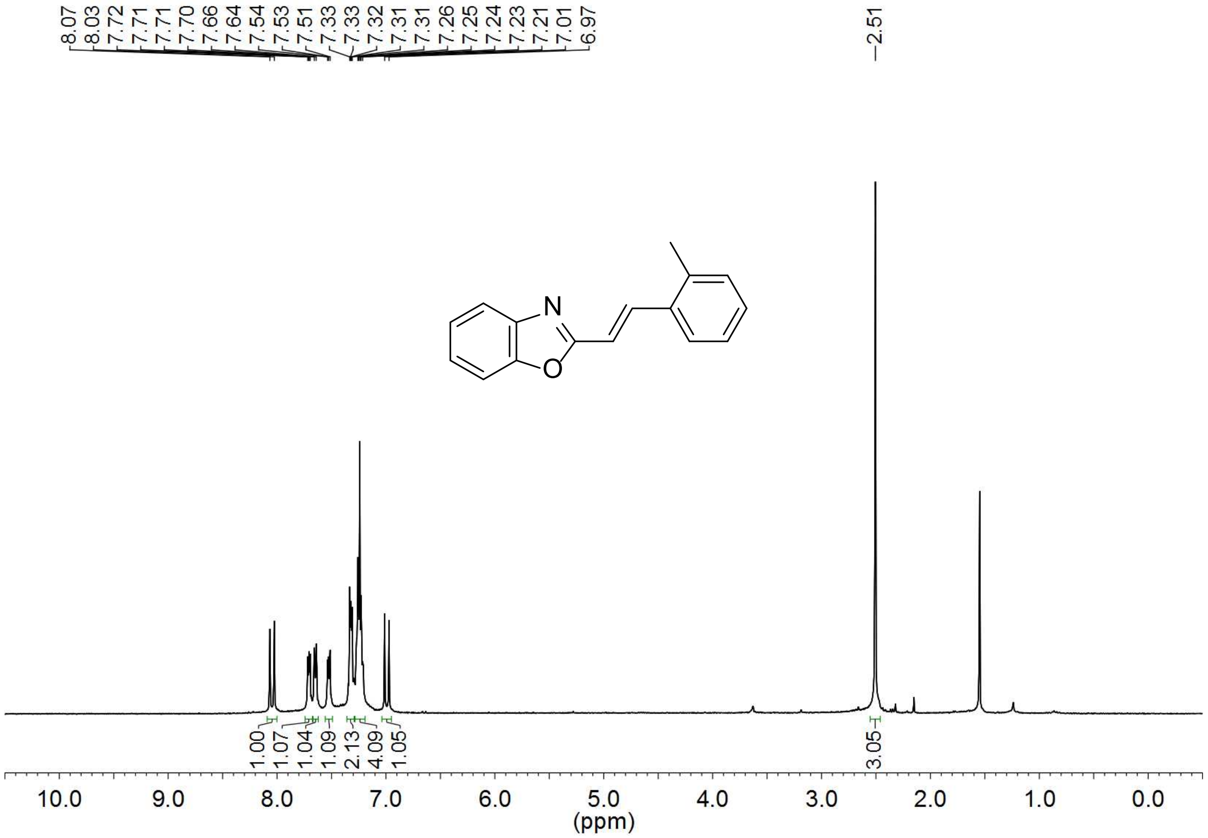

160.7
160.1
151.2
135.9
135.5
129.2
129.1
127.3
126.0
122.4
121.0
114.6
114.2
55.5
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

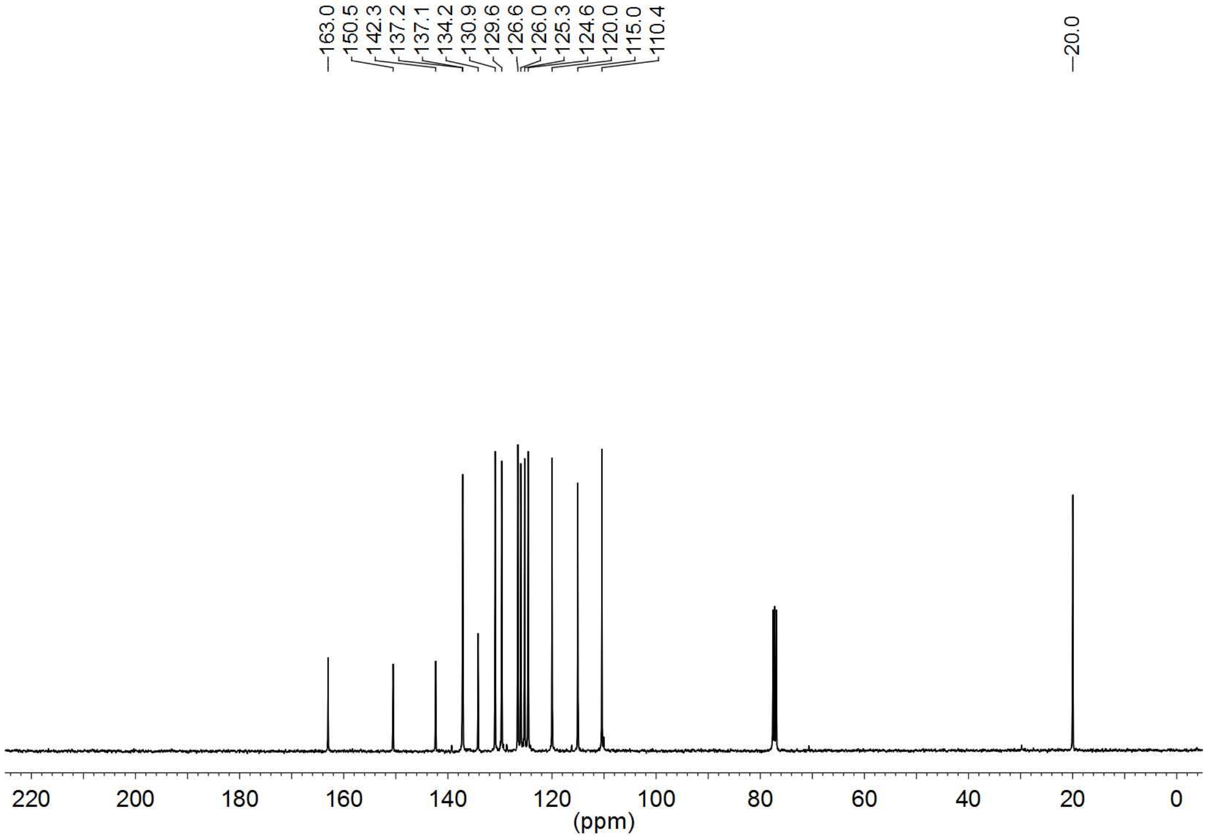

7.79
7.75
7.55
7.54
7.53
7.53
7.40
7.39
7.39
7.38
7.24
6.96
6.92
3.98
O
O
N
O
O
O
1.00
2.03
3.01
1.01
5.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

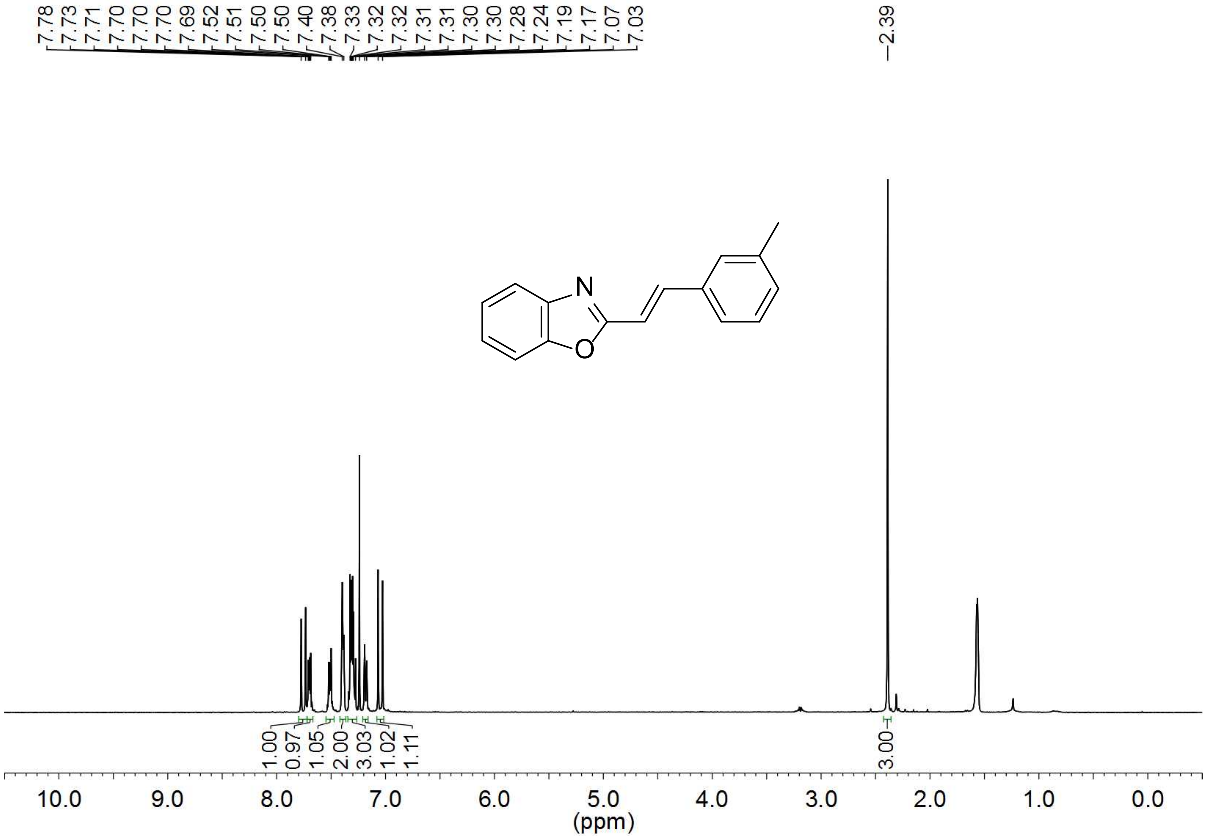

162.2
160.8
157.2
141.5
140.9
137.3
134.5
130.3
129.0
127.7
111.9
52.9
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

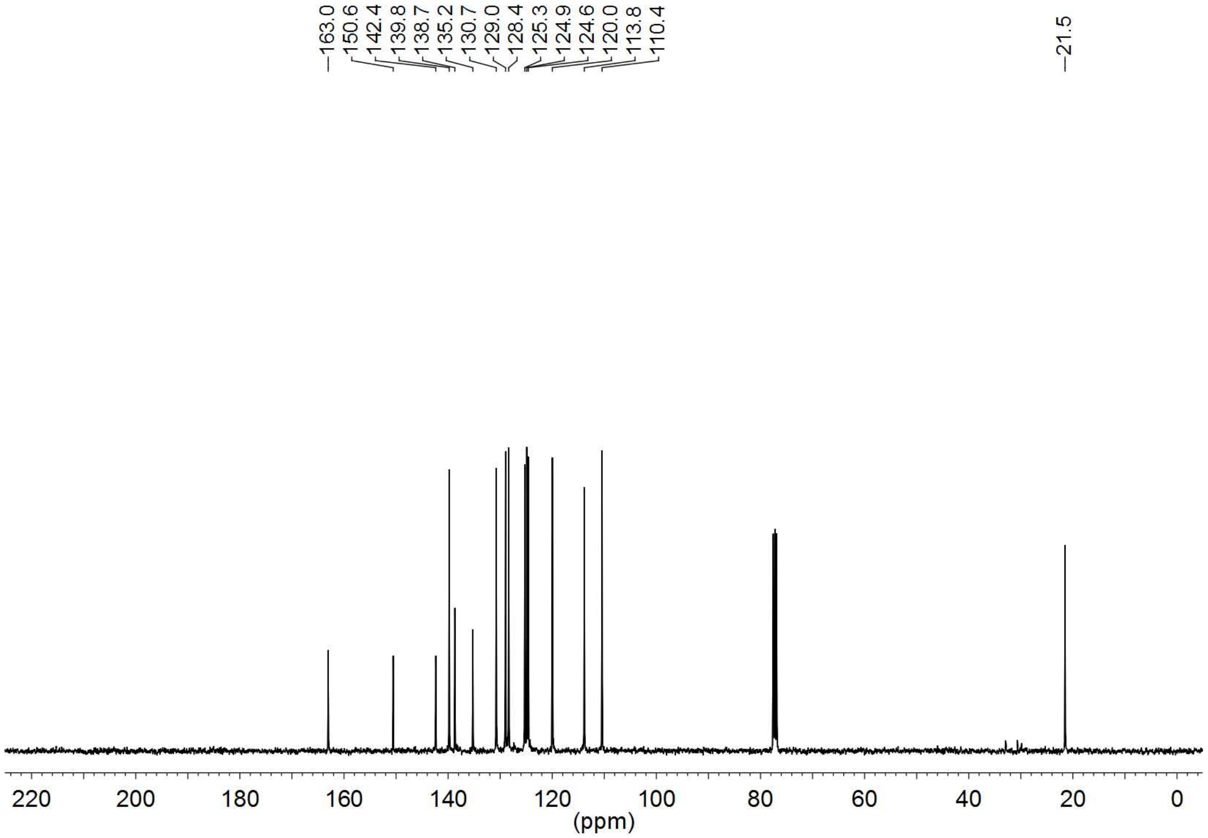

7.93
7.87
7.55
7.54
7.53
7.53
7.52
7.35
7.35
7.34
7.34
7.33
7.22
7.21
6.91
6.91
6.86
6.80
3.80
N
N
1.00
2.01
3.02
1.02
2.06
3.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

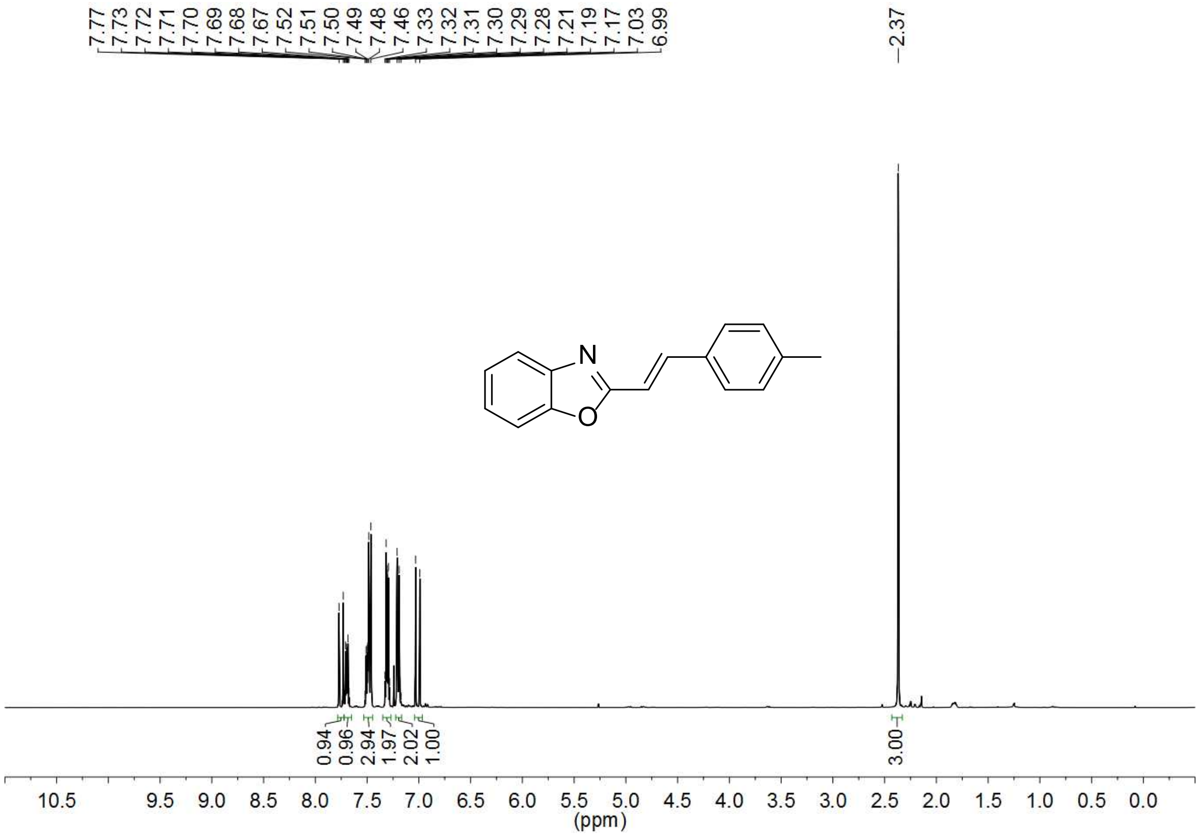

143.9
141.9
134.5
130.7
129.2
128.1
122.2
121.3
106.8
34.6
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

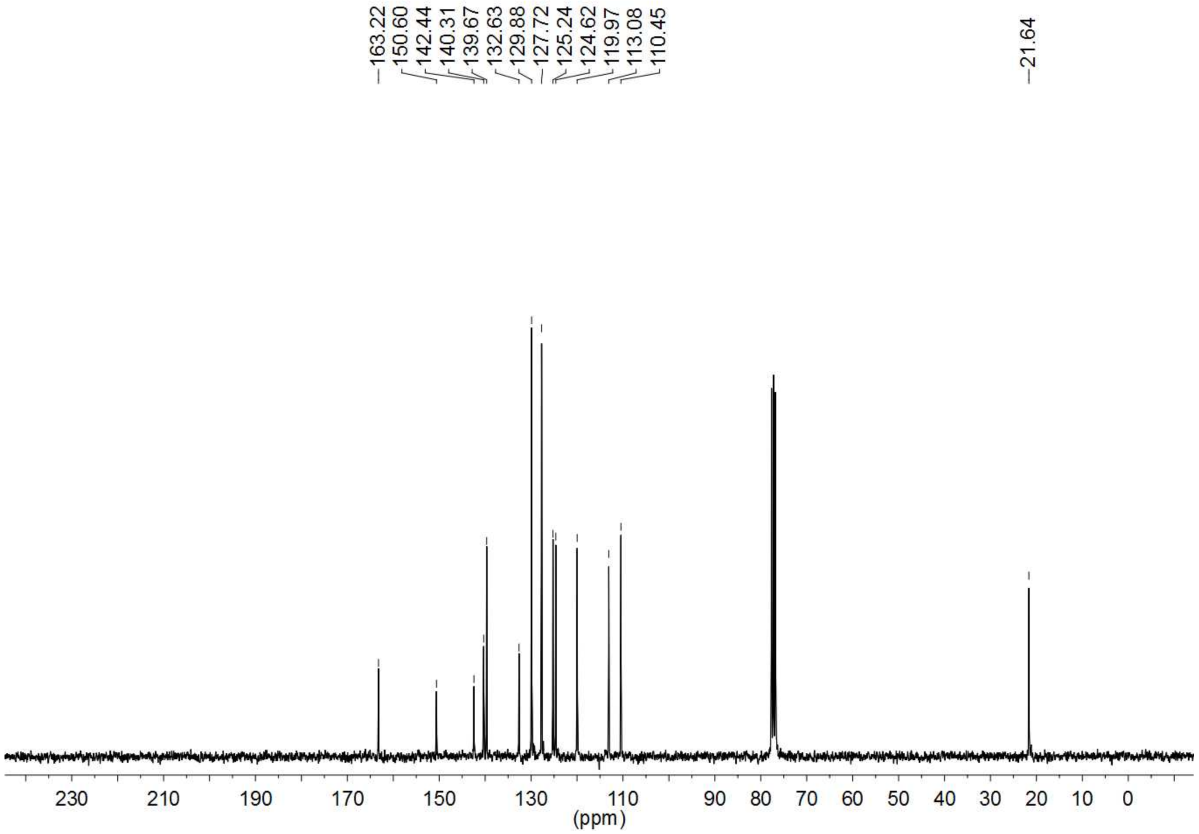

8.07
8.03
7.72
7.71
7.71
7.70
7.66
7.64
7.54
7.53
7.51
7.33
7.33
7.32
7.31
7.31
7.26
7.25
7.24
7.23
7.21
7.01
6.97
2.51
N
O
1.00
1.07
1.04
1.09
2.13
4.09
1.05
3.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

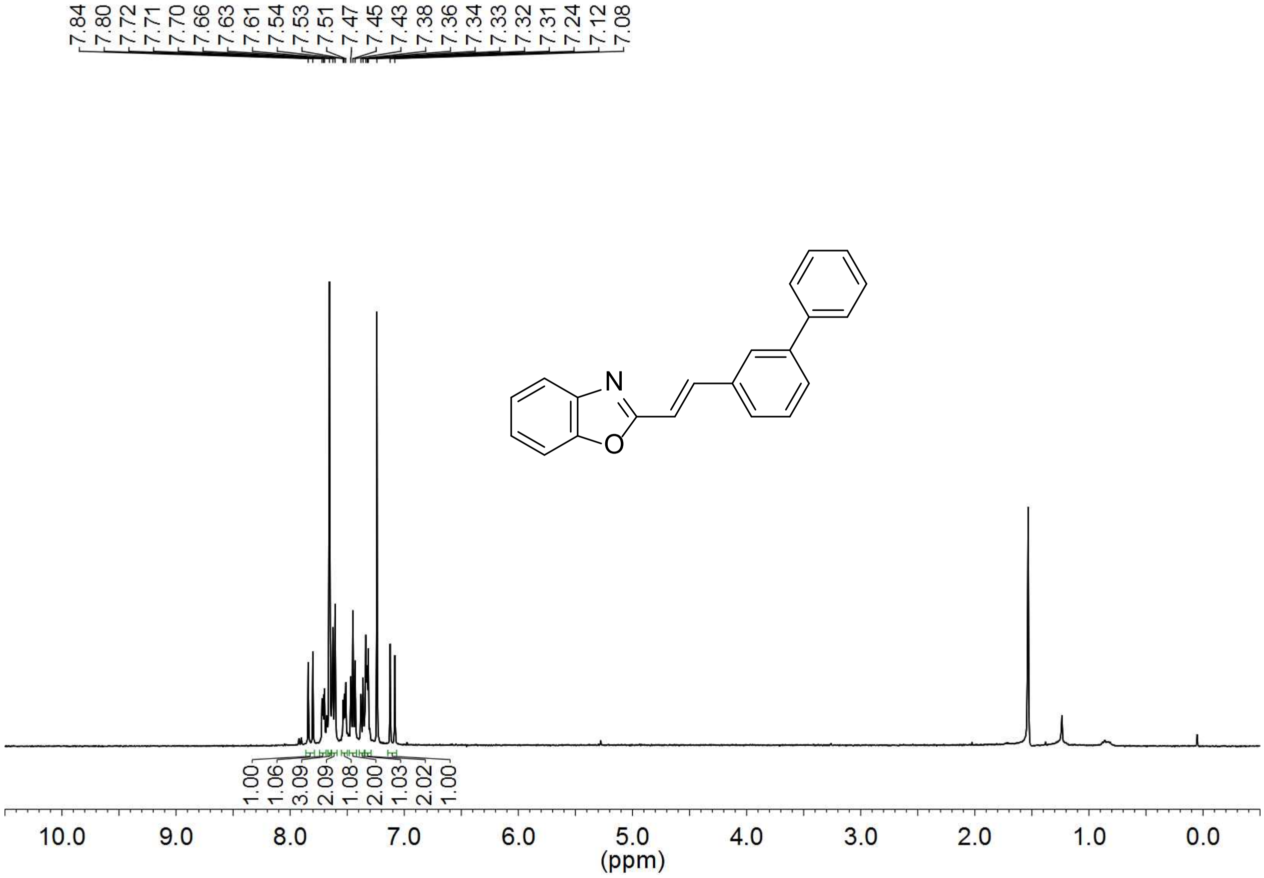

163.0
150.5
142.3
137.2
137.1
134.2
130.9
129.6
126.6
126.0
125.3
124.6
120.0
115.0
110.4
20.0
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

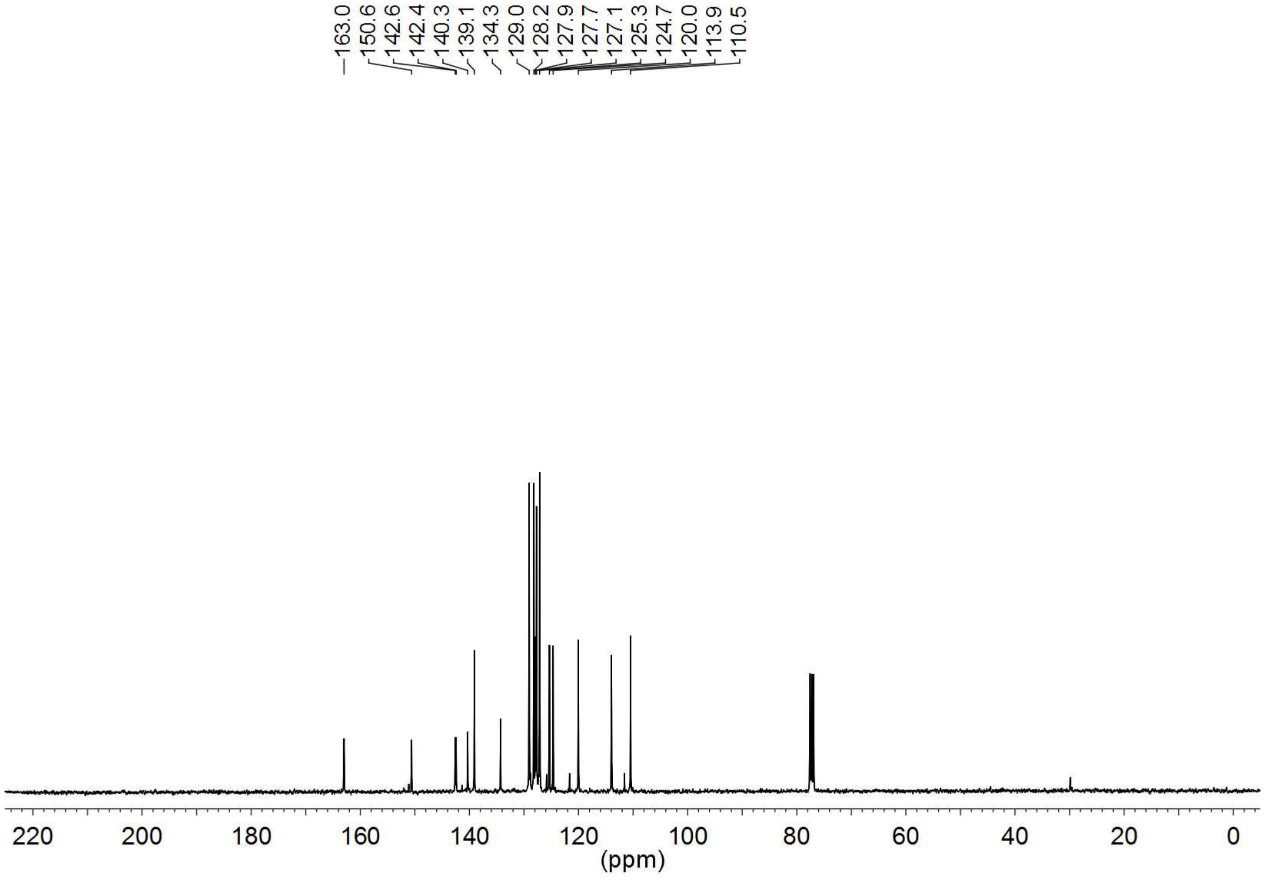

7.78
7.73
7.71
7.70
7.70
7.70
7.69
7.52
7.51
7.50
7.50
7.40
7.38
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.28
7.24
7.19
7.17
7.07
7.03
2.39
N
O
1.00
0.97
1.05
2.00
3.03
1.02
1.11
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

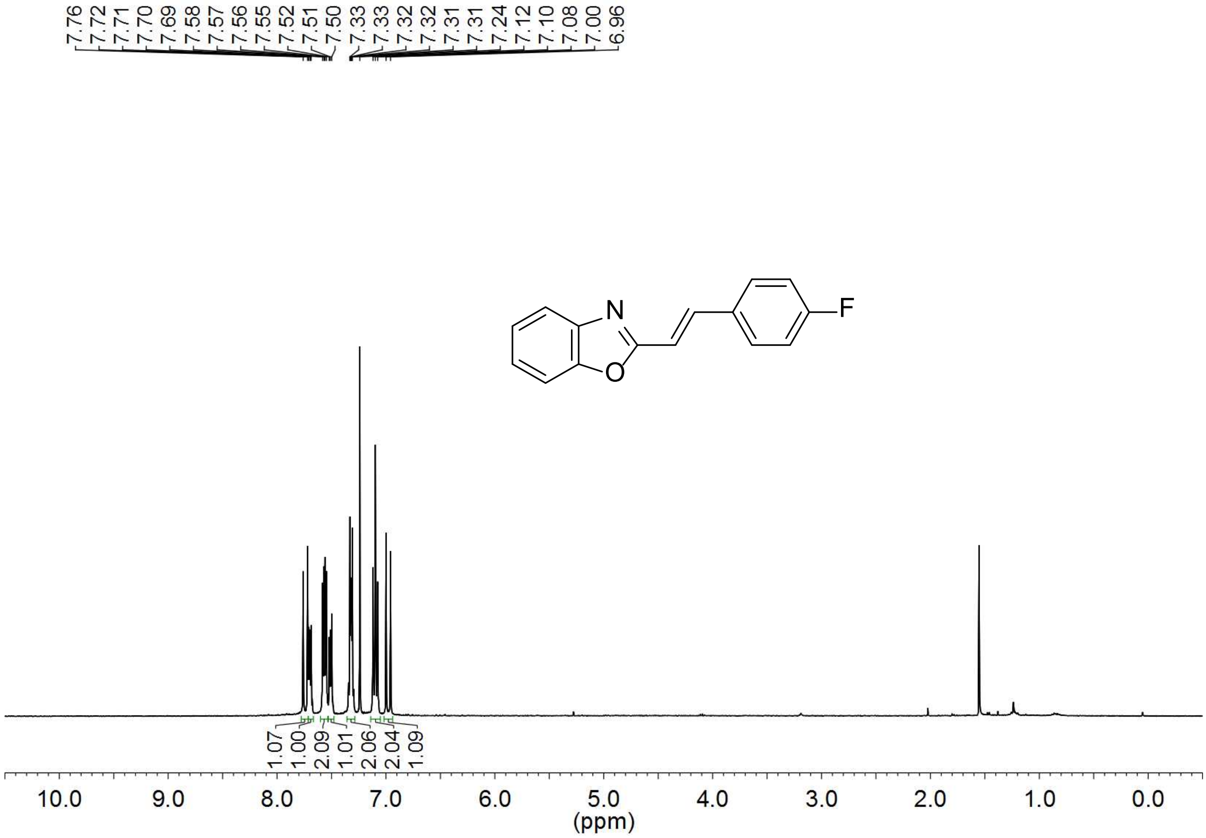

163.0
150.6
142.4
139.8
138.7
135.2
130.7
129.0
128.4
125.3
124.9
124.6
120.0
113.8
110.4
21.5
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

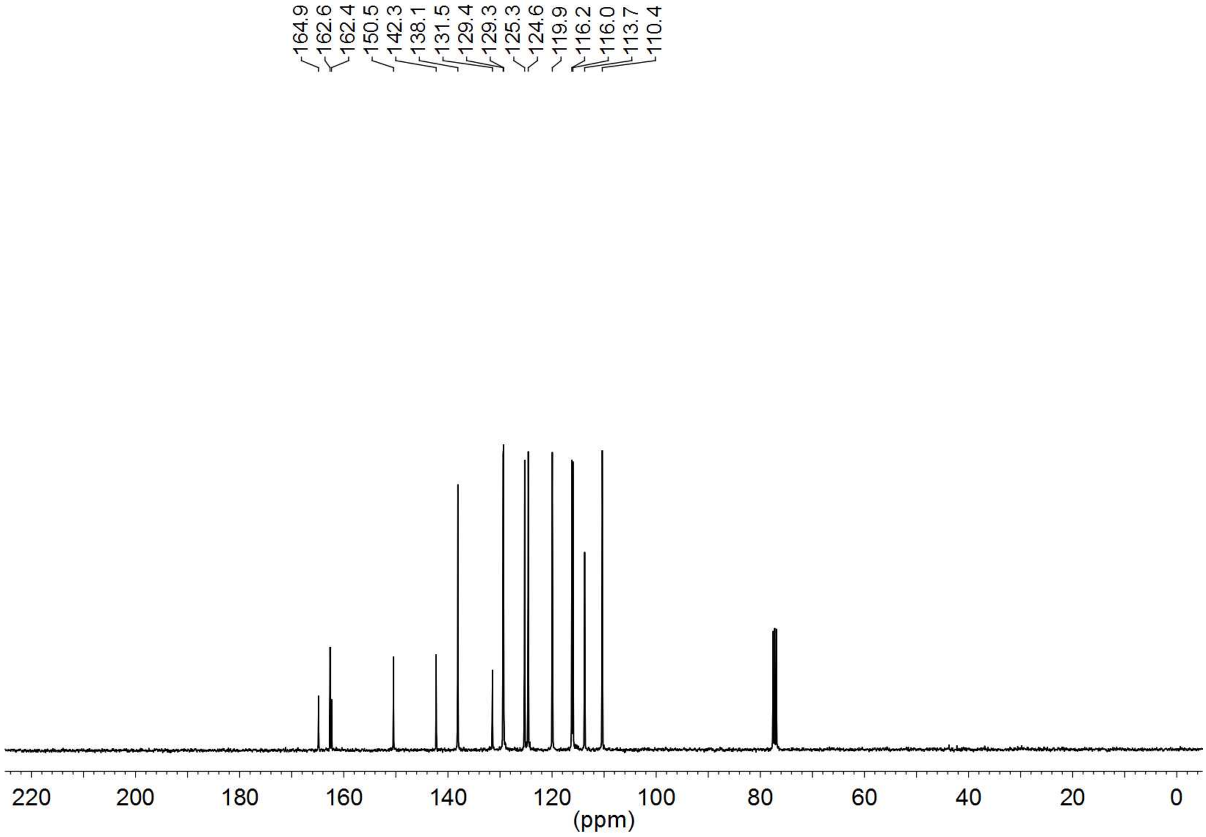

7.77
7.73
7.72
7.71
7.70
7.69
7.68
7.67
7.52
7.51
7.50
7.49
7.48
7.46
7.33
7.32
7.31
7.30
7.29
7.28
7.21
7.19
7.17
7.03
6.99
2.37
N
O
0.94
0.96
2.94
1.97
2.02
1.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

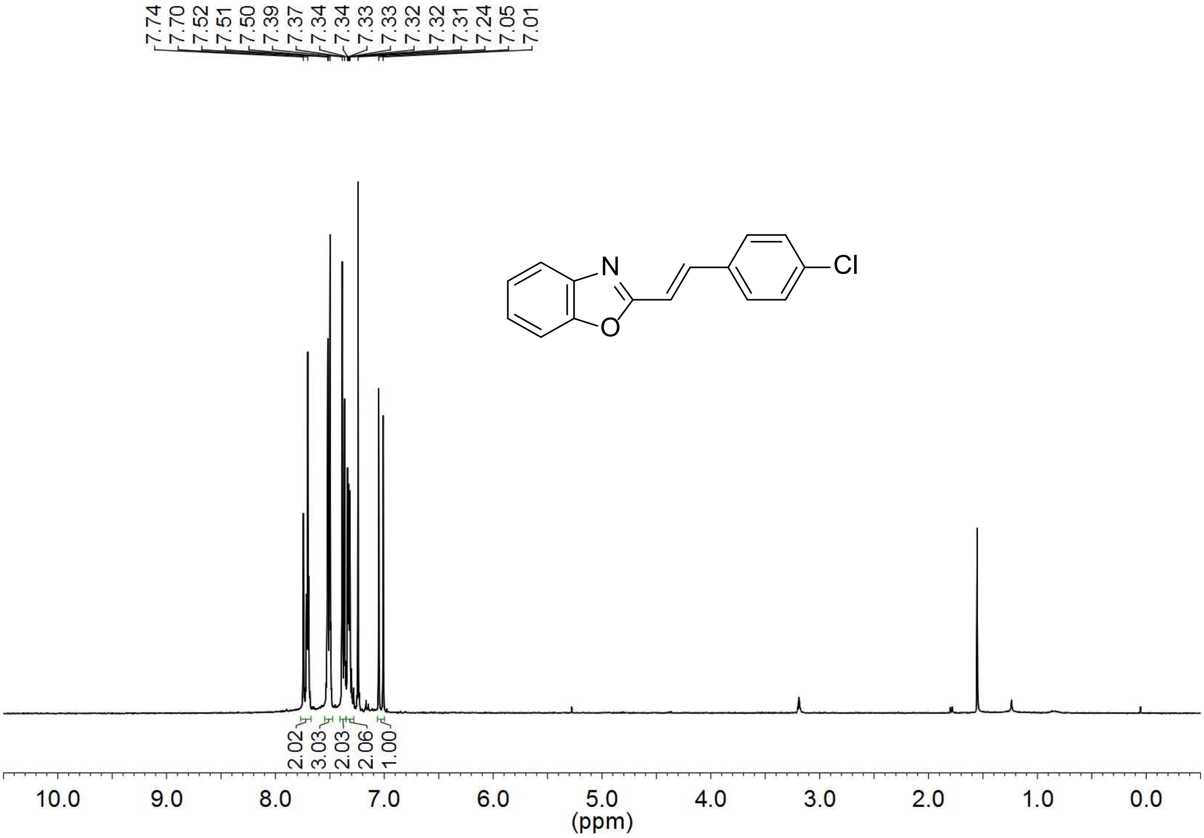

163.22
150.60
142.44
140.31
139.67
132.63
129.88
127.72
125.24
124.62
119.97
113.08
110.45
21.64
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

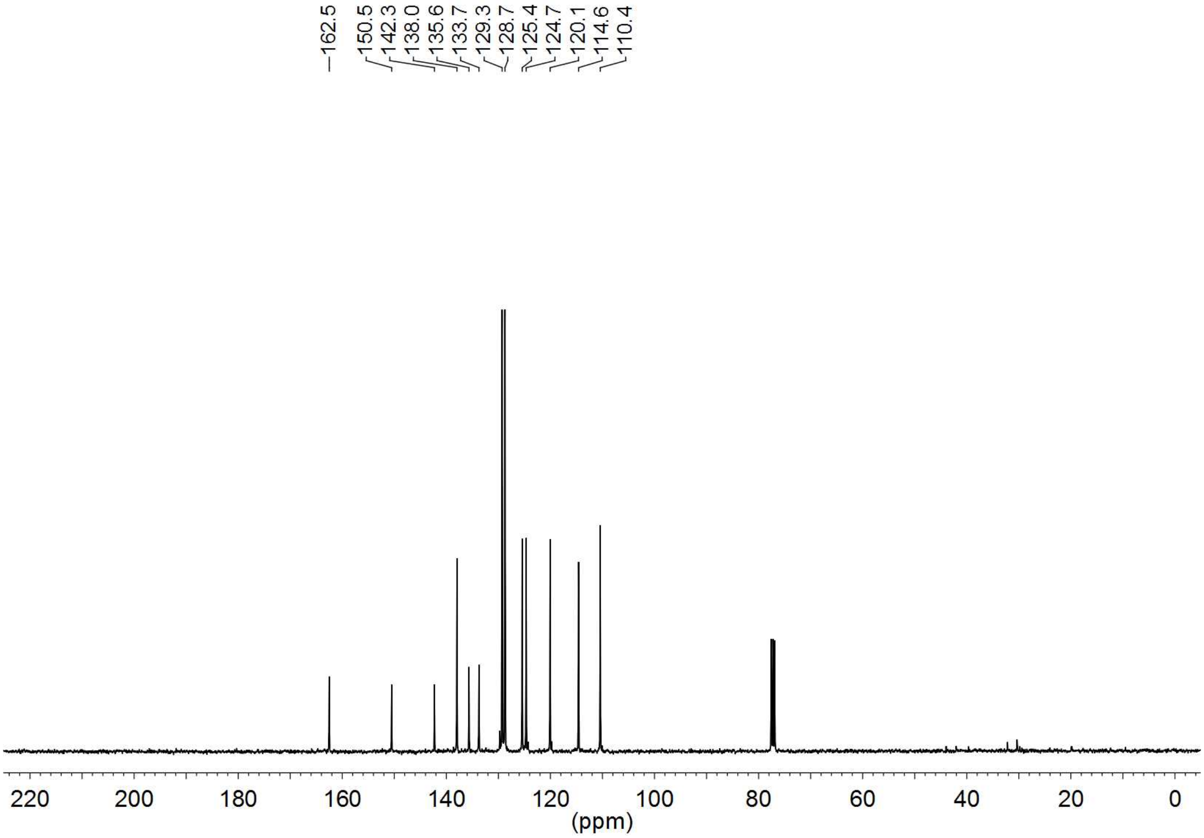

7.84
7.80
7.72
7.71
7.70
7.66
7.63
7.61
7.54
7.53
7.51
7.47
7.45
7.43
7.38
7.36
7.34
7.33
7.32
7.31
7.24
7.12
7.08
N
O
1.00
1.06
3.09
2.09
1.08
2.00
1.03
2.02
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

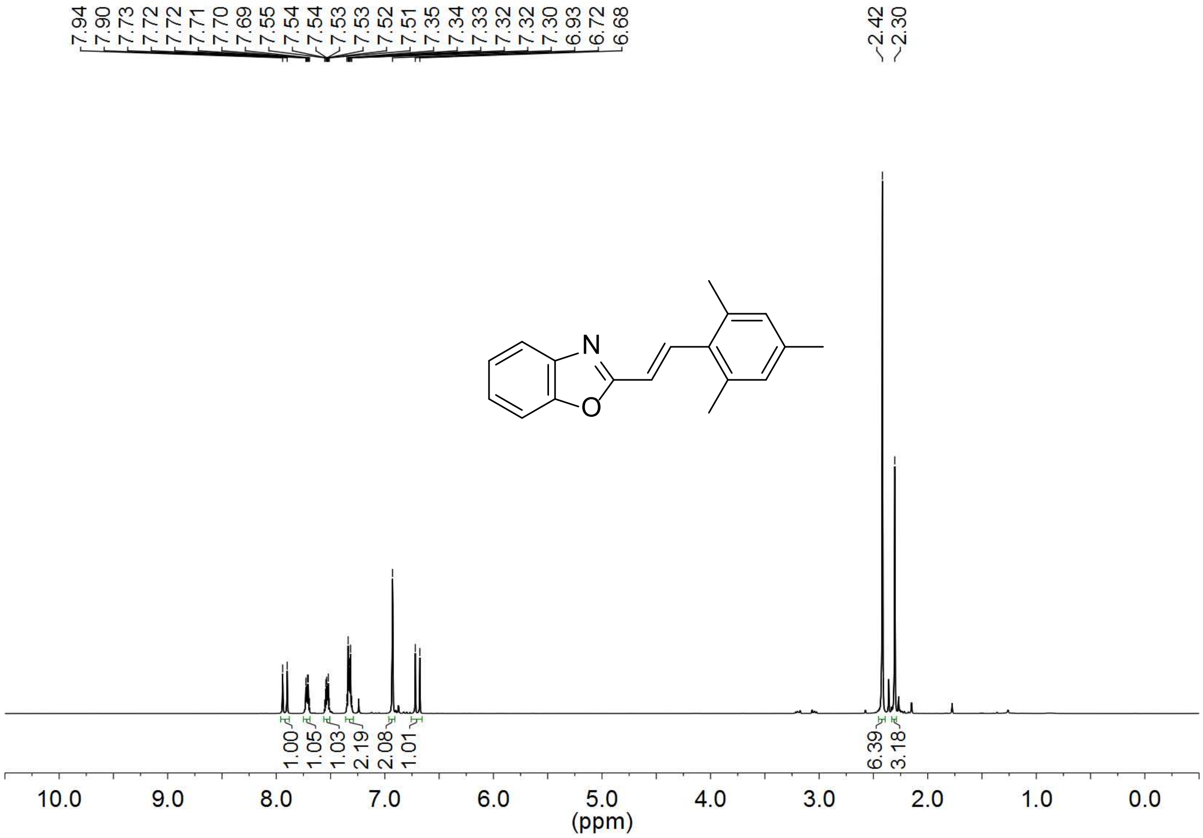

163.0
150.6
142.6
142.4
140.3
139.1
134.3
129.0
128.2
127.9
127.7
127.1
125.3
124.7
120.0
113.9
110.5
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

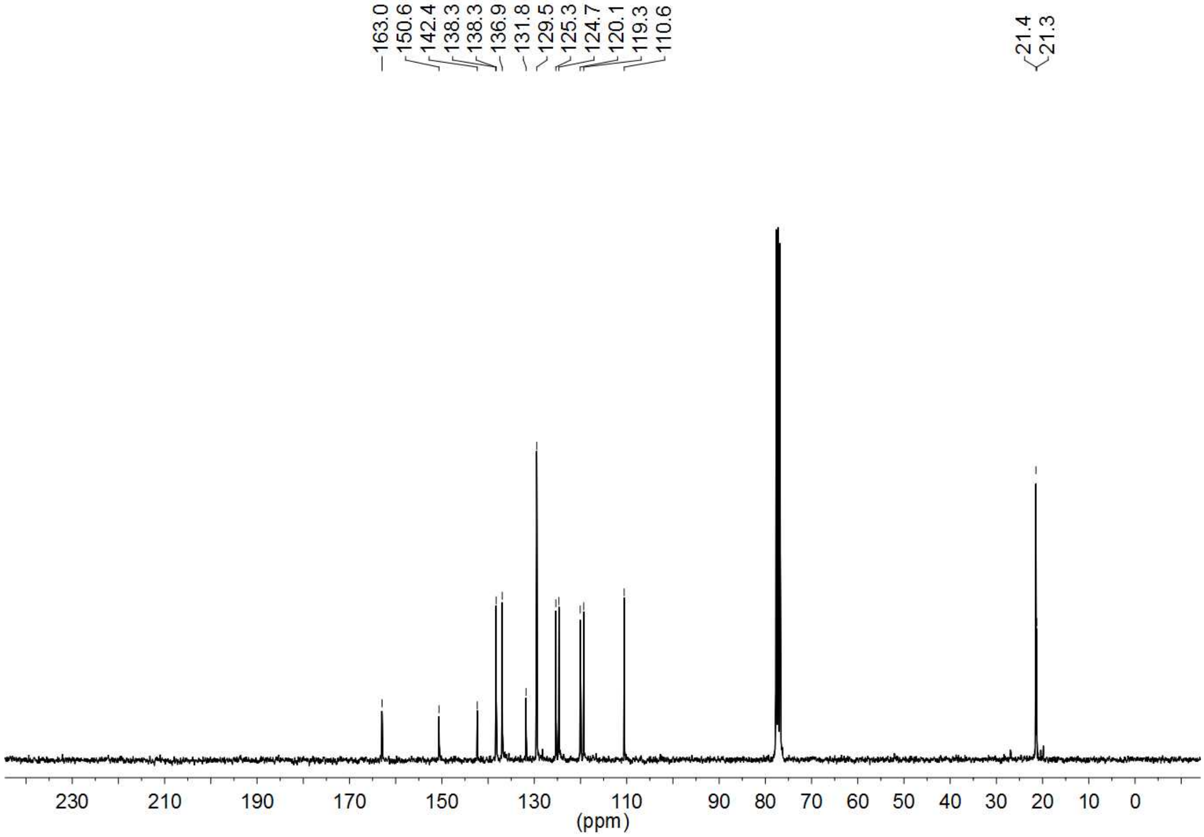

7.76
7.72
7.71
7.70
7.69
7.58
7.57
7.56
7.55
7.52
7.51
7.50
7.33
7.33
7.32
7.32
7.31
7.31
7.24
7.12
7.10
7.08
7.00
6.96
N
O
F
1.07
1.00
2.09
1.01
2.06
2.04
1.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

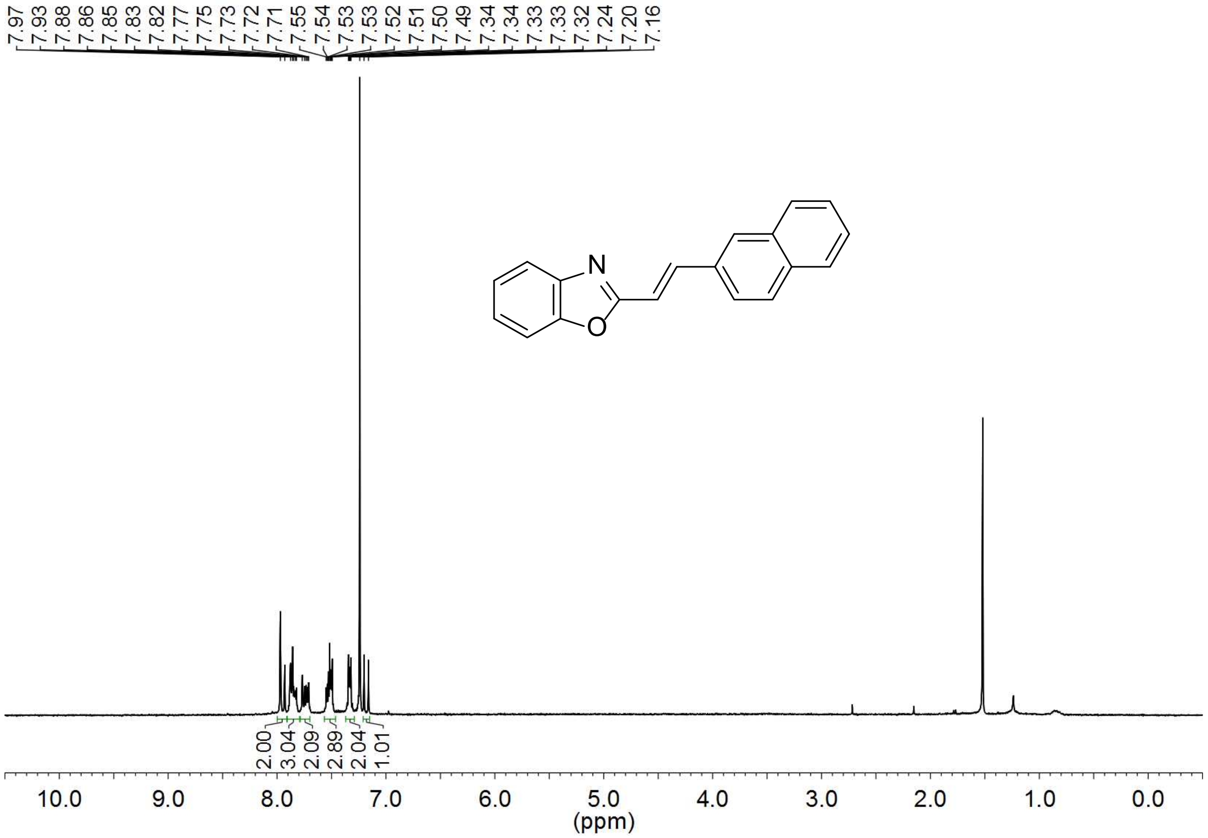

164.9
162.6
162.4
150.5
142.3
138.1
131.5
129.4
129.3
125.3
124.6
119.9
116.2
116.0
113.7
110.4
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

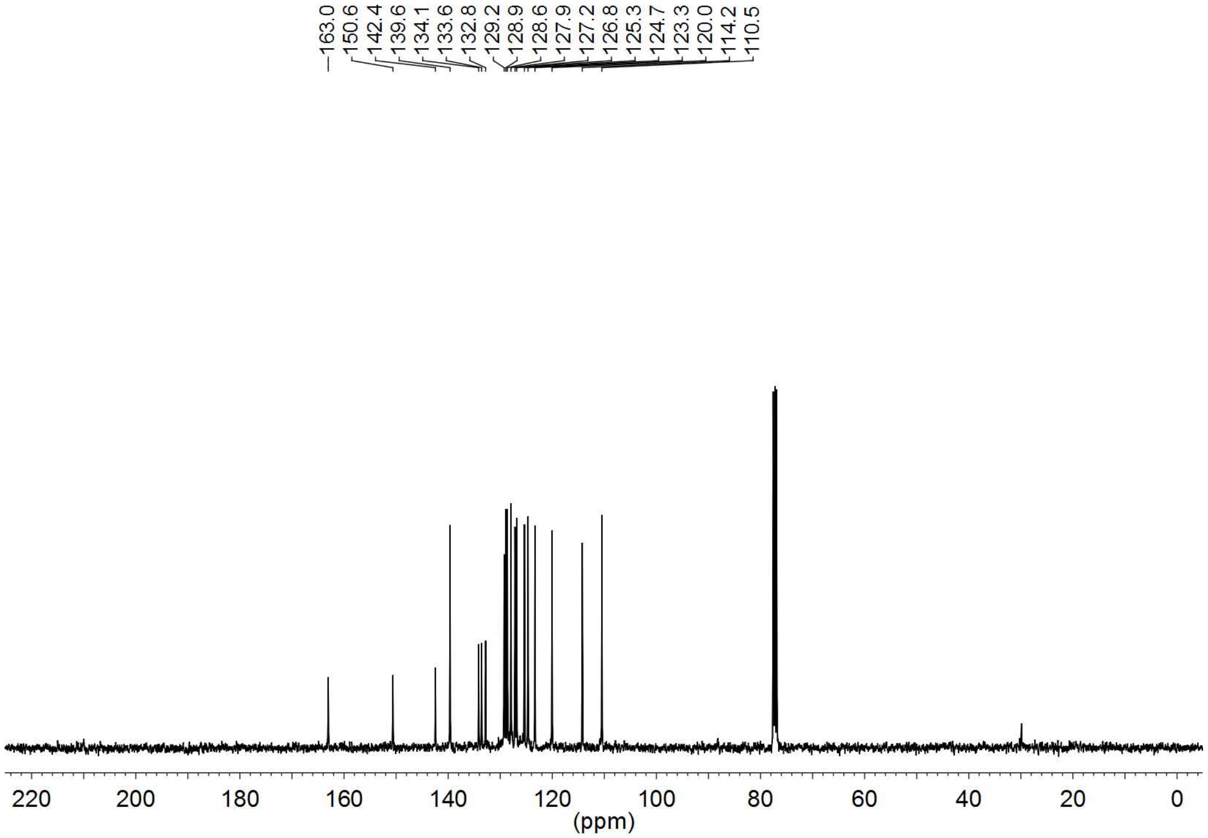

7.74
7.70
7.52
7.51
7.50
7.39
7.37
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.24
7.05
7.01
N
O
Cl
2.02
3.03
2.03
2.06
1.00
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

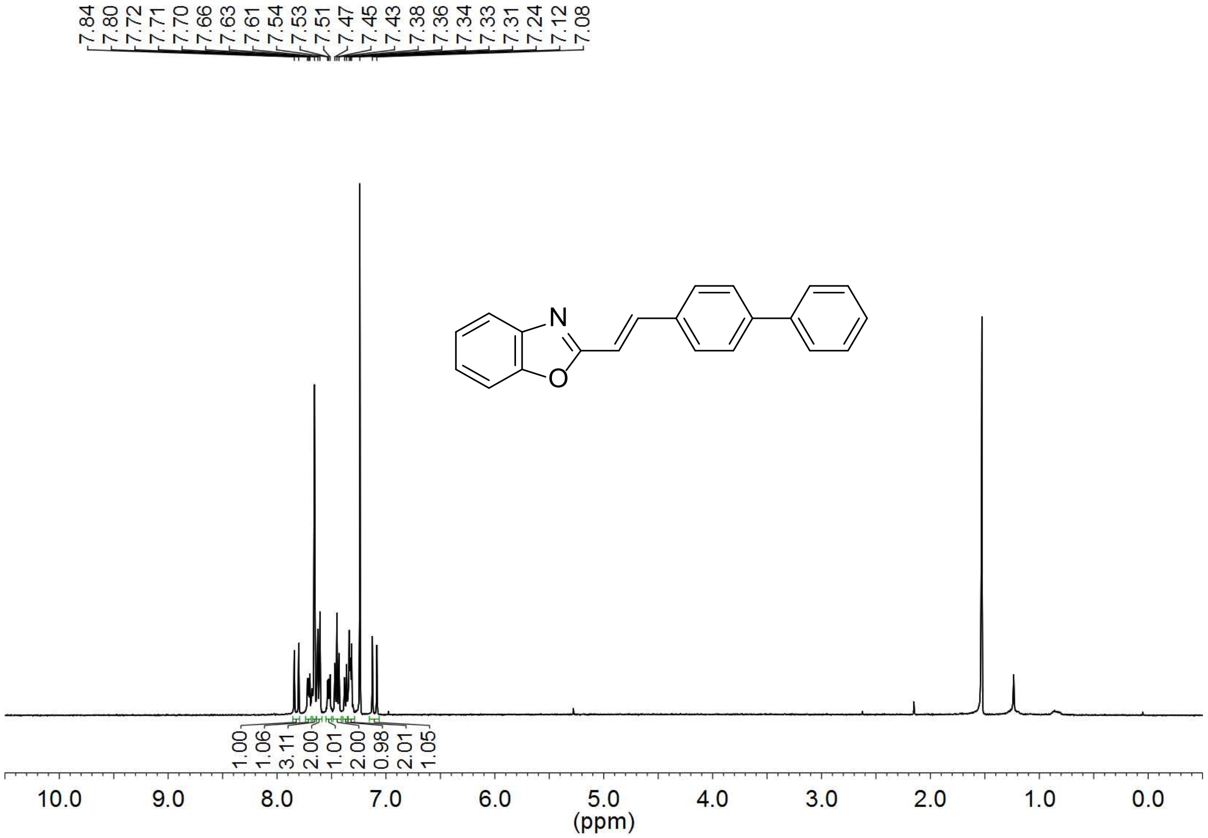

162.5
150.5
142.3
138.0
135.6
133.7
129.3
128.7
125.4
124.7
120.1
114.6
110.4
220
200
180
160
140
120
(ppm)
100
80
60
40
20
0

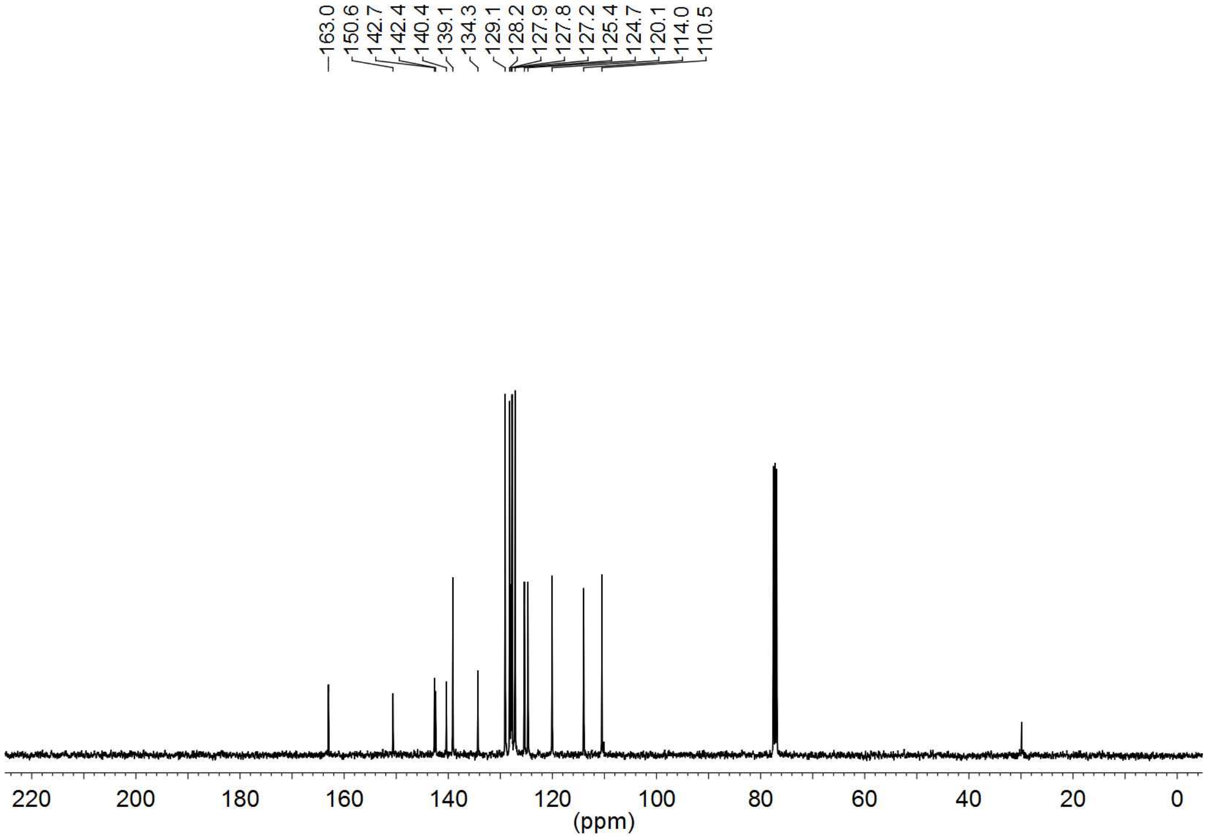

7.94
7.90
7.73
7.72
7.72
7.71
7.70
7.69
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.35
7.34
7.33
7.32
7.32
7.30
6.93
6.72
6.68
2.42
2.30
N
O
1.00
1.05
1.03
2.19
2.08
1.01
6.39
3.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

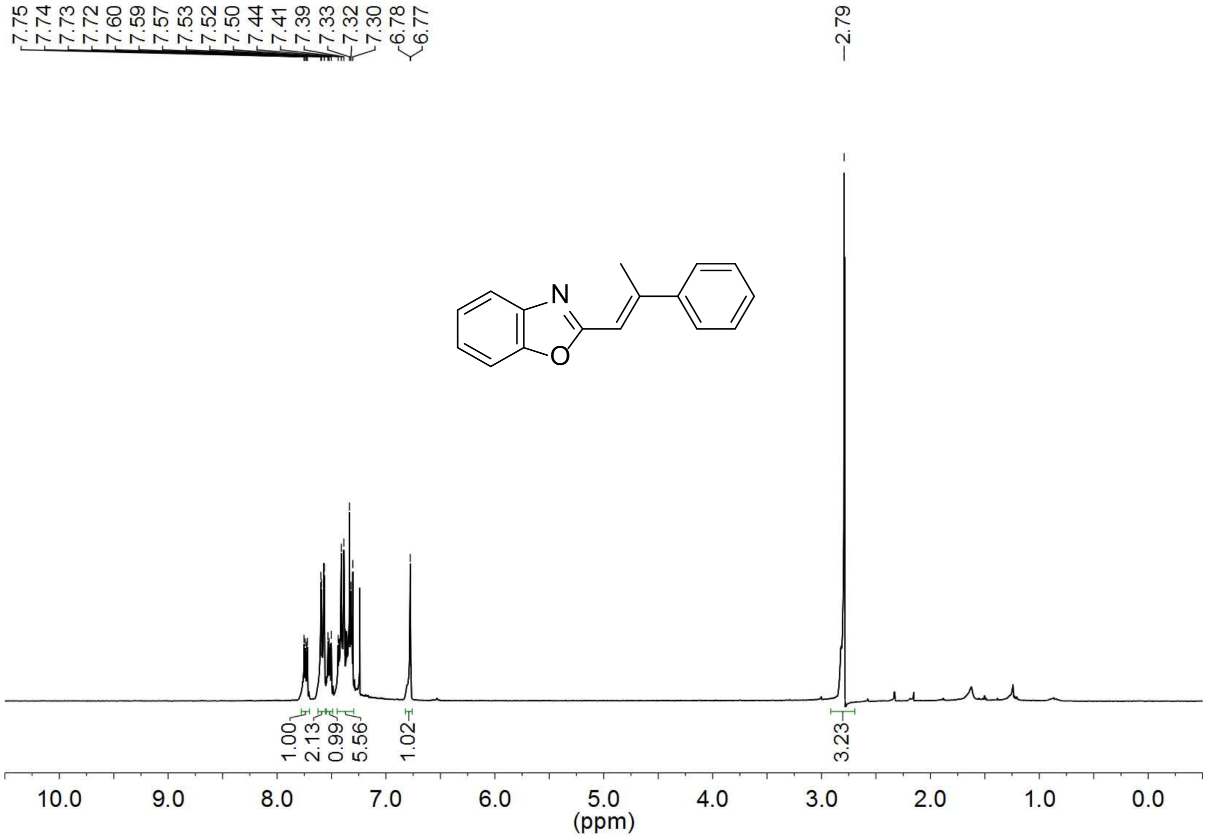

163.0
150.6
142.4
138.3
138.3
136.9
131.8
129.5
125.3
124.7
120.1
119.3
110.6
21.4
21.3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

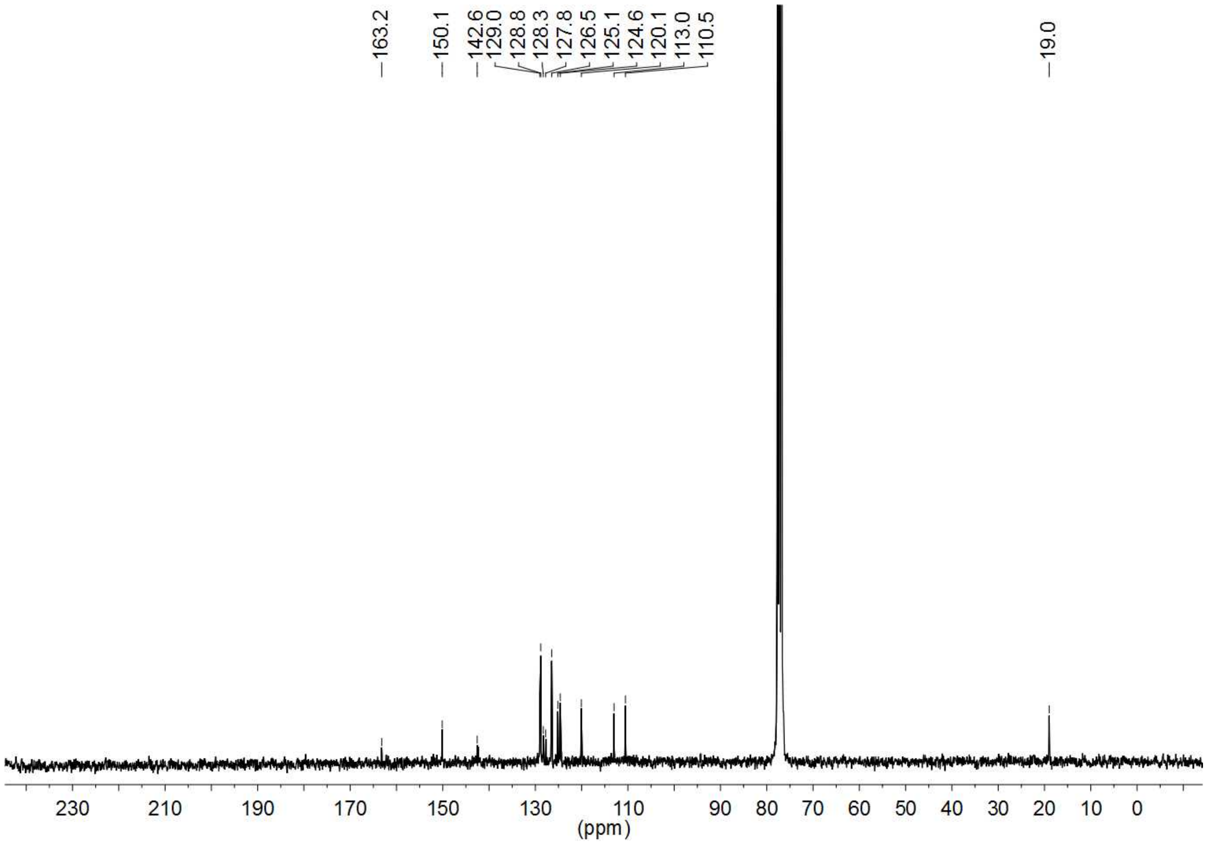

7.97
7.93
7.88
7.86
7.85
7.83
7.82
7.77
7.75
7.73
7.72
7.71
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.34
7.34
7.33
7.33
7.32
7.24
7.20
7.16
N
O
2.00
3.04
2.09
2.89
2.04
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

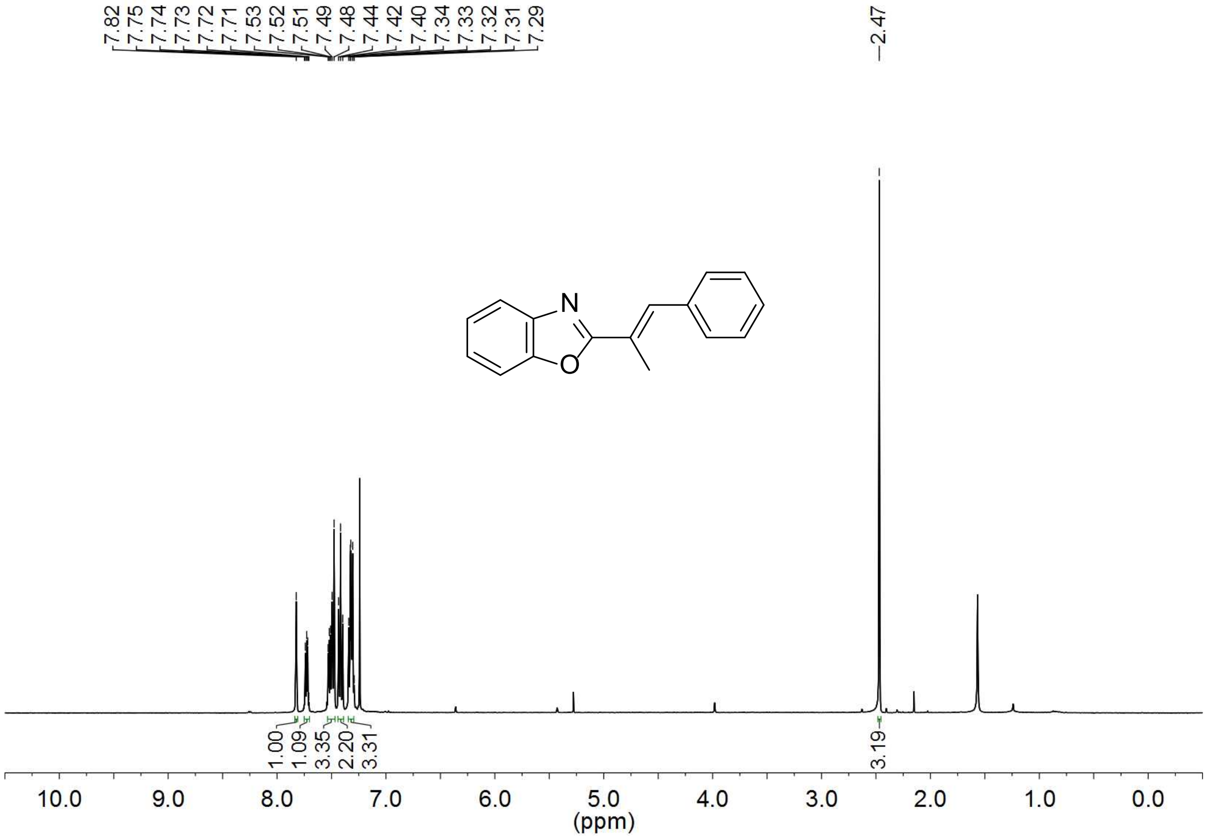

163.0
150.6
142.4
139.6
134.1
133.6
132.8
129.2
128.9
128.6
127.9
127.2
126.8
125.3
124.7
123.3
120.0
114.2
110.5
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

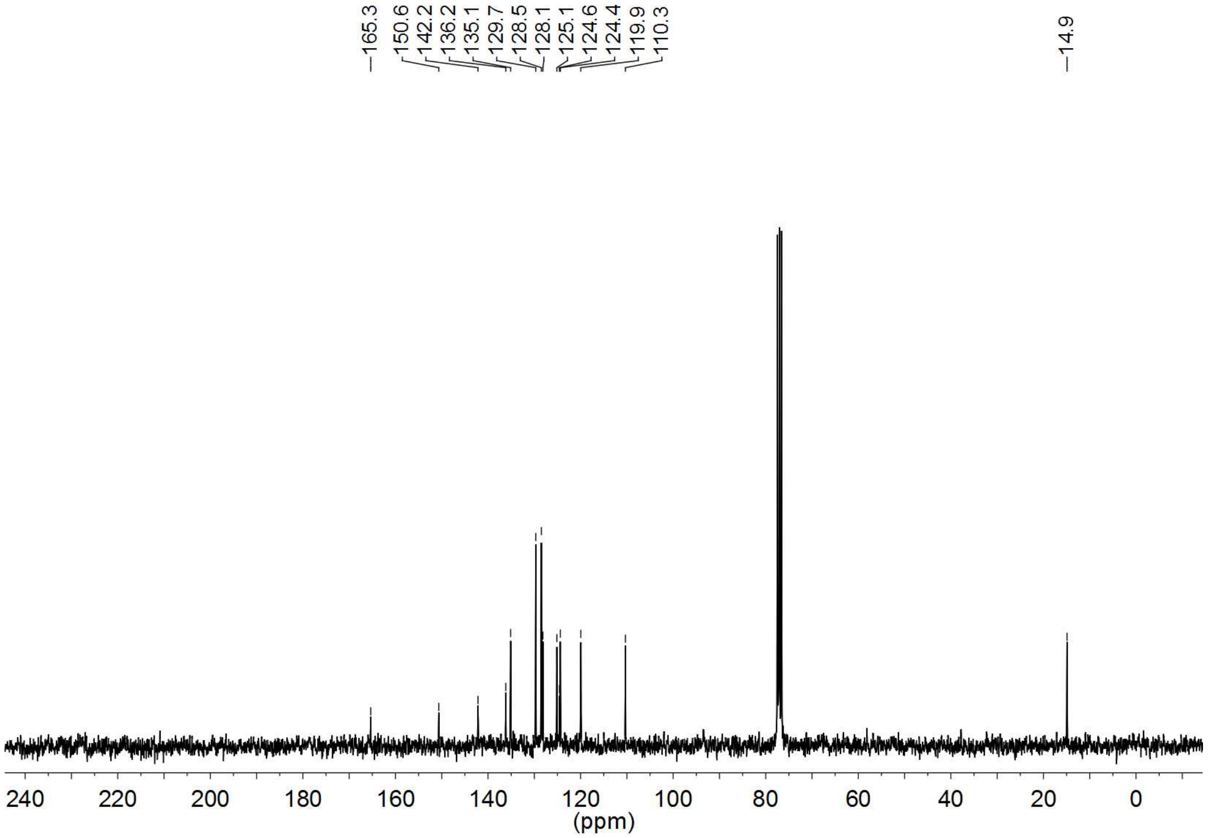

7.84
7.80
7.72
7.71
7.70
7.66
7.63
7.61
7.54
7.53
7.51
7.47
7.45
7.43
7.38
7.36
7.34
7.33
7.31
7.24
7.12
7.08
N
O
1.00
1.06
3.11
2.00
1.01
2.00
0.98
2.01
1.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

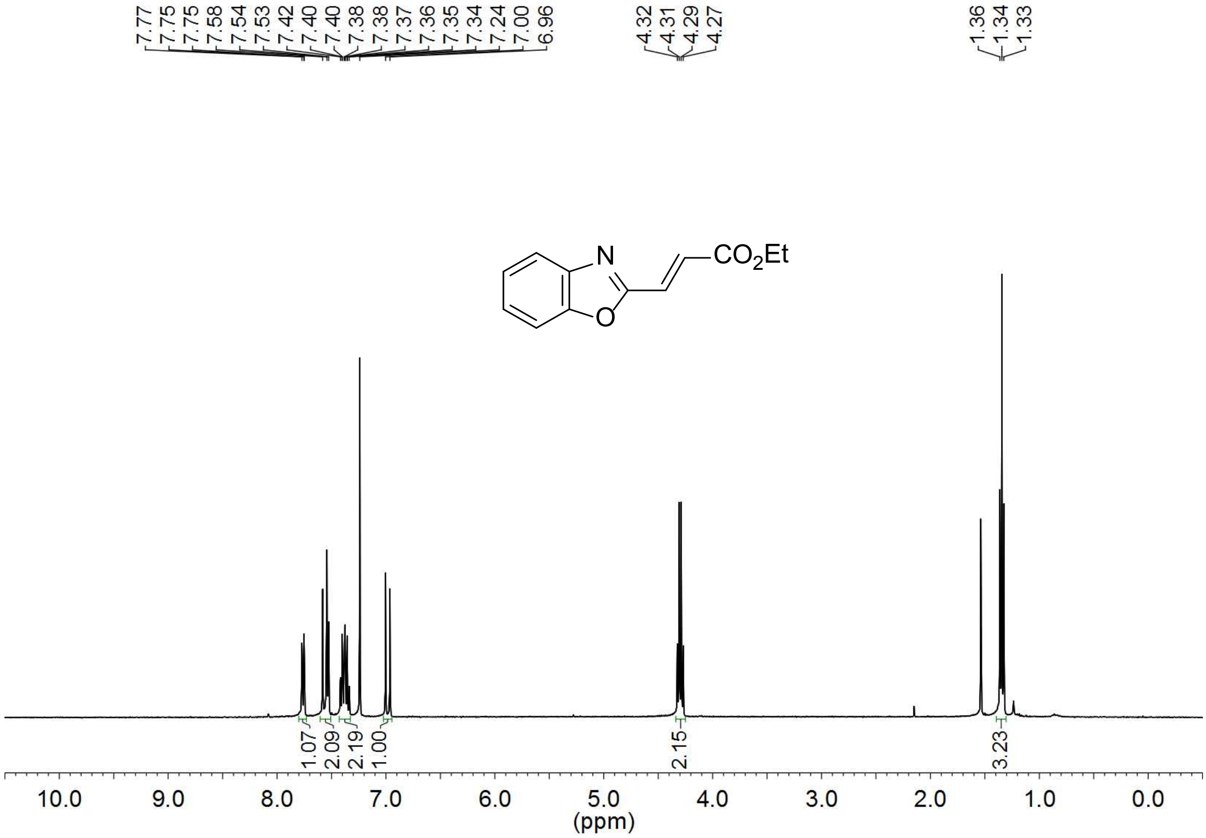

163.0
150.6
142.7
142.4
140.4
139.1
134.3
129.1
128.2
127.9
127.8
127.2
125.4
124.7
120.1
114.0
110.5
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

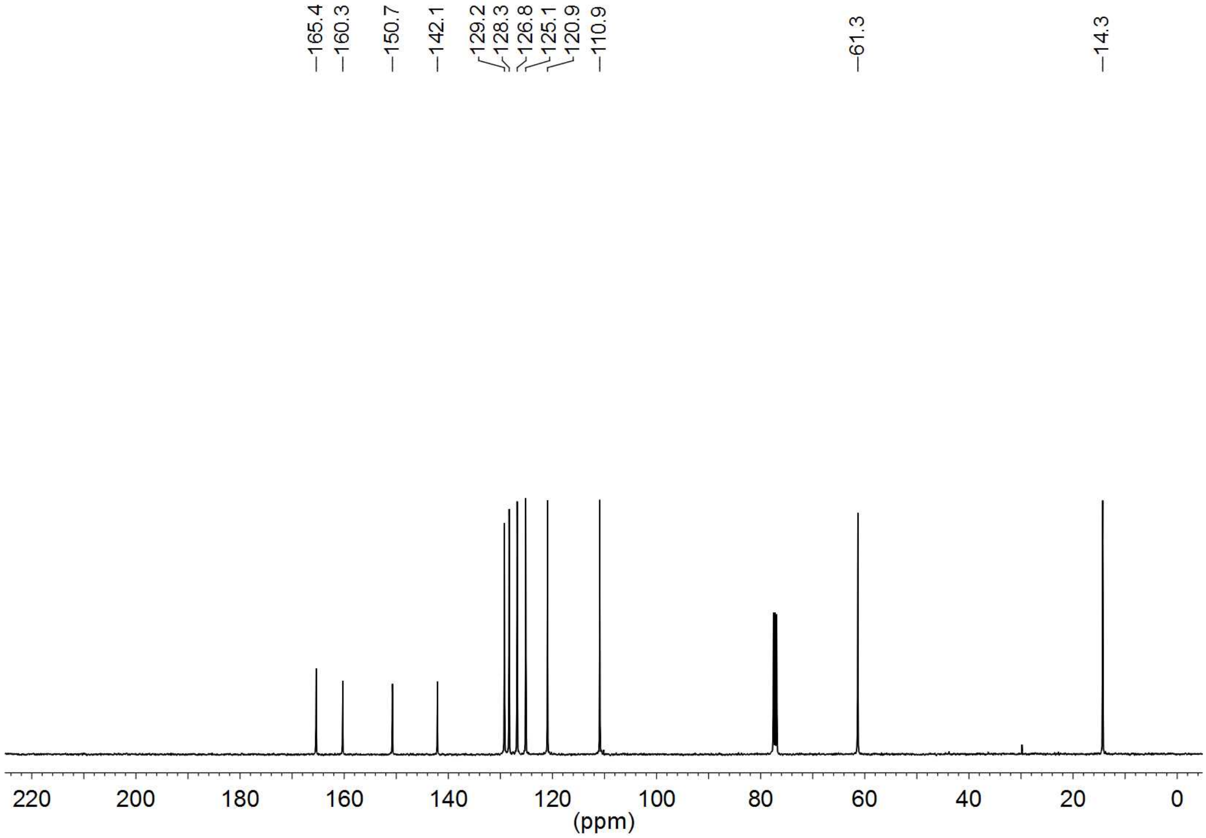

7.75
7.74
7.73
7.72
7.60
7.59
7.57
7.53
7.52
7.50
7.44
7.41
7.39
7.33
7.32
7.30
6.78
6.77
2.79
N
O
1.00
2.13
0.99
5.56
1.02
3.23
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

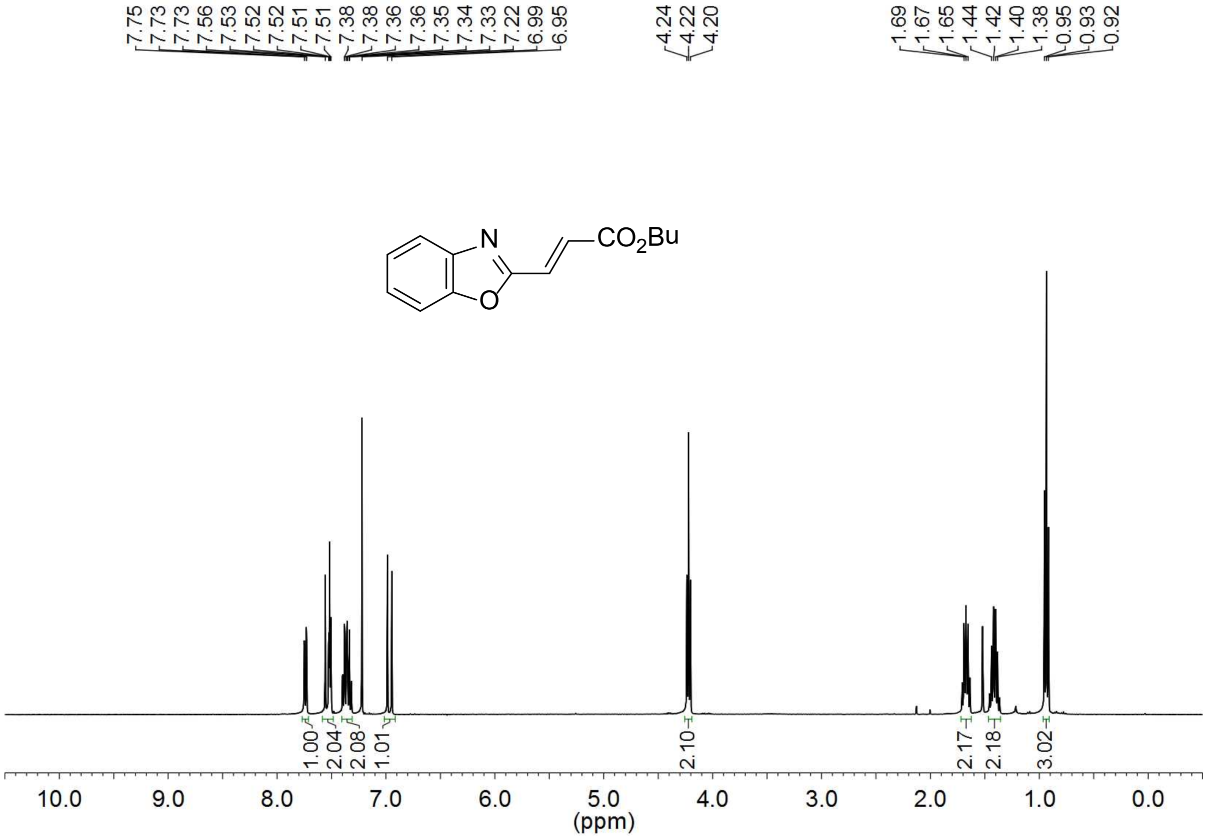

163.2
150.1
142.6
129.0
128.8
128.3
127.8
126.5
125.1
124.6
120.1
113.0
110.5
19.0
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)

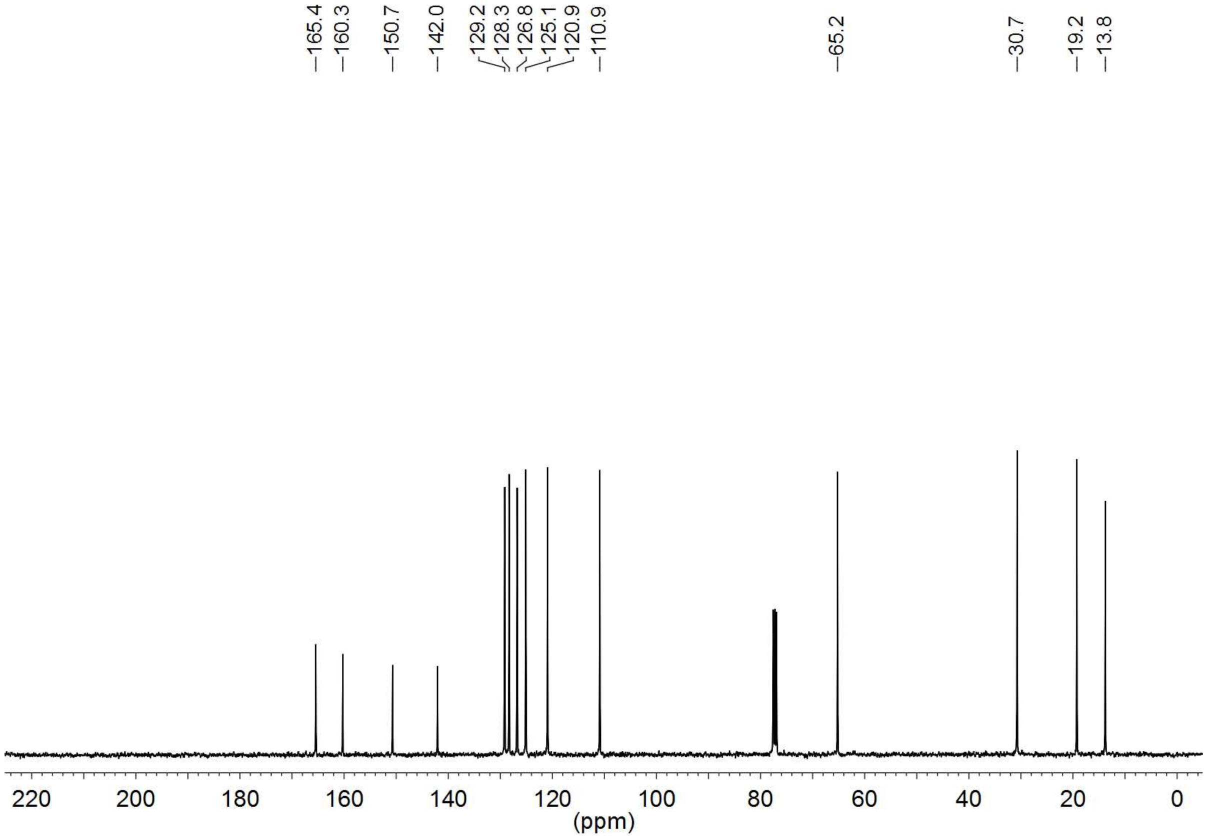

7.82
7.75
7.74
7.73
7.72
7.71
7.53
7.52
7.51
7.49
7.48
7.44
7.42
7.40
7.34
7.33
7.32
7.31
7.29
2.47
N
O
1.00
1.09
3.35
2.20
3.31
3.19
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

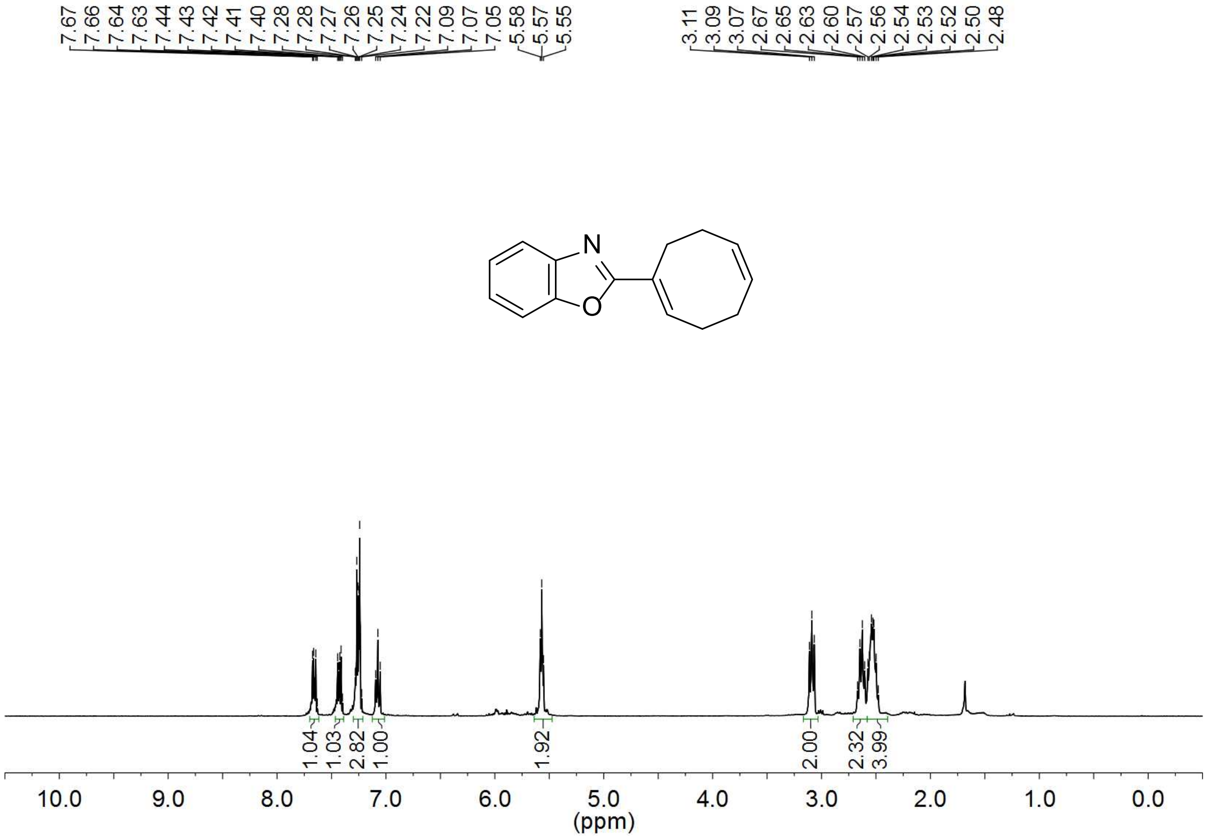

165.3
150.6
142.2
136.2
135.1
129.7
128.5
128.1
125.1
124.6
124.4
119.9
110.3
14.9
240
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

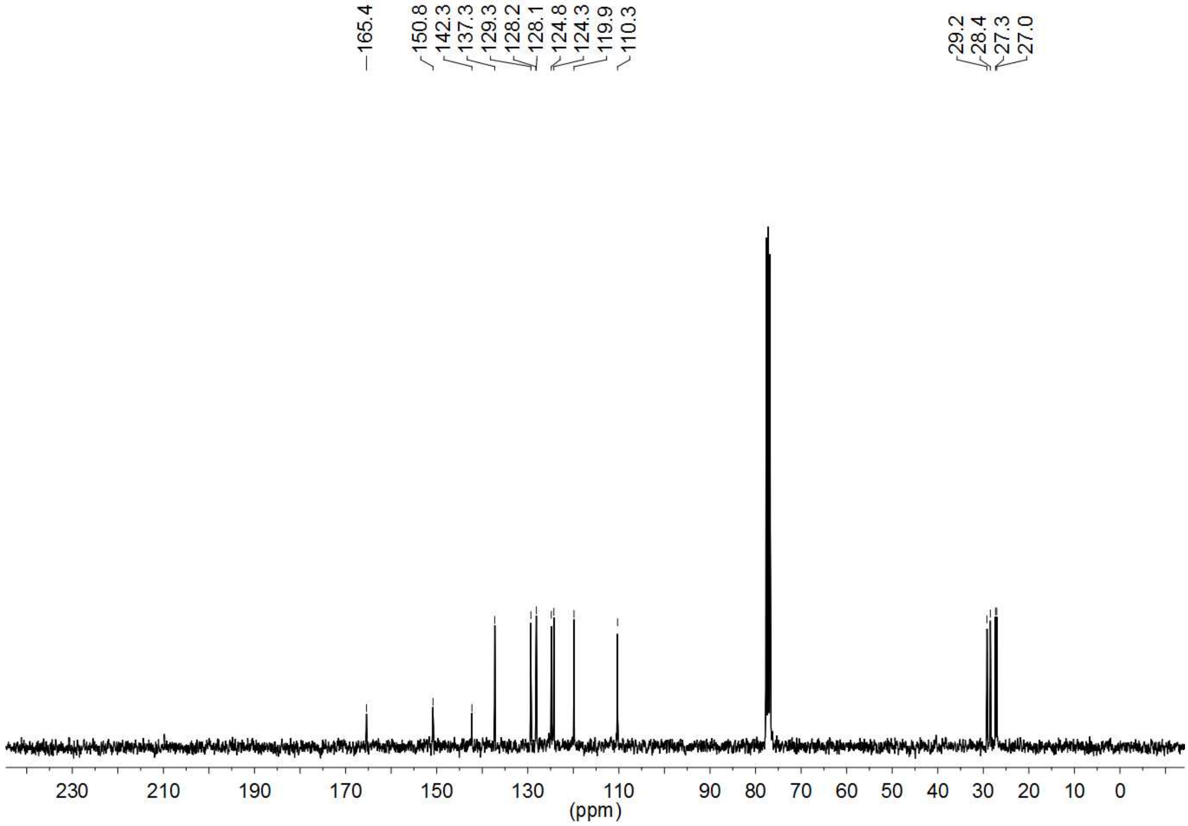

7.77
7.75
7.75
7.58
7.54
7.53
7.42
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.24
7.00
6.96
4.32
4.31
4.29
4.27
1.36
1.34
1.33
N
O
CO2Et
1.07
2.09
2.19
1.00
2.15
3.23
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

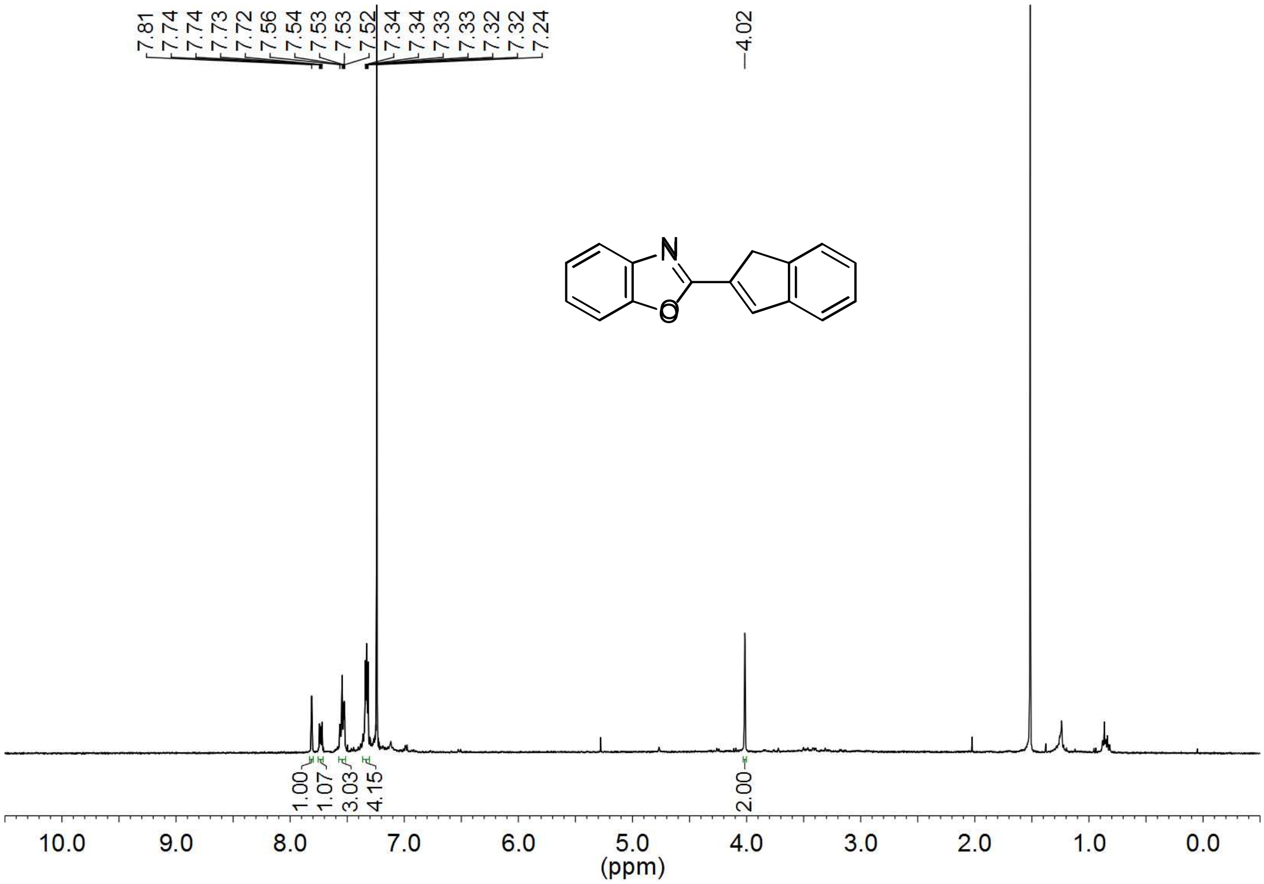

165.4
160.3
150.7
142.1
129.2
128.3
126.8
125.1
120.9
110.9
61.3
14.3
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

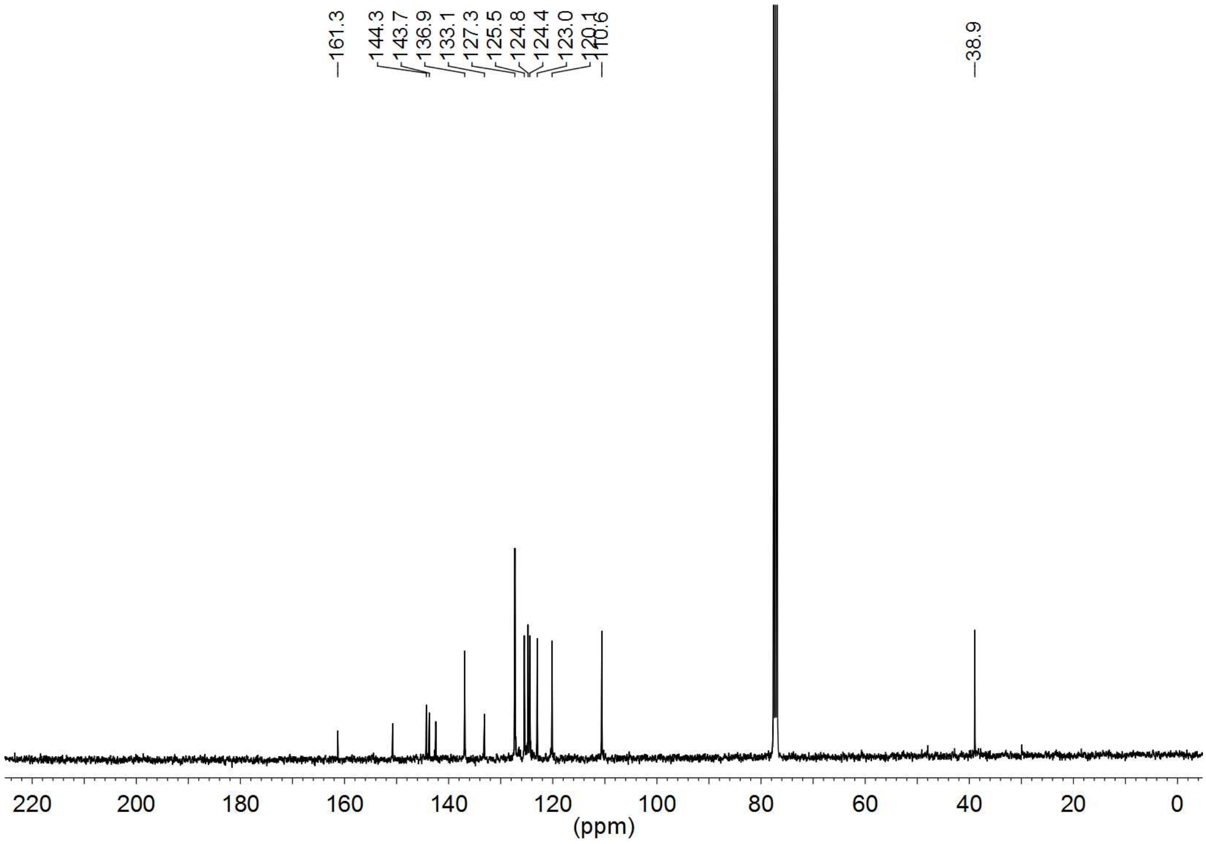

7.75
7.73
7.73
7.56
7.53
7.52
7.52
7.51
7.51
7.38
7.38
7.36
7.36
7.35
7.34
7.33
7.22
6.99
6.95
4.24
4.22
4.20
1.69
1.67
1.65
1.44
1.42
1.40
1.38
0.95
0.93
0.92
N
O
CO2Bu
1.00
2.04
2.08
1.01
2.10
2.17
2.18
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

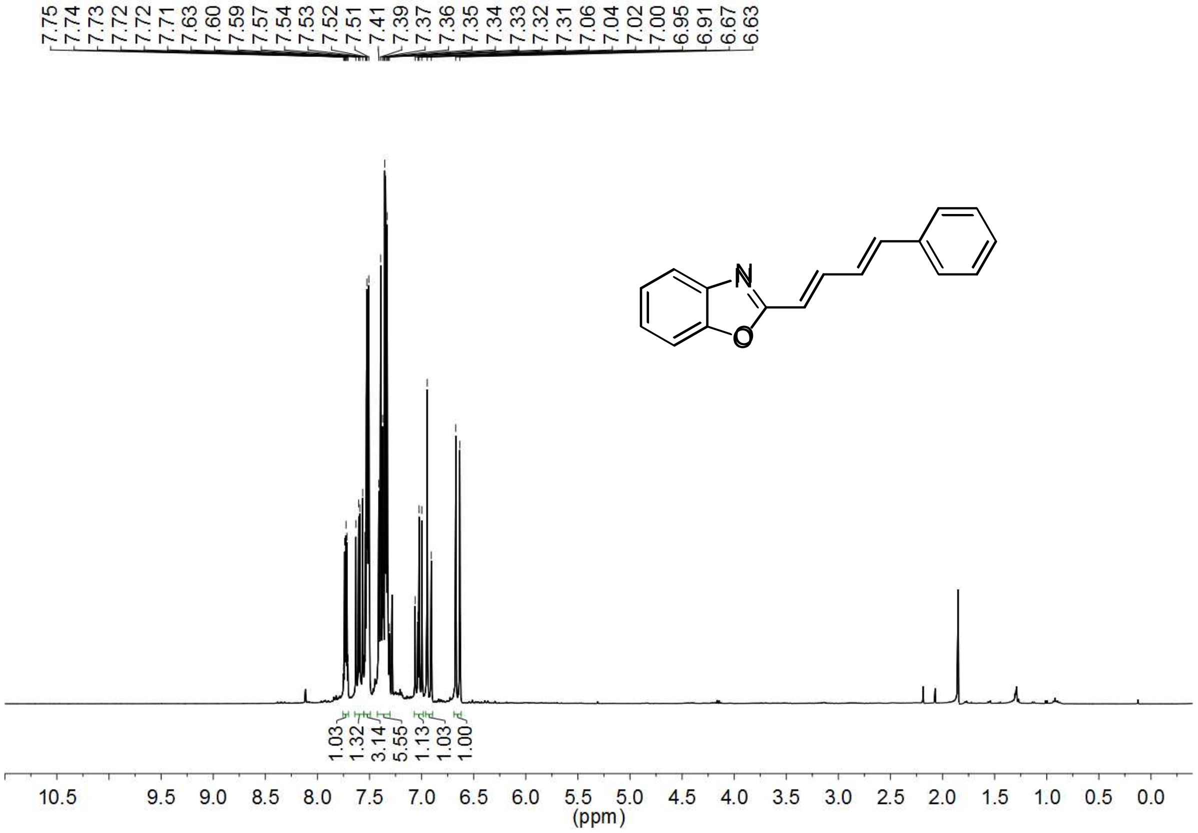

165.4
160.3
150.7
142.0
129.2
128.3
126.8
125.1
120.9
110.9
65.2
30.7
19.2
13.8
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

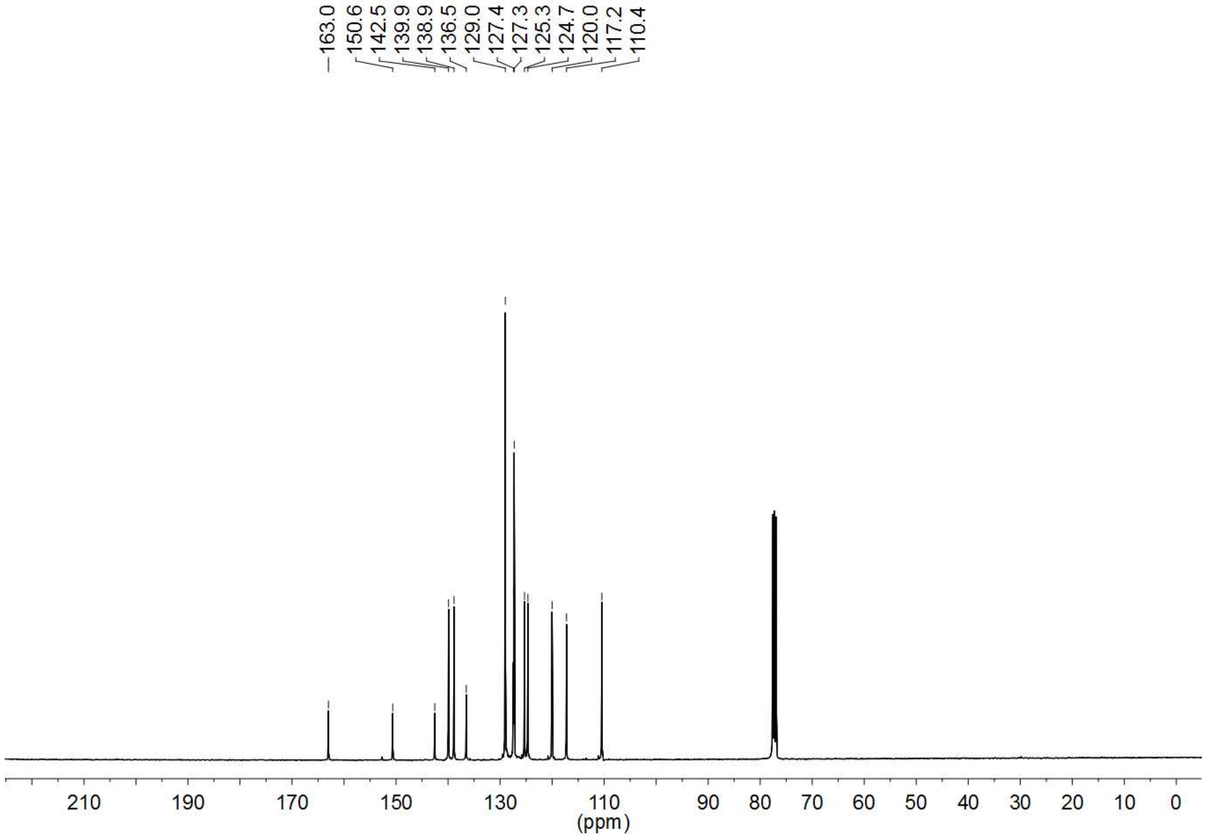

7.67
7.66
7.64
7.63
7.44
7.43
7.42
7.41
7.40
7.28
7.28
7.27
7.26
7.25
7.24
7.22
7.09
7.07
7.05
5.58
5.57
5.55
3.11
3.09
3.07
2.67
2.65
2.63
2.60
2.57
2.56
2.54
2.53
2.52
2.50
2.48
N
O
1.04
1.03
2.82
1.00
1.92
2.00
2.32
3.99
10.0
9.0
8.0
7.0
6.0
5.0
(ppm)
4.0
3.0
2.0
1.0
0.0

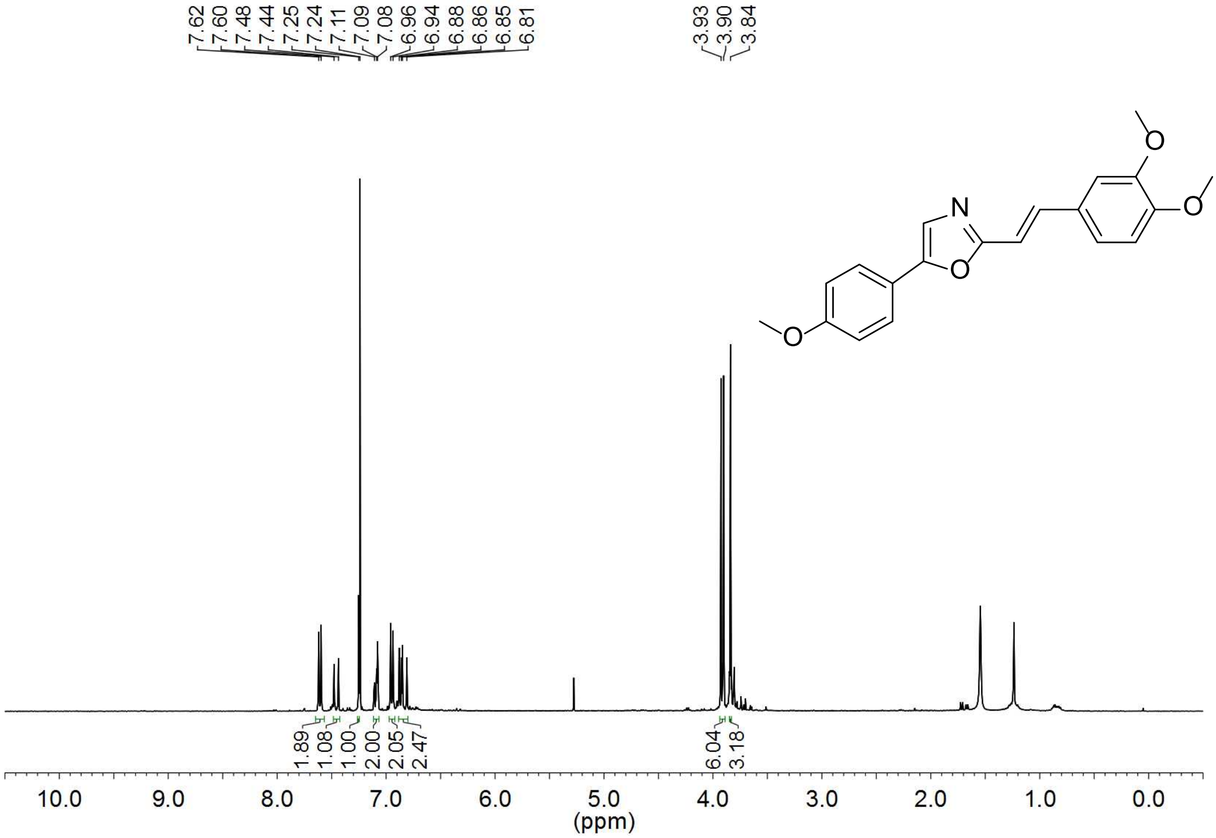

165.4
150.8
142.3
137.3
129.3
128.2
128.1
124.8
124.3
119.9
110.3
29.2
28.4
27.3
27.0
230
210
190
170
150
130
110
(ppm)
90
80
70
60
50
40
30
20
10
0

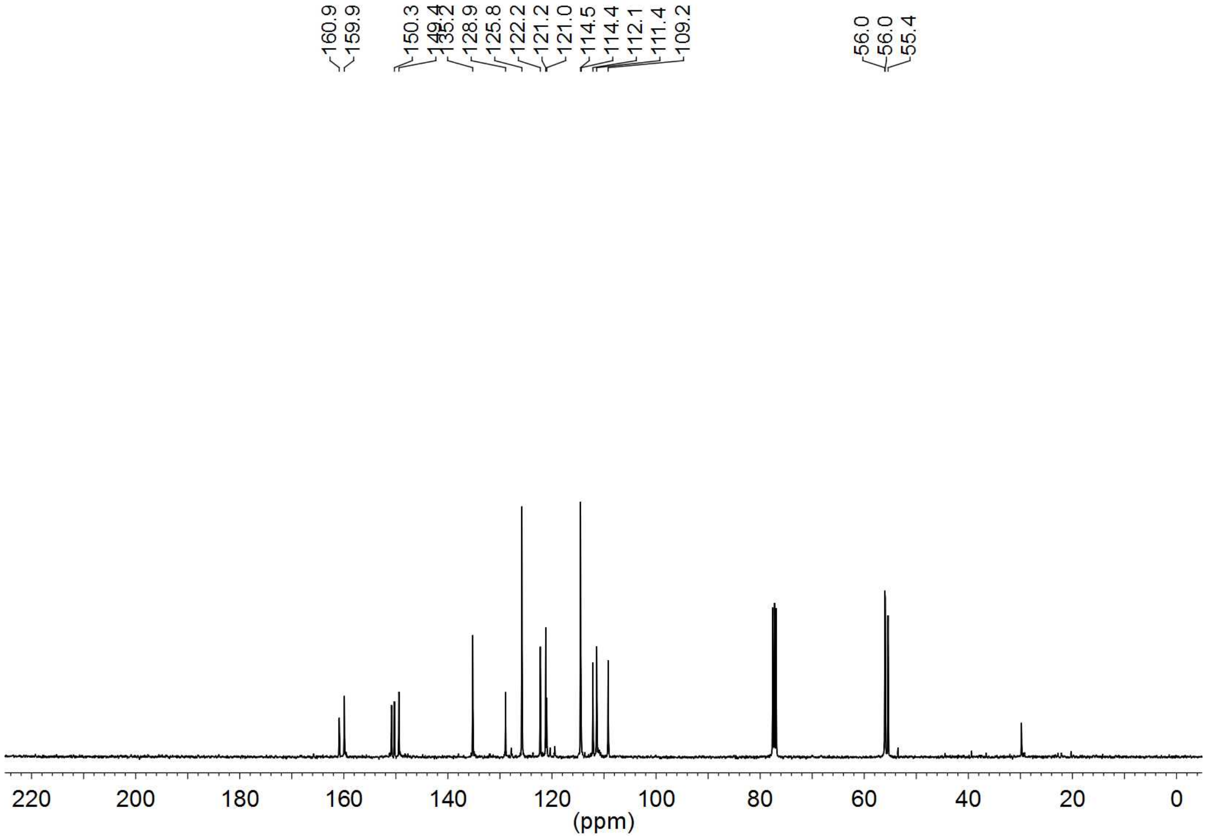

7.81
7.74
7.74
7.73
7.72
7.56
7.54
7.53
7.53
7.52
7.34
7.34
7.33
7.33
7.32
7.32
7.24
4.02
N
O
1.00
1.07
3.03
4.15
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

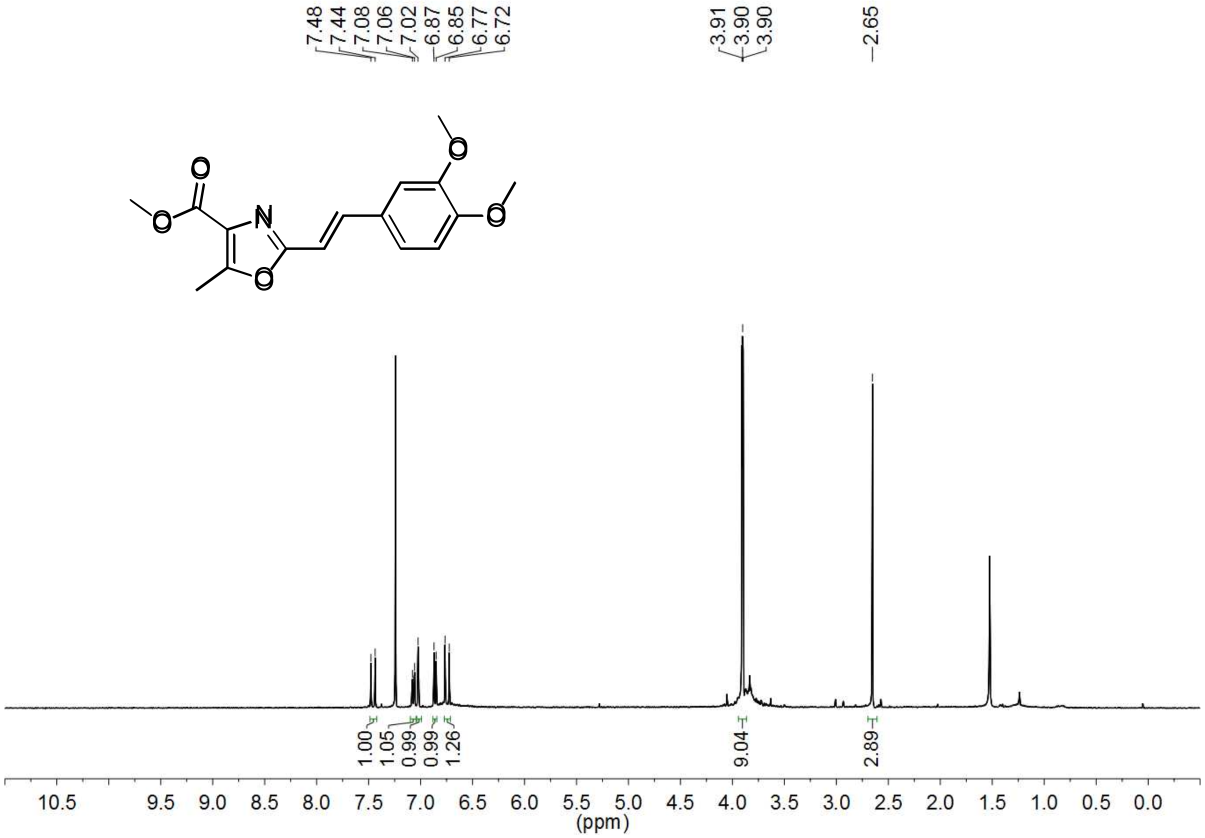

161.3
144.3
143.7
136.9
133.1
127.3
125.5
124.8
124.4
123.0
120.1
110.6
38.9
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

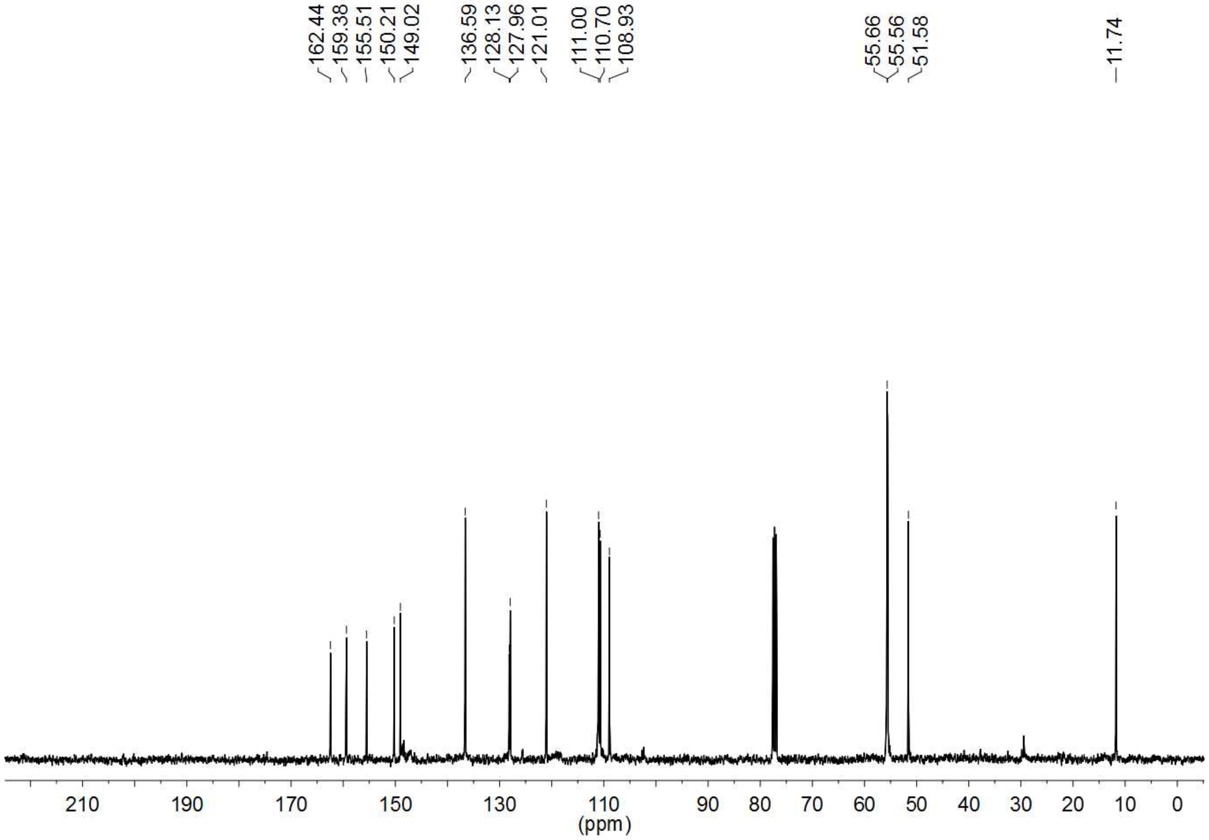

7.75
7.74
7.73
7.72
7.72
7.71
7.63
7.60
7.59
7.57
7.54
7.53
7.52
7.51
7.41
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.06
7.04
7.02
7.00
6.95
6.91
6.67
6.63
N
O
1.03
1.32
3.14
5.55
1.13
1.03
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


163.0
150.6
142.5
139.9
138.9
136.5
129.0
127.4
127.3
125.3
124.7
120.0
117.2
110.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)


7.62
7.60
7.48
7.44
7.25
7.24
7.11
7.09
7.08
6.96
6.94
6.88
6.86
6.85
6.81
3.93
3.90
3.84
N
O
O
O
O
1.89
1.08
1.00
2.00
2.05
2.47
6.04
3.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


160.9
159.9
150.3
149.4
135.2
128.9
125.8
122.2
121.2
121.0
114.5
114.4
112.1
111.4
109.2
56.0
56.0
55.4
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


7.48
7.44
7.08
7.06
7.02
6.87
6.85
6.77
6.72
3.91
3.90
3.90
2.65
1.00
1.05
0.99
0.99
1.26
9.04
2.89
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


162.44
159.38
155.51
150.21
149.02
136.59
128.13
127.96
121.01
111.00
110.70
108.93
55.66
55.56
51.58
11.74
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
(ppm)