Supplementary Information

Dehydrogenative cycloisomerization-arylation reaction of *N*-propargyl carboxamides catalyzed by iodoarene/sulfonyl chloride/sulfoxide systems

Miwa Shoji,[a] Yuki Umakoshi,[a] Akira Tsubouchi,[a] Akira Yoshimura[b] and Akio Saito[a]*

[a] Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
[b] Faculty of Pharmaceutical Sciences, Aomori University, Aomori 030-0943, Japan.
* Correspondence: akio-sai@cc.tuat.ac.jp; Tel.: +81-42-388-7667

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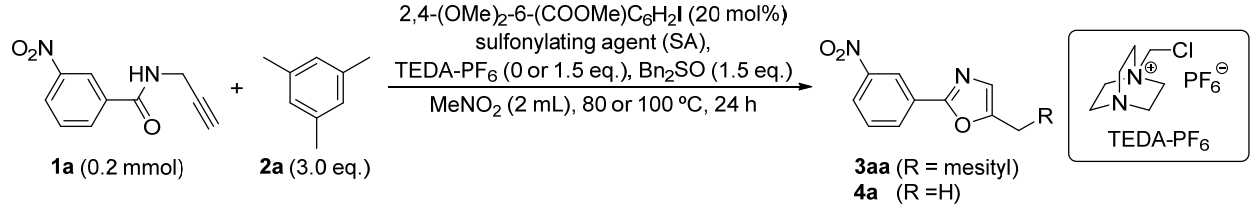
1. Optimization of Reaction Conditions

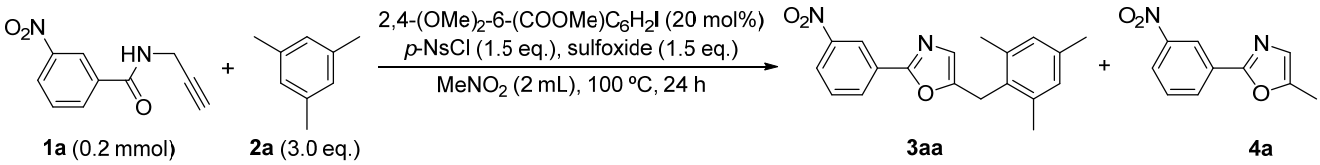
Table S1. Additive effects of sulfonating agents (SAs) and TEDA-PF_6 for the formation of **3a**



entry	SAs (eq.)	TEDA-PF_6 (eq.)	Temp. (ºC)	**3aa**[a] (%)	**4a**[a] (%)
1	*o*-NsCl (1.5)	1.5	100	47	4
2	*o*-NsCl (3.0)	1.5	100	56 (49)	6
3	*m*-NsCl (1.5)	1.5	100	48	8
4	*p*-NsCl (1.5)	1.5	100	51 (48)	5
5	TsCl (1.5)	1.5	100	27	7
6	TsCl (3.0)	1.5	100	43 (34)	17
7	Tf_2O (1.5)	1.5	100	17	trace
8	Tf_2O (1.5)	1.5	80	7	trace
9	Tf_2O (3.0)	1.5	80	12	trace
10	*o*-NsCl (1.5)	0.0	100	79 (52)	9
11	*m*-NsCl (1.5)	0.0	100	75 (<70)[b]	7
12	*p*-NsCl (1.5)	0.0	100	65 (55)	4
13	*p*-NsCl (3.0)	0.0	100	50	23
14	TsCl (1.5)	0.0	100	30	5
15	MsCl (1.5)	0.0	100	22	5
16	BzCl (1.5)	0.0	100	37	4

[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show the isolated yields. [b] Contains impurities of unknown structure.

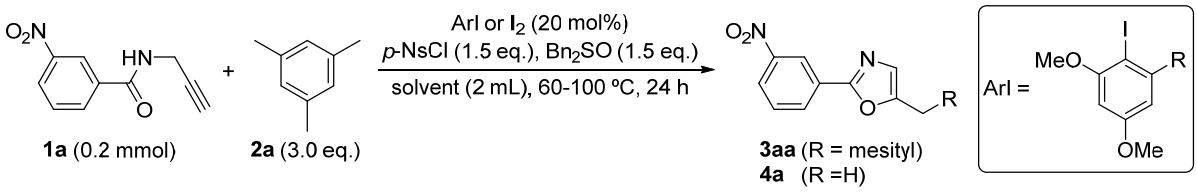
Table S2. Evaluation of sulfoxides for the formation of **3a**



entry	Sulfoxides (eq.)	**3aa**[a] (%)	**4a**[a] (%)	**1a**[a] (%)
1	Bn_2SO	65 (55)	4	0
2	Ph_2SO	trace	18	27
3	dibenzothiophene S-oxide	trace	90	4
4	Me_2SO	42	6	0
5	PhS(O)Me	65 (47)[b]	ND[c]	0

[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show the isolated yields. [b] Contains impurities of unknown structure. [c] ND = not determined.

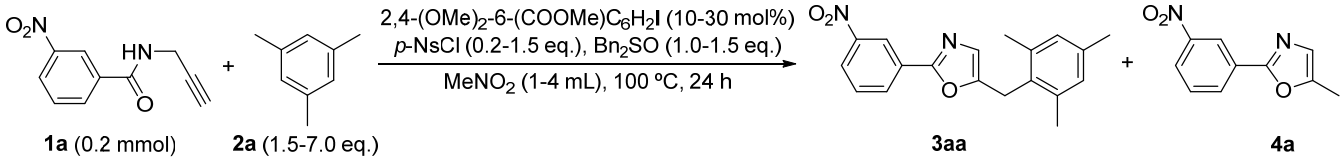
Table S3. Evaluation of iodoarene (ArI) precatalysts and solvents for the formation of **3a**



entry	ArI or I_2	Solvent	Temp. (ºC)	**3aa**[a] (%)	**4a**[a] (%)	**1a**[a] (%)
1	ArI (R = COOMe)	$MeNO_2$	100	65 (55)	4	0
2	ArI (R = COOH)	$MeNO_2$	100	72 (54)	4	0
3	ArI (R = CONHMe)	$MeNO_2$	100	65 (49)	4	0
4	ArI (R = OMe)	$MeNO_2$	100	66 (<58)[b]	7	0
5	I_2	$MeNO_2$	100	62 (<43)[b]	10	0
6	ArI (R = COOMe)	DCE	80	trace	trace	25
7	ArI (R = COOMe)	HFIP	60	36	trace	32
8	ArI (R = COOMe)	MeCN	85	35	45	0
9	ArI (R = COOMe)	EtCN	100	32	10	0
10	ArI (R = COOMe)	1,4-dioxane	100	0	0	40
11	ArI (R = COOMe)	DMF	100	0	trace	0
12	ArI (R = COOMe)	DMSO	100	0	0	0
13	ArI (R = COOMe)	$MeNO_2$	80	28	trace	0

[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show the isolated yields. [b] Contains impurities of unknown structure.

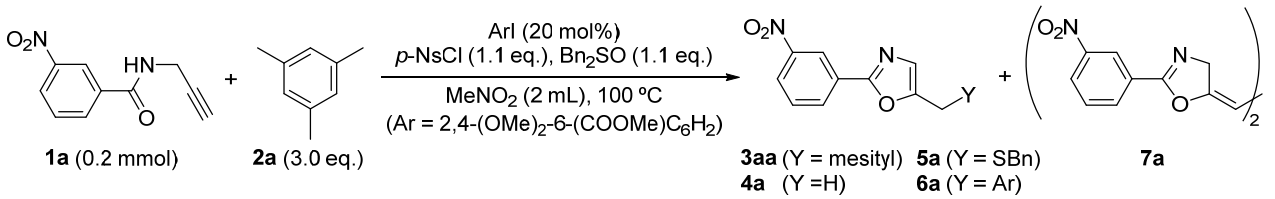
Table S4. Evaluation of the amount of each reagent for the formation of **3a**



entry	**2a** (eq.)	ArI (mol%)	*p*-NsCl (eq.)	Bn_2SO (eq.)	$MeNO_2$ (mL)	**3aa**[a] (%)	**4a**[a] (%)
1	3.0	20	1.5	1.5	2	65 (55)	4
2	3.0	20	1.5	1.5	1	69 (49)	6
3	3.0	20	1.5	1.5	4	70 (<62)[b]	4
4[c]	3.0	20	0.2	1.5	2	36	8
5	3.0	20	1.2	1.2	2	70	7
6	3.0	20	1.1	1.1	2	70 (58)	6
7	3.0	20	1.0	1.0	2	63	6
8	3.0	10	1.1	1.1	2	57	11
9	3.0	30	1.1	1.1	2	66	50
10	1.5	20	1.1	1.1	2	56	9
11	5.0	20	1.1	1.1	2	87 (67)	14
12	7.0	20	1.1	1.1	2	75 (58)	trace

[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show the isolated yields. [b] Contains impurities of unknown structure. [c] Recovery of **1a**: 14%.

Table S5. Evaluation of reaction times for the formation of **3a**



1a (0.2 mmol) **2a** (3.0 eq.) **3aa** (Y = mesityl) **5a** (Y = SBn) **7a**
4a (Y =H) **6a** (Y = Ar)

entry	Time (h)	**3aa**[a] (%)	**4a**[a] (%)	**5a**[a] (%)	**6a**[a] (%)	**7a**[a] (%)	**1a**[a] (%)
1	1	9	0	18	trace	7	22
2	8	47	5	13	trace	5	0
3	15	58 (47)	7	trace	trace	4	0
4	24	65 (55)	4	trace	trace	trace	0
5	30	80 (57)	5	trace	trace	trace	0

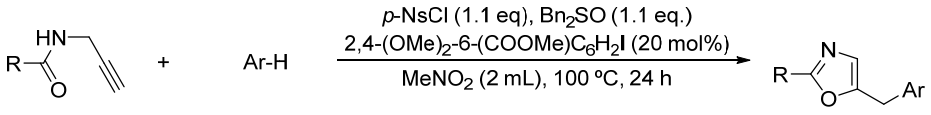
[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show the isolated yields.

2. General Information

All reactions were carried out under an argon atmosphere. *N*-Propargyl carboxamides **1a**,[1a] **1b**,[1a] **1c**,[1b] **1d**,[1a] **1e**,[1c] **1f**,[1a] **1g**,[1a] **1h**,[1a] **1i**,[1d] **1j**[1e] and 2,4-$(OMe)_2$-6-$(COOMe)C_6H_2I$[2] were prepared by the method reported in the literatures. Arenes **2a-k**, *p*-NsCl and Bn_2SO were commercial products used without purification. All solvents were purchased as the "anhydrous" and used without further purification. For the thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Medium pressure liquid chromatography (MPLC) was carried out with YAMAZEN EPCLC-W-Prep 2XY.

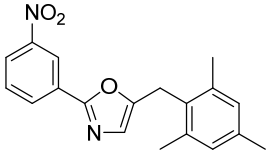
^1H and ^{13}C NMR spectra were measured at 500 and 125 MHz in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^1H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). HRMS were recorded on Bruker Daltonics micrOTOF-QII by ESI-TOF method.

3. Preparation and Characterization of Arylated Oxazoles 3 (Scheme 2 and 3)

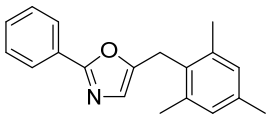


1 (0.2 mmol) **2a-2d, 2g-2j** (5.0 eq.) **2e, 2f** (10.0 eq.) **3**

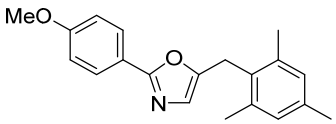
To a solution of *N*-propargyl carboxamide **1** (0.2 mmol), 2,4-$(OMe)_2$-6-$(COOMe)C_6H_2I$ (12.9 mg, 0.04 mmol) and dibenzyl sulfoxide (50.7 mg, 0.22 mmol) in $MeNO_2$ (2.0 mL) were added aromatic compound **2** (1.0 mmol for **2a**-**2d** and **2g-2j**; 2.0 mmol for **2e** and **2f**) and *p*-NsCl (48.8 mg, 0.22 mmol). After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a short silica gel column using ethyl acetate. The filtrate was concentrated in vacuo to dryness, and then the residue was purified by medium-pressure liquid chromatography (MPLC) or preparative thin-layer chromatography (PTLC) to give oxazole **3**.



2-(3-Nitrophenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3aa**): MPLC (hexane/EtOAc = 90:10), 42.9 mg (67%). Yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.36 (s, 6H), 4.06 (s, 2H), 6.67 (s, 1H), 6.91 (s, 2H), 7.62 (dd, *J* = 8.0, 8.0 Hz, 1H), 8.26 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.80 (dd, *J* = 1.7, 1.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.9, 26.0, 120.9, 124.3, 124.9, 129.2, 129.3, 129.4, 129.8, 131.5, 136.70, 136.74, 148.6, 152.3, 158.7. The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



2-Phenyl-5-(2,4,6-trimethylbenzyl)oxazole (**3ba**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 36.0 mg (65%). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.37 (s, 6H), 4.04 (s, 2H), 6.63 (s, 1H), 6.91 (s, 2H), 7.38-7.50 (m, 3H), 7.98 (d, *J* = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.9, 26.0, 124.2, 125.9, 127.7, 128.7, 129.1, 129.9, 136.4, 136.7, 150.9, 160.9 (note that two carbon peaks overlap with each other). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



2-(4-Methoxyphenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3ca**): PTLC (hexane/EtOAc = 14:1), 40.8 mg (66%). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 2.36 (s, 6H), 3.85 (s, 3H), 4.01 (s, 2H), 6.57 (s, 1H), 6.90 (s, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.9, 26.0, 55.3, 114.1, 120.6, 123.9, 127.6, 127.6, 129.1, 130.1, 136.4, 136.8, 150.2, 161.0 (note that two carbon peaks overlap with each other). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]

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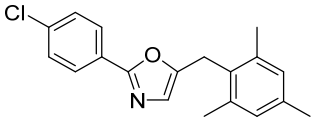
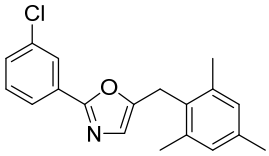
[1] (*a*) N. Asari, Y. Takemoto, Y. Shinomoto, T. Yagyu, A. Yoshimura, V. V. Zhdankin, and A. Saito, *Asian J. Org. Chem.*, 2016, **5**, 1314; (*b*) S. Punna, S. Meunier and M. G. Finn, *Org. Lett.*, 2004, **6**, 2777; (*c*) L. Willand, M. Desroses, P. Toto, B. Dirié, Z. Lens, V. Villelet, P. Rucktooa, C. Locht and A. Baulard, *ACS Chem. Biol.*, 2010, **5**, 1007.; (*d*) W.-C. Cheng, C.-K. Lin, H.-Y. Li, Y.-C. Chang, S.-J. Lu, Y.-S. Chen and S.-Y. Chang, *Chem. Commun.*, 2018, **54**, 2647; (*e*) N. Wang, B. Chen and S. Ma, *Asian J. Org. Chem.*, 2014, **3**, 723.

[2] M. Ehrlich and T. Carell, *Eur. J. Org. Chem.*, 2013, **2013**, 77.

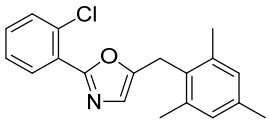
[3] Y. Umakoshi, Y. Takemoto, A. Tsubouchi, V. V. Zhdankin, A. Yoshimura and A. Saito, *Adv. Synth. Catal.*, 2022, **364**, 2053.



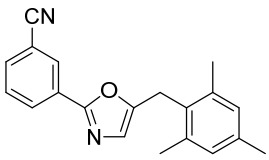
2-(4-Chlorophenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3da**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 43.7 mg (70%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.36 (s, 6H), 4.03 (s, 2H), 6.63 (s, 1H), 6.91 (s, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.8, 20.8, 25.9, 124.3, 126.1, 127.2, 128.9, 129.1, 129.7, 135.9, 136.5, 136.7, 151.2, 160.0. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



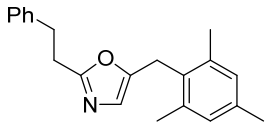
2-(3-Chlorophenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3ea**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 44.4 mg (71%). ^{1}H NMR (500MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.36 (s, 6H), 4.04 (s, 2H), 6.64 (s, 1H), 6.91 (s, 2H), 7.34-7.41 (m, 2H), 7.86 (ddd, *J* = 6.9, 2.3, 2.3 Hz, 1H), 7.97 (dd, *J* = 2.3, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.8, 25.9, 124.0, 124.4, 126.0, 129.1, 129.2, 129.6, 129.9, 130.0, 134.7, 136.5, 136.7, 151.5, 159.6. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



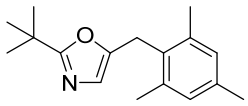
2-(2-Chlorophenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3fa**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 36.5 mg (59%).^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 2.37 (s, 6H), 4.05 (s, 2H), 6.75 (s, 1H), 6.89 (s, 2H), 7.29-7.37 (m, 2H), 7.45-7.50 (m, 1H), 7.91-7.96 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.9, 26.0, 124.3, 126.5, 126.7, 129.1, 129.9, 130.56, 130.61, 131.1, 132.1, 136.5, 136.8, 151.4, 158.7. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



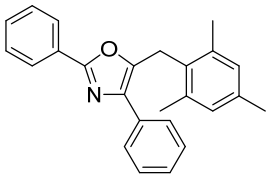
2-(3-Cyanophenyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3ga**): MPLC (hexane/EtOAc = 90:10), 34.5 mg (57%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.36 (s, 6H), 4.05 (s, 2H), 6.68 (s, 1H), 6.91 (s, 2H), 7.55 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.68 (ddd, *J* = 8.0, 1.7, 1.7 Hz, 1H), 8.19 (ddd, *J* = 8.0, 1.7, 1.7 Hz, 1H), 8.24 (dd, *J* = 1.7, 1.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.8, 25.9, 113.1, 118.1, 124.7, 128.8, 129.1, 129.3, 129.4, 129.6, 129.8, 133.0, 136.6, 136.7, 152.1, 158.7. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



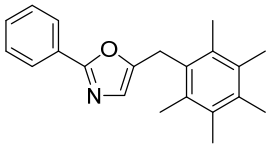
2-Phenethyl-5-(2,4,6-trimethylbenzyl)oxazole (**3ha**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 6.3 mg (10%). Yellow solid. IR (neat) ν cm^{-1}; 2924, 2856, 1603, 1572, 1496, 1454. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 2.30 (s, 6H), 2.98-3.09 (m, 4H), 3.90 (s, 2H), 6.39 (s, 1H), 6.88 (s, 2H), 7.14-7.23 (m, 3H), 7.25-7.29 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.8, 20.9, 25.8, 30.1, 33.1, 122.5, 126.3, 128.3, 128.5, 129.0, 130.1, 136.3, 136.8, 140.5, 150.3, 163.1. HRMS (ESI): *m/z* calcd. for $C_{21}H_{23}NO^{+}$ $[M + H]^{+}$ 306.1852; found 306.1860.



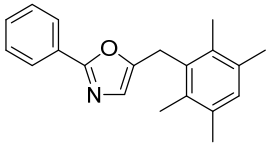
2-(*tert*-Butyl)-5-(2,4,6-trimethylbenzyl)oxazole (**3ia**): MPLC (hexane/EtOAc = 90:10), 18.0 mg (35%). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.35 (s, 9H), 2.27 (s, 3H), 2.31 (s, 6H), 3.91 (s, 2H), 6.34 (s, 1H), 6.87 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 19.8, 20.8, 25.9, 28.6, 33.6, 122.1, 129.0, 130.2, 136.2, 136.7, 150.0, 170.2. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



2,4-Diphenyl-5-(2,4,6-trimethylbenzyl)oxazole (**3ja**): MPLC (hexane/EtOAc = 90:10), 33.7 mg (48%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 9H), 4.28 (s, 2H), 6.87 (s, 2H), 7.36-7.45 (m, 4H), 7.50 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.93-7.99 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 20.2, 20.8, 26.1, 126.1, 127.4, 127.5, 127.6, 128.5, 128.6, 128.9, 129.9, 130.9, 132.4, 136.1, 136.2, 136.8, 145.6, 159.7. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]

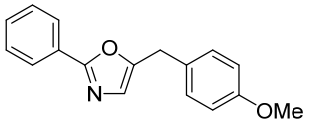


5-(2,3,4,5,6-Pentamethylbenzyl)-2-phenyloxazole (**3bb**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 37.2 mg (61%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 6H), 2.29 (s, 3H), 2.34 (s, 6H), 4.15 (s, 2H), 6.65 (s, 1H), 7.40-7.47 (m, 3H), 7.99-8.04 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 16.7, 16.9, 17.0, 27.5, 124.5, 126.0, 127.8, 128.6, 129.9, 130.1, 132.5, 132.8, 133.9, 151.5, 160.8. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



2-Phenyl-5-(2,3,5,6-tetramethylbenzyl)oxazole (**3bc**): PTLC (hexane/EtOAc = 10:1), 36.1 mg (62%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.27 (s, 12H), 4.13 (s, 2H), 6.61 (s, 1H), 6.95 (s, 1H), 7.39-7.47 (m, 3H), 7.97-8.02 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 15.7, 20.6, 27.0, 124.5, 126.0, 127.7, 128.7, 129.9, 130.6, 132.80, 132.85, 133.9,

151.2, 160.8. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



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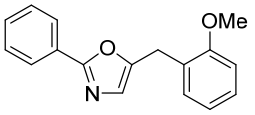
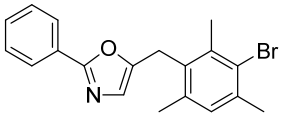


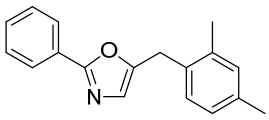
5-(4-Methoxybenzyl)-2-phenyloxazole (**3bd**) and **5-(2-Methoxybenzyl)-2-phenyloxazole** (**3bd'**): PTLC (hexane/EtOAc = 10:1), 28.4 mg (54%) and 7.5 mg (14%).

3bd: Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.80 (s, 3H), 4.01 (s, 2H), 6.83 (s, 1H) 6.88 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.38-7.47 (m, 3H), 7.97-8.02 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 31.3, 55.3, 114.1, 124.6, 126.0, 127.7, 128.6, 128.7, 129.7, 130.0, 151.8, 158.5, 161.1. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]

3bd': Pale pink solid. IR (neat) ν cm^{-1}; 2957, 2924, 2837, 1598, 1550, 1494, 1464, 1450, 1438, 1120, 1107, 754, 692. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 4.07 (s, 2H), 6.81 (s, 1H), 6.88-6.95 (m, 2H), 7.20 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.24-7.28 (m, 1H), 7.40-7.45 (m, 3H), 7.98-8.02 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 26.3, 55.4, 110.5, 120.6, 124.7, 125.2, 126.0, 127.8, 128.2, 128.6, 129.8, 130.0, 151.4, 157.3, 160.8. HRMS (ESI): *m/z* calcd. for $C_{17}H_{16}NO_2^+$ $[M + H]^+$ 266.1176; found 266.1183.



5-(3-Bromo-2,4,6-trimethylbenzyl)-2-phenyloxazole (**3be**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 28.3 mg (40%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 2.39 (s, 3H), 2.51 (s, 3H), 4.11 (s, 2H), 6.62 (s, 1H), 6.99 (s, 1H), 7.39-7.51 (m, 3H), 7.94-8.04 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.9, 20.5, 24.1, 27.5, 124.5, 126.0, 126.2, 127.6, 128.7, 130.0, 130.4, 131.9, 135.5, 136.7, 137.0, 150.3, 161.1. The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



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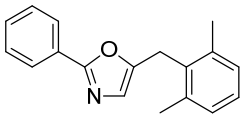
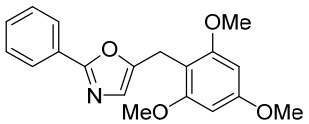
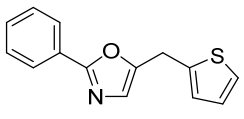


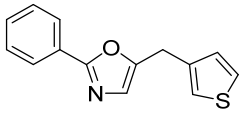
5-(2,4-Dimethylbenzyl)-2-phenyloxazole (**3bf**) **and 5-(2,6-Dimethylbenzyl)-2-phenyloxazole** (**3bf'**): MPLC (hexane/EtOAc = 90:10) then reverse phase MPLC (MeCN only), 30.2 mg (57%, **3bf**:**3bf'** = 85:15). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.32 (s, 0.85×3H), 2.34 (s, 0.85×3H), 2.41 (s, 0.15×6H), 4.01 (s, 0.85×2H), 4.08 (s, 0.15×2H), 6.63 (s, 0.15×1H), 6.75 (s, 0.85×1H), 7.00 (d, *J* = 7.5 Hz, 0.85×1H), 7.03 (s, 0.85×1H), 7.06-7.15 (m, 0.85×1H+0.15×3H), 7.38-7.48 (m, 3H), 7.96-8.02 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.3 (major), 20.0 (minor), 20.9 (major), 26.3 (minor), 29.5 (major), 124.3 (minor), 124.7 (major), 125.96 (minor), 126.02 (major), 126.9 (major), 127.0 (minor), 127.7, 128.3 (minor), 128.7, 129.5 (major), 129.9, 131.3 (major), 131.7 (major), 133.0 (minor), 136.1 (major), 136.8 (major), 136.9 (minor), 150.6 (minor), 151.3 (major), 160.96 (minor), 161.04 (major). The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]



2-Phenyl-5-(2,4,6-trimethoxybenzyl)oxazole (**3bg**): MPLC (hexane/EtOAc = 90:10), 35.3 mg (54%). White solid, mp 107-108 ºC. IR (KBr) ν cm^{-1}; 2957, 2937, 2840, 1609, 1549, 1502, 1455, 1439, 1371. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (s, 6H), 3.83 (s, 3H), 4.01 (s, 2H), 6.17 (s, 2H), 6.62 (s, 1H), 7.35-7.44 (m, 3H), 7.95-8.00 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 19.3, 55.3, 55.8, 90.6, 105.5, 123.6, 125.9, 128.1, 128.6, 129.5, 152.5, 159.0, 160.1, 160.3. HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}NO_4^+$ $[M + H]^+$ 326.1387; found 326.1388.



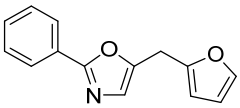
and



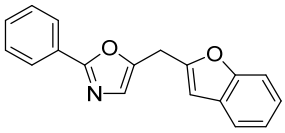
2-Phenyl-5-(thiophen-2-ylmethyl)oxazole (**3bh**) and **2-phenyl-5-(thiophen-3-ylmethyl)oxazole** (**3bh'**): MPLC (hexane/EtOAc = 90:10), 15.4 mg (32%) and 3.5 mg (7%).

3bh: Orange solid, mp 54-55 °C. IR (KBr) ν cm^{-1}; 2924, 2892, 2851, 1599, 1585, 1490, 1447, 1120, 1104. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.28 (s, 2H), 6.92-7.02 (m, 3H), 7.21 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39-7.50 (m, 3H), 7.99-8.09 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 26.5, 124.5, 124.8, 126.0, 126.1, 127.0, 127.6, 128.7, 130.1, 138.6, 150.4, 161.3. HRMS (ESI): *m/z* calcd. for $C_{14}H_{12}NOS^+$ $[M + H]^+$ 242.0634; found 242.0640.

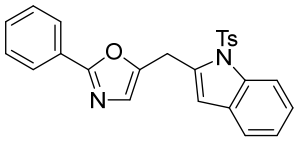
3bh': Pink solid, mp 51-54 °C. IR (KBr) ν cm^{-1}; 2959, 2926, 2893, 2857, 1599, 1584, 1490, 1447, 1127, 1120, 1104. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.09 (s, 2H), 6.88 (s, 1H), 7.04 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.11 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.31 (dd, *J* = 5.2, 2.9 Hz, 1H), 7.40-7.48 (m, 3H), 7.99-8.02 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 26.9, 122.1, 124.6, 126.07, 126.08, 127.6, 128.1, 128.7, 130.1, 136.6, 150.9, 161.2. HRMS (ESI): *m/z* calcd. for $C_{14}H_{12}NOS^+$ $[M + H]^+$ 242.0634; found 242.0637.



5-(Furan-2-ylmethyl)-2-phenyloxazole (**3bi**): MPLC (hexane/EtOAc = 90:10), 19.8 mg (44%). Colorless oil. IR (neat) ν cm^{-1}; 2958, 2925, 2853, 1599, 1550, 1506, 1448, 1150, 1121, 1102, 736, 691. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.11 (s, 2H), 6.17 (d, *J* = 2.9 Hz, 1H), 6.34 (dd, *J* = 2.9, 1.7 Hz, 1H), 6.95 (s, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.40-7.48 (m, 3H), 7.97-8.06 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 25.2, 106.9, 110.5, 125.1, 126.1, 127.5, 128.7, 130.1, 141.9, 148.5, 150.0, 161.2. HRMS (ESI): *m/z* calcd. for $C_{14}H_{12}NO_2^+$ $[M + H]^+$ 226.0863; found 226.0868.



5-(Benzofuran-2-ylmethyl)-2-phenyloxazole (**3bj**): MPLC (hexane/EtOAc = 90:10), 27.5 mg (50%). Pale yellow solid, mp 62-64°C. IR (KBr) ν cm^{-1}; 2952, 2922, 2851, 1601, 1586, 1456, 1120, 1105, 1074, 764, 752, 711, 691. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.27 (s, 2H), 6.56 (s,1H), 7.05 (s, 1H), 7.21 (dd, *J* = 7.5, 6.9 Hz, 1H), 7.24-7.29 (m, 1H), 7.41-7.49 (m, 4H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.98-8.07 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 25.7, 104.0, 111.0, 120.6, 122.8, 123.9, 125.6, 126.2, 127.4, 128.5, 128.7, 130.2, 147.6, 153.1, 154.9, 161.5. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_2^+$ $[M + H]^+$ 276.1019; found 276.1025.



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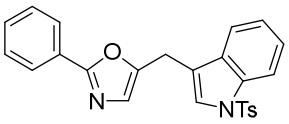


2-Phenyl-5-[(1-tosyl-1*H*-indol-2-yl)methyl]oxazole (**3bk**) and **2-phenyl-5-[(1-tosyl-1*H*-indol-3-yl)methyl]oxazole** (**3bk'**): MPLC (hexane/EtOAc = 80:20), 11.6 mg (14%) and 29.6 mg (35%).

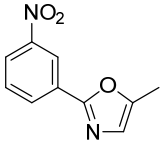
3bk: Yellow oil. IR (neat) ν cm^{-1}; 2924, 2853, 1597, 1567, 1484, 1450, 1370, 1175, 1121. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 4.54 (s, 2H), 6.42 (s, 1H), 6.99 (s, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.23 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.6, 6.9, 1.2 Hz, 1H), 7.40-7.47 (m, 4H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.94-8.00 (m, 2H), 8.17 (dd, *J* = 8.6, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 21.5, 25.9, 111.0, 114.8, 120.6, 123.7, 124.5, 126.0, 126.1, 126.2, 127.4, 128.7, 129.2, 129.9, 130.2, 135.9, 136.2, 137.2, 144.9, 148.4, 161.3. HRMS (ESI): *m/z* calcd. for $C_{25}H_{21}N_2O_3S^+$ $[M + H]^+$ 429.1267; found 429.1260.

3bk': Yellow oil. IR (neat) ν cm^{-1}; 2954, 2923, 2852, 1597, 1567, 1491, 1447, 1368, 117, 1119. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.32 (s, 3H), 4.12 (s, 2H), 6.83 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.34 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.41-7.47 (m, 3H), 7.48 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.95-7.99 (m, 2H), 8.01 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 21.5, 22.0, 113.8, 117.8, 119.4, 123.3, 124.2, 124.9, 125.0, 126.1, 126.7, 127.5, 128.7, 129.8, 130.2, 135.1, 135.3, 144.9, 149.7, 161.2 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{25}H_{21}N_2O_3S^+$ $[M + H]^+$ 429.1267; found 429.1266.

4. Control Experiments

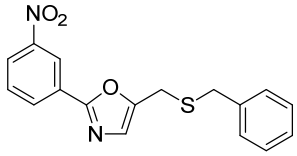
(*a*) Time course of reaction of **1a** with **2a** (Figure 1)

To a solution of *N*-propargyl carboxamide **1a** (40.8 mg, 0.2 mmol), 2,4-$(OMe)_2$-6-(COOMe)C_6H_2I (12.9 mg, 0.04 mmol) and dibenzyl sulfoxide (50.7 mg, 0.22 mmol) in $MeNO_2$ (2.0 mL) were added mesitylene (**2a**, 83.5 μL, 0.6 mmol) and *p*-NsCl (48.8 mg, 0.22 mmol). After being stirred at 100 °C for 1 h, the reaction mixture was filtered through a short silica gel column using ethyl acetate. The filtrate was concentrated in vacuo to dryness, and then the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the residue was measured, using dibromomethane (20 μL) as an internal standard. The yields of **3aa** (δ = 4.06 ppm), **4a** (δ = 2.44 ppm), **5a** (δ = 3.68 and 3.77 ppm) and **6a** (δ = 4.45 ppm) were determined from the obtained spectrum. The same procedure was followed for reaction times of 8, 15 and 24 h.

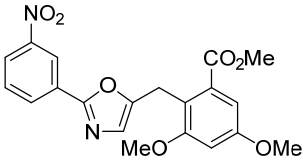


5-Methyl-2-(3-nitrophenyl)oxazole (**4a**): R_f = 0.54 (hexane:AcOEt = 2:1). Brown solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm; 2.43 (s, 3H), 6.90 (s, 1H), 7.63 (dd, *J* =8.2, 7.8 Hz, 1H) 8.25 (ddd, *J* = 8.2, 2.0, 1.1 Hz, 1H), 8.32 (ddd, *J* = 7.8, 2.0, 1.1 Hz, 1H), 8.82 (t, *J* = 2.0 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm; 10.9, 120.8, 124.2, 124.9, 129.4, 129.9, 131.5, 148.7, 150.3, 158.5. The ^{1}H and ^{13}C NMR spectra of **4a** were identical to data reported in the literature.[4]

[4] G. C. Senadi, W.-P. Hu, J.-S. Hsiao, J. K. Vandavasi, C.-Y. Chen, J.-J. Wang, *Org. Lett.* **2012**, *14*, 4478–4481.



5-[(Benzylthio)methyl]-2-(3-nitrophenyl)oxazole (**6a**): R_f = 0.48 (hexane: AcOEt = 2:1). pale yellow solid, mp 91-96. IR (KBr) ν cm^{-1}; 2931, 2912, 2862, 1595, 1580, 1547, 1526, 1496, 1456, 1346, 1140, 1119, 1105, 1071. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.68 (s, 2H), 3.77 (s, 2H), 7.01 (s, 1H), 7.23-7.29 (m, 1H), 7.31-7.38 (m, 4H), 7.65 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.28 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.83 (d, *J* = 1.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 24.9, 36.0, 121.0, 124.6, 126.2, 127.3, 128.6, 128.9, 129.9, 131.6, 137.1, 148.5, 150.1, 159.2 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{17}H_{15}N_2O_3S^+$ $[M + H]^+$ 327.0798; found 327.0805.



Methyl 3,5-dimethoxy-2-{[2-(3-nitrophenyl)oxazol-5-yl]methyl}benzoate (**7a**): R_f = 0.26 (hexane: AcOEt = 2:1). yellow, sticky solid. IR (KBr) ν cm^{-1}; 2950, 2841, 1604, 1583, 1547, 1526, 1459, 1435, 1353, 1322, 1298, 1280, 1244, 1213, 1205, 1189, 1164, 1136, 1121, 1104, 1065. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 3.86 (s, 3H), 3.92 (s, 3H), 4.46 (s, 2H), 6.66 (d, *J* = 2.3 Hz, 1H), 6.73 (s, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.0, 8.0 Hz, 1H), 8.23 (dd, *J* = 8.0, 2.3 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.78 (d, *J* = 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 22.2, 52.3, 55.5, 55.9, 102.4, 105.8, 118.5, 120.7, 124.0, 124.4, 129.5, 129.8, 131.4, 131.7, 148.5, 153.4, 158.0, 158.9, 159.3, 167.7. HRMS (ESI): *m/z* calcd. for $C_{20}H_{19}N_2O_7^+$ $[M + H]^+$ 399.1187; found 399.1195.

(*b*) Reaction of **1a** with BnSH under the optimized conditions (Scheme 4a)

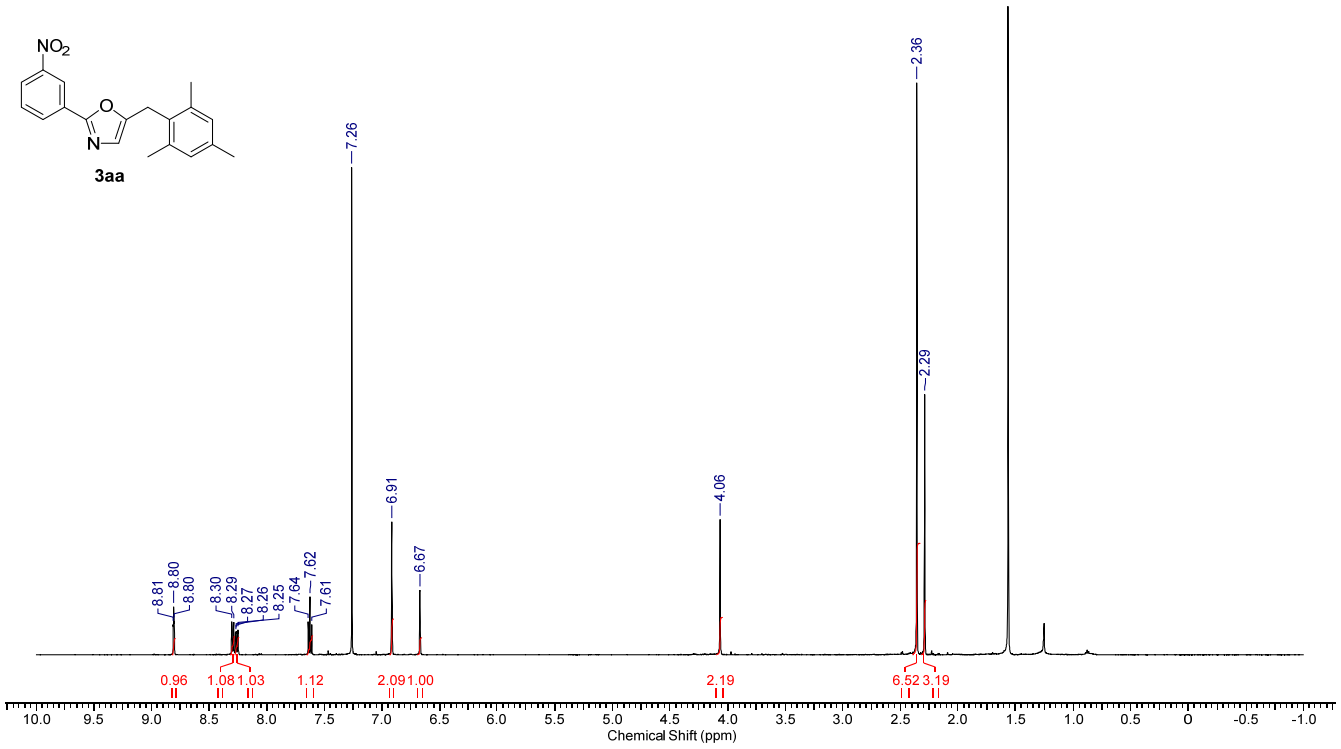
To a solution of *N*-propargyl carboxamide **1a** (40.8 mg, 0.2 mmol), 2,4-$(OMe)_2$-6-$(COOMe)C_6H_2I$ (12.9 mg, 0.04 mmol) and dibenzyl sulfoxide (50.7 mg, 0.22 mmol) in $MeNO_2$ (2.0 mL) were added BnSH (117.2 μL, 1.0 mmol) and *p*-NsCl (48.8 mg, 0.22 mmol). After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a short silica gel column using ethyl acetate. The filtrate was concentrated in vacuo to dryness, and then the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the residue was measured, using dibromomethane (20 μL) as an internal standard. The yields of **3aa** (δ = 4.06 ppm), **4a** (δ = 2.44 ppm), **5a** (δ = 3.68 and 3.77 ppm) and **6a** (δ = 4.45 ppm) were determined from the obtained spectrum.

(*c*) Reaction of **6a** with **2a** under the optimized conditions (Scheme 4b)

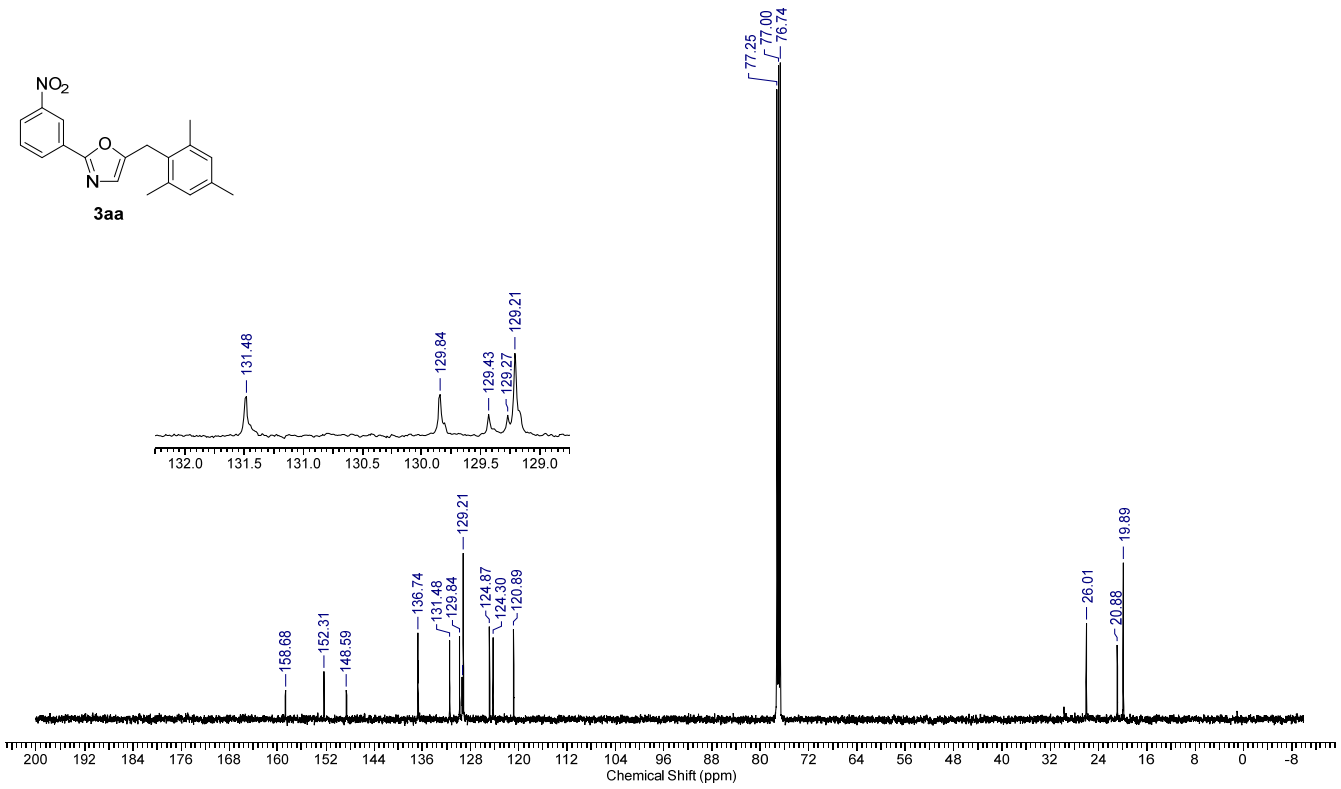
To a solution of *N*-propargyl carboxamide **6a** (20.4 mg, 0.1 mmol), 2,4-$(OMe)_2$-6-$(COOMe)C_6H_2I$ (6.4 mg, 0.02 mmol) and dibenzyl sulfoxide (25.3 mg, 0.11 mmol) in $MeNO_2$ (1.0 mL) were added mesitylene (**2a**, 69.1 μL, 0.5 mmol) and *p*-NsCl (24.4 mg, 0.11 mmol). After being stirred at 100 °C for 24 h, the reaction mixture was filtered through a short silica gel column using ethyl acetate. The filtrate was concentrated in vacuo to dryness, and then the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the residue was measured, using dibromomethane (20 μL) as an internal standard. The yields of **3aa** (δ = 4.06 ppm), **4a** (δ = 2.44 ppm), **5a** (δ = 3.68 and 3.77 ppm) and **6a** (δ = 4.45 ppm) were determined from the obtained spectrum.

5. ^{1}H and ^{13}C NMR Spectra of 3aa-3ja, 3bb-3bj, 4a, 5a and 6a

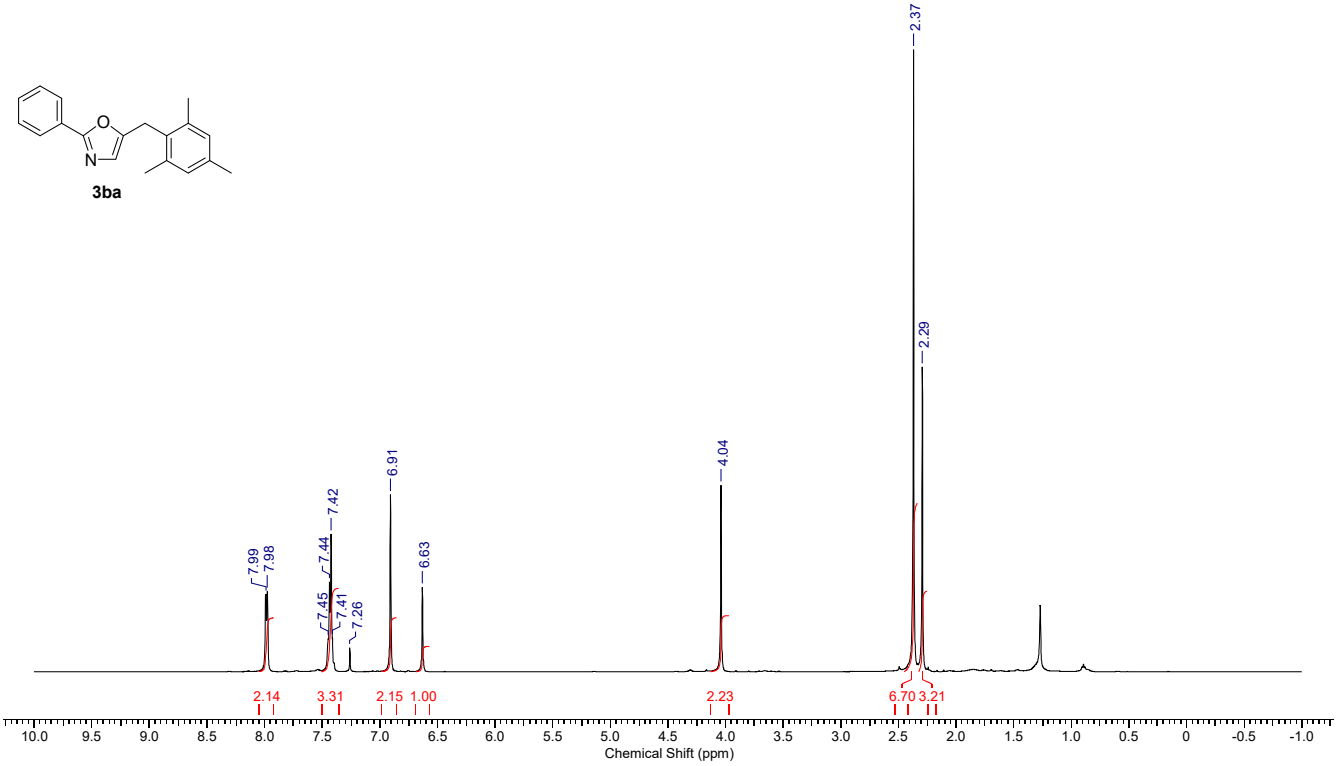
^{1}H NMR (500 MHz, $CDCl_3$) of **3aa**



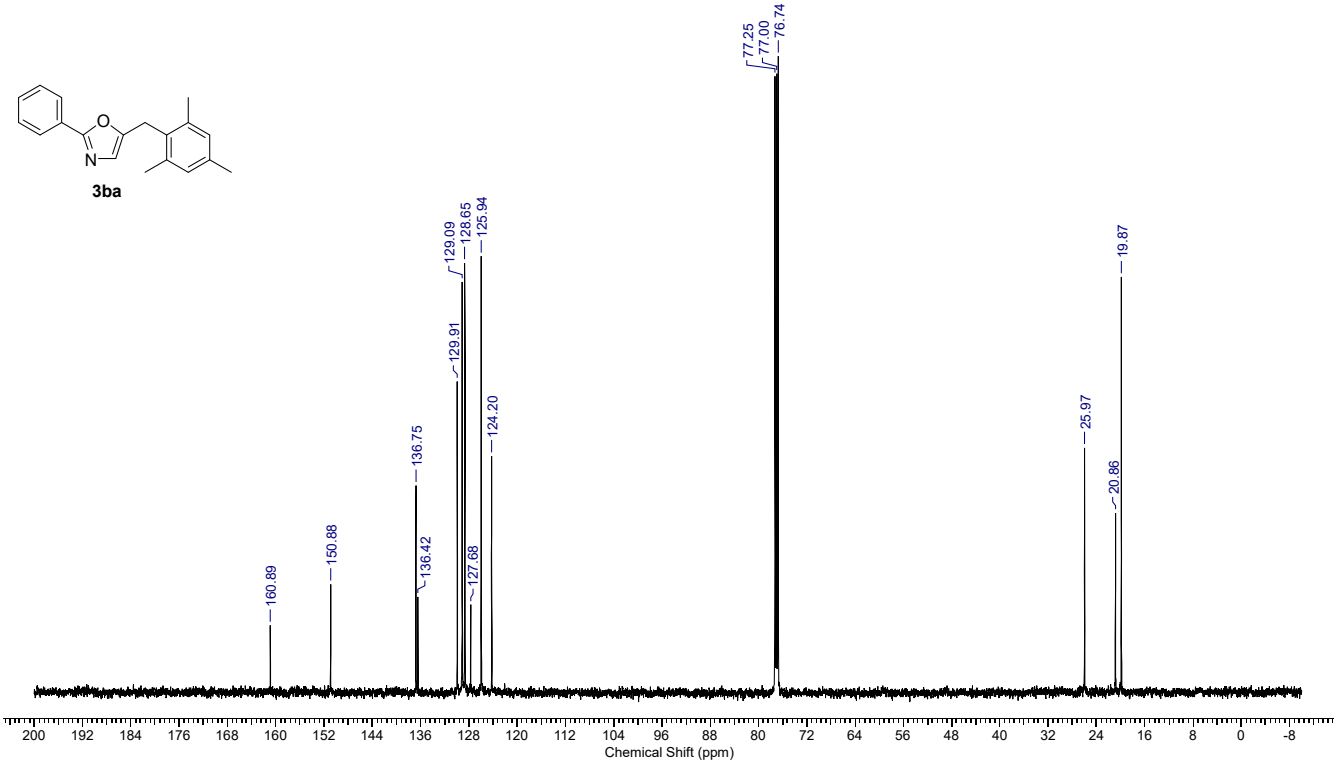
^{13}C NMR (125 MHz, $CDCl_3$) of **3aa**



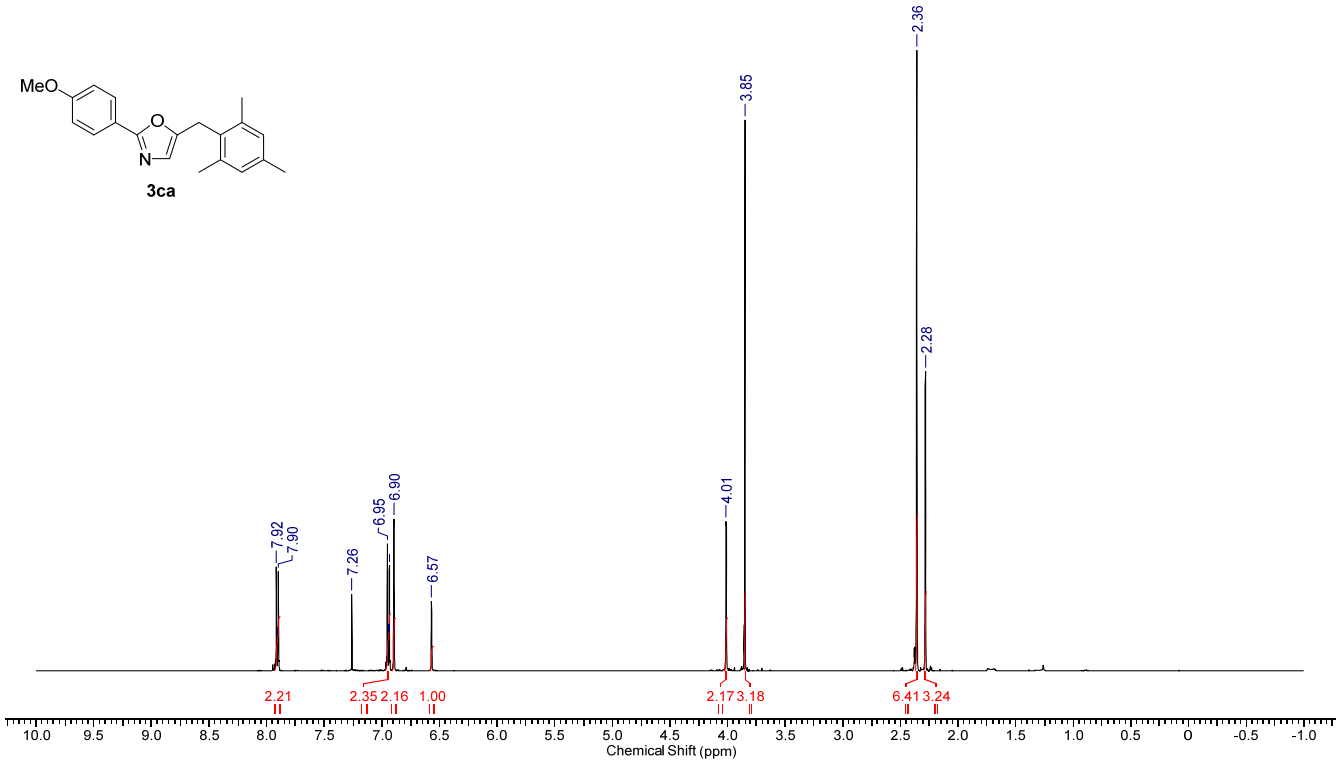
^{1}H NMR (500 MHz, $CDCl_3$) of **3ba**



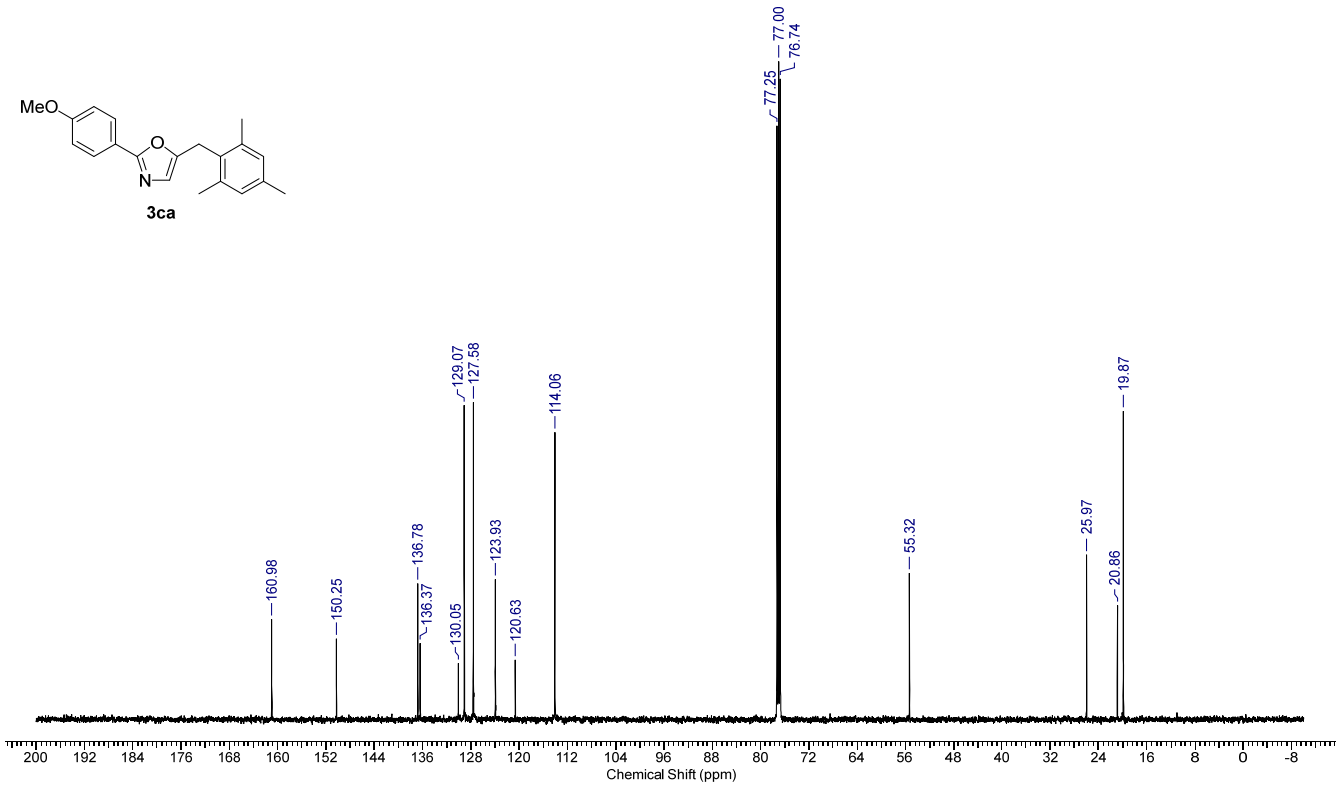
^{13}C NMR (125 MHz, $CDCl_3$) of **3ba**



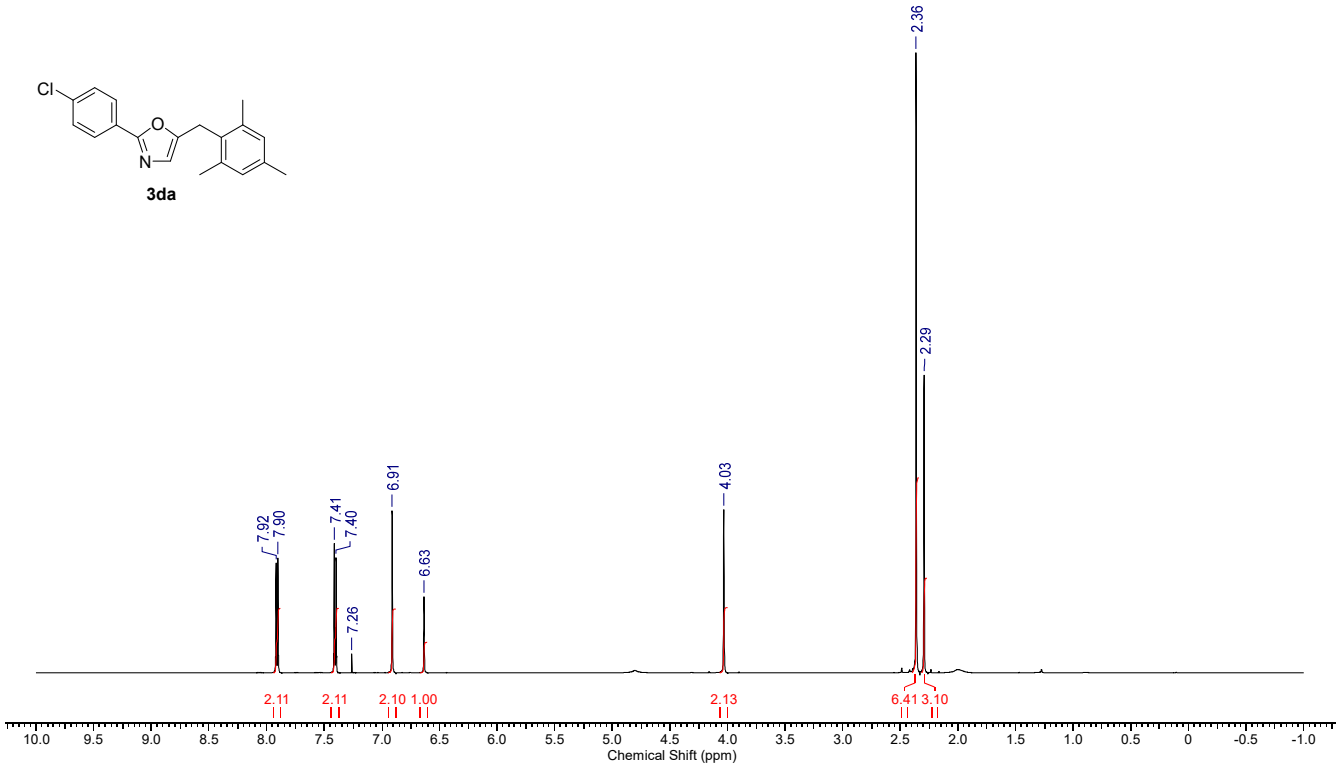
^{1}H NMR (500 MHz, $CDCl_3$) of **3ca**



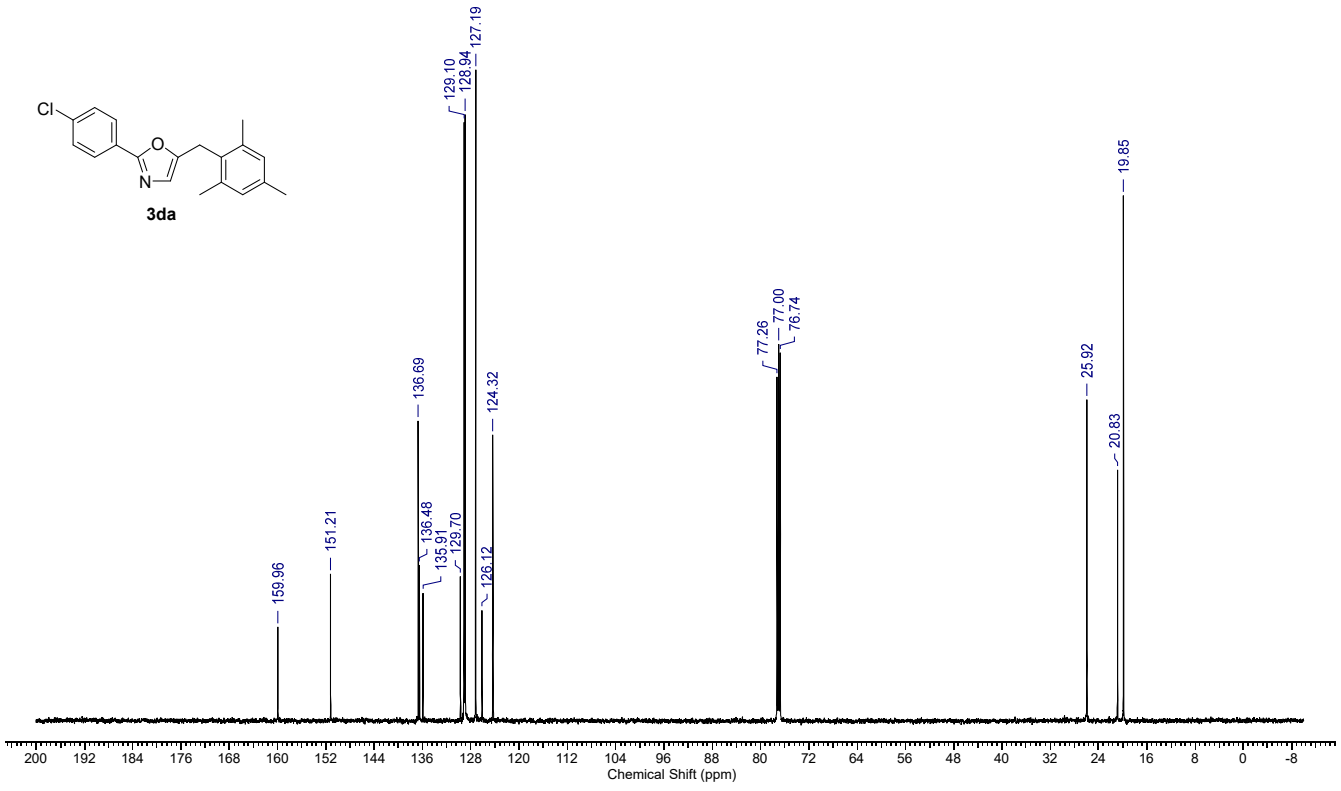
^{13}C NMR (125 MHz, $CDCl_3$) of **3ca**



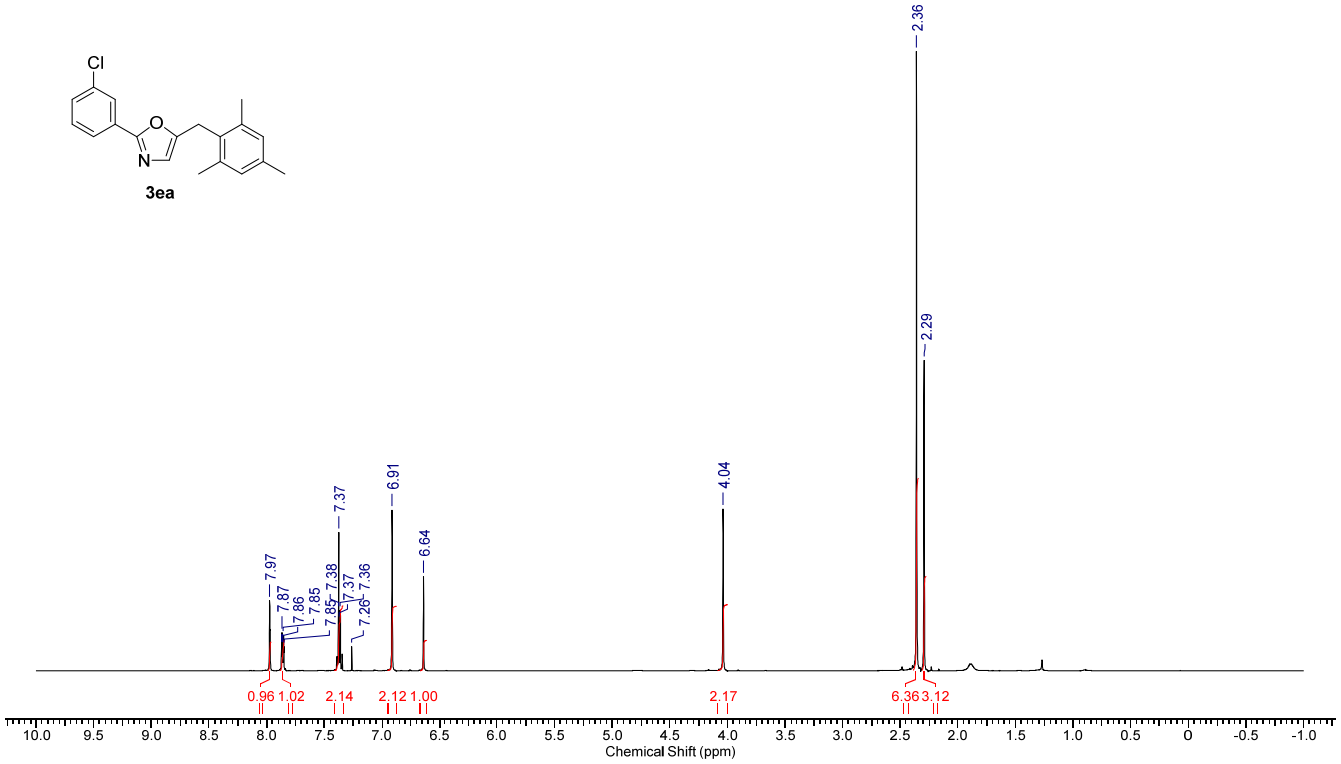
^{1}H NMR (500 MHz, $CDCl_3$) of **3da**



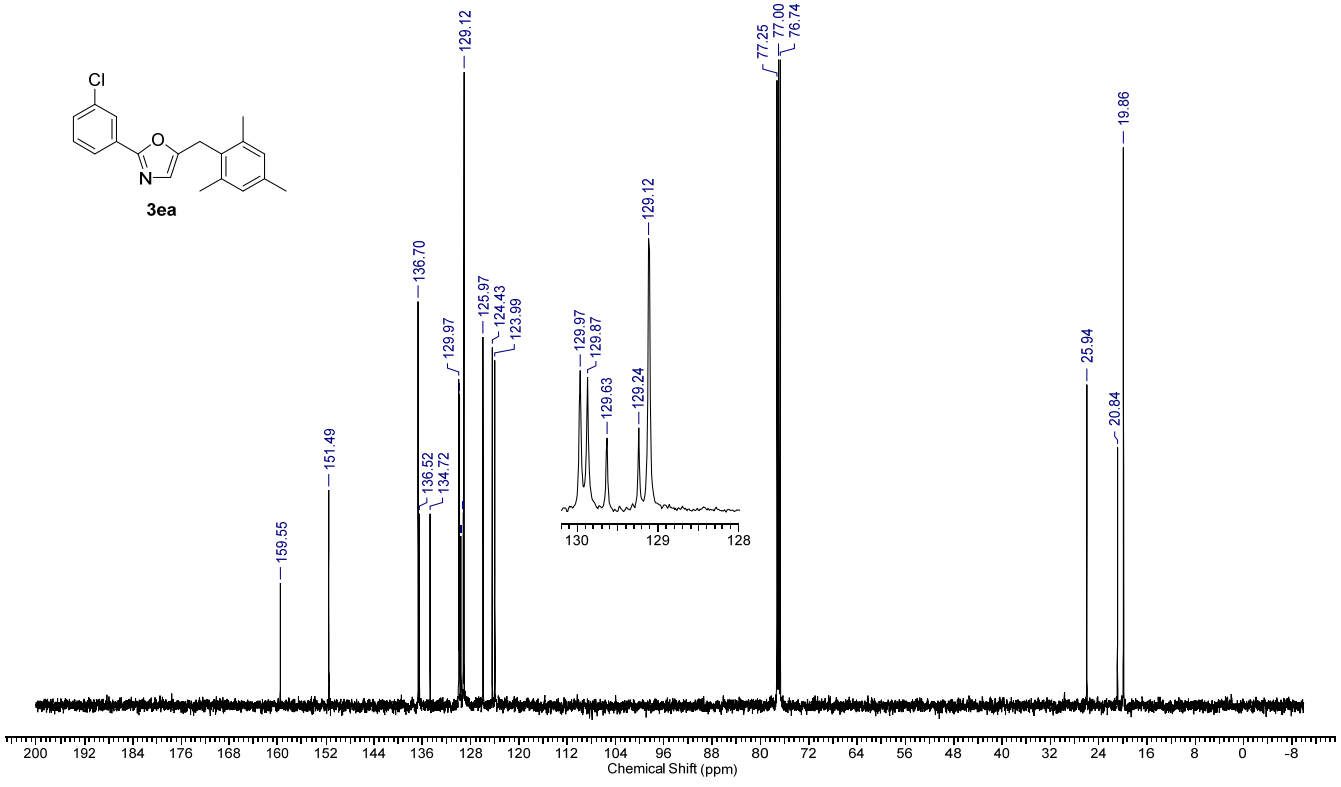
^{13}C NMR (125 MHz, $CDCl_3$) of **3da**



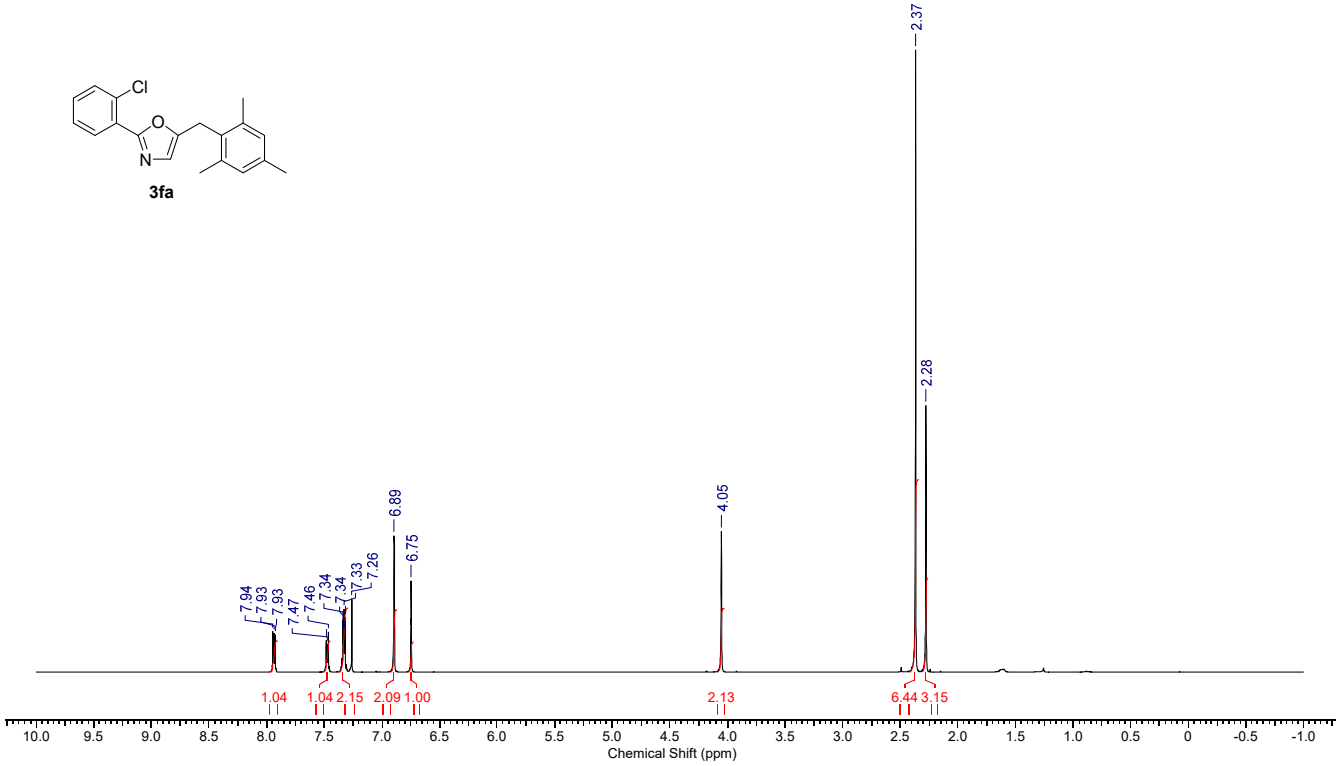
^{1}H NMR (500 MHz, $CDCl_3$) of **3ea**



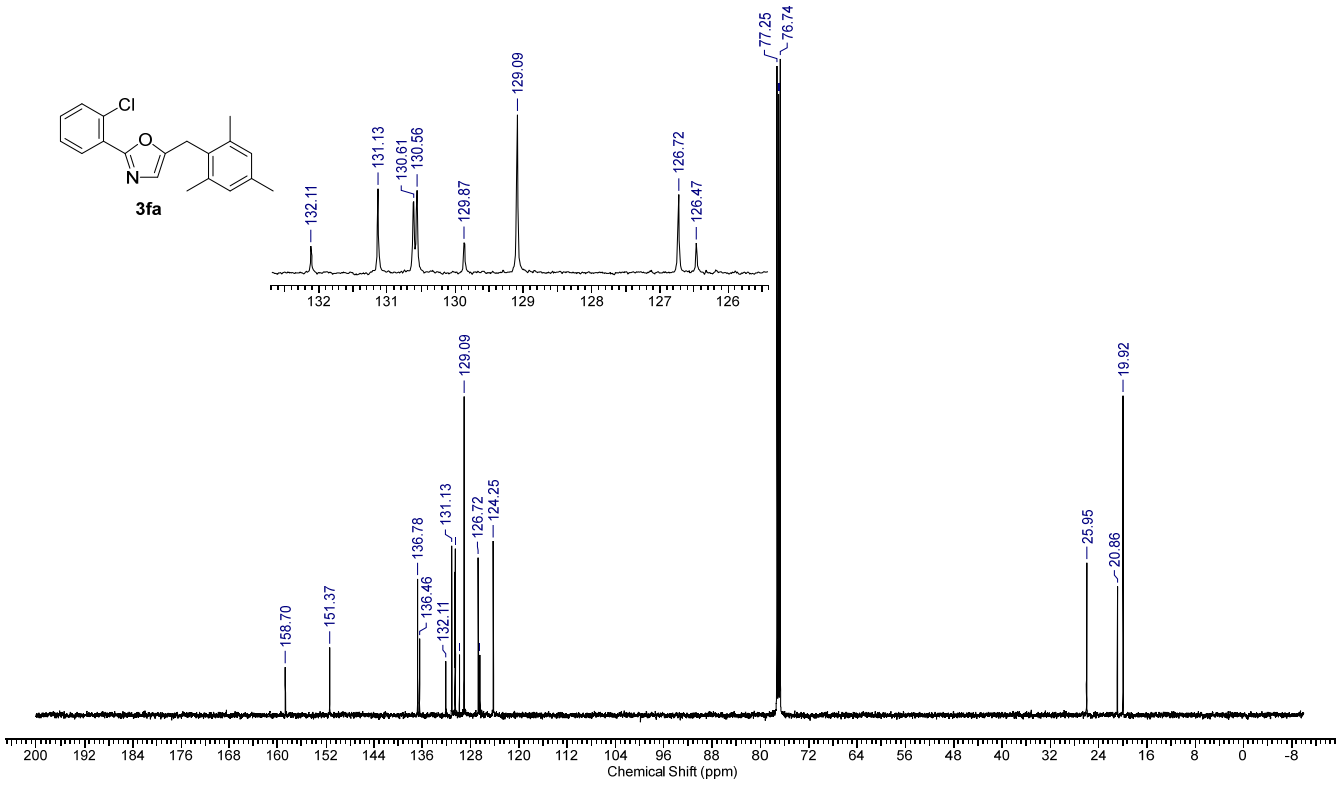
^{13}C NMR (125 MHz, $CDCl_3$) of **3ea**



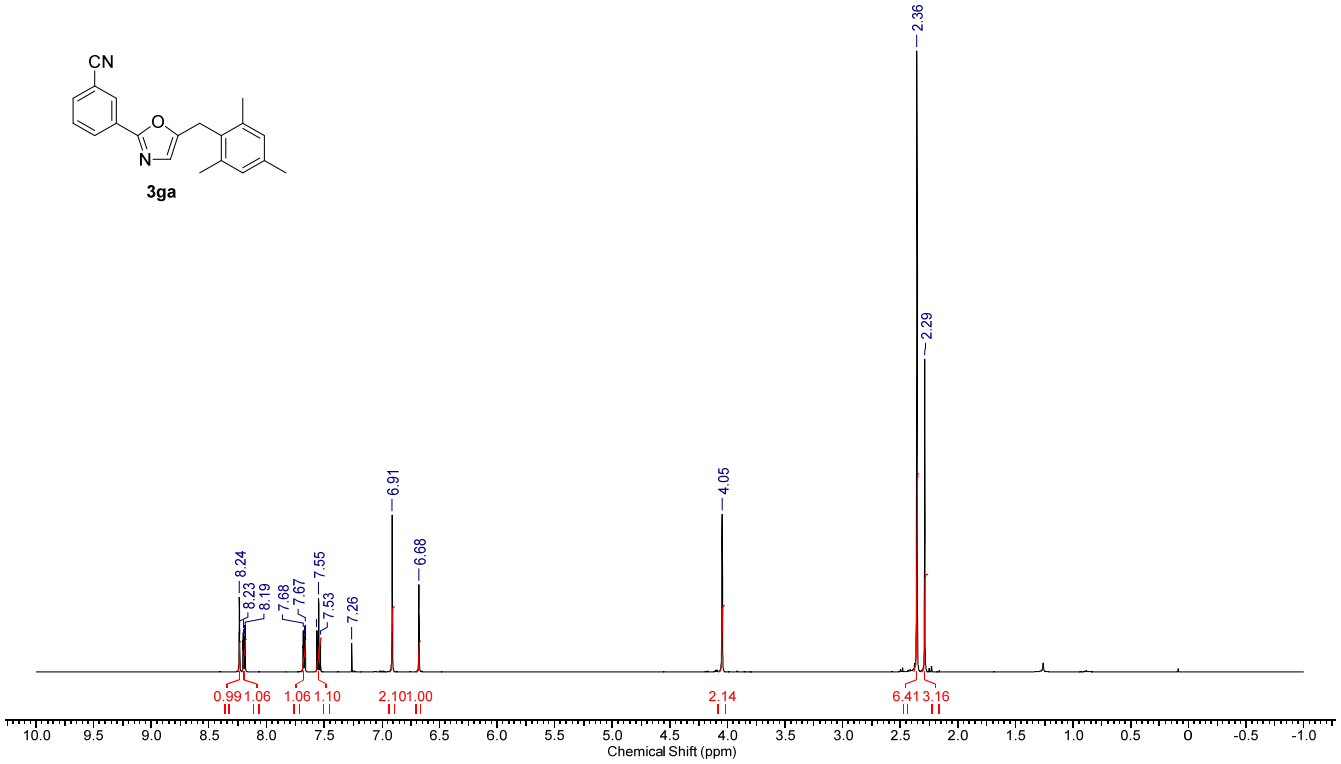
^{1}H NMR (500 MHz, $CDCl_3$) of **3fa**



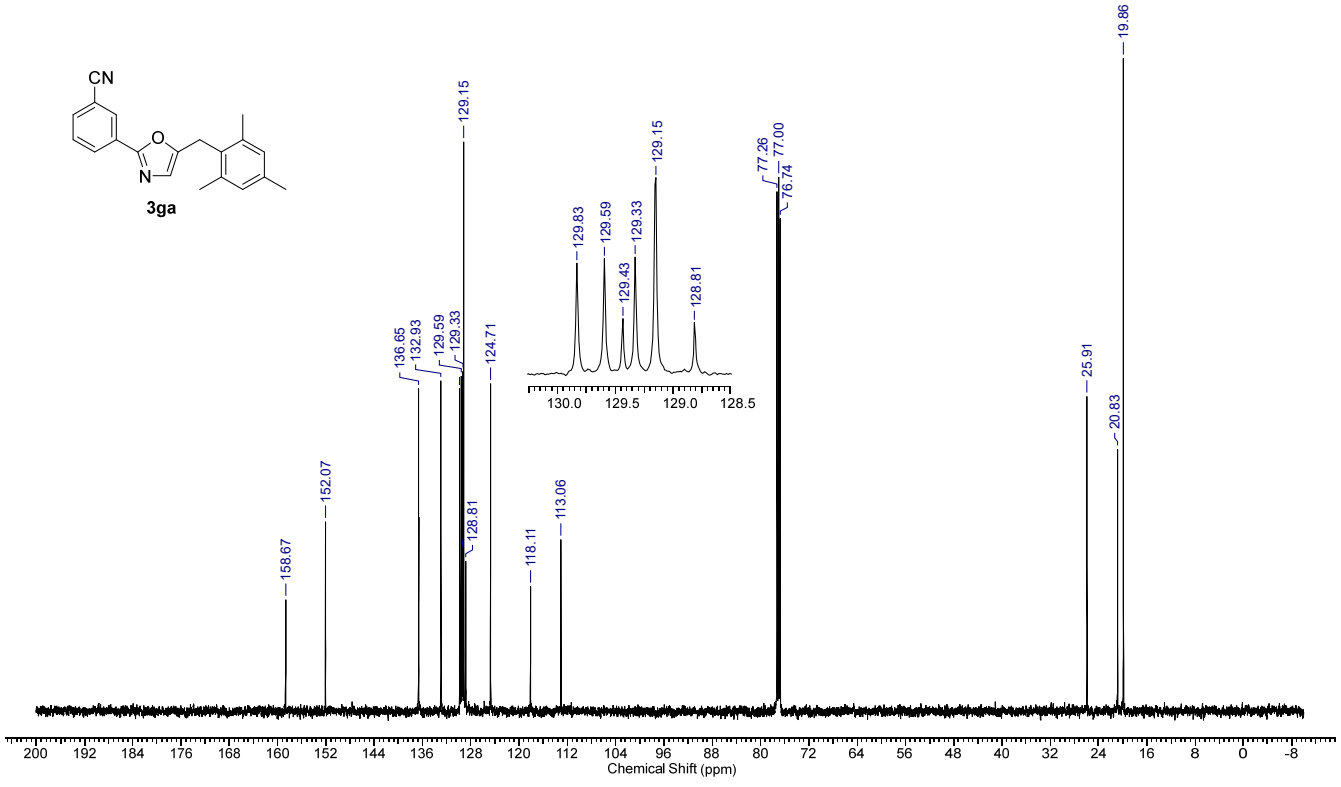
^{13}C NMR (125 MHz, $CDCl_3$) of **3fa**



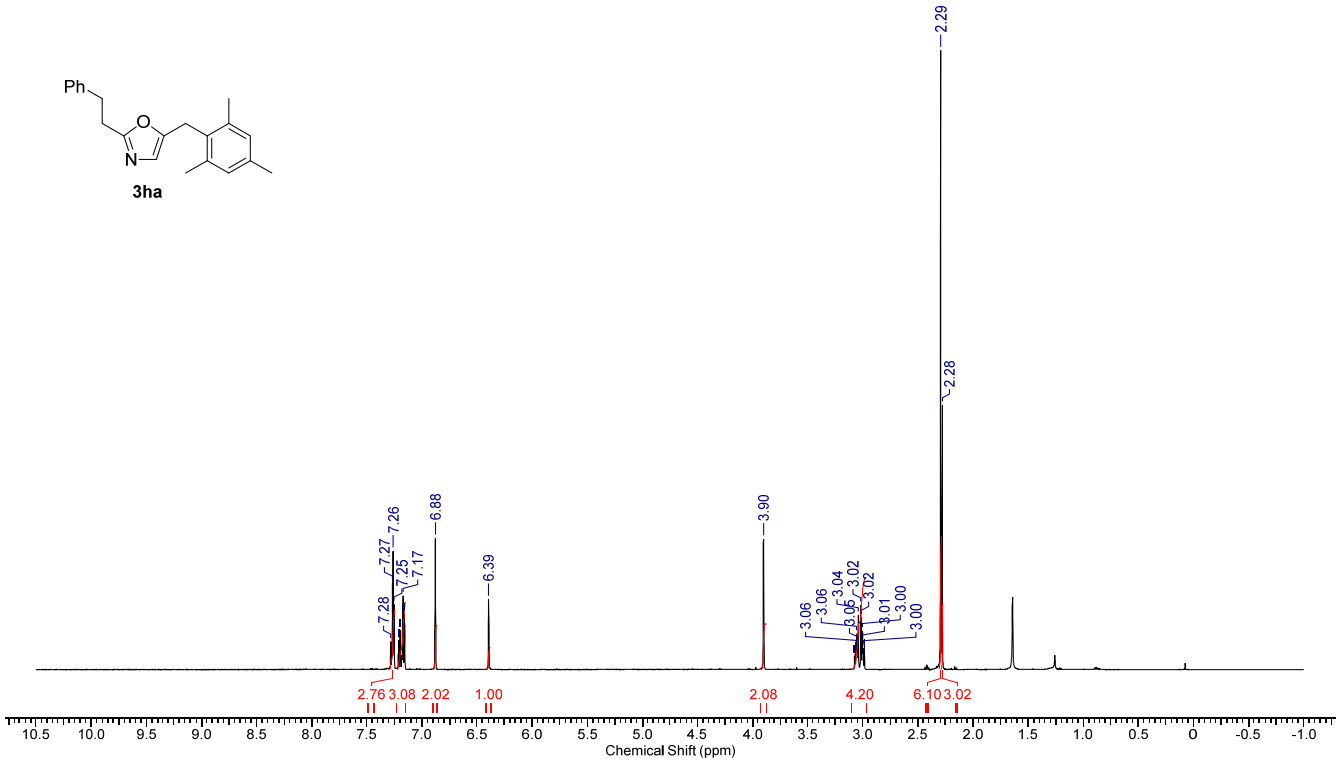
^{1}H NMR (500 MHz, $CDCl_3$) of **3ga**



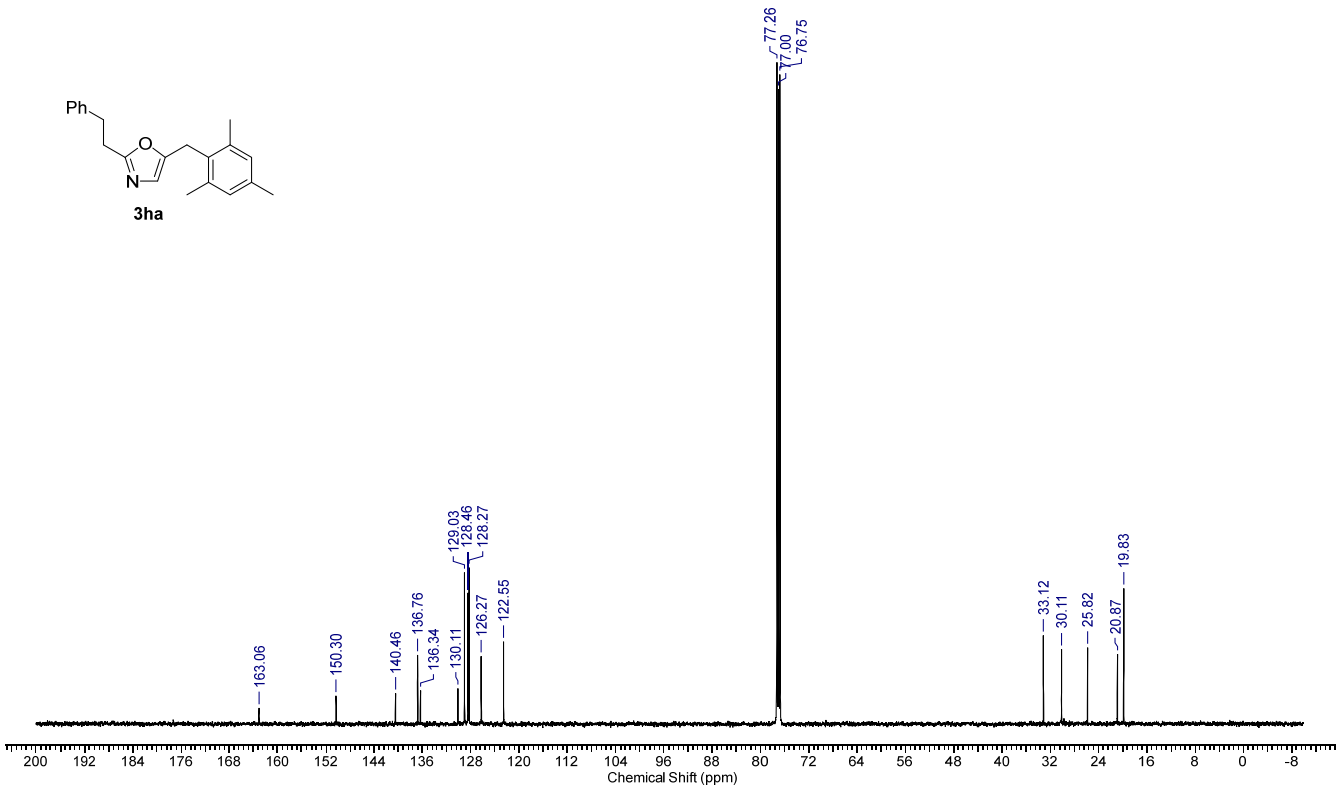
^{13}C NMR (125 MHz, $CDCl_3$) of **3ga**



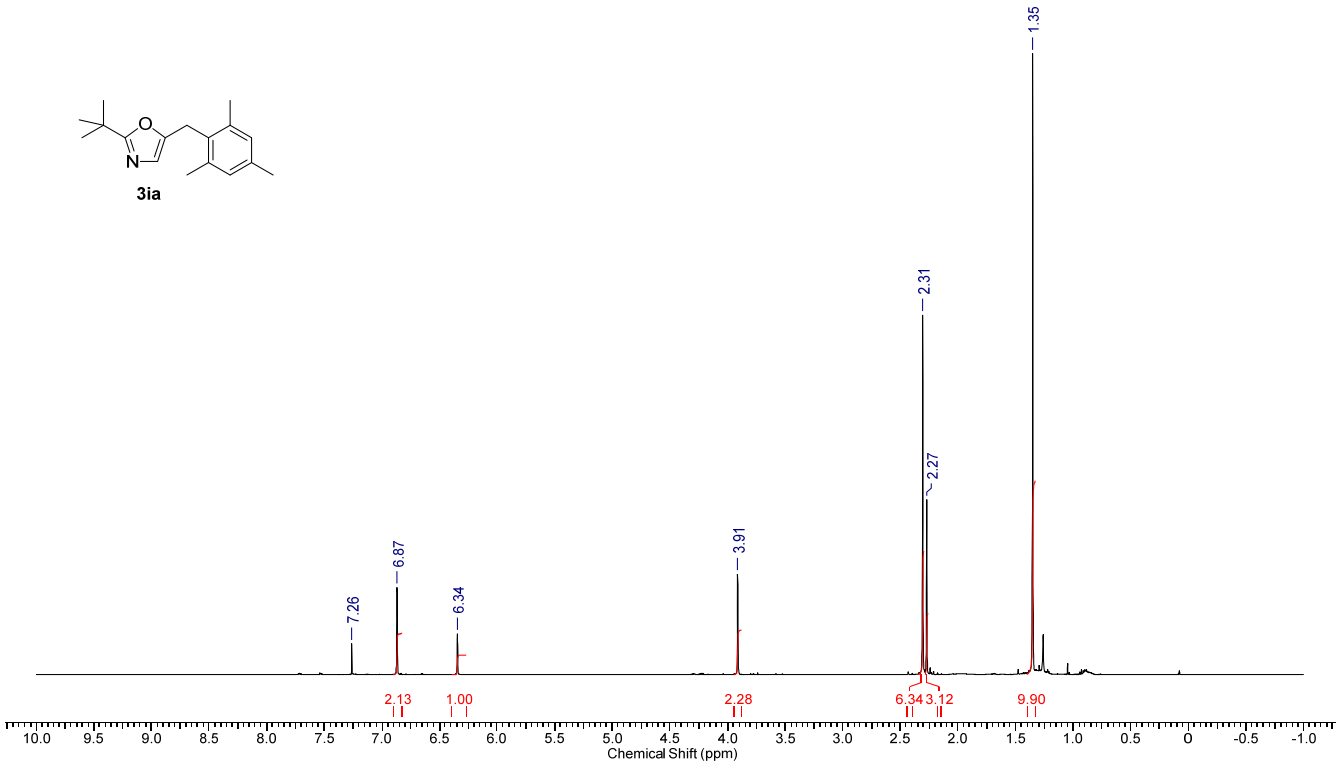
^{1}H NMR (500 MHz, $CDCl_3$) of **3ha**



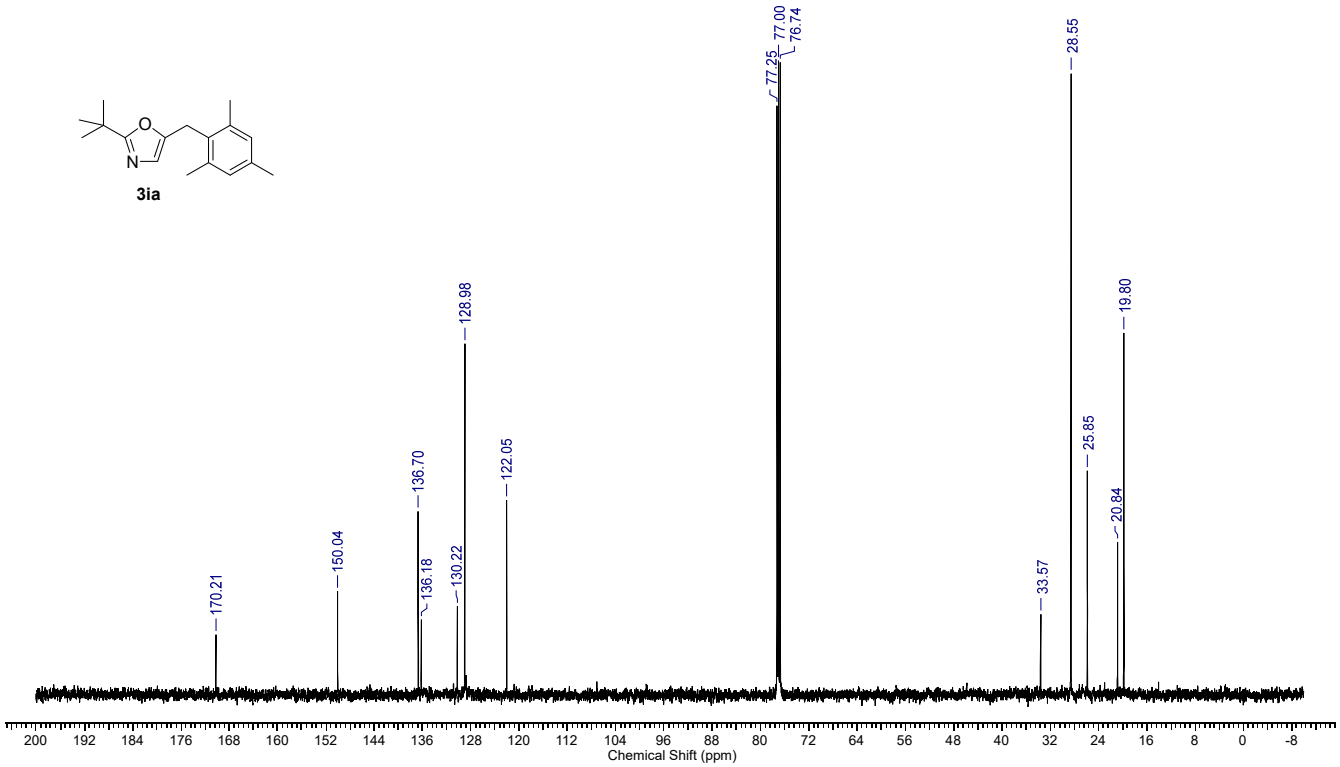
^{13}C NMR (125 MHz, $CDCl_3$) of **3ha**



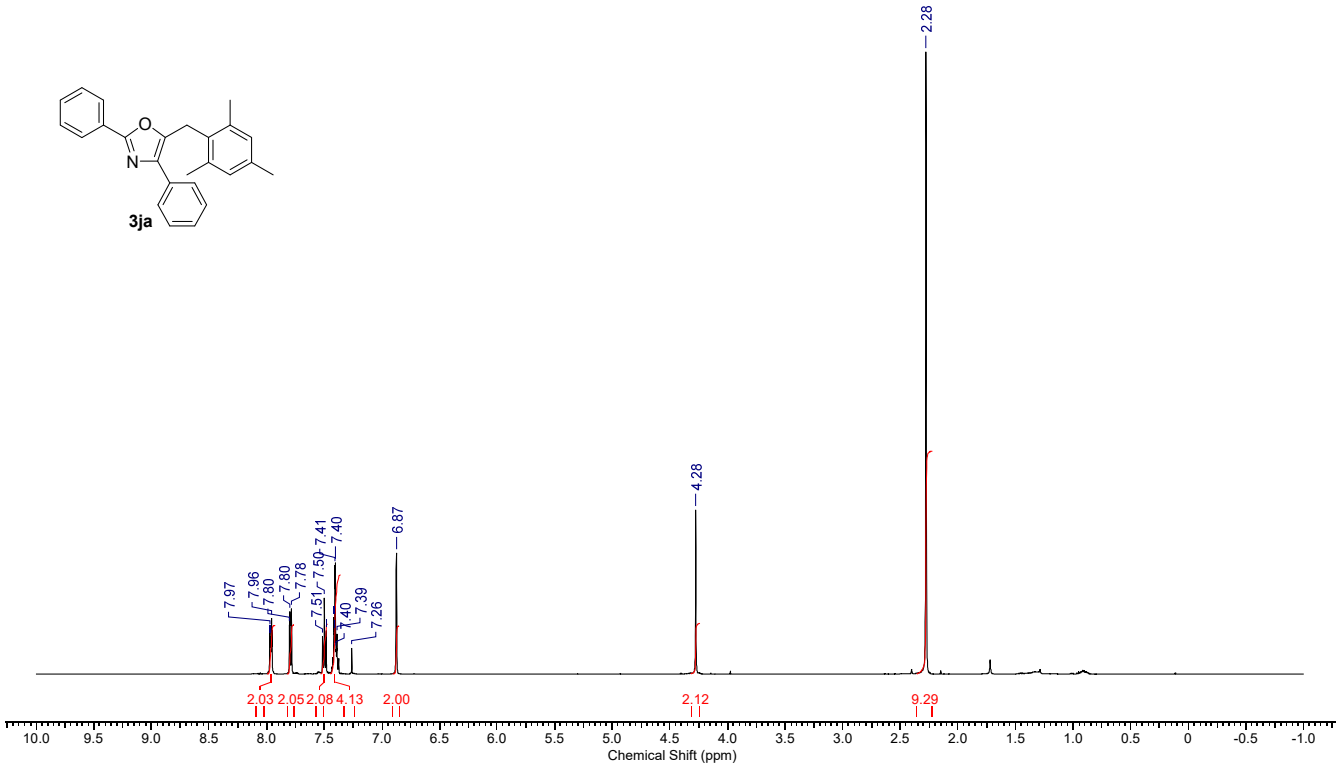
^{1}H NMR (500 MHz, $CDCl_3$) of **3ia**



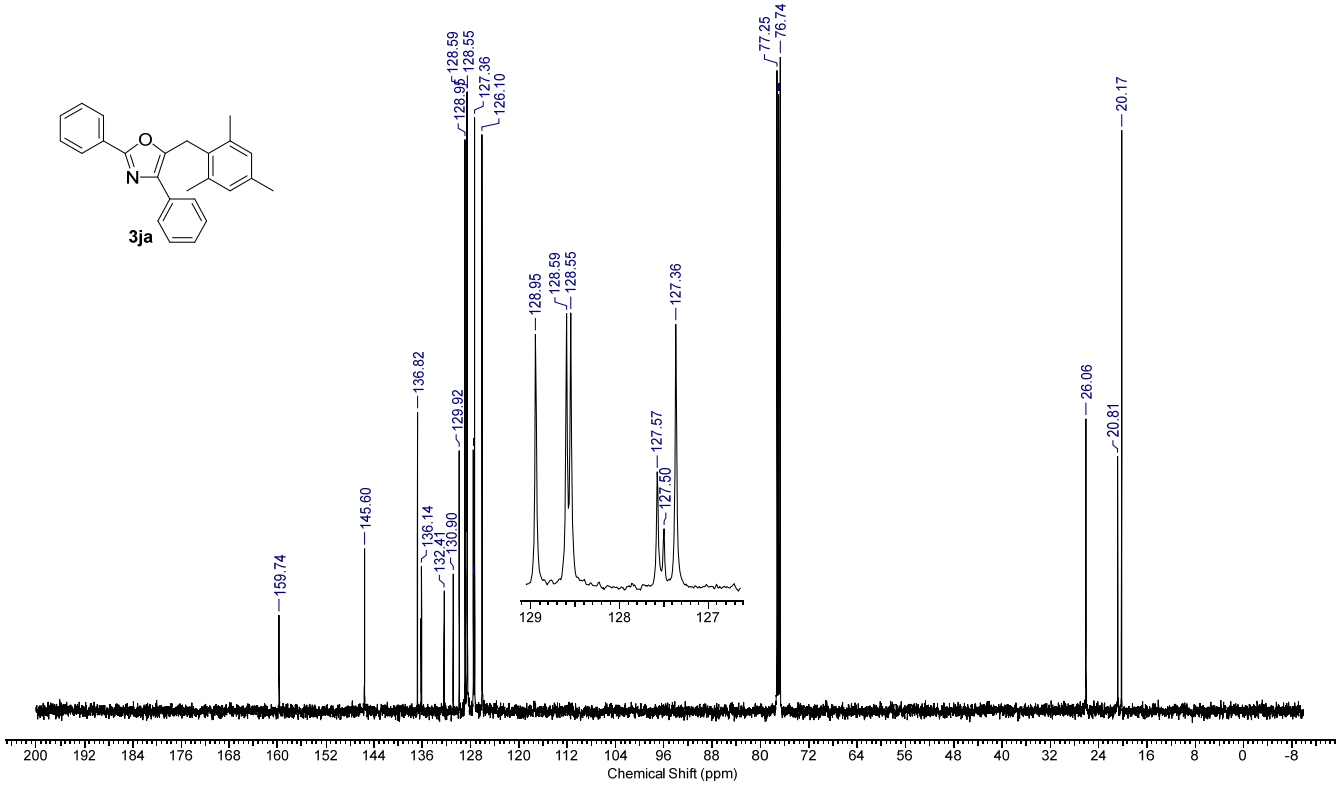
^{13}C NMR (125 MHz, $CDCl_3$) of **3ia**



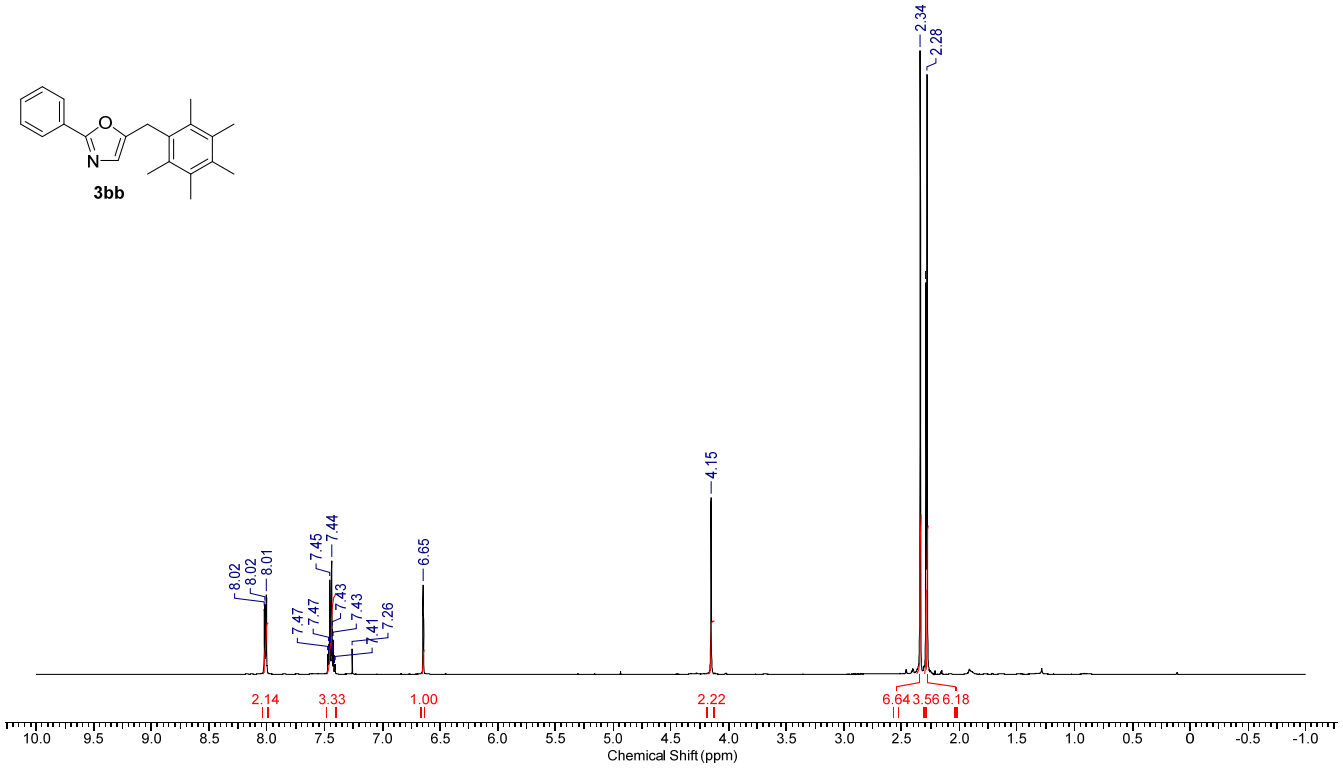
^{1}H NMR (500 MHz, $CDCl_3$) of **3ja**



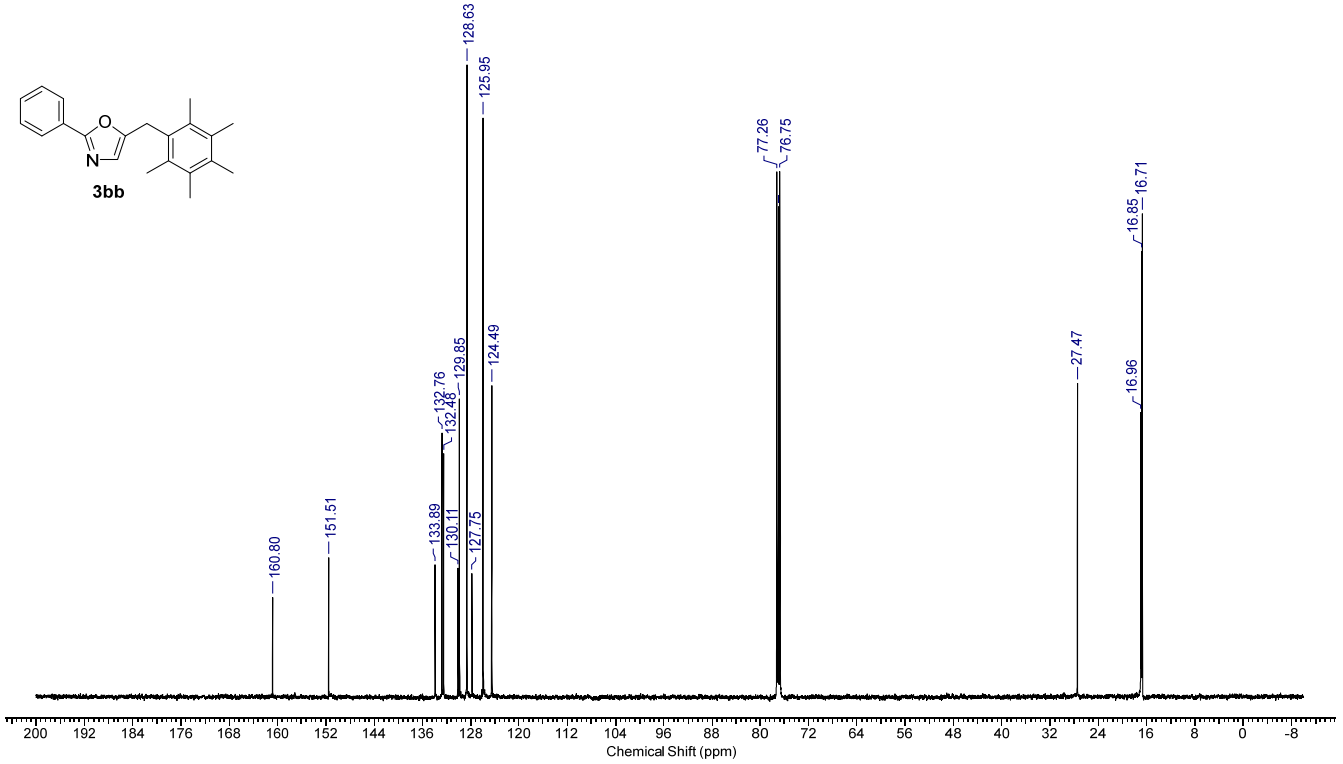
^{13}C NMR (125 MHz, $CDCl_3$) of **3ja**



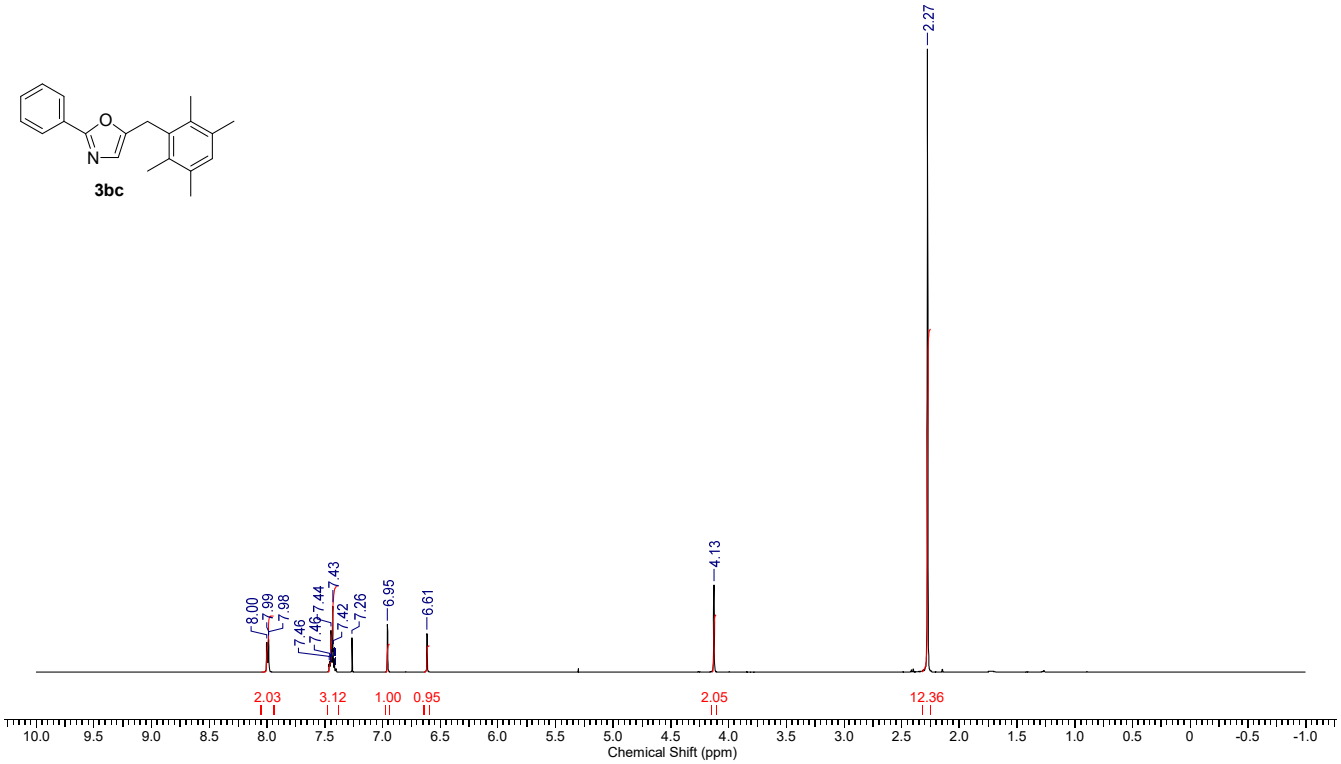
^{1}H NMR (500 MHz, $CDCl_3$) of **3bb**



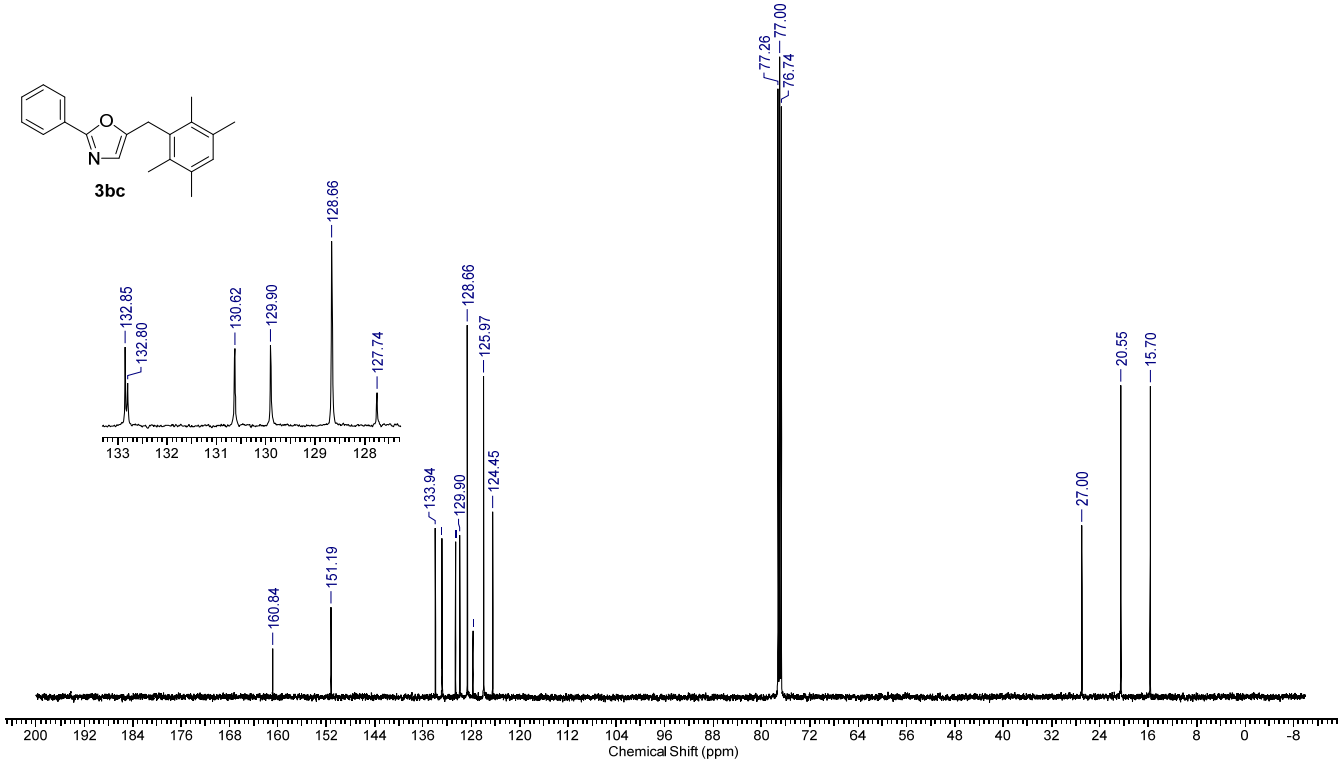
^{13}C NMR (125 MHz, $CDCl_3$) of **3bb**



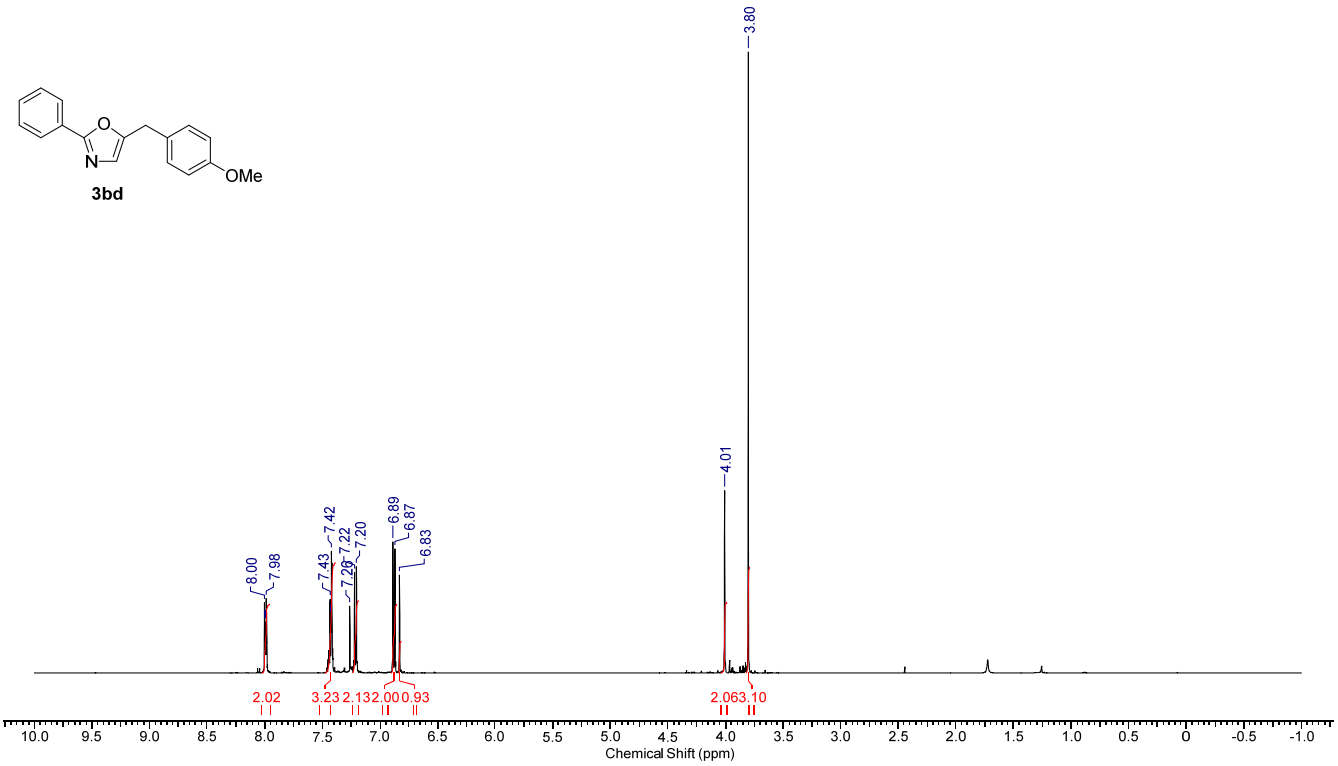
^{1}H NMR (500 MHz, $CDCl_3$) of **3bc**



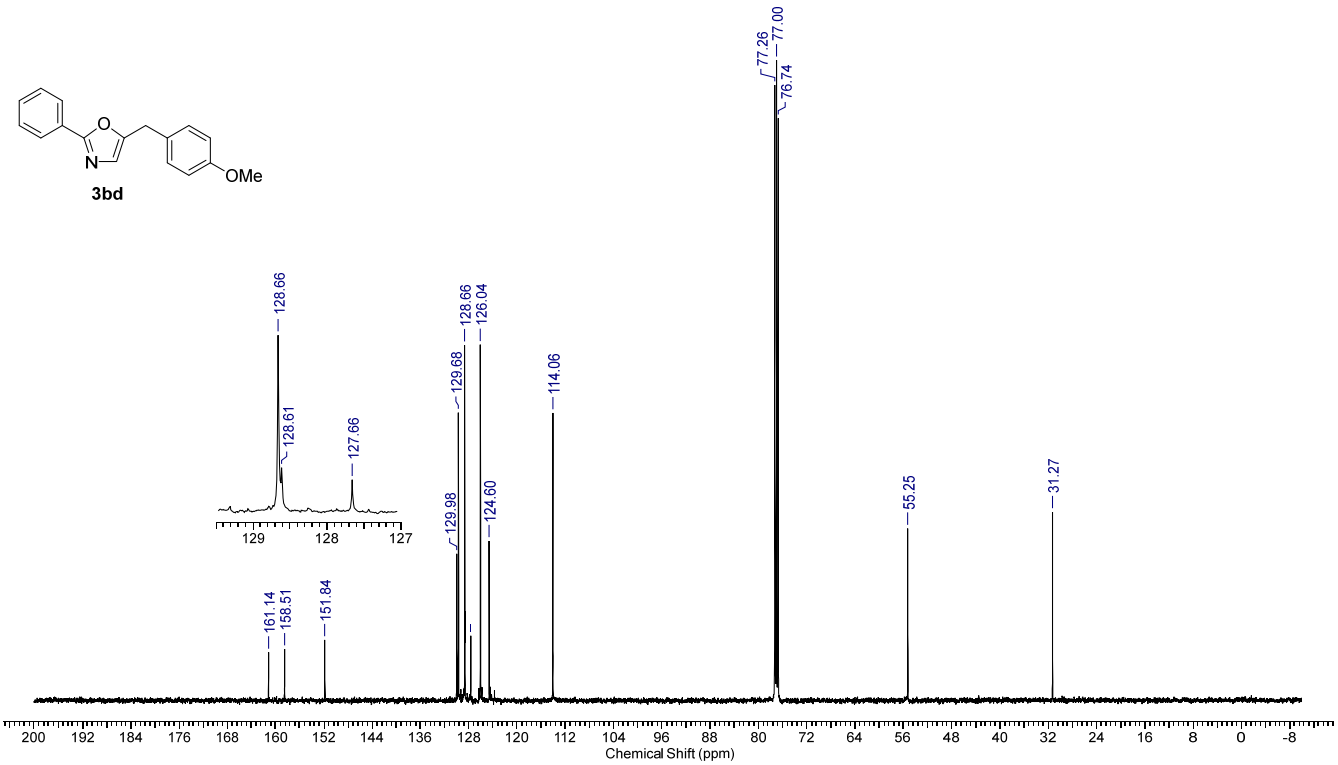
^{13}C NMR (125 MHz, $CDCl_3$) of **3bc**



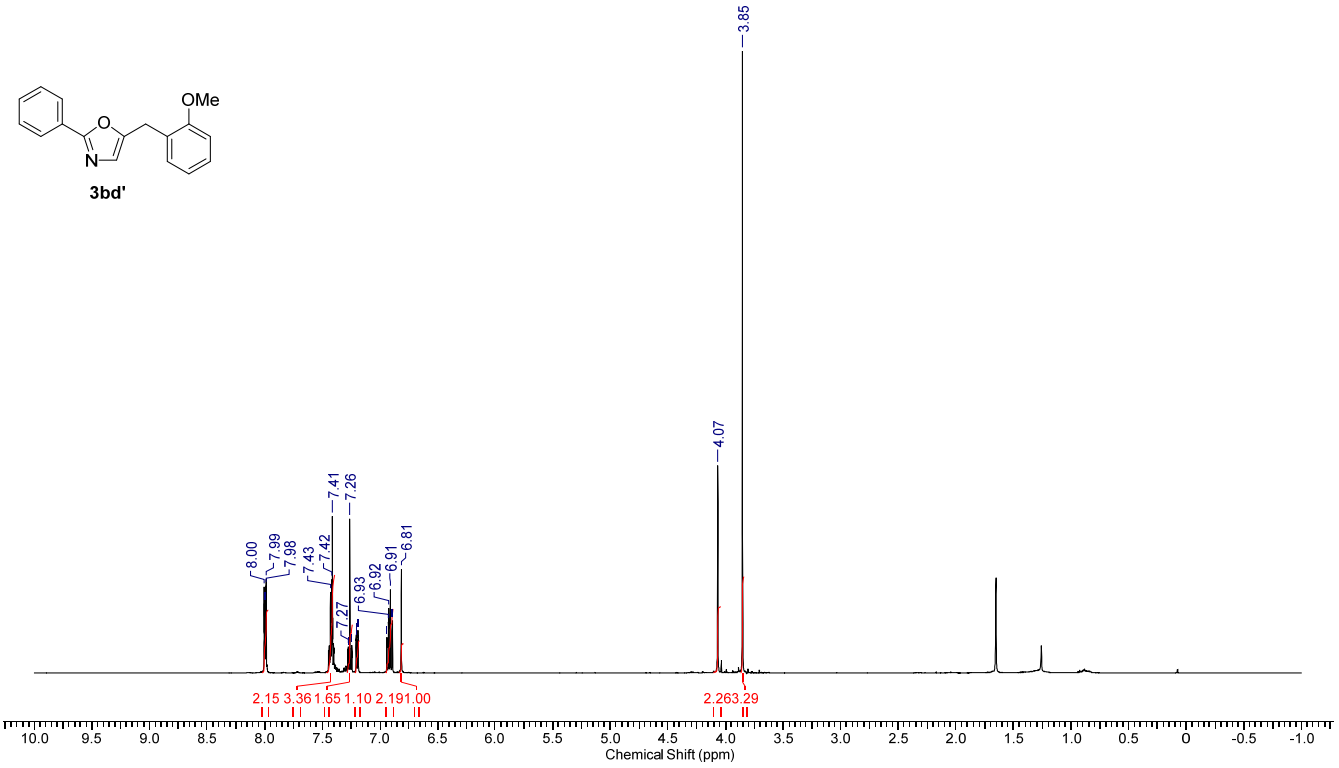
^{1}H NMR (500 MHz, $CDCl_3$) of **3bd**



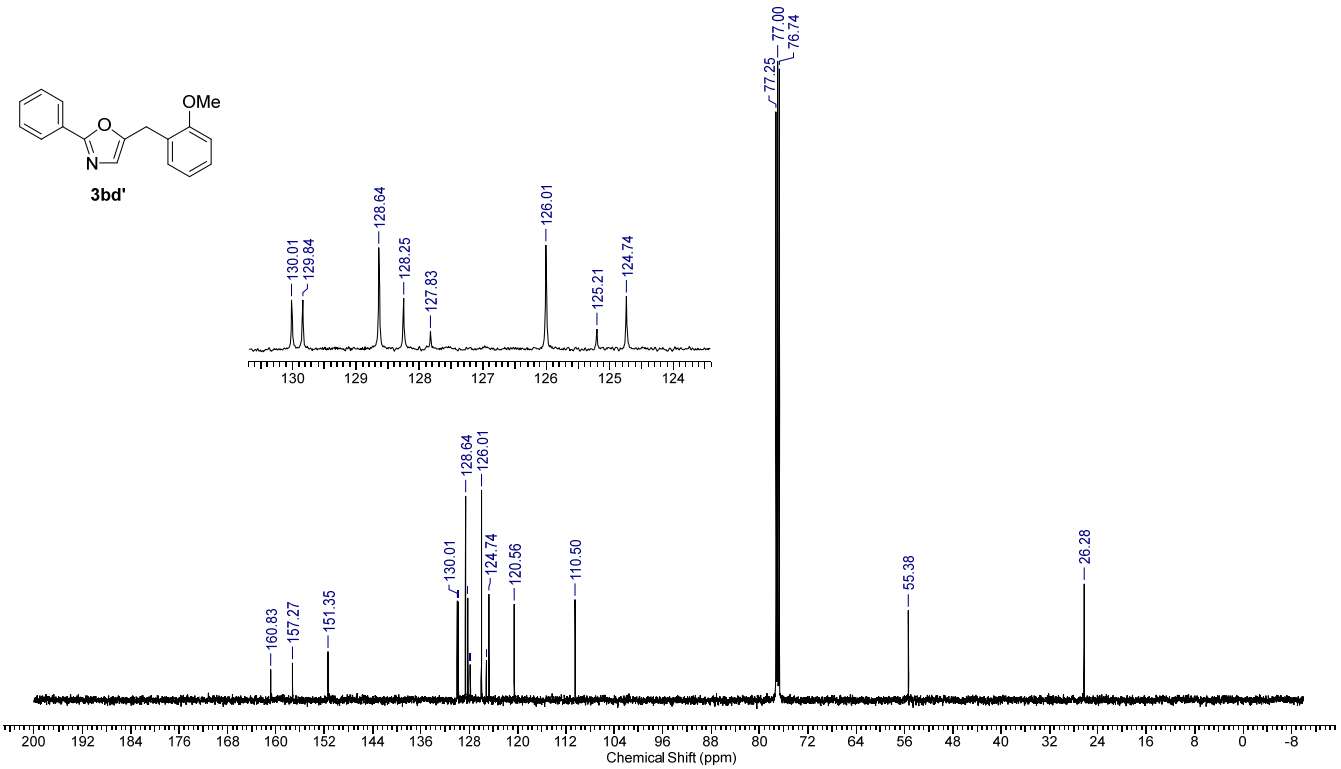
^{13}C NMR (125 MHz, $CDCl_3$) of **3bd**



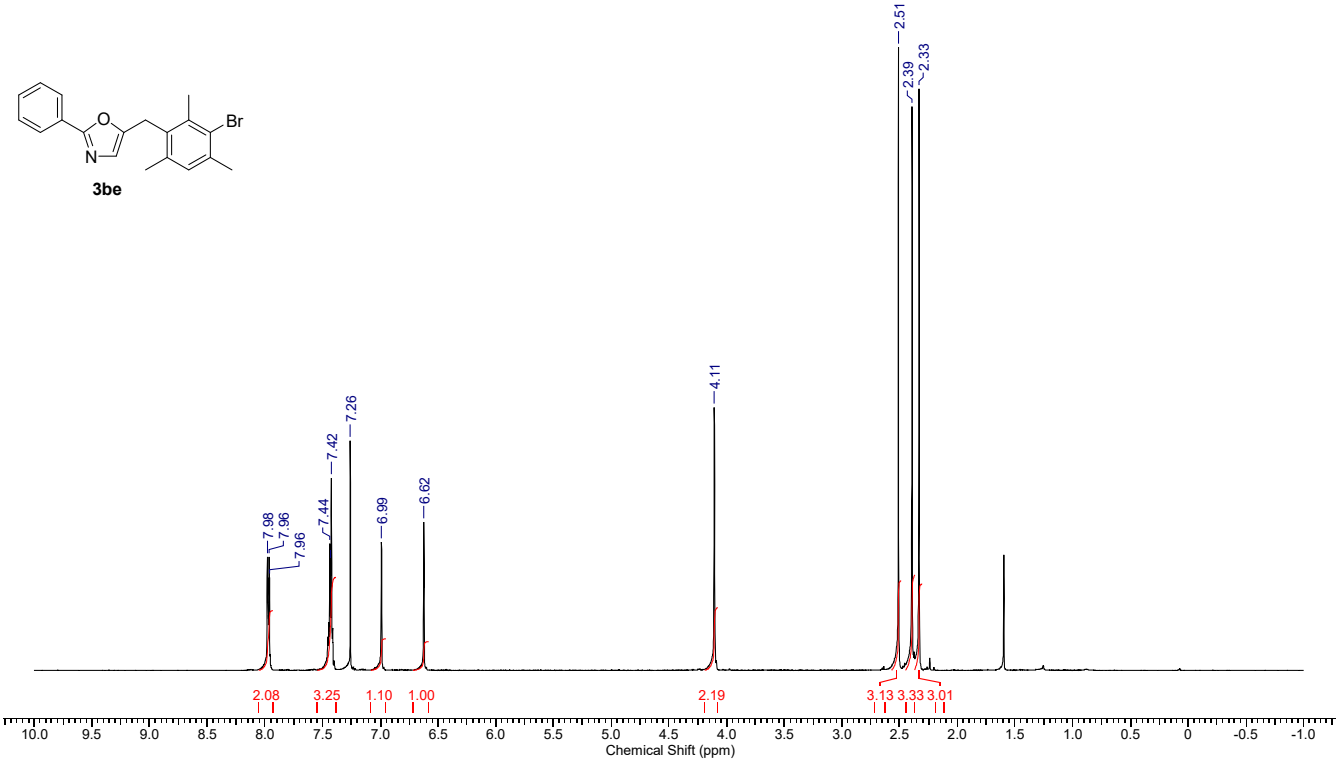
^{1}H NMR (500 MHz, $CDCl_3$) of **3bd'**



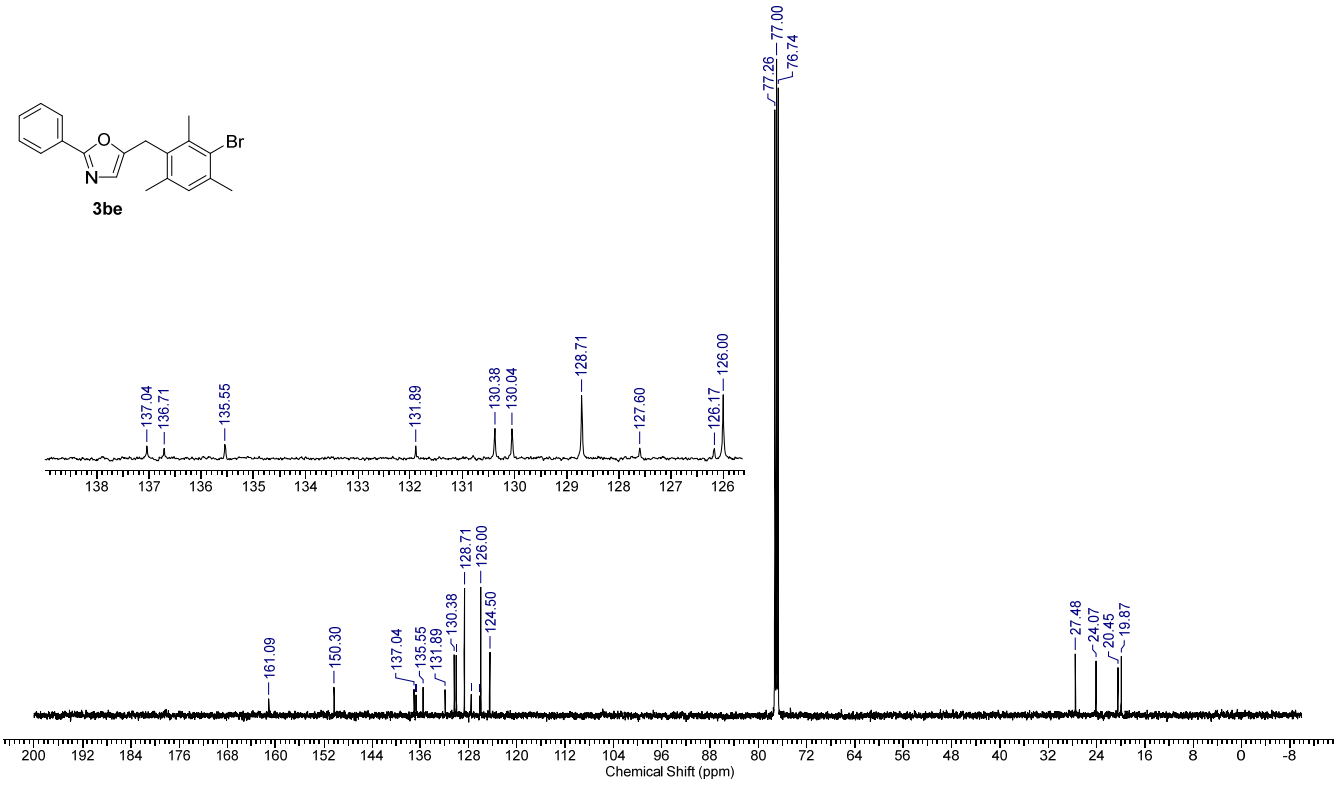
^{13}C NMR (125 MHz, $CDCl_3$) of **3bd'**



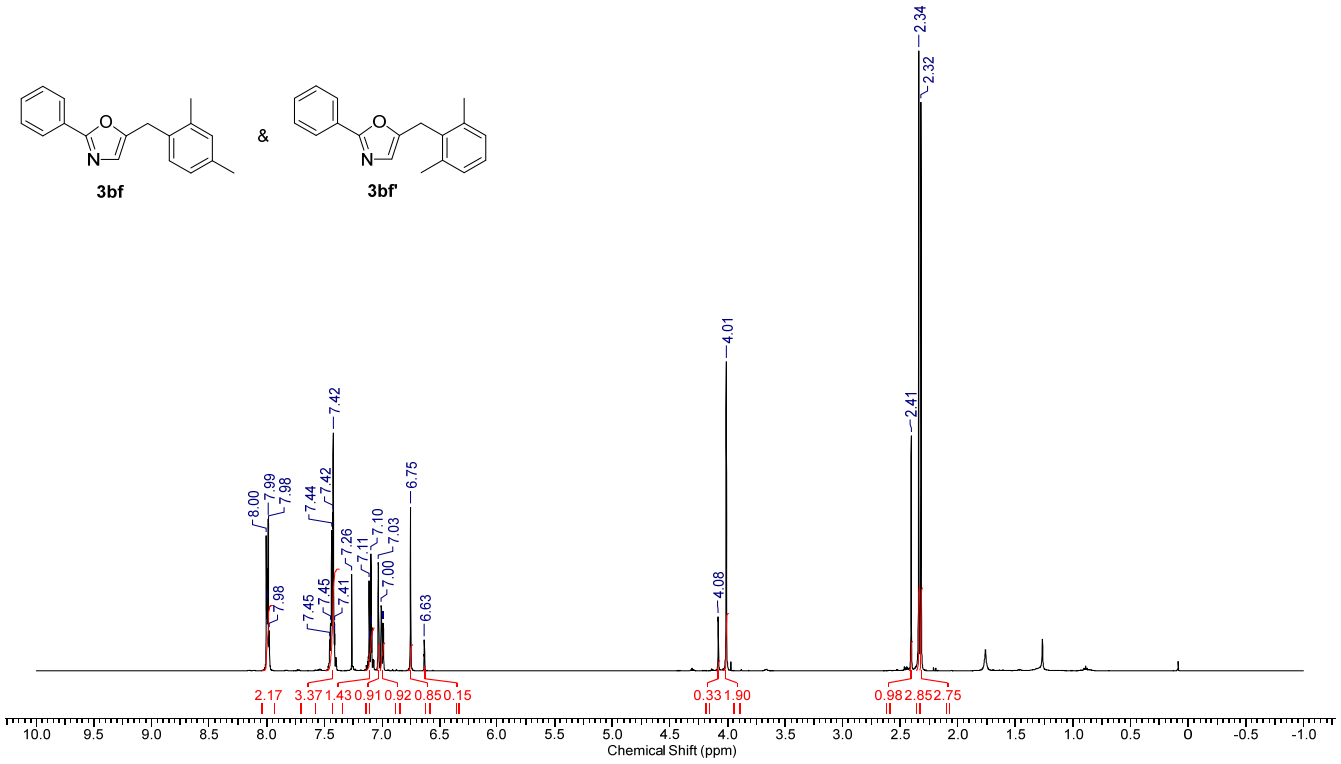
^{1}H NMR (500 MHz, $CDCl_3$) of **3be**



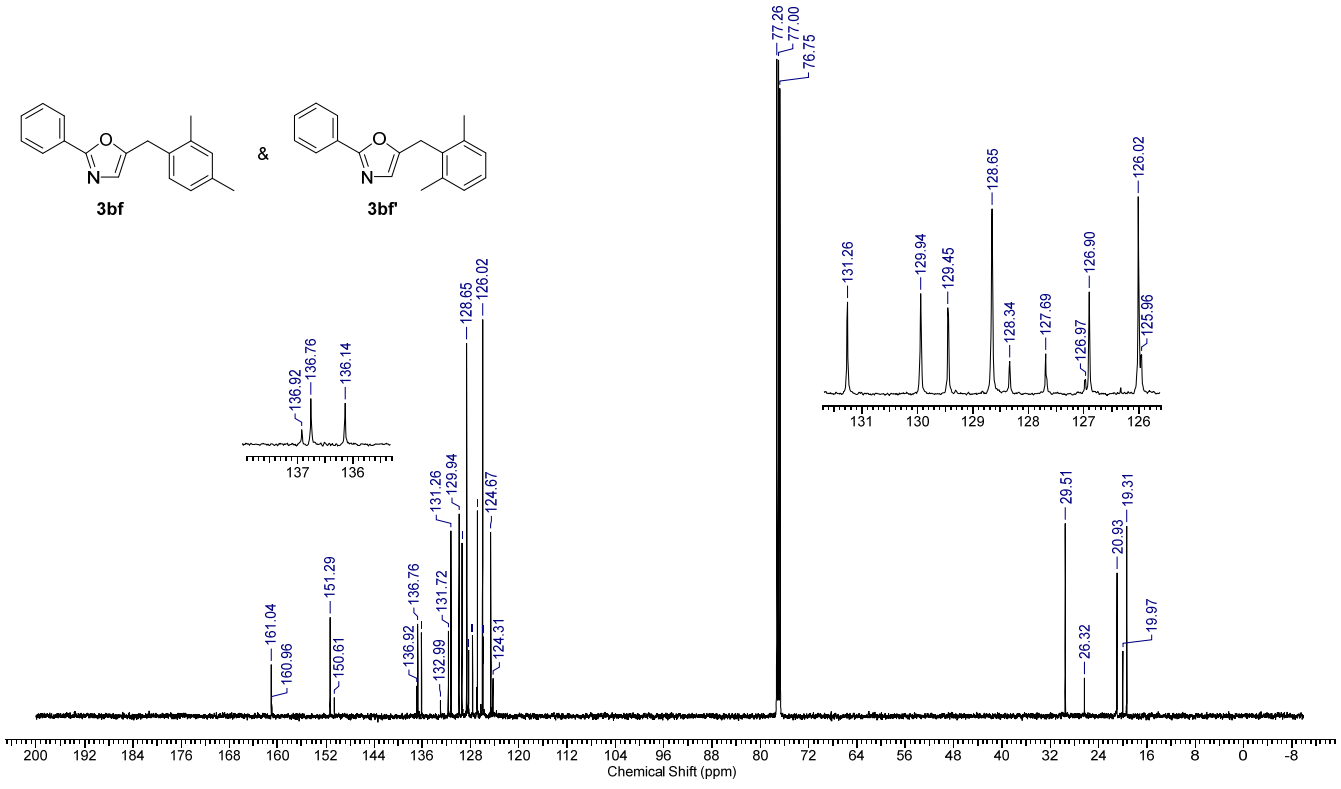
^{13}C NMR (125 MHz, $CDCl_3$) of **3be**



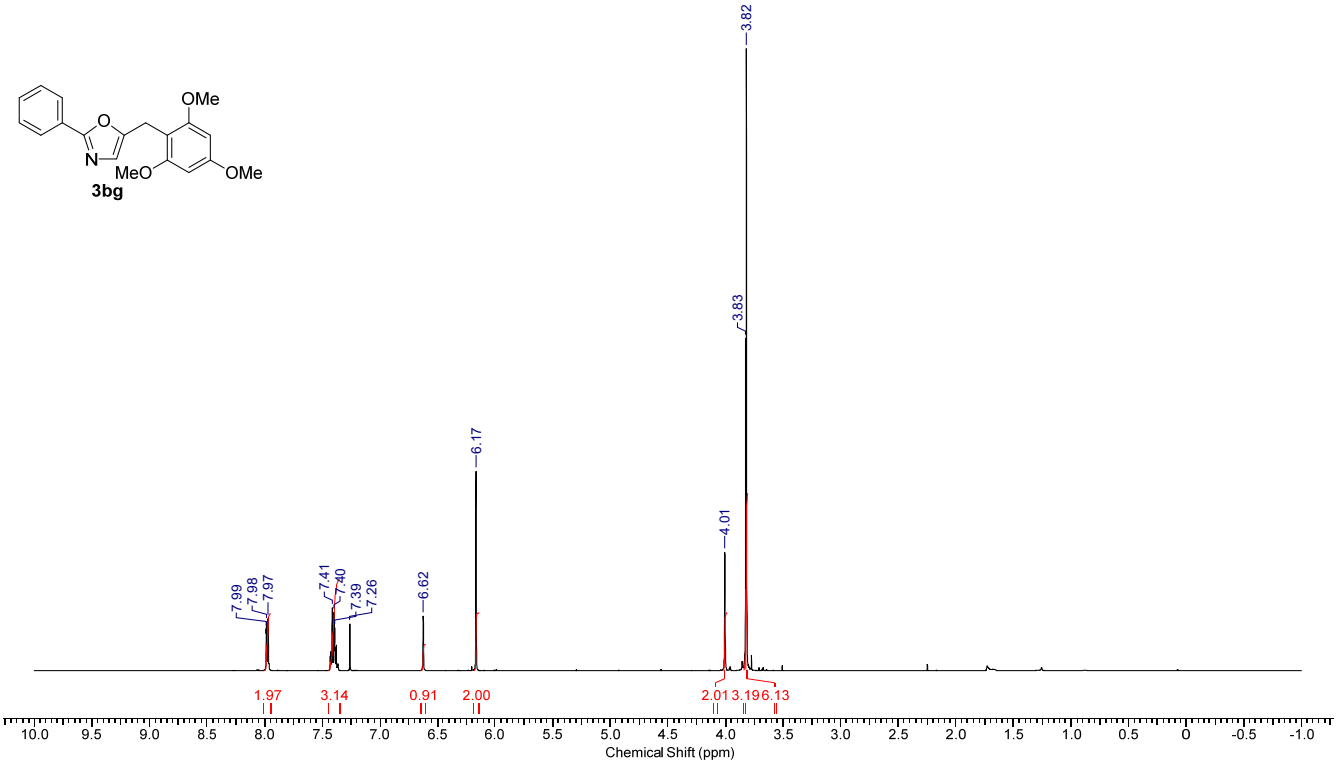
^{1}H NMR (500 MHz, $CDCl_3$) of **3bf** and **3bf'**



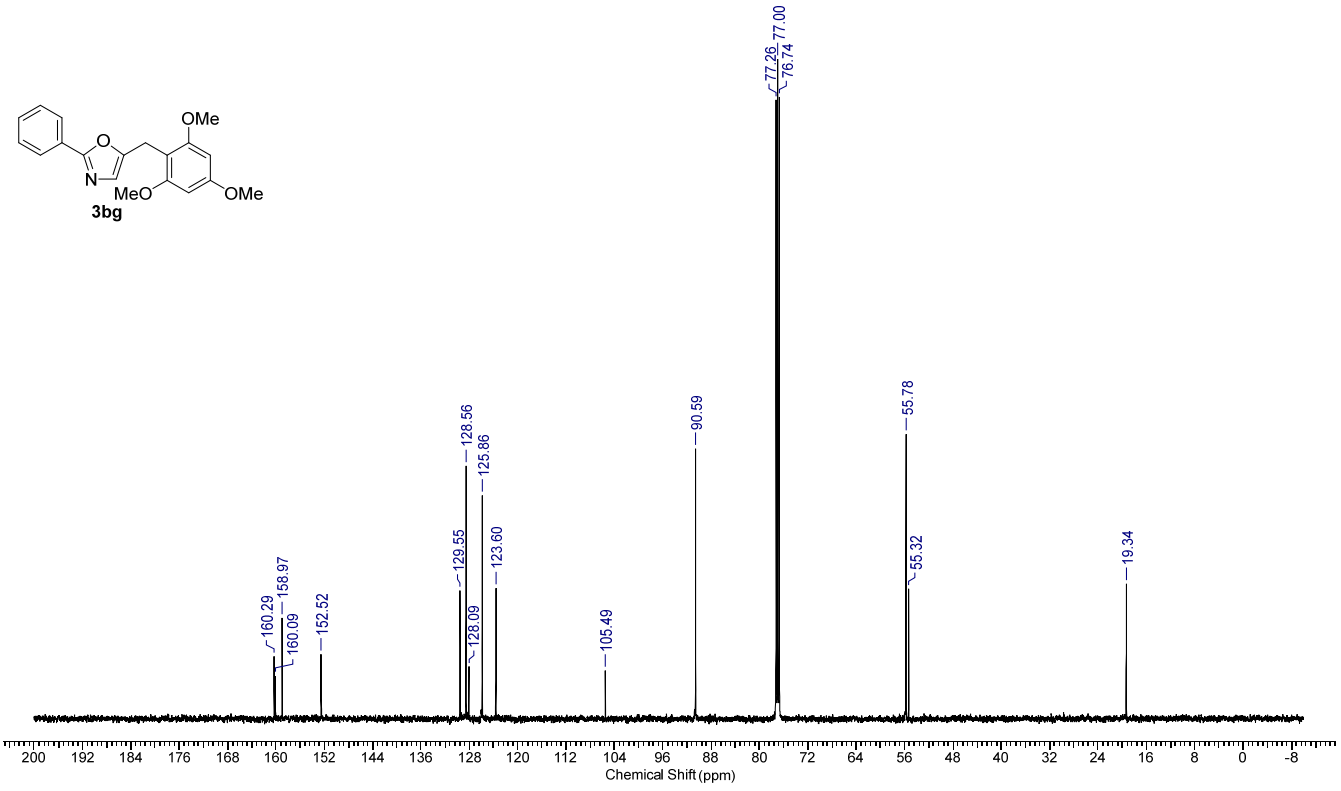
^{13}C NMR (125 MHz, $CDCl_3$) of **3bf** and **3bf'**



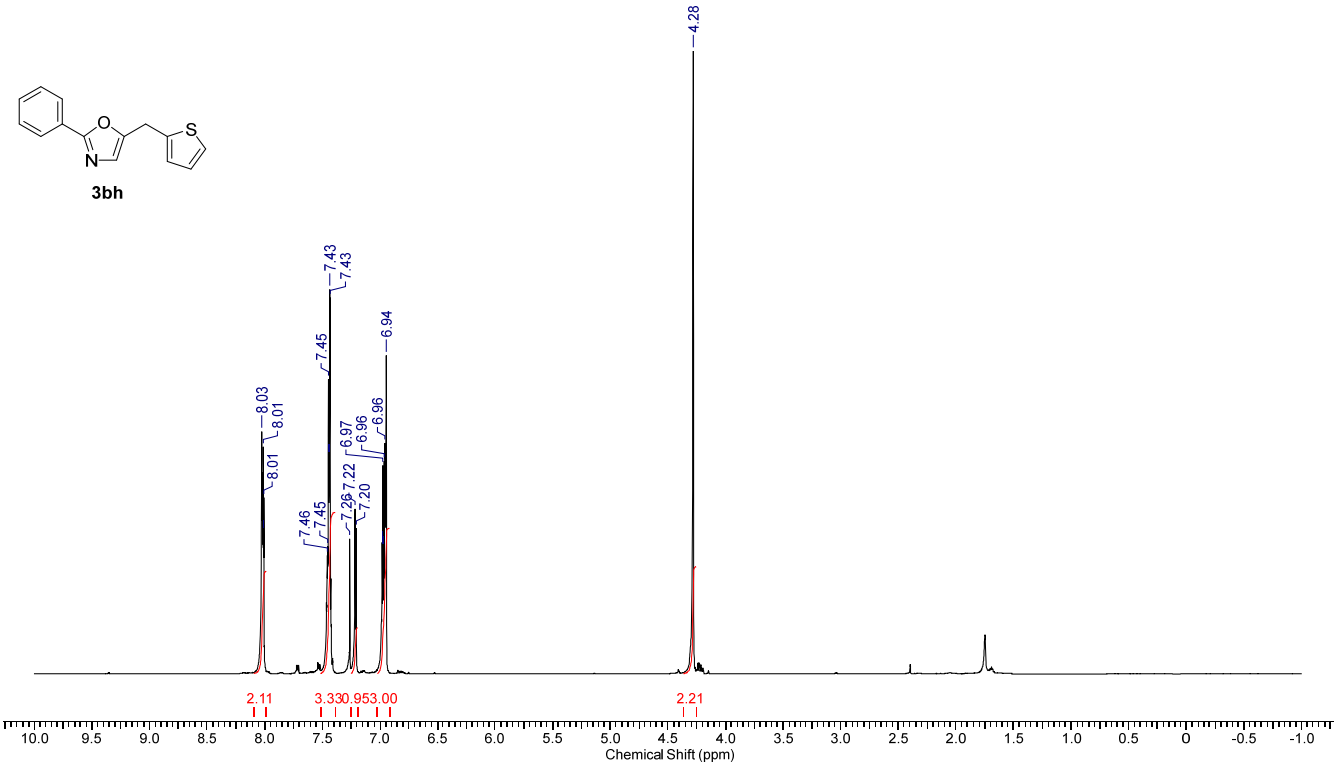
^{1}H NMR (500 MHz, $CDCl_3$) of **3bg**



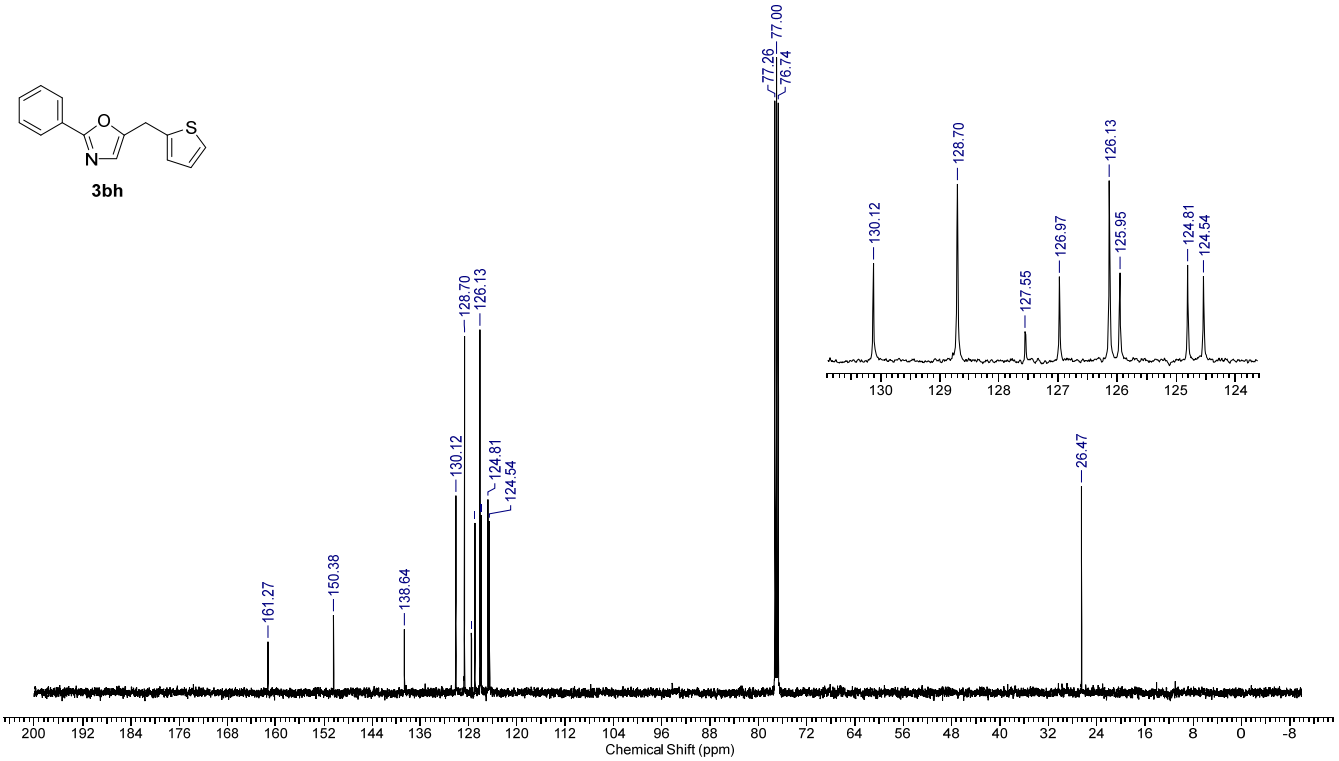
^{13}C NMR (125 MHz, $CDCl_3$) of **3bg**



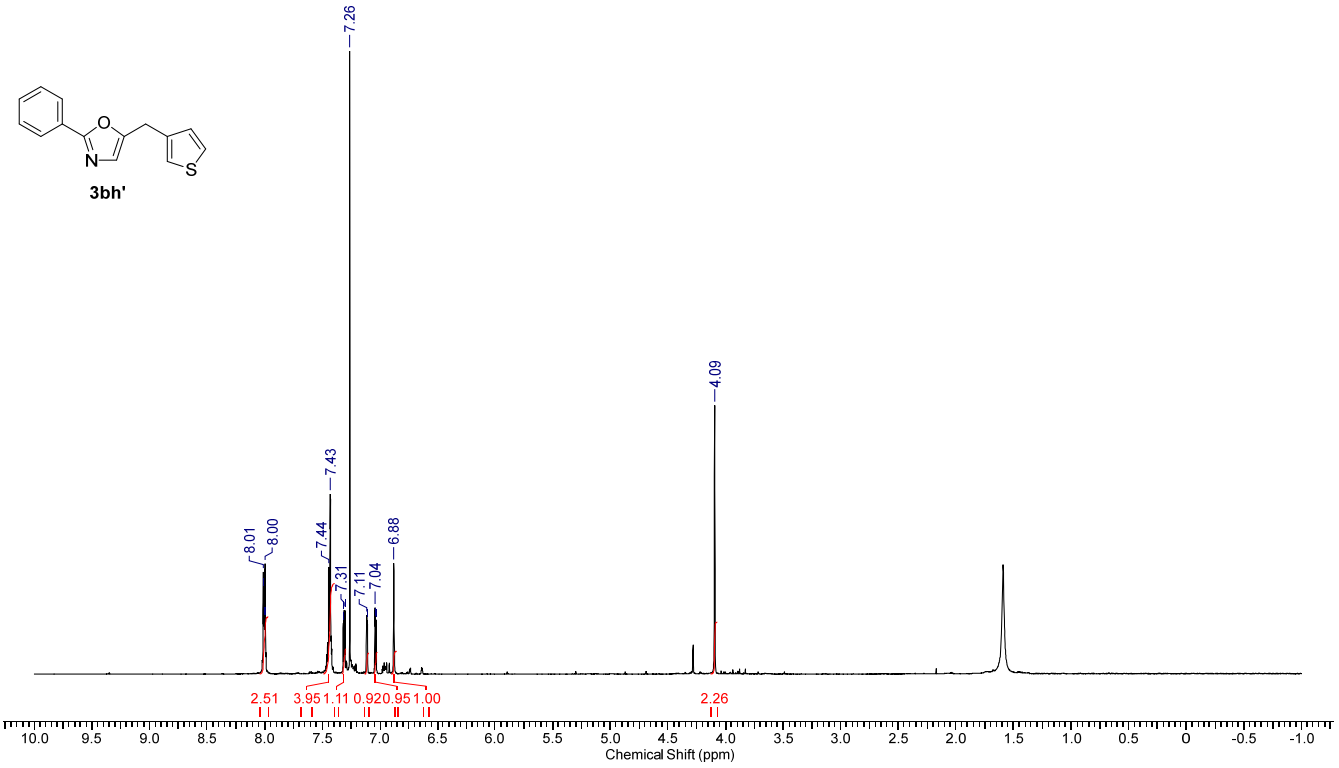
^{1}H NMR (500 MHz, $CDCl_3$) of **3bh**



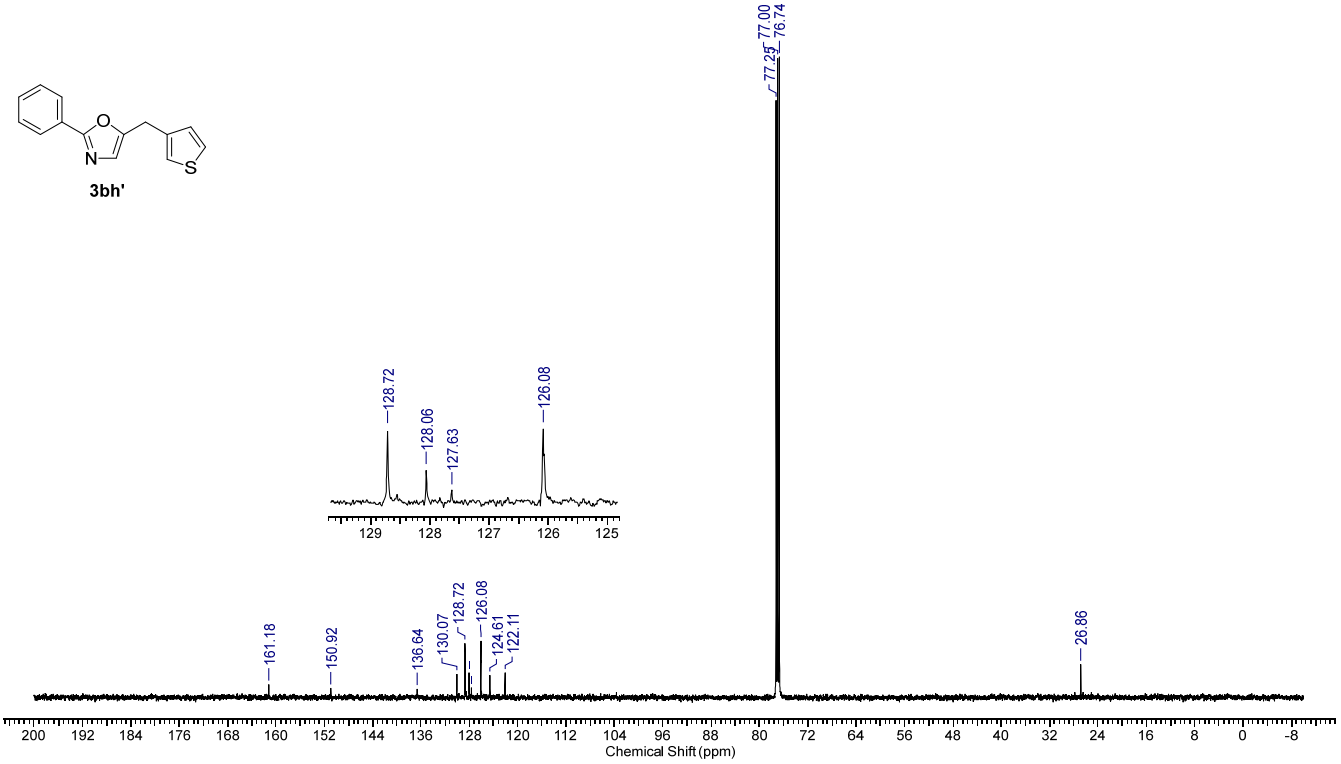
^{13}C NMR (125 MHz, $CDCl_3$) of **3bh**



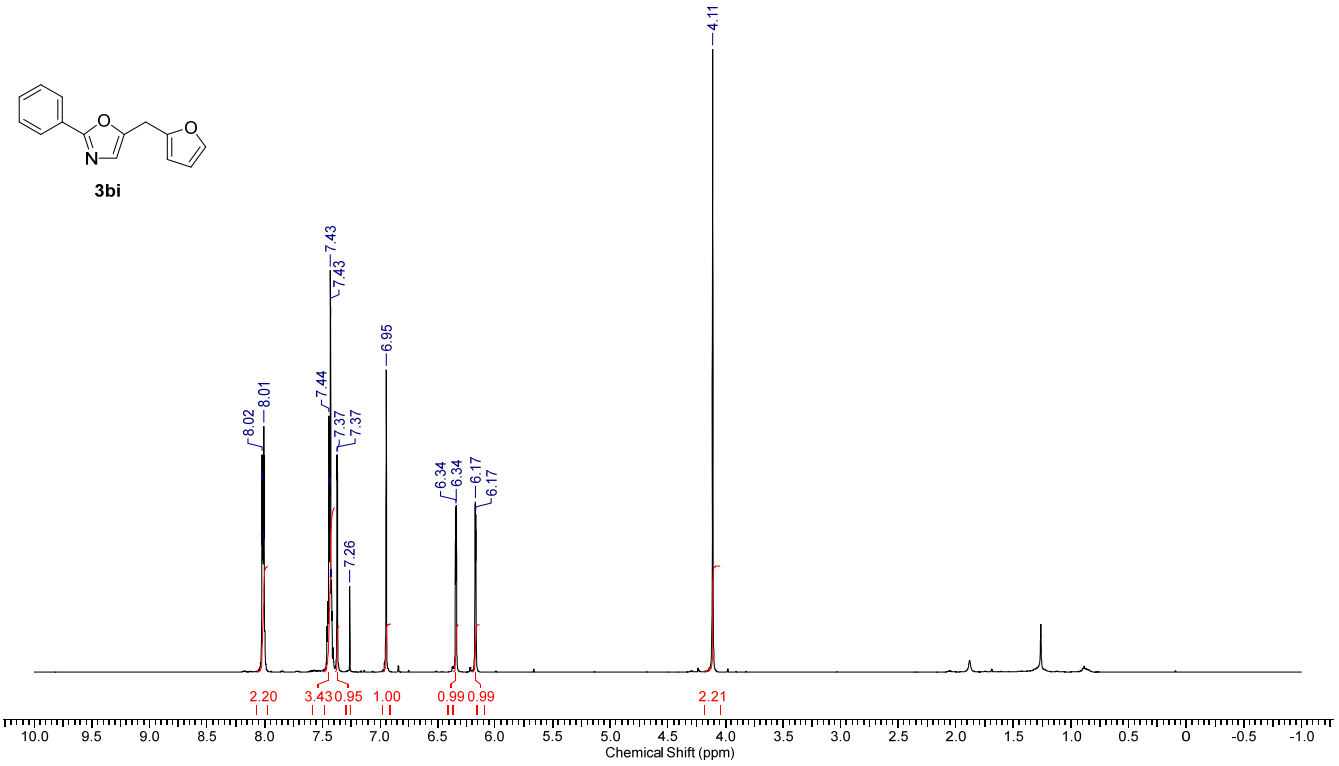
^{1}H NMR (500 MHz, $CDCl_3$) of **3bh'**



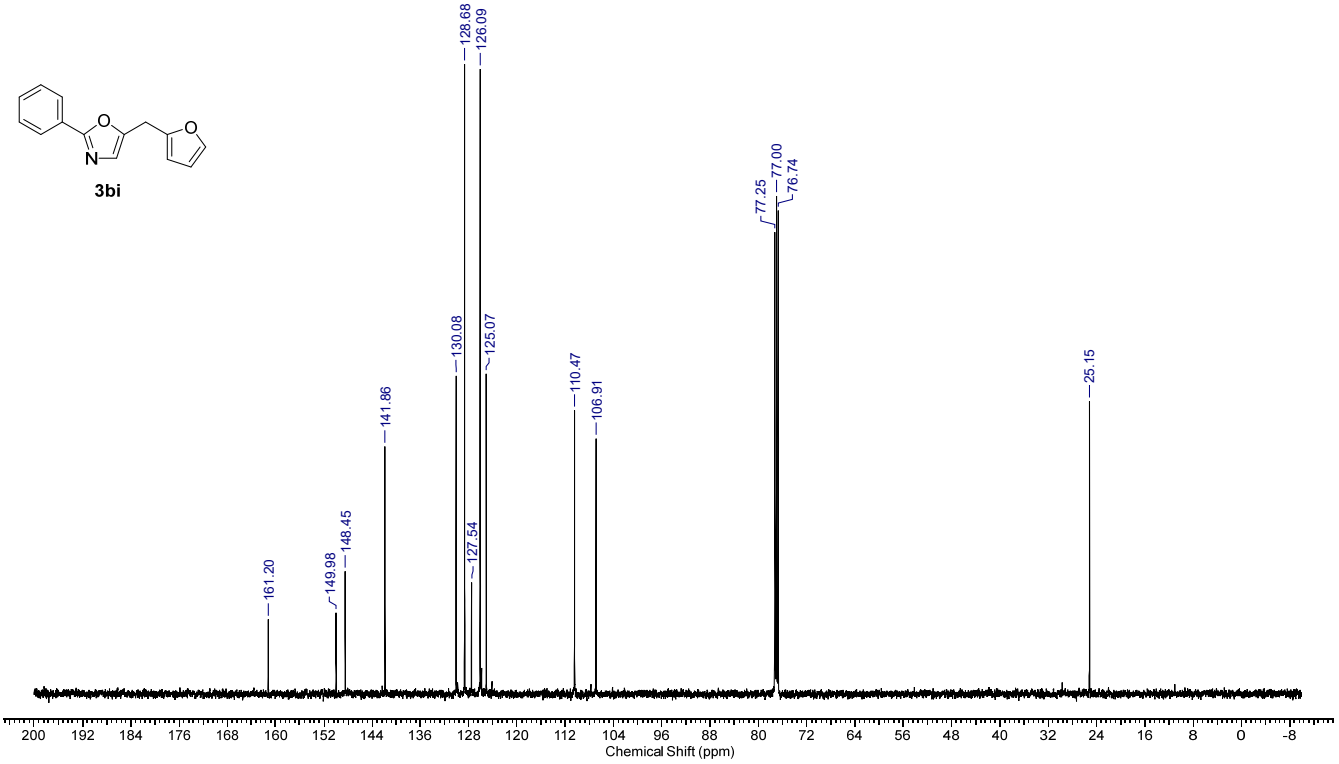
^{13}C NMR (125 MHz, $CDCl_3$) of **3bh'**



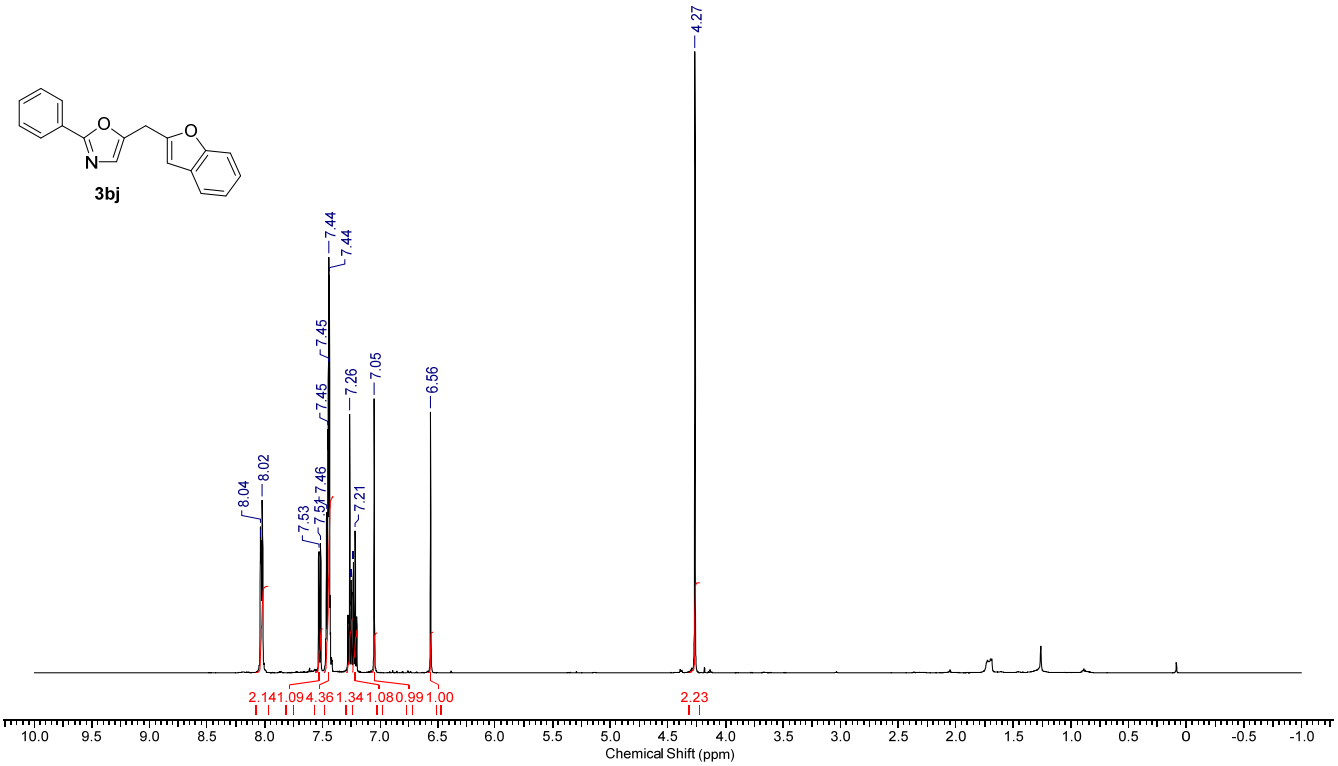
^{1}H NMR (500 MHz, $CDCl_3$) of **3bi**



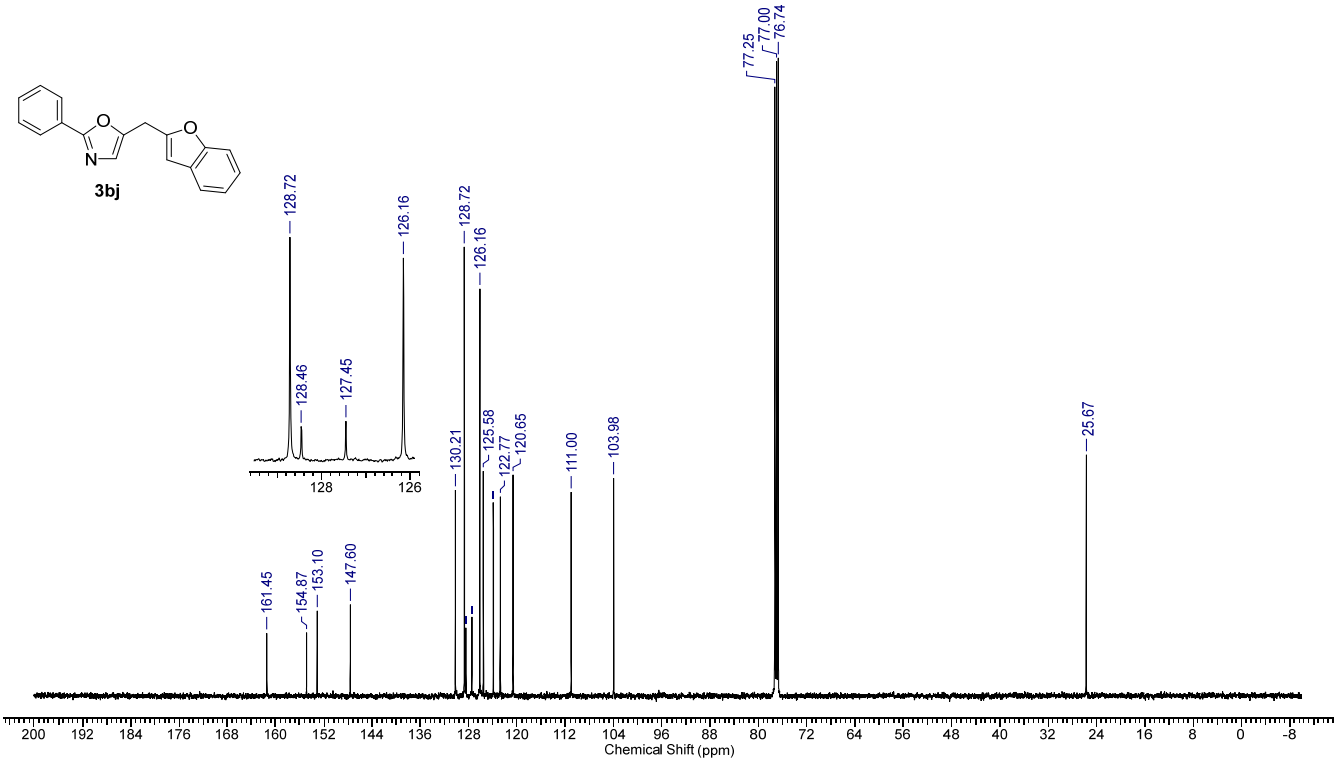
^{13}C NMR (125 MHz, $CDCl_3$) of **3bi**



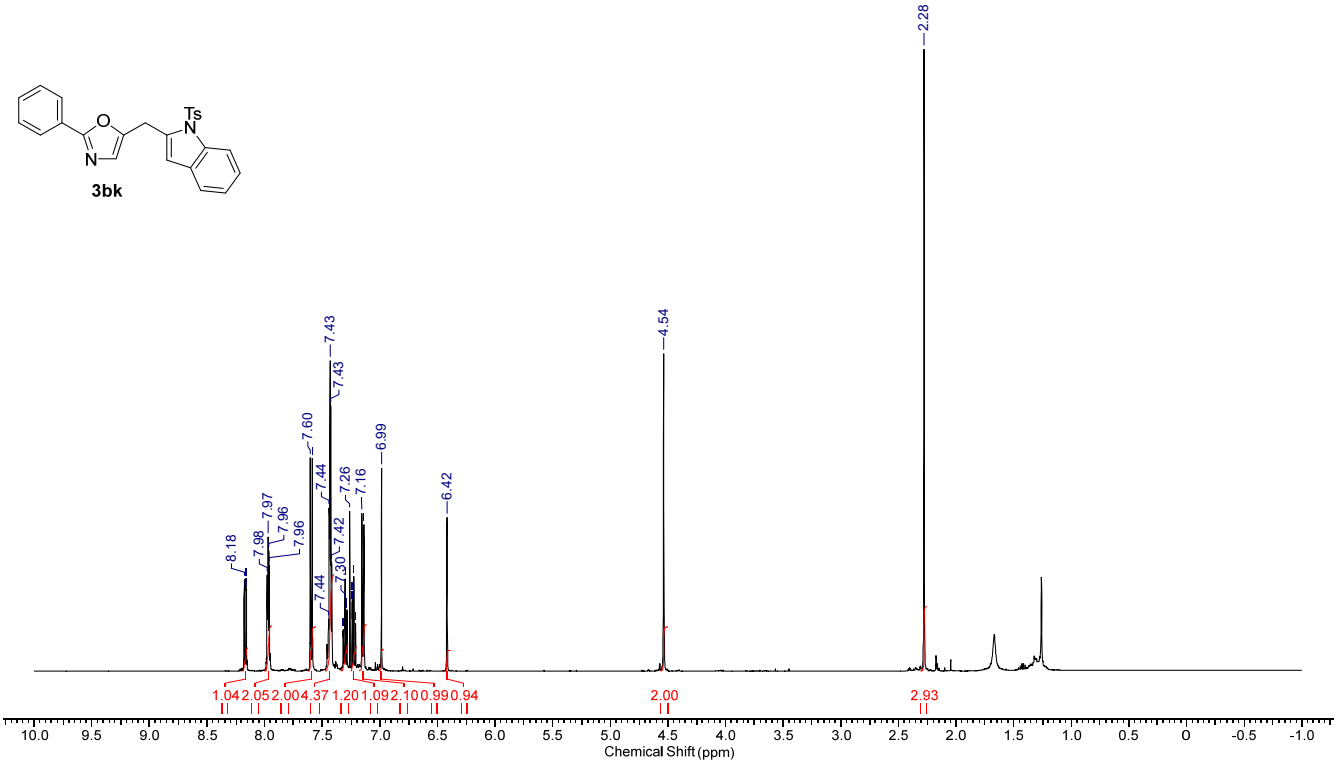
^{1}H NMR (500 MHz, $CDCl_3$) of **3bj**



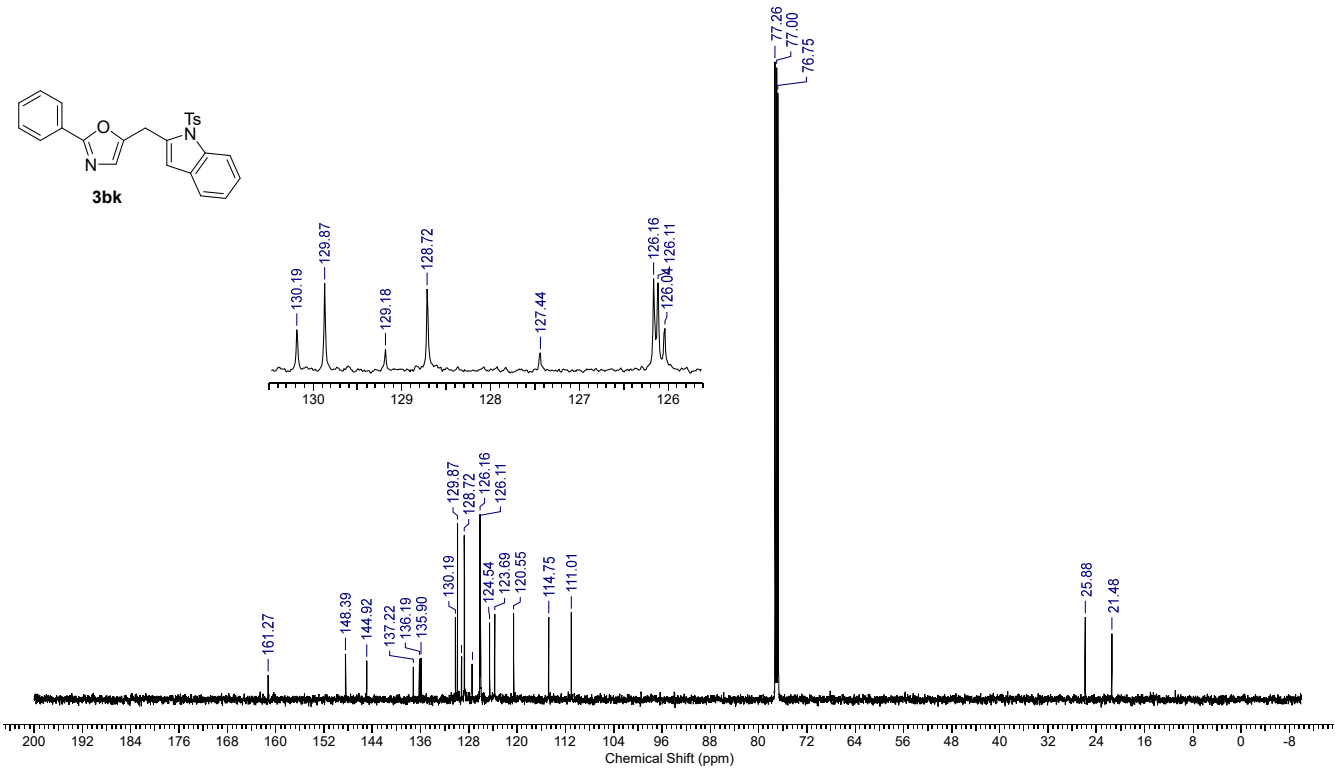
^{13}C NMR (125 MHz, $CDCl_3$) of **3bj**



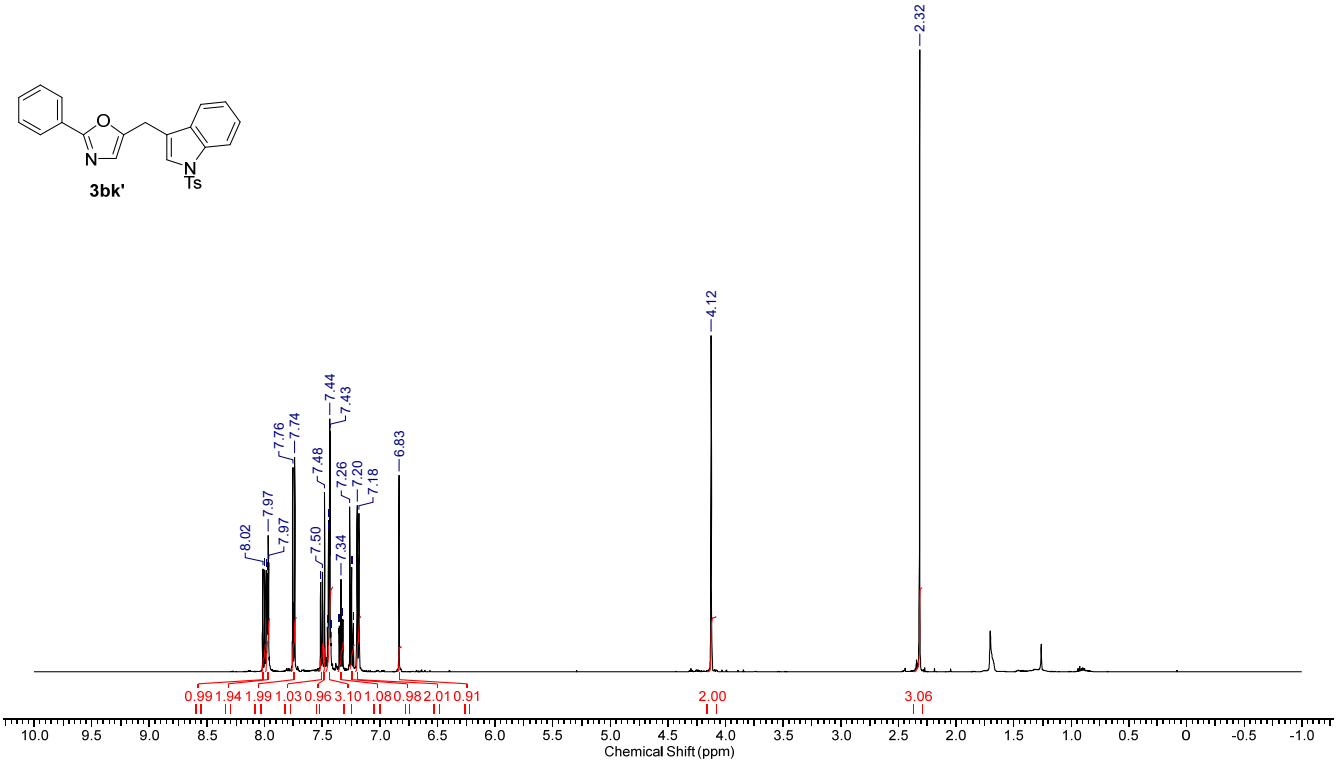
^{1}H NMR (500 MHz, $CDCl_3$) of **3bk**



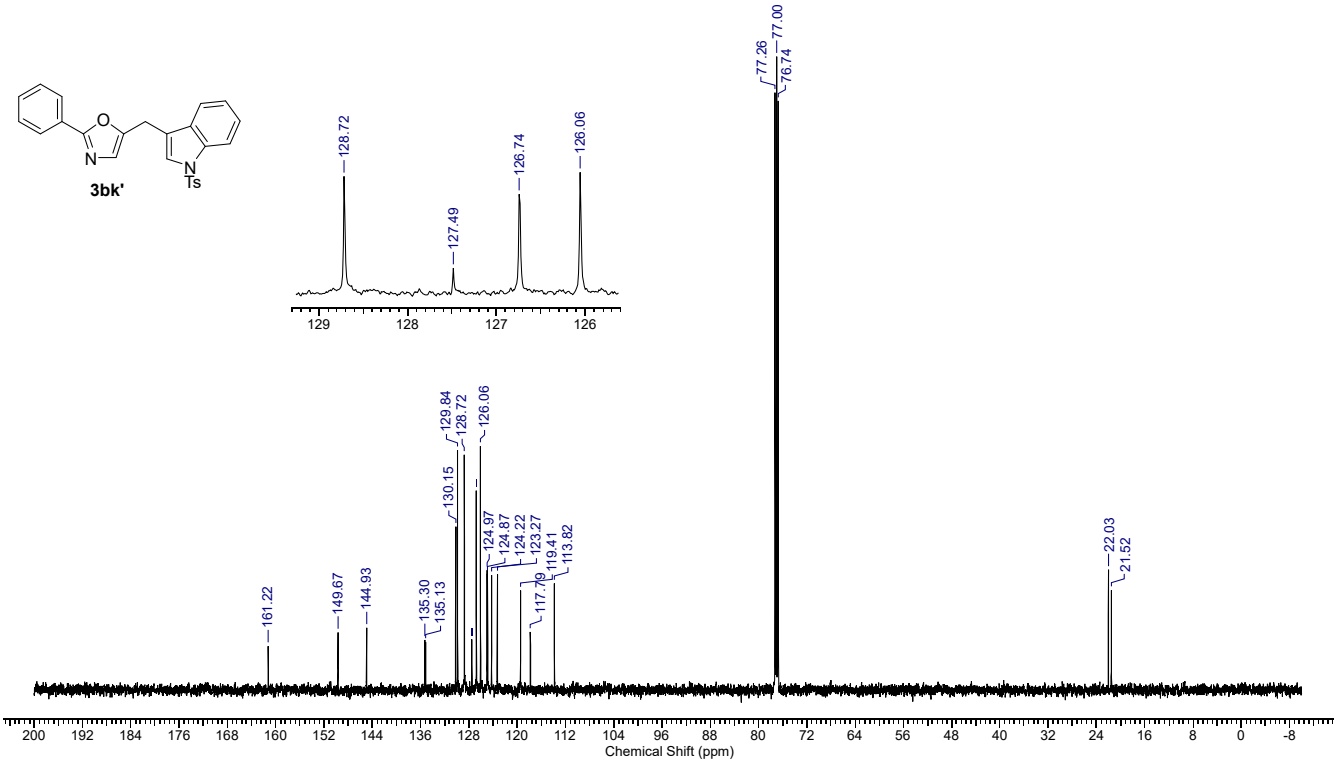
^{13}C NMR (125 MHz, $CDCl_3$) of **3bk**



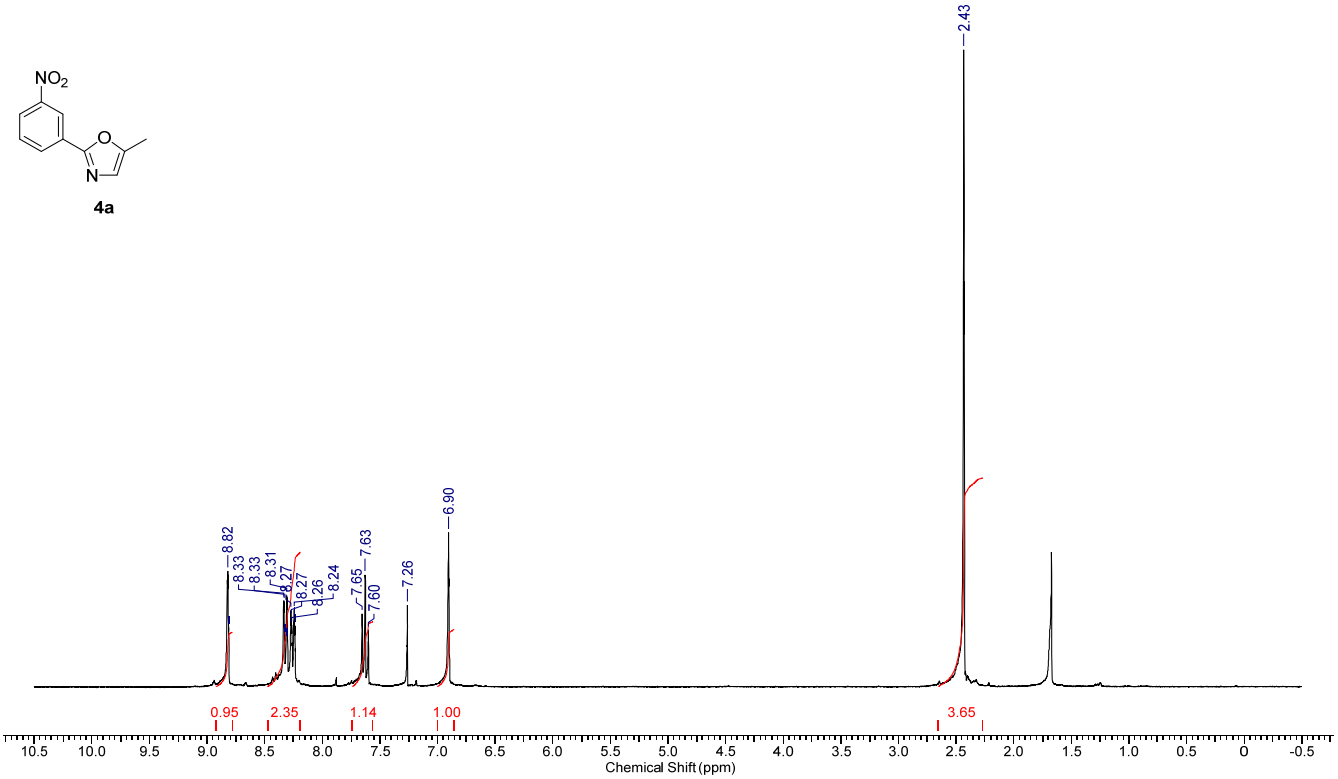
^{1}H NMR (500 MHz, $CDCl_3$) of **3bk'**



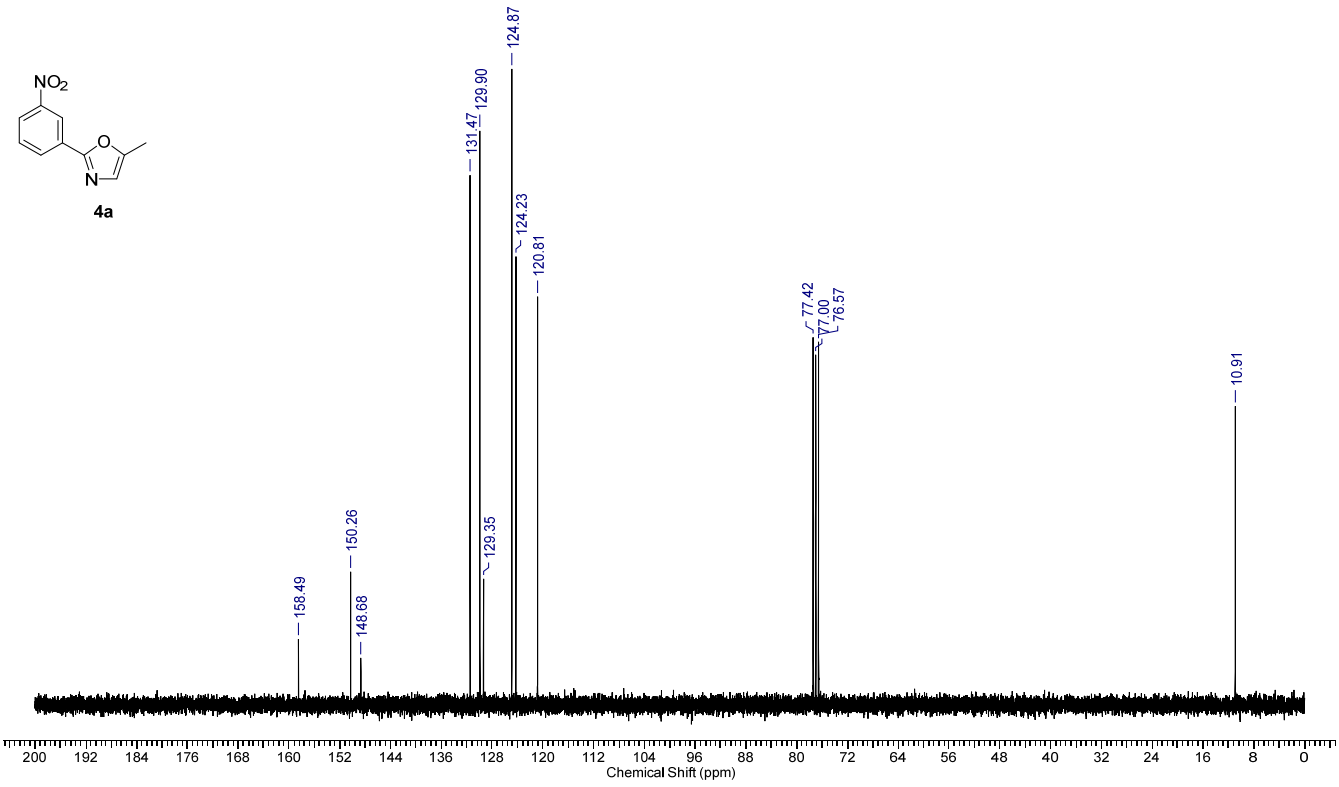
^{13}C NMR (125 MHz, $CDCl_3$) of **3bk'**



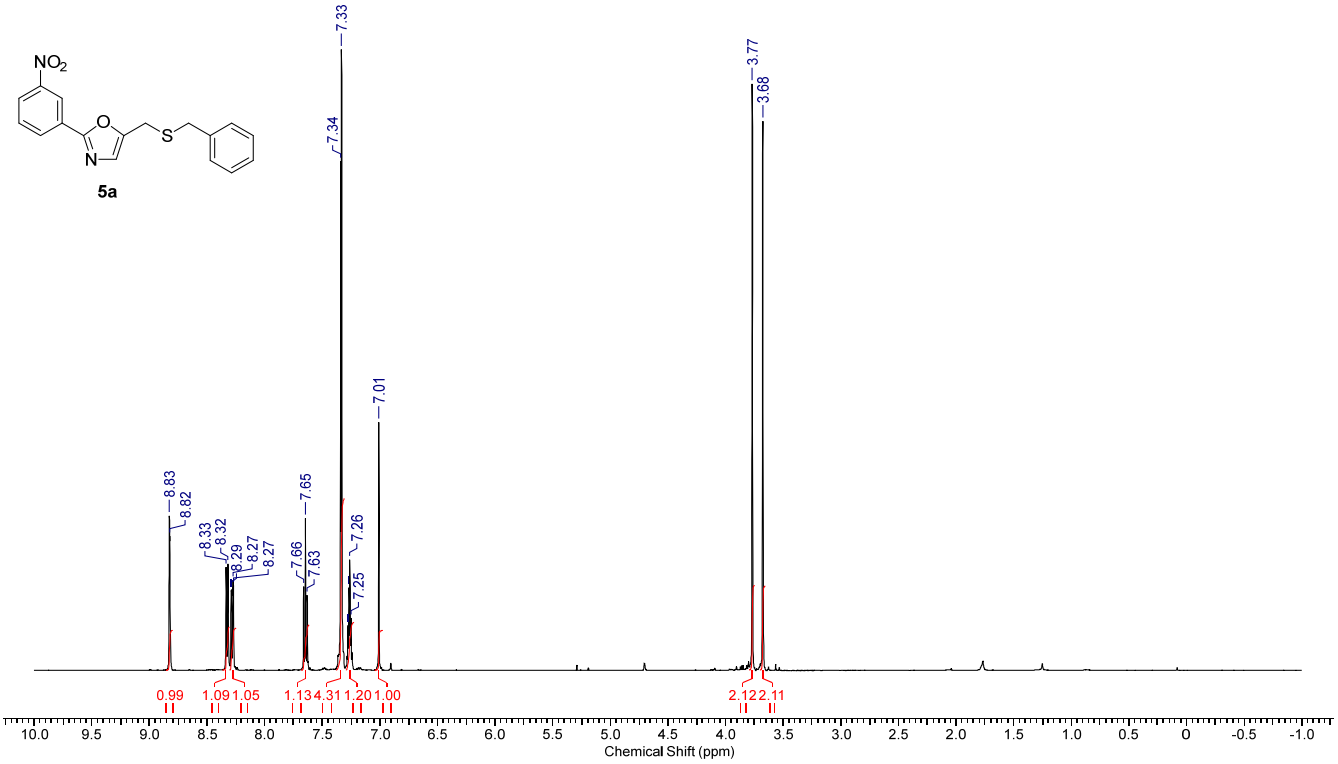
^{1}H NMR (500 MHz, $CDCl_3$) of **4a**



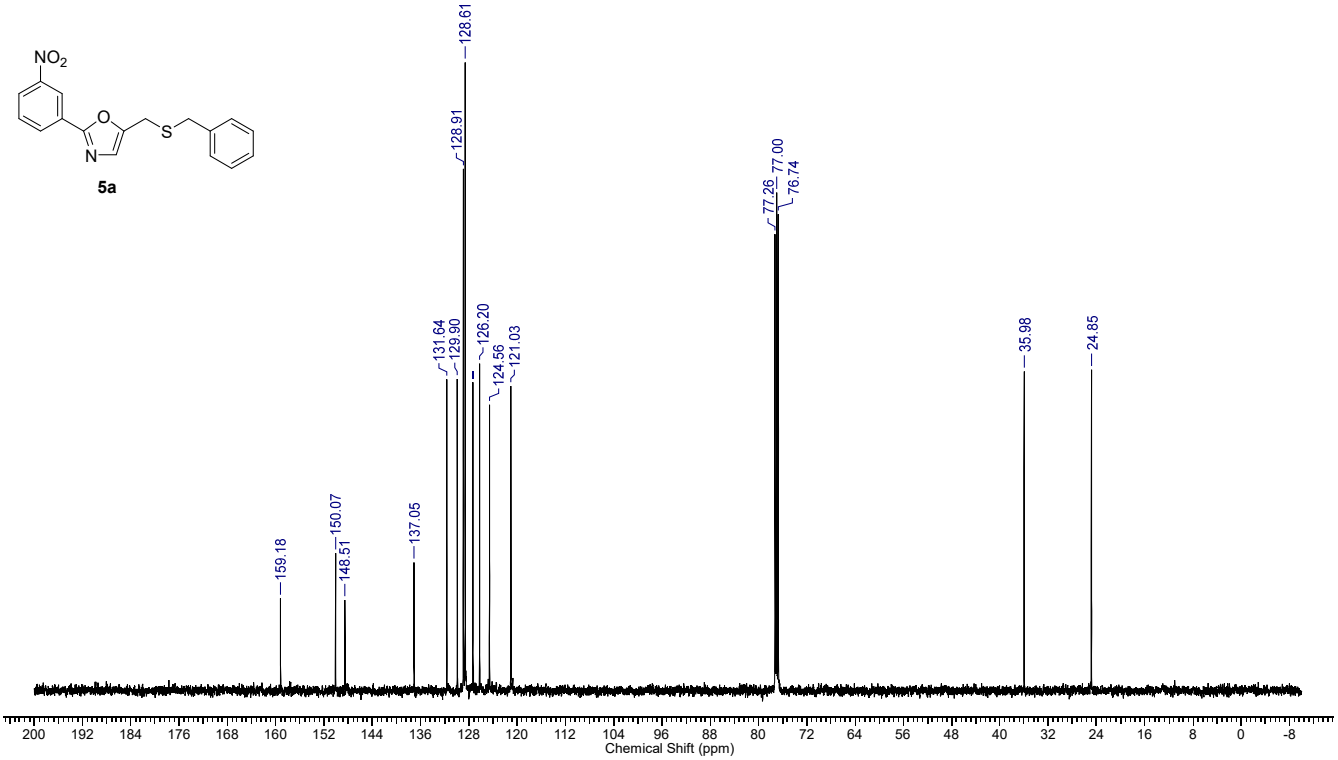
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



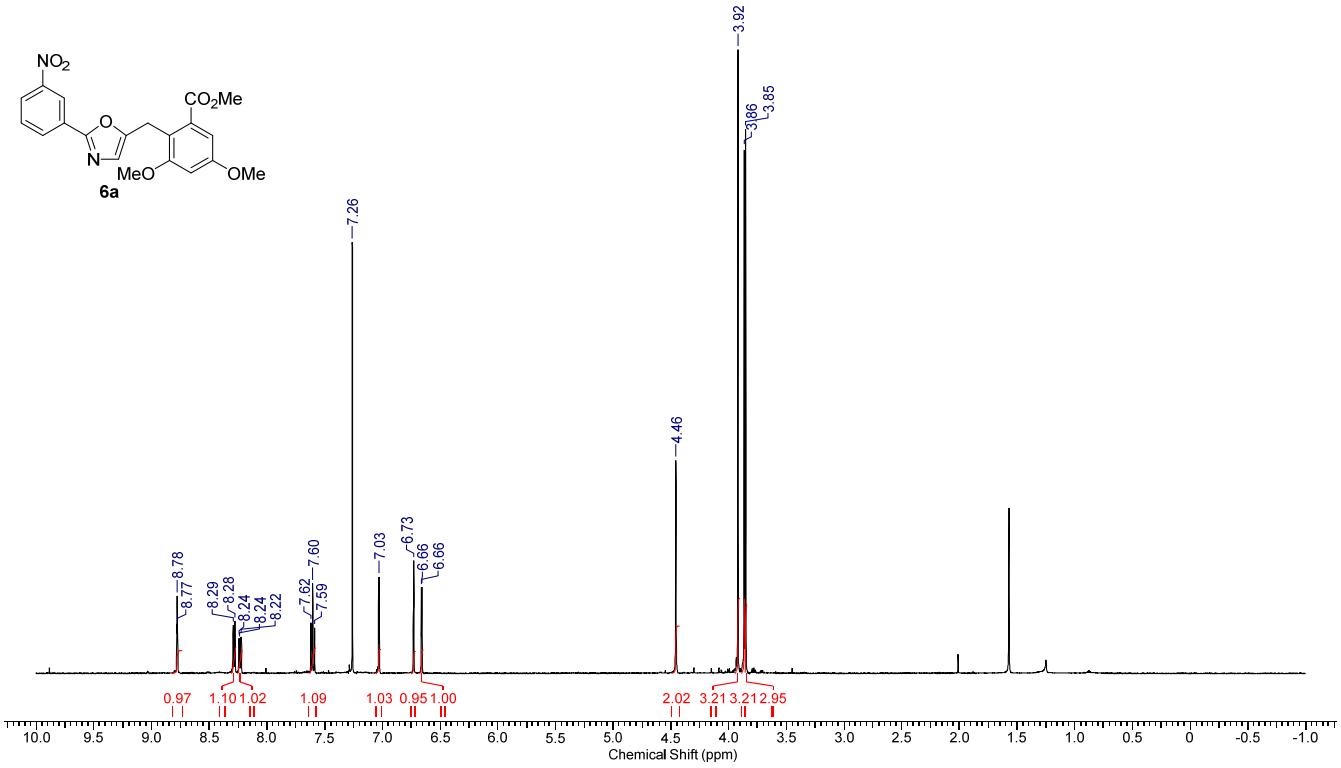
^{1}H NMR (500 MHz, $CDCl_3$) of **5a**



^{13}C NMR (125 MHz, $CDCl_3$) of **5a**



^{1}H NMR (500 MHz, $CDCl_3$) of **6a**



^{13}C NMR (125 MHz, $CDCl_3$) of **6a**