Supporting Information

Iron-Catalyzed Direct α-Arylation of Ethers with Azoles

Arkaitz Correa,[†] Béla Fiser[§] and Enrique Gómez-Bengoa[§]*

[†] *Department of Organic Chemistry I, University of the Basque Country (UPV/EHU)*
Joxe Mari Korta R&D Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián (Spain)
E-mail: arkaitz.correa@ehu.es
[§] *Department of Organic Chemistry I, University of the Basque Country (UPV/EHU),*
P.O. Box 1072, 20080 Donostia-San Sebastián (Spain)

General Considerations

Reagents. Commercially available materials were used without further purification. Anhydrous iron(II) fluoride (FeF_2, 99% purity) was purchased from Strem Chemicals. 1,2-Dichloroethane (spectrophotometric grade, ≥99%), *tert*-butyl hydroperoxide solution (TBHP, 5.0-6.0 M in decane) and *tert*-butyl peroxybenzoate (technical, ≥95.0%) were purchased from Sigma-Aldrich.

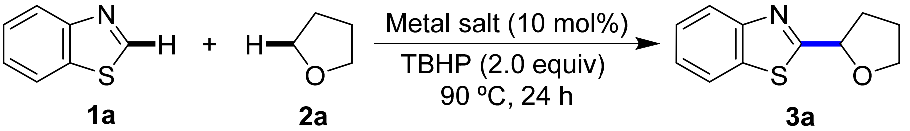
Analytical methods. ^1H NMR and ^{13}C NMR spectra and melting points (where applicable) are included for all compounds. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz at 20 ^oC. All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm), unless otherwise indicated. All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77 ppm), unless otherwise indicated, and were obtained with ^1H decoupling, Coupling constants, *J*, are reported in hertz. Melting points were measured using open glass capillaries in a Büchi SMP-20 apparatus. Mass spectra were acquired on a time of flight (TOF) mass spectrometer (SYNAPT G2 HDMS from Waters, Milford, MA, USA) equipped with an electrospray source in positive mode (ESI^+). The chromatographic separation was performed using an ACQUITY UPLC system from Waters (Milford, MA, USA) equiped with an Acquity UPLC BEH C18 1.7 µm, 50 x 2.1 mm column at 30 °C. Mobile phases consisted of 0.1% formic acid in water (A) and 0.1% formic acid in methanol (B). Separation was carried out in 5 min: initial conditions were 5 % B, raised to 100 % B over 2.5 min, held at 100 % B until 4 min, decreased to 5 % B over 0.1 min and held at 5 % B until 5 min for re-equilibration of the system. Flow rate was 0.25 mL/min and injection volume was 5 µL. Infrared spectra were recorded on a Bruker Alpha P. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh). The yields reported in tables 2-3 correspond to isolated yields and represent an average of at least two independent runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in the tables of the manuscript.

Optimization Details

General Procedure: Cross-Dehydrogenative Coupling of 1a with THF

A reaction tube containing a stirring bar was charged with **1a** (0.5 mmol), metal source (10 mol%), oxidant (if solid) and additive (50 mol%), if applicable. The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated three times). Then, oxidant (if liquid), THF (1 mL) and solvent (if applicable) were subsequently added under argon atmosphere by syringe and the resulting solution was warmed up to the corresponding temperature and stirred for 24 hours. The mixture was then allowed to warm to room temperature, filtered off through a pad of celite and washed with CH_2Cl_2. The resulting crude was evaporated and purified by conventional flash chromatography (hexanes/AcOEt 9/1). The purity of the corresponding product **3a** was verified by ^{1}H NMR.

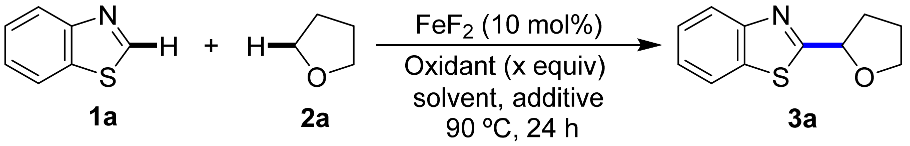
Table S1: Influence of the nature of the catalyst on the CDC of 1a and THF



Entry	Metal	3a (%)[a]
1	none	6
2	**FeF_2**	**62**
3	**FeF_3**	**61**
4	$FeCl_2$	traces
5	$FeCl_3$	traces
6	$Fe(acac)_3$	35
7	Fe_2O_3	traces
8	$Fe(OAc)_2$	43
9	$Co(acac)_2$	traces
10	$Co(acac)_3$	38
11	CoF_2	47
12	$Cu(OTf)_2$	25
13	CuF_2	29
14	$CuCl_2$	traces
15	$CuBr_2$	traces
16	CuCl	traces
17	Cu_2O	19
18	CuO	26
19[b]	TBAI	traces

[a] Yield of isolated product after column chromatography. [b] 30 mol% of catalyst

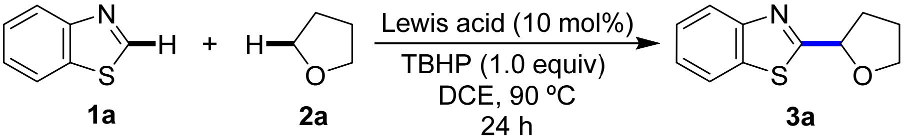
Table S2: Optimization experiments of the CDC of 1a with THF



Entry	Oxidant (equiv)	Solvent	Additive	3a (%)[a]
1	TBHP (2.0)	none	none	62 (54)[b]
2	TBHP (1.0)	none	none	62
3	TBHP (0.5)	none	none	51
4	TBHPaq (2.0)	none	none	41
5	CHP (2.0)	none	none	traces
6	H_2O_2 (2.0)	none	none	traces
7	*t*BuOO*t*Bu (2.0)	none	none	traces
8	$(NH_4)_2S_2O_8$ (2.0)	none	none	0
9	DDQ (2.0)	none	none	0
10	BzOOBz (2.0)	none	none	traces
11	BzOO*t*Bu (2.0)	none	none	51
12	TBHP (1.0)	none	NaI	0
13	TBHP (1.0)	none	KF	0
14	TBHP (1.0)	AcOEt	none	50
15	**TBHP (1.0)**	**DCE**	**none**	**82 (62)[b]**
16[c]	TBHP (1.0)	DCE	none	60
17[d]	TBHP (1.0)	DCE	none	46

[a] Yield of isolated product after column chromatography. [b] Under air. [c] 80 ºC. [d] 5 mol% of catalyst. CHP = Cumene hydroperoxide

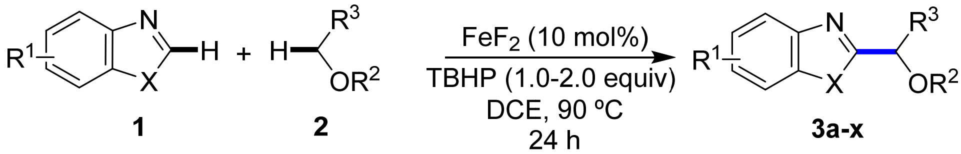
Table S3: Experiments in the presence of Lewis acids



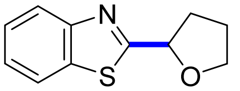
Entry	Lewis acid	3a (%)[a]
1	none	14
2	FeF_2	82
3	$Sc(OTf)_3$	28
4	$Bi(OTf)_3$	21
5	$GaCl_3$	traces
6	$AlCl_3$	traces

[a] Yield of isolated product after column chromatography.

Iron-Catalyzed Direct α-Arylation of Ethers with Azoles (Table 2-3)

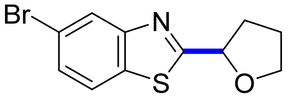


General Procedure: A reaction tube containing a stirring bar was charged with azole **1** (if solid) (0.5 mmol, 1.0 equiv) and FeF_2 (0.05 mmol, 10 mol%). The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated up to three times). The azole **1** (if liquid) (0.5 mmol, 1.0 equiv), ether **2** (0.5 mL), 1,2-dichloroethane (0.5 mL) and TBHP (1.0 equiv, 100 μL, 5.0-6.0 M in decane) were then added under argon atmosphere. The reaction tube was next warmed up to 90 ºC and stirred for 24 hours. The mixture was then allowed to warm to room temperature, filtered off through a pad of celite and washed with CH_2Cl_2. The resulting mixture was concentrated under reduced pressure and the corresponding product was purified by flash chromatography (hexanes/AcOEt 9/1). The yields reported in the manuscript refer to isolated yields and represent an average of at least two independent runs.



(**3a**)

2-(Tetrahydrofuran-2-yl)benzothiazole (3a) (Table 2). Following the general procedure, using benzothiazole (**1a**) (0.50 mmol, 54 μL) and THF (0.5 mL) provided 81 mg (80% yield) of the corresponding coupling product **3a** as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 41.2, 8.1 Hz, 2H), 7.39 (dt, J = 40.6, 7.5 Hz, 2H), 5.34 (t, J = 7.8 Hz, 1H), 4.14 (q, J = 7.1 Hz, 1H), 3.99 (q, J = 7.4 Hz, 1H), 2.50 (dt, J = 14.9, 7.4 Hz, 1H), 2.25 (dt, J = 12.8, 6.3 Hz, 1H), 2.02 (p, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.3, 153.5, 134.6, 125.8, 124.7, 122.6, 121.7, 78.6, 69.3, 33.3, 25.6 ppm.



(**3b**)

5-Bromo-2-(tetrahydrofuran-2-yl)benzothiazole (3b) (Table 2). Following the general procedure, using 5-bromobenzothiazole (**1b**) (0.50 mmol, 107 mg) and THF (0.5 mL) provided 77 mg (54% yield) of the corresponding coupling product **3b** as a white solid.

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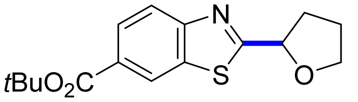
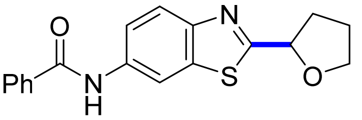
[1] T. He, L. Yu, L. Zhang, L. Wang, M. Wang, *Org. Lett.* **2011**, *13*, 5016-5019.

Mp 57-58 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* δ 8.11 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 5.32 (t, *J* = 7.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 4.00 (q, *J* = 7.4 Hz, 1H), 2.51 (tt, *J* = 11.4, 5.8 Hz, 1H), 2.25 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.13-1.93 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 178.5, 154.6, 133.5, 127.9, 125.6, 122.8, 119.5, 78.6, 69.5, 33.3, 25.7 ppm. IR (neat, cm^{-1}): 1512, 1428, 1074, 917, 860. MS (ESI$^+$) *m/z* (%) 283 (M+H). HRMS *calcd.* for ($C_{11}H_{11}NOSBr$): 283.9745, *found* 283.9746.



(3c)

***Tert*-butyl 2-(tetrahydrofuran-2-yl)benzothiazole-6-carboxylate (3c) (Table 2)**. Following the general procedure, using *tert*-butyl benzothiazole-6-carboxylate[2] (**1c**) (0.50 mmol, 117 mg), TBHP (2.0 equiv, 200 μL) and THF (1 mL) provided 91 mg (60% yield) of the corresponding coupling product **3c** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.53 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 5.34 (t, *J* = 8.0, 1H), 4.16 (q, *J* = 7.1 Hz, 1H), 4.01 (q, *J* = 7.4 Hz, 1H), 2.53 (dt, *J* = 15.0, 7.6 Hz, 1H), 2.27 (dq, *J* = 12.8, 6.4 Hz, 1H), 2.04 (dd, *J* = 9.0, 6.2 Hz, 2H), 1.62 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 179.9, 165.3, 156.3, 134.5, 128.5, 127.1, 123.7, 122.2, 81.4, 78.8, 69.5, 33.3, 28.2, 25.7 ppm. IR (neat, cm^{-1}): 1698, 1290, 899. MS (ESI$^+$) *m/z* (%) 306 (M+H). HRMS *calcd.* for ($C_{16}H_{20}NO_3S$): 306.1164, *found* 306.1165.



(3d)

***N*-[2-(Tetrahydrofuran-2-yl)benzothiazol-6-yl]benzamide (3d) (Table 2)**. Following the general procedure, using 2-(benzothiazol-6-yl)benzamide[3] (**1d**) (0.50 mmol, 127 mg), TBHP (2.0 equiv, 200 μL) and THF (1 mL) provided 127 mg (78% yield) of the corresponding coupling product **3d** as a white solid. Mp 160-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.53 (s, 1H), 8.30 (br s, 1H), 7.87 (d, *J* = 7.5 Hz, 3H), 7.66-7.35 (m, 4H), 5.40-5.15 (m, 1H), 4.13 (p, *J* = 6.9 Hz, 1H), 3.98 (q, *J* = 7.5 Hz, 1H), 2.51-2.46 (m, 1H), 2.26-2.21 (m, 1H), 2.02 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 175.6, 166.2, 150.2, 135.4, 135.1, 134.5, 131.7, 128.4, 127.0, 122.5, 119.4, 113.2, 78.5, 69.2, 33.2, 25.5 ppm. IR (neat, cm^{-1}): 3274, 1642, 1570, 1520, 1490, 1329, 933. MS (ESI$^+$) *m/z* (%) 325 (M+H). HRMS *calcd.* for ($C_{18}H_{17}N_2O_2S$): 325.1011, *found* 325.1009.

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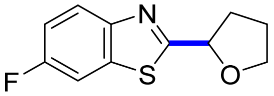
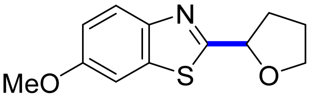
[2] Y. Tani, K. Kobayashi, K. Nomura, *PCT Int. Appl.* **2013**, WO 2013088898 A1.

[3] M. Chakrabarty, A. Mukherji, S. Karmakar, R. Mukherjee, K. Nagai, A. Geronikaki, P. Eleni, *ARKIVOC* **2010**, *11*, 265-290.



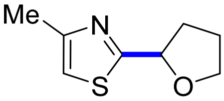
(3e)

6-Fluoro-2-(tetrahydrofuran-2-yl)benzothiazole (3e) (Table 2). Following the general procedure, using 6-fluorobenzothiazole (**1e**) (0.50 mmol, 76.5 mg), TBHP (2.0 equiv, 200 μL) and THF (1 mL) provided 58 mg (51% yield) of the corresponding coupling product **3e** as a white solid. The spectroscopic data correspond to those previously reported in the literature.[4] Mp 53-54 ºC, (Lit. 74-76 ºC). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (dd, J = 8.9, 4.8 Hz, 1H), 7.53 (dd, J = 8.1, 2.6 Hz, 1H), 7.17 (td, J = 8.9, 2.6 Hz, 1H), 5.29 (t, J = 7.8 Hz, 1H), 4.13 (q, J = 7.2 Hz, 1H), 3.98 (q, J = 7.4 Hz, 1H), 2.48 (dt, J = 14.9, 7.5 Hz, 1H), 2.24 (dq, J = 13.0, 6.5 Hz, 2H), 2.02 (p, J = 8.0, 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 176.0 (d, J = 3.0 Hz), 160.1 (d, J = 246.4 Hz), 150.1, 135.6 (d, J = 11.1 Hz), 123.5 (d, J = 9.1 Hz), 114.4 (d, J = 24.2 Hz), 107.8 (d, J = 26.2 Hz), 78.5, 69.4, 33.2, 25.6 ppm.



(3f)

6-Methoxy-2-(tetrahydrofuran-2-yl)benzothiazole (3f) (Table 2). Following the general procedure, using 6-methoxybenzothiazole (**1f**) (0.50 mmol, 82.5 mg), TBHP (2.0 equiv, 200 μL) and THF (1 mL) provided 73 mg (62% yield) of the corresponding coupling product **3f** as a white solid. The spectroscopic data correspond to those previously reported in the literature.[4] Mp 80-82 ºC, (Lit. 81-83 ºC). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, J = 8.9 Hz, 1H), 7.32 (s, 1H), 7.05 (dd, J = 8.9, 2.6 Hz, 1H), 5.32 (t, J = 8.0 Hz, 1H), 4.13 (q, J = 7.1 Hz, 1H), 3.98 (q, J = 7.4 Hz, 1H), 3.85 (s, 3H), 2.48 (dt, J = 14.8, 7.6 Hz, 1H), 2.25 (dt, J = 12.7, 6.3 Hz, 1H), 2.02 (p, J = 7.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 176.0 (d, J = 3.0 Hz), 160.1 (d, J = 246.4 Hz), 150.1, 135.6 (d, J = 11.1 Hz), 123.5 (d, J = 9.1 Hz), 114.4 (d, J = 24.2 Hz), 107.8 (d, J = 26.2 Hz), 78.5, 69.4, 33.2, 25.6 ppm.



(3g)

4-Methyl-2-(tetrahydrofuran-2-yl)thiazole (3g) (Table 2). Following the general procedure, using 4-methylthiazole (**1g**) (0.50 mmol, 46 μL), TBHP (2.0 equiv, 200 μL) and THF (1 mL) provided 44 mg (53% yield) of the corresponding coupling product **3g** as a colorless oil. The spectroscopic data correspond to those previously reported in the

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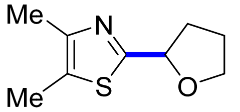
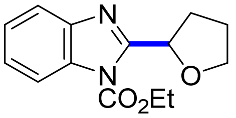
[4] Xie, Z.; Cai, Y.; Hu, H.; Lin, C.; Jiang, J.; Chen, Z.; Wang, L.; Pan, Y. *Org. Lett.* **2013**, *15*, 4600-4603.

literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (s, 1H), 5.20 (dd, *J* = 7.6, 5.5 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 1H), 3.92 (q, *J* = 7.4 Hz, 1H), 2.41 (s, 3H), 2.05-1.96 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 152.5, 112.9, 69.1, 33.4, 25.6, 16.9 ppm.



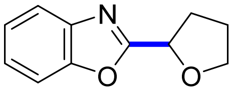
(3h)

4,5-Dimethyl-2-(tetrahydrofuran-2-yl)thiazole (3h) (Table 2). Following the general procedure, using 4,5-dimethylthiazole (**1h**) (0.50 mmol, 53 μL) and THF (0.5 mL) provided 48 mg (52% yield) of the corresponding coupling product **3h** as a colorless oil. The spectroscopic data correspond to those previously reported in the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (t, *J* = 6.2 Hz, 1H), 4.16-3.97 (m, 1H), 3.89-3.91 (m, 1H), 2.42-2.38 (m, 1H), 2.30 (d, *J* = 4.9 Hz, 6H), 2.12-1.94 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.9, 147.5, 125.8, 78.2, 69.0, 33.3, 25.6, 14.5, 11.2 ppm.



(3i)

Ethyl 2-(tetrahydrofuran-2-yl)-1*H*-benzimidazole-1-carboxylate (3i) (Table 2). Following the general procedure, using ethyl 1*H*-benzimidazole-1-carboxylate[5] (**1i**) (0.50 mmol, 95 mg) and THF (0.5 mL) provided 66 mg (50% yield) of the corresponding coupling product **3i** as a white solid. Mp 74-75 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.82 (m, 1H), 7.81-7.69 (m, 1H), 7.37-7.27 (m, 2H), 5.72 (t, *J* = 7.9 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 4.26-4.07 (m, 1H), 3.99 (q, *J* = 7.2 Hz, 1H), 2.57-2.21 (m, 2H), 2.10-1.98 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 150.1, 141.8, 132.9, 124.8, 124.4, 120.2, 114.8, 75.1, 69.1, 64.2, 31.1, 25.0, 14.1 ppm. IR (neat, cm^{-1}): 1741, 1472, 1300, 1074. MS (ESI$^+$) *m/z* (%) 261 (M+H). HRMS *calcd.* for ($C_{14}H_{17}N_2O_3$): 261.1239, *found* 261.1235.



(3j)

2-(Tetrahydrofuran-2-yl)benzoxazole (3j) (Table 2). Following the general procedure, using benzoxazole (**1j**) (0.50 mmol, 60 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and THF (1 mL) provided 64 mg (72% yield) of the corresponding coupling product **3j** as a colorless oil which was found to be thermally unstable. In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the

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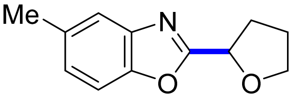
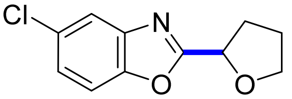
[5] A. P. Venkova, S. Statkova-Abeghea, *Synth. Commun.* **1998**, *28*, 1857-1864.

benzoic acid side-product. The spectroscopic data correspond to those previously reported in the literature.[6] ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75-7.65 (m, 1H), 7.55-7.44 (m, 1H), 7.37-7.27 (m, 2H), 5.20 (t, J = 6.7 Hz, 1H), 4.11 (q, J = 7.3 Hz, 1H), 4.00 (q, J = 7.3 Hz, 1H), 2.39 (q, J = 7.2 Hz, 2H), 2.20-2.02 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.2, 150.8, 140.8, 125.1, 124.3, 120.1, 110.7, 73.9, 69.3, 30.7, 25.7 ppm.



(**3k**)

5-Methyl-2-(tetrahydrofuran-2-yl)benzoxazole (3k) (Table 2). Following the general procedure, using 5-methylbenzoxazole (**1k**) (0.50 mmol, 66 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 µL) and THF (1 mL) provided 65 mg (65% yield) of the corresponding coupling product **3k** as a colorless oil which was found to be thermally unstable. In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The spectroscopic data correspond to those previously reported in the literature.[6] ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.48 (s, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 5.17 (t, J = 6.8 Hz, 1H), 4.11 (q, J = 7.3 Hz, 1H), 3.99 (q, J = 7.3 Hz, 1H), 2.44 (s, 3H), 2.37 (q, J = 7.1 Hz, 2H), 2.18-2.01 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.2, 149.0, 140.9, 134.1, 126.2, 119.9, 110.0, 73.9, 69.2, 30.7, 25.7, 21.4 ppm.



(**3l**)

5-Chloro-2-(tetrahydrofuran-2-yl)benzoxazole (3l) (Table 2). Following the general procedure, using 5-chlorobenzoxazole (**1l**) (0.50 mmol, 77 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 µL) and THF (1 mL) provided 63 mg (57% yield) of the corresponding coupling product **3k** as a colorless oil which was found to be thermally unstable. In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68 (s, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.7 Hz, 1H), 5.18 (t, J = 6.8 Hz, 1H), 4.11 (q, J = 7.3 Hz, 1H), 4.00 (q, J = 7.2 Hz, 1H), 2.40-2.33 (m, 2H), 2.26-1.95 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ 167.7, 149.4, 141.9, 129.8, 125.5, 120.1, 111.5, 73.8, 69.4, 30.8, 25.8 ppm. IR (neat, cm^{-1}): 1655, 1449, 1375, 799. MS (ESI$^+$) *m/z* (%) 224 (M+H). HRMS *calcd.* for (C$_{11}$H$_{11}$NO$_2$Cl): 224.0478, *found* 224.0473.

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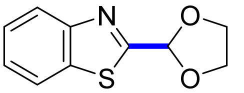
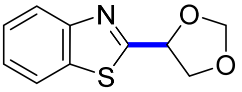
[6] T. Okitsu, K. Nagase, N. Nishio, A. Wada, *Org. Lett.* **2012**, *14*, 708-711.

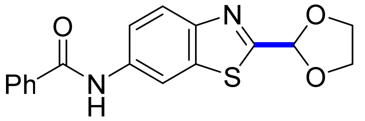


(**3m**)



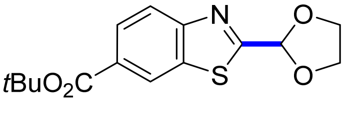
(**3m'**)

2-(1,3-Dioxolan-2-yl)benzothiazole (3m) (Table 3). Following the general procedure, using benzothiazole (**1a**) (0.50 mmol, 54 µL) and 1,3-dioxolane (0.5 mL) provided 75 mg (73% yield) of the corresponding coupling product **3m** as a colorless oil along with 10 mg (9% yield) of the isomer 2-(1,3-dioxolan-4-yl)benzothiazole (**3m’**) (82% overall yield, 9:1, **3m**:**3m’**). The spectroscopic data correspond to those previously reported in the literature.[4] **3m:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.21 (s, 1H), 4.30-3.87 (m, 5H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 153.0, 134.7, 126.0, 125.5, 123.5, 121.7, 100.3, 65.5 ppm. **3m’**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 5.52-5.36 (m, 1H), 5.30 (s, 1H), 5.11 (s, 1H), 4.38 (t, J = 7.8 Hz, 1H), 4.22 (dd, J = 8.6, 4.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 153.2, 134.6, 126.2, 125.2, 122.9, 121.8, 96.3, 75.1, 71.0 ppm.



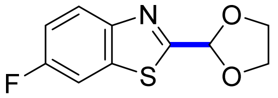
(**3n**)

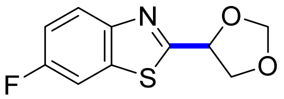
***N*-(2-(1,3-Dioxolan-2-yl)benzothiazol-6-yl)benzamide (3n) (Table 3)**. Following the general procedure, 2-(benzothiazol-6-yl)benzamide[3] (**1d**) (0.50 mmol, 127 mg) and 1,3-dioxolane (0.5 mL) provided 109 mg (67% yield) of the corresponding coupling product **3n** as a white solid. Mp 199-200 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.58 (s, 1H), 8.75 (s, 1H), 8.05 (t, J = 10.4 Hz, 3H), 7.88 (d, J = 8.9 Hz, 1H), 7.62 (dt, J = 14.5, 7.1 Hz, 3H), 6.21 (s, 1H), 4.20-4.09 (m, 4H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.9, 165.8, 148.8, 137.2, 134.9, 134.7, 131.7, 128.4, 127.7, 123.1, 120.1, 120.0, 112.9, 112.8, 99.6, 65.4 ppm. IR (neat, cm^{-1}): 3285, 1645, 1568, 1518, 1358, 1083. MS (ESI$^+$) *m/z* (%) 327 (M+H). HRMS *calcd.* for ($C_{17}H_{15}N_2O_3S$): 327.0803, *found* 327.0807.



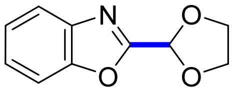
(**3o**)

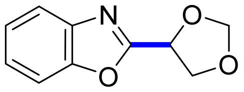
***Tert*-butyl 2-(1,3-dioxolan-2-yl)benzothiazole-6-carboxylate (3o) (Table 3)**. Following the general procedure, using *tert*-butyl benzothiazole-6-carboxylate[2] (**1c**) (0.50 mmol, 117 mg) and 1,3-dioxolane (0.5 mL) provided 98 mg (64% yield) of the corresponding coupling product **3o** as a white solid. Mp 93-95 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.22-7.98 (m, 2H), 6.25 (s, 1H), 4.31-4.07 (m, 4H), 1.64 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 165.0, 155.7, 134.6, 129.3, 127.2, 123.8, 123.2, 100.2, 81.4, 65.7, 28.1 ppm. IR (neat, cm^{-1}): 1698, 1368, 1264, 1135, 899. MS (ESI^{+}) *m/z* (%) 308 (M+H). HRMS *calcd.* for ($C_{15}H_{18}NO_4S$): 308.0957, *found* 308.0949.


(3p)

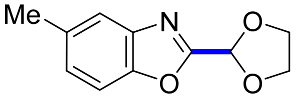

(3p')

6-Fluoro-2-(1,3-dioxolan-2-yl)benzothiazole (3p) (Table 3). Following the general procedure, using 6-fluorobenzothiazole (**1e**) (0.50 mmol, 76.5 mg), TBHP (2.0 equiv, 200 µL) and 1,3-dioxolane (1 mL) provided 65 mg (62% yield) of the corresponding coupling product **3p** as a white solid oil along with 13 mg (12% yield) of the isomer 6-fluoro-2-(1,3-dioxolan-4-yl)benzothiazole (**3p'**) (74% overall yield, 9:1, **3p**:**3p'**). The spectroscopic data correspond to those previously reported in the literature.[4] Mp 93-94 ºC, (Lit. 89-90 ºC). **3p:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.20 (td, *J* = 8.9, 2.5 Hz, 1H), 6.18 (s, 1H), 4.23-3.99 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8 (d, *J* = 3.0 Hz), 160.5 (d, *J* = 247.4 Hz), 149.7, 135.9 (d, *J* = 11.1 Hz), 124.6 (d, *J* = 10.1 Hz), 114.9 (d, *J* = 25.2 Hz), 107.9 (d, *J* = 27.3 Hz), 100.2, 65.6 ppm. **3p':** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.60 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.37-7.13 (m, 1H), 5.46 (dd, *J* = 6.8, 4.4 Hz, 1H), 5.32 (s, 1H), 5.12 (s, 1H), 4.38 (t, *J* = 7.9 Hz, 1H), 4.25 (dd, *J* = 8.7, 4.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.3 (d, *J* = 3.0 Hz), 160.4 (d, *J* = 3.0 Hz), 149.7, 135.6 d, *J* = 11.1 Hz), 123.8 (d, *J* = 10.1 Hz), 114.1 (d, *J* = 25.2 Hz), 107.9 (d, *J* = 26.3 Hz), 96.3, 74.9, 71.0 ppm.

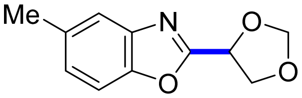

(3q)


(3q')

2-(1,3-Dioxolan-2-yl)benzoxazole (3q) (Table 3). Following the general procedure, using benzoxazole (**1j**) (0.50 mmol, 60 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 µL) and 1,3-dioxolane (1 mL) provided 68 mg (72% yield) of the corresponding coupling product as an inseparable mixture (85:15, **3q:3q'**). In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The signals corresponding to the major isomer are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 6.0 Hz, 2H), 6.19 (s, 1H), 4.29 (s, 2H), 4.14 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8, 150.6, 140.3, 125.8, 124.6, 120.7, 111.0, 97.1, 65.7 ppm. IR (neat, cm^{-1}): 1453, 1113, 935, 841. MS (ESI^{+}) *m/z* (%) 192 (M+H). HRMS *calcd.* for ($C_{10}H_9NO_3$): 192.0582, *found* 192.0657.

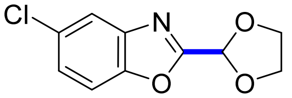


(**3r**)

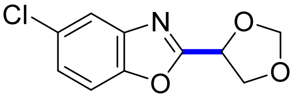


(**3r'**)

2-(1,3-Dioxolan-2-yl)-5-methylbenzoxazole (3r) (Table 3). Following the general procedure, using 5-methylbenzoxazole (**1k**) (0.50 mmol, 66 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and 1,3-dioxolane (1 mL) provided 65 mg (63% yield) of the corresponding coupling product as an inseparable mixture (85:15, **3r:3r'**). In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The signals corresponding to the major isomer are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 6.16 (s, 1H), 4.28 (s, 2H), 4.12 (s, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9, 148.9, 140.4, 134.5, 127.0, 120.5, 110.3, 97.1, 65.6, 21.4 ppm. IR (neat, cm^{-1}): 1481, 1258, 1101, 851. MS (ESI$^+$) *m/z* (%) 206 (M+H). HRMS *calcd.* for ($C_{11}H_{11}NO_3$): 206.0739, *found* 206.0813.

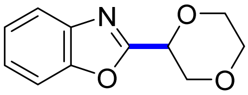


(**3s**)



(**3s'**)

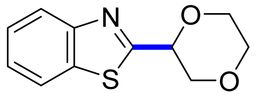
5-Chloro-2-(1,3-Dioxolan-2-yl)benzoxazole (3s) (Table 3). Following the general procedure, using 5-chlorobenzoxazole (**1l**) (0.50 mmol, 77 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and 1,3-dioxolane (1 mL) provided 69 mg (62% yield) of the corresponding coupling product as an inseparable mixture (6:4, **3s:3s'**). In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The signals corresponding to the major isomer are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.66 (m, 1H), 7.45 (dd, J = 8.6, 3.2 Hz, 1H), 7.37-7.28 (m, 1H), 6.16 (s, 1H), 4.27 (s, 2H), 4.13 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.2, 149.2, 141.4, 130.2, 126.2, 120.6, 111.8, 96.9, 65.7 ppm. IR (neat, cm^{-1}): 1450, 1159, 960, 915. MS (ESI$^+$) *m/z* (%) 226 (M+H). HRMS *calcd.* for ($C_{10}H_9NO_3Cl$): 226.0271, *found* 226.0271.



(**3t**)

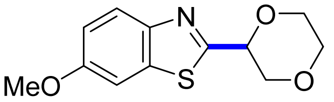
2-(1,4-Dioxan-2-yl)benzoxazole (3t) (Table 3). Following the general procedure, using benzoxazole (**1j**) (0.50 mmol, 60 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and dioxane (1 mL) provided 78 mg (77% yield) of the corresponding coupling product **3t** as a white solid. In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The spectroscopic data correspond to those previously reported in the literature. Mp 60-62 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.64 (m, 1H), 7.57-7.47 (m, 1H), 7.37-7.28 (m, 2H), 4.95 (dd, *J* = 9.2, 3.0 Hz, 1H), 4.18 (dd, *J* = 11.9, 3.0 Hz, 1H), 4.07-3.85 (m, 3H), 3.85-3.71 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.6, 150.5, 140.5, 125.4, 124.6, 120.3, 110.8, 71.0, 68.4, 66.5, 66.3 ppm.



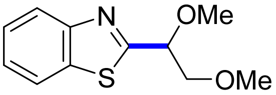
(**3u**)

2-(1,4-Dioxan-2-yl)benzothiazole (3u) (Table 3). Following the general procedure, using benzothiazole (**1a**) (0.50 mmol, 54 μL), TBHP (2.0 equiv, 200 μL) and dioxane (1 mL) provided 65 mg (59% yield) of the corresponding coupling product **3u** as a white solid. The spectroscopic data correspond to those previously reported in the literature.[4] Mp 71-72 ºC, (Lit. 66-68 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 5.06 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.32 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.99 (td, *J* = 11.0, 9.9, 5.6 Hz, 2H), 3.88-3.61 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8, 152.8, 134.3, 125.9, 124.9, 122.9, 121.6, 75.2, 70.3, 66.8, 66.2 ppm.

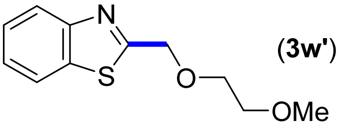


(**3v**)

2-(1,4-Dioxan-2-yl)-6-methoxybenzothiazole (3v) (Table 3). Following the general procedure, using 6-methoxybenzothiazole (**1f**) (0.50 mmol, 82 mg), TBHP (2.0 equiv, 200 μL) and dioxane (1 mL) provided 63 mg (51% yield) of the corresponding coupling product **3v** as a white solid. The spectroscopic data correspond to those previously reported in the literature.[4] Mp 105-107 ºC, (Lit. 96-98 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.9 Hz, 1H), 7.35 (s, 1H), 7.08 (dd, *J* = 8.8, 2.7 Hz, 1H), 5.02 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.42-4.19 (m, 1H), 4.09-3.60 (m, 5H), 3.87 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 157.6, 147.3, 135.8, 123.4, 115.5, 104.0, 75.2, 70.4, 66.9, 66.3, 55.7 ppm.

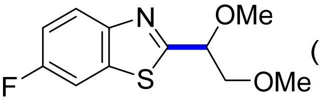


(**3w**)



(**3w'**)

2-(1,2-Dimethoxyethyl)benzothiazole (3w) (Table 3). Following the general procedure, using benzothiazole (**1a**) (0.50 mmol, 54 μL), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and 1,2-dimethoxyethane (1 mL) provided 51 mg (46% yield) of the corresponding coupling product **3w** as a colorless oil along with 26 mg (23% yield) of 2-[(2-methoxyethoxy)methyl]benzothiazole **3w’** (69% overall yield, 7:3 **3w**:**3w’**). In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. The spectroscopic data correspond to those previously reported in the literature.[1] **3w**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 4.83 (dd, J = 6.4, 3.8 Hz, 1H), 3.79 (qd, J = 10.4, 5.1 Hz, 2H), 3.51 (s, 3H), 3.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 152.8, 134.9, 125.9, 125.1, 122.9, 121.7, 81.0, 75.1, 59.3, 58.4 ppm. **3w’**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 4.97 (s, 2H), 3.78 (t, J = 4.5 Hz, 2H), 3.68-3.52 (m, 2H), 3.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0, 152.5, 134.6, 125.7, 124.7, 122.5, 121.4, 71.4, 70.3, 70.3, 58.7 ppm.



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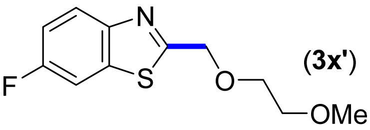
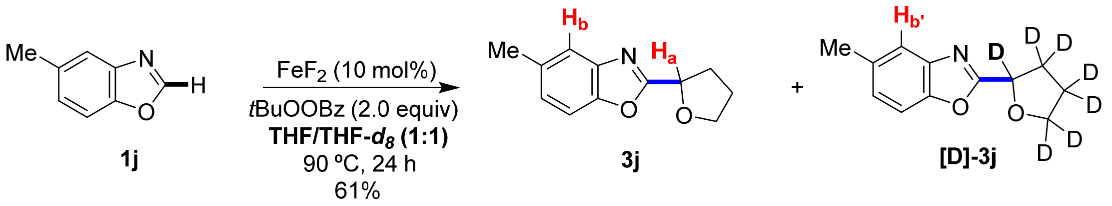
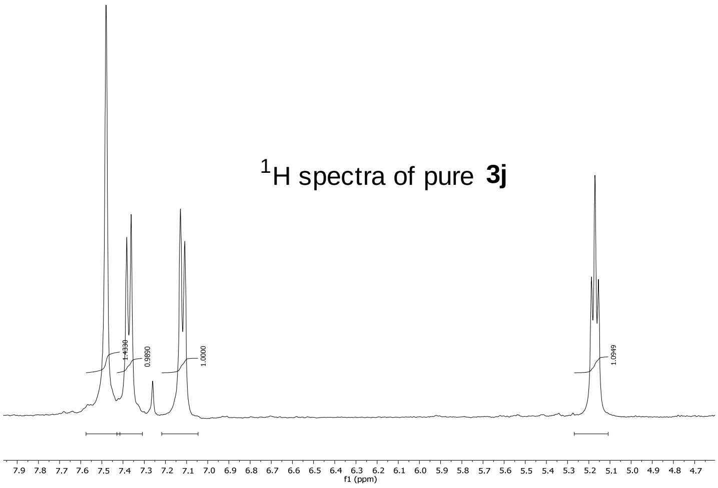


(**3x'**)

2-(1,2-Dimethoxyethyl)-6-fluorobenzothiazole (3x) (Table 3). Following the general procedure, using 6-fluorobenzothiazole (**1e**) (0.50 mmol, 77 mg), *tert*-butyl perbenzoate (2.0 equiv, 190 μL) and 1,2-dimethoxyethane (1 mL) provided 66 mg (54% yield) of the corresponding coupling product **3x** as a colorless oil along with 13 mg (11% yield) of 2-6-fluoro-[(2-methoxyethoxy)methyl]benzothiazole **3x’** (65% overall yield, 8:2 **3m**:**3m’**). In this case, the reaction crude was washed with NaOH 1M before purification by column chromatography to remove the benzoic acid side-product. **3x**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J = 8.9, 4.8 Hz, 1H), 7.55 (dd, J = 7.9, 2.6 Hz, 1H), 7.18 (td, J = 9.0, 2.7 Hz, 1H), 4.78 (dd, J = 6.4, 3.8 Hz, 1H), 3.78 (qd, J = 10.5, 5.0 Hz, 2H), 3.51 (s, 3H), 3.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2 (d, J = 4.0 Hz), 160.3 (d, J = 246.4 Hz), 149.5, 136.1 (d, J = 11.1 Hz), 123.9 (d, J = 9.1 Hz), 114.6 (d, J = 25.2 Hz), 107.9 (d, J = 27.3 Hz), 75.0, 59.4, 58.45 ppm. IR (neat, cm^{-1}): 1566, 1454, 1127, 813. MS (ESI$^+$) *m/z* (%) 242 (M+H). HRMS *calcd.* for ($C_{11}H_{13}NO_2SF$): 242.0651, *found* 242.0649. **3w’**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J = 9.0, 4.8 Hz, 1H), 7.56 (dd, J = 8.1, 2.6 Hz, 1H), 7.20 (td, J = 9.1, 2.6 Hz, 1H), 4.95 (s, 3H), 3.85-3.72 (m, 2H), 3.69-3.56 (m, 2H), 3.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1 (d, J = 4.0 Hz), 160.3 (d, J = 246.4 Hz) 149.4, 136.0 (d, J = 11.1 Hz), 123.8 (d, J = 9.1 Hz), 114.7 (d, J = 24.2 Hz) 108.0 (d, J = 26.3 Hz), 71.8, 70.7, 70.6, 59.1 ppm. IR (neat, cm^{-1}): 1566, 1453, 1046, 816. MS (ESI$^+$) *m/z* (%) 242 (M+H). HRMS *calcd.* for ($C_{11}H_{13}NO_2SF$): 242.0651, *found* 242.0651.



Kinetic Isotope Effect (KIE) experiment with benzoxazole 1j: A reaction tube containing a stirring bar was charged with 5-methylbenzoxazole **1j** (0.5 mmol, 66 mg) and FeF_2 (0.05 mmol, 4.76 mg). The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated up to three times). Then **THF** (0.5 mL), **THF-*d*$_8$** (0.5 mL) and *tert*-butyl perbenzoate (2.0 equiv, 190 µL) were then added under argon atmosphere. The reaction tube was next warmed up to 90 ºC and stirred for 24 hours. The mixture was then allowed to warm to room temperature, washed with NaOH 1M and extracted with CH_2Cl_2. The resulting mixture was concentrated under reduced pressure and the corresponding product (**3j** and **[D]-3j**) was purified by flash chromatography (hexanes/AcOEt 9/1). The KIE value was calculated by analysis of the ^{1}H NMR spectra:


^{1}H spectra of pure **3j**

KIE = 3.18

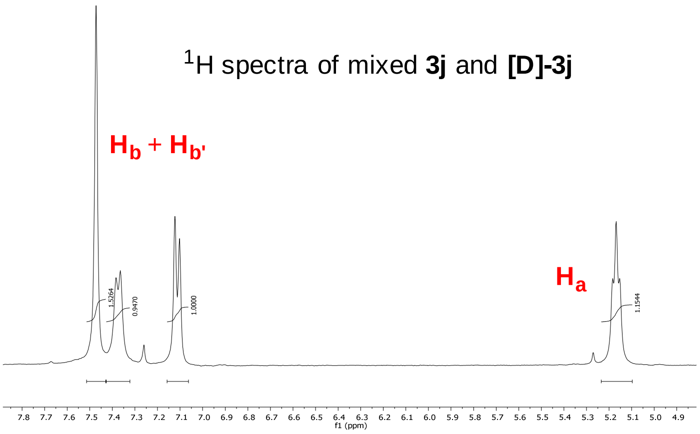
H_a = 1.1609

$H_b + H_{b'}$ = 1.5263

$H_a = H_b$

$H_{b'}$ = 1.5263 - H_b = 0.3654

KIE = $H_b/H_{b'}$ = 1.1609/0.3654 = 3.18


^{1}H spectra of mixed **3j** and **[D]-3j**

Computational Methods

All reported structures were optimized at DFT level by using the M06[7] hybrid functional as implemented in Gaussian 09.[8] Optimizations were carried out by using the standard 6-311++G(d,p) basis set for C, H, O, and N, and the SDD basis set for Fe.[9] Implicit solvent (Tetrahydrofuran) was included in all the optimizations by means of a CPCM solvent model system.[10] Reported energy values correspond to Gibbs Free (G) energies. The critical stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies, and the intrinsic reaction coordinates (IRC)[11] were followed to verify the energy profiles connecting those transition structures to the correct associated local minima.

Computational Discussion

Computational data confirm that the homolytic cleavage of the peroxide substrate *t*BuOOH to form the hydroxide and *t*-butoxide radical species is a highly endergonic process, with an uphill Gibbs Free energy of 5.1 kcal/mol (Figure S1.1). Thus, in the absence of iron catalyst, this step is probably rate-determining, severely limiting the feasibility of the background reaction. However, FeF_2 helps stabilizing the arising radical species by formation of a very stable Fe(III) complex, which lies ca. 80 kcal/mol lower in energy than the starting reactants. Two possible product combinations are outlined in Figures S1.2 and S1.3, showing the preferential formation of $FeF_2(OH)$ complex and *tert*-butoxy radical by more than 6 kcal/mol *vs* the alternative formation of FeF_2(O*t*Bu) and hydroxyl radical. Finally, doublet and quartet spin states were considered for $F_2Fe(OH)$ and F_2Fe(O*t*Bu), the latter (quartet) being lower in energy by more than 5 kcal/mol in

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[7] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[8] Gaussian 09, Revision D.01; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[9] P. Fuentealba, H. Preuss, H. Stoll, L. v. Szentpály, *Chem. Phys. Lett.* **1982**, *89*, 418-22.

[10] a) E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys*. **1997**, *107*, 3032-3047; b) M. Cossi, V. Barone, B. Mennuci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253-260; c) J. Tomasi, B. Mennucci, E. Cancès, *J. Mol. Struct. (Theochem)* **1999**, *464*, 211-226.

[11] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523-5527.

both species, regardless the computational conditions used. Thus, only energy values for high spin Fe(III) are shown in the figures and Table S4.

$$tBuO\text{-}OH \rightleftharpoons tBuO^{\cdot} + {}^{\cdot}OH \qquad \Delta G_R = +5.1 \qquad (1)$$

$$FeF_2 + tBuO\text{-}OH \rightleftharpoons F_2Fe(OtBu) + {}^{\cdot}OH \qquad \Delta G_R = -76.5 \qquad (2)$$

$$FeF_2 + tBuO\text{-}OH \rightleftharpoons F_2Fe(OH) + {}^{\cdot}OtBu \qquad \Delta G_R = -82.9 \qquad (3)$$

Figure S1. Gibbs Free energies for the homolytic cleavage of TBHP in the absence or presence of FeF_2 catalyst.

Next, the deprotonation of the O-C-**H** in the THF molecule **2a** is predicted to be an easy process, with an activation energy of only 12.5 kcal/mol (**TS1**, Figure S2.1). As mentioned before, we have found a significant experimental kinetic isotope effect between **2a** and **2a**-*d*, indicating that this step should be the rate-determining step in our reaction. In this regard, its low activation energy can be accepted if we consider also the low concentration of the *tert*-butoxide radical in the reaction media. This radical will be probably involved in an equilibrium between its free form and a Fe(III)-O*t*Bu complex, by combination with the Fe(II) catalyst. This equilibrium would compromise the availability of the free radical, decreasing the deprotonation rate in Figure S2.1. In agreement with the experimental findings, the deuterium cleavage in **2a**-*d* presents an activation energy of 13.6 kcal/mol (Figure S2.2), corresponding to a computed KIE of 5.3. The subsequent SET event that affords a highly electrophilic oxonium cation **5** (Figure S2.3) and a hydroxide anion is also a favorable process, lying ca. 5 kcal/mol lower in energy than the sum of the starting Fe(III) complex and radical species.

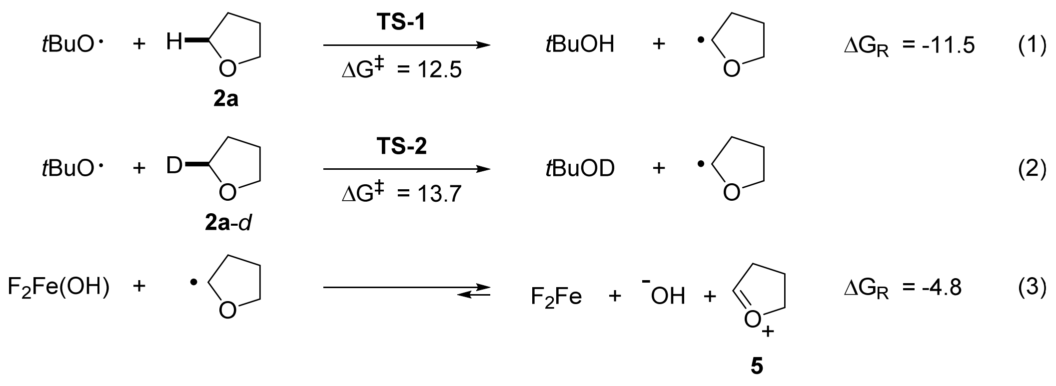

Figure S2. Computed formation of the electrophilic oxonium species **5.**

Finally, we also confirmed that the hydroxide anion formed in the previous step is basic enough to easily deprotonate the azole **1a** through **TS3** (Figure S3.1) with a low activation energy of only 10.1 kcal/mol in a slightly exergonic process (-0.6 kcal/mol). The low energy barrier of **TS-3** confirms the radical-mediated deprotonation event in Figure S2.1 (**TS-1**) as the rate-determining step. Obviously, the final C-C bond formation should be a barrierless step in an extremely favorable process, where the product **3a** lies 82 kcal/mol lower in energy than the sum of the anionic/cationic species (Figure S3.2).

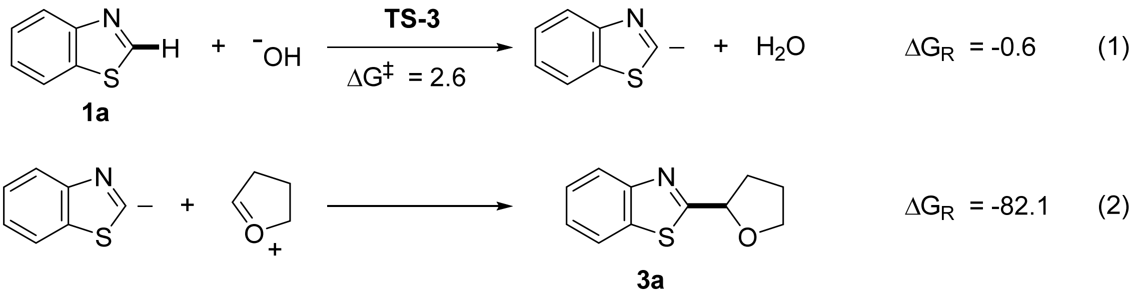

Figure S3. Final steps in the formation of product **3a.**

Table S3. Energies of all stationary points shown in the study

	M06/6-311++G** Electronic energy	Correction to G	M06/6-311++G** Gibbs Free	relative **G** M06	Frequency
		All Stationary points			
THF	-232.351720	0.085652	-232.266068		
THF-*d*	-232.351720	0.081945	-232.269774		
***t*BuOOH**	-308.699834	0.107074	-308.592760		
***t*BuOO (rad)**	-308.058556	0.094603	-307.963913		
***t*BuOO- (anion)**	-308.188813	0.095351	-308.095300		
FeF_2	-323.570284	-0.023838	-323.594122		
1a	-722.529832	0.070589	-722.459243		
1a-rad	-721.846442	0.057355	-721.789087		
1a-anion	-722.001791	0.055967	-721.945824		
H_2O	-76.425040	0.003861	-76.421179		
HO (rad)	-75.725808	-0.008335	-75.734143		
HO- (anion)	-75.899517	-0.007333	-75.906850		
***t*BuO (rad)**	-232.905755	0.091324	-232.814431		
***t*BuO- (anion)**	-233.059196	0.092137	-232.967059		
***t*BuOH**	-233.583257	0.105659	-233.477598		
FeF_2(O*t*Bu)	-556.662891	0.088311	-556.574580		
FeF_2(OH)	-399.516823	0.012334	-399.504489		
THF rad	-231.695062	0.073852	-231.621210		
THF-cation	-231.541397	0.077445	-231.463952		
TS1	-465.256306	0.195739	-465.060567		
TS2	-465.256306	0.193903	-465.062402		
TS3	-798.432676	0.070805	-798.361870		
3a	-953.700125	0.159535	-953.540591		

equation S1.1

***t*BuOOH**	-308.592760		
***t*BuO (rad)+ HO (rad)**	-308.584574	5.1	
equation S1.2			
FeF_2 + *t*BuOOH	-632.186882		
FeF_2(O*t*Bu) + HO (rad)	-632.308723	-76.5	
equation S1.3			
FeF_2 + *t*BuOOH	-632.186882		
FeF_2(OH) + *t*BuO (rad)	-632.318920	-82.9	
equation S2.1			
THF + *t*BuO (rad)	-465.080499		
THF (rad) + *t*BuOH	-465.098808	-11.5	
TS1	-465.060567	12.5	-1341.2
equation S2.2			
THF-*d* + *t*BuO (rad)	-464.747372		
TS2	-465.062402	13.7	-1027.9
equation S2.3			
FeF_2(OH) + THF (rad)	-555.050494		
FeF_2 + -OH +THF(cation)	-555.058074	-4.8	
equation S3.1			
1a + -OH	-798.366093		
1a (anion) + H_2O	-798.367003	-0.6	
TS3	-798.361870	2.6	-1663.7
equation S3.2			
1a(anion) + THF(cation)	-953.409776		
3a	-953.540591	-82.1	

Atomic Coordinates for the compounds described in the Manuscript and Supporting Information

THF

```
                  Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.079952   -0.524977    0.213713
      2          8           0       -0.063795   -1.199305   -0.277408
      3          6           0       -1.170128   -0.388172    0.086601
      4          6           0       -0.680623    1.068114    0.035336
      5          6           0        0.839252    0.932467   -0.138998
      6          1           0        1.153835   -0.655583    1.307270
      7          1           0        1.965619   -0.966095   -0.249390
      8          1           0       -1.988468   -0.604953   -0.604265
      9          1           0       -1.499736   -0.650972    1.103841
     10          1           0       -1.132845    1.622000   -0.790775
     11          1           0        1.127900    1.111692   -1.179510
     12          1           0        1.407593    1.619695    0.492286
     13          1           0       -0.934260    1.594060    0.959901
 ---------------------------------------------------------------------
```

tBuOOH

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.383687   -0.000715    0.033610
      2          6           0       -1.552845   -0.117458   -0.924581
      3          1           0       -1.505930   -1.055636   -1.486165
      4          1           0       -1.558716    0.717387   -1.631953
      5          1           0       -2.490383   -0.098733   -0.360763
      6          6           0       -0.321369   -1.195055    0.966395
      7          1           0       -0.232523   -2.125244    0.394707
      8          1           0       -1.236754   -1.247058    1.564616
      9          1           0        0.523884   -1.120282    1.656662
     10          6           0       -0.427201    1.308983    0.795700
     11          1           0       -0.455574    2.155151    0.101619
     12          1           0        0.445707    1.415353    1.444834
     13          1           0       -1.325084    1.345090    1.421458
     14          8           0        0.744474   -0.011277   -0.875571
     15          8           0        1.961621    0.115249   -0.146782
     16          1           0        2.297222   -0.792343   -0.152943
 ---------------------------------------------------------------------
```

tBuOO (rad)

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.363625    0.000217    0.046305
      2          6           0        1.489320   -0.001067   -0.960073
      3          1           0        1.447078    0.888308   -1.596003
      4          1           0        1.446899   -0.892052   -1.593723
      5          1           0        2.447296   -0.000534   -0.431901
      6          6           0        0.335528    1.259857    0.879345
      7          1           0        0.302279    2.148355    0.241278
      8          1           0        1.243266    1.307434    1.488685
      9          1           0       -0.528671    1.267897    1.548426
     10          6           0        0.336373   -1.257167    0.883011
     11          1           0        0.304889   -2.147381    0.247232
     12          1           0       -0.528681   -1.264501    1.551012
     13          1           0        1.243376   -1.302017    1.493606
     14          8           0       -0.849534   -0.001731   -0.831508
     15          8           0       -1.966317   -0.000338   -0.173509
 ---------------------------------------------------------------------
```

*t*BuOO (anion)

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.321373   -0.000004    0.009263
      2          6           0        1.541238   -0.000016   -0.899260
      3          1           0        1.543231    0.888613   -1.540751
      4          1           0        1.543097   -0.888558   -1.540872
      5          1           0        2.463757   -0.000128   -0.307395
      6          6           0        0.325839    1.250788    0.879904
      7          1           0        0.339590    2.149097    0.250966
      8          1           0        1.208675    1.270735    1.530631
      9          1           0       -0.572663    1.278470    1.501079
     10          6           0        0.325791   -1.250776    0.879936
     11          1           0        0.339911   -2.149111    0.251044
     12          1           0       -0.572929   -1.278553    1.500799
     13          1           0        1.208399   -1.270563    1.530977
     14          8           0       -0.777520   -0.000026   -0.882717
     15          8           0       -2.045794    0.000032   -0.166725
 ---------------------------------------------------------------------
```

FeF$_2$

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         26           0        0.000000    0.449256    0.000000
      2          9           0        1.459668   -0.649047    0.000000
      3          9           0       -1.459668   -0.648802    0.000000
 ---------------------------------------------------------------------
```

1a

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
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      2          6           0        0.092532    0.829909    0.000018
      3          6           0        1.383388    1.363752   -0.000077
      4          6           0        2.462849    0.502417   -0.000119
      5          6           0        2.275324   -0.885760   -0.000112
      6          6           0        1.006107   -1.435428   -0.000072
      7          6           0       -2.099109    0.787662    0.000419
      8          1           0        1.514260    2.441378   -0.000089
      9          1           0        3.471038    0.904296   -0.000177
     10          1           0        3.139786   -1.542158   -0.000170
```

```
   11        1        0       0.865349   -2.511124   -0.000111
   12        1        0      -3.128866    1.130539    0.000254
   13        7        0      -1.076767    1.567409    0.000081
   14       16        0      -1.785130   -0.935761   -0.000043
 ---------------------------------------------------------------------
```

1a (rad)

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
    1        1        0      -3.039816   -1.636024    0.000025
    2        1        0      -0.729434   -2.521600    0.000023
    3       16        0       1.879820   -0.850946   -0.000007
    4        1        0      -3.462453    0.793730    0.000027
    5        1        0      -1.564756    2.406377   -0.000055
    6        6        0       0.139915   -0.543059    0.000017
    7        6        0      -0.910262   -1.452015    0.000028
    8        6        0      -1.393394    1.334873   -0.000050
    9        6        0       2.091215    0.881524   -0.000091
   10        7        0       1.078158    1.612247    0.000132
   11        6        0      -0.091386    0.843964   -0.000033
   12        6        0      -2.440024    0.430211   -0.000010
   13        6        0      -2.200691   -0.947678    0.000000
 ---------------------------------------------------------------------
```

***t*BuO (rad)**

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
    1        8        0       0.000086    0.288812    1.419434
    2        6        0      -0.000010   -0.030575    0.086001
    3        6        0      -1.264507   -0.789078   -0.301690
    4        1        0      -2.154218   -0.214211   -0.028470
    5        1        0      -1.298572   -1.753137    0.215573
    6        1        0      -1.284184   -0.978685   -1.379929
    7        6        0       0.000456    1.364183   -0.593189
    8        1        0      -0.892065    1.929681   -0.315613
    9        1        0       0.000549    1.198129   -1.675524
   10        1        0       0.893235    1.929163   -0.315397
   11        6        0       1.263986   -0.789910   -0.301677
   12        1        0       1.297485   -1.753916    0.215721
   13        1        0       2.154076   -0.215557   -0.028612
   14        1        0       1.283457   -0.979676   -1.379892
 ---------------------------------------------------------------------
```

***t*BuO (anion)**

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          8           0        0.000480   -0.001999    1.494289
      2          6           0        0.000044   -0.000146    0.134472
      3          6           0       -0.155052    1.427741   -0.429070
      4          1           0        0.668848    2.056840   -0.067383
      5          1           0       -1.095450    1.865068   -0.068621
      6          1           0       -0.158109    1.462923   -1.528920
      7          6           0        1.313288   -0.578816   -0.431585
      8          1           0        2.162387    0.016622   -0.070847
      9          1           0        1.344756   -0.592837   -1.531475
     10          1           0        1.446744   -1.607182   -0.070676
     11          6           0       -1.158739   -0.847165   -0.431191
     12          1           0       -2.115703   -0.447658   -0.070624
     13          1           0       -1.068201   -1.880159   -0.070428
     14          1           0       -1.186358   -0.867315   -1.531090
 ---------------------------------------------------------------------
```

***t*BuOH**

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          8           0        0.067611   -0.000076    1.447645
      2          6           0       -0.006714   -0.000106    0.014965
      3          6           0       -1.486280   -0.010937   -0.309227
      4          1           0       -1.976508    0.873435    0.110757
      5          1           0       -1.963231   -0.903528    0.108792
      6          1           0       -1.640755   -0.011075   -1.392821
      7          6           0        0.655418    1.255650   -0.528217
      8          1           0        0.175396    2.149016   -0.115528
      9          1           0        0.581109    1.294881   -1.620384
     10          1           0        1.719120    1.280430   -0.262530
     11          6           0        0.674393   -1.245145   -0.529239
     12          1           0        0.208082   -2.146369   -0.117868
     13          1           0        1.738363   -1.254209   -0.263458
     14          1           0        0.601029   -1.284198   -1.621490
     15          1           0        0.995609    0.005448    1.703682
 ---------------------------------------------------------------------
```

FeF$_2$(O*t*Bu)

```
                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
```

```
 ---------------------------------------------------------------------
      1         26           0        1.422858    0.090316   -0.000770
      2          9           0        2.461639   -1.397008    0.000461
      3          9           0        0.942805    1.830507    0.000719
      4          8           0       -0.317106   -0.743476   -0.004248
      5          6           0       -1.564395   -0.127573    0.000346
      6          6           0       -1.784232    0.692187   -1.260741
      7          1           0       -1.629494    0.074954   -2.150764
      8          1           0       -1.082389    1.531052   -1.281494
      9          1           0       -2.804356    1.087708   -1.281252
     10          6           0       -2.509549   -1.361473   -0.006927
     11          1           0       -2.350904   -1.961451   -0.905005
     12          1           0       -3.533000   -0.972159   -0.002971
     13          1           0       -2.348714   -1.974067    0.882175
     14          6           0       -1.781960    0.676377    1.271914
     15          1           0       -1.079099    1.514276    1.302809
     16          1           0       -1.627176    0.047650    2.153843
     17          1           0       -2.801520    1.073017    1.298494
 ---------------------------------------------------------------------
```

$FeF_2(OH)$

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         26           0       -0.000626   -0.147754   -0.058011
      2          9           0       -1.642355   -0.608327    0.074360
      3          9           0        1.639387   -0.614625    0.073851
      4          8           0        0.003693    1.606962   -0.079542
      5          1           0        0.013447    1.992474    0.810721
 ---------------------------------------------------------------------
```

THF (cation)

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.542947   -1.107808    0.030556
      2          8           0       -0.807525   -0.946621   -0.118237
      3          6           0       -1.112924    0.420233    0.182516
      4          6           0        0.128139    1.187410   -0.228369
      5          6           0        1.242017    0.202810    0.147179
      6          1           0        0.935981   -2.030725   -0.377143
      7          1           0       -2.020998    0.689095   -0.359949
      8          1           0       -1.300785    0.513281    1.261719
      9          1           0        0.120423    1.357334   -1.310399
     10          1           0        0.209921    2.154499    0.272080
     11          1           0        2.119408    0.278778   -0.504408
     12          1           0        1.595175    0.394841    1.172702
```

```
---------------------------------------------------------------------
```

THF (rad)

```
                         Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic              Coordinates (Angstroms)
Number      Number       Type              X           Y           Z
---------------------------------------------------------------------
      1          6           0        1.100759   -0.450634   -0.049347
      2          8           0        0.117167   -1.219400   -0.064790
      3          6           0       -1.151600   -0.439171    0.114278
      4          6           0       -0.729477    0.992906   -0.141029
      5          6           0        0.781571    0.962870    0.103205
      6          1           0        2.087306   -0.905944   -0.125723
      7          1           0       -1.858537   -0.869519   -0.590676
      8          1           0       -1.455355   -0.655374    1.139286
      9          1           0       -0.938776    1.282010   -1.172589
     10          1           0       -1.244814    1.684936    0.523496
     11          1           0        1.392329    1.590761   -0.550499
     12          1           0        1.072995    1.232503    1.132390
---------------------------------------------------------------------
```

TS1

```
                         Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic              Coordinates (Angstroms)
Number      Number       Type              X           Y           Z
---------------------------------------------------------------------
      1          6           0       -1.249785   -0.556674    0.773506
      2          8           0       -1.649002    0.778229    0.886433
      3          6           0       -2.378117    1.111637   -0.305699
      4          6           0       -3.178058   -0.153596   -0.626381
      5          6           0       -2.209308   -1.277227   -0.190374
      6          1           0       -1.123707   -0.984114    1.772206
      7          1           0       -2.984679    1.992459   -0.083328
      8          1           0       -1.671336    1.355721   -1.111256
      9          1           0       -4.092118   -0.178065   -0.024868
     10          1           0       -3.461696   -0.216800   -1.680012
     11          1           0       -2.726960   -2.112173    0.290357
     12          1           0       -1.650503   -1.678192   -1.041546
     13          1           0       -0.150739   -0.622106    0.240150
     14          6           0        2.002372    0.008206   -0.081698
     15          6           0        3.163180   -0.335045   -1.042527
     16          1           0        4.053790    0.245338   -0.778855
     17          1           0        3.405790   -1.399552   -0.982304
     18          1           0        2.883884   -0.101387   -2.073498
     19          6           0        2.384538   -0.373211    1.360175
     20          1           0        3.279011    0.164496    1.692902
     21          1           0        1.571391   -0.128732    2.051872
     22          1           0        2.578913   -1.447880    1.425251
     23          6           0        1.652238    1.504337   -0.182599
     24          1           0        1.399574    1.760322   -1.216371
```

```
    25        1         0        0.789938    1.737088    0.449551
    26        1         0        2.490447    2.134688    0.134535
    27        8         0        0.934832   -0.789688   -0.547834
 ---------------------------------------------------------------------
```

TS2

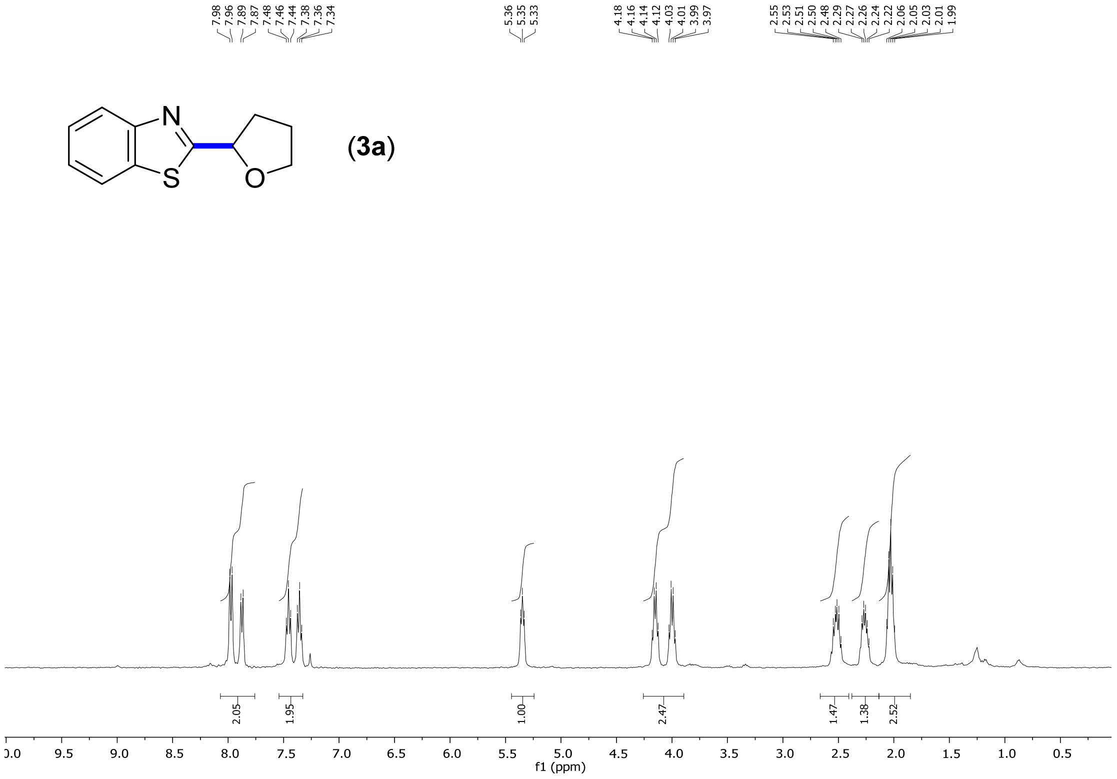
```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -1.248056   -0.655699    0.725122
      2          8           0       -1.567934    0.673136    0.946326
      3          6           0       -2.245731    1.137269   -0.223219
      4          6           0       -3.117822   -0.032571   -0.632584
      5          6           0       -2.234897   -1.235540   -0.280372
      6          1           0       -1.115653   -1.175050    1.678634
      7          1           0       -2.785752    2.047819    0.041117
      8          1           0       -1.500268    1.374384   -0.998259
      9          1           0       -4.034209   -0.038295   -0.033934
     10          1           0       -3.398660    0.001314   -1.686950
     11          1           0       -2.803567   -2.069249    0.139358
     12          1           0       -1.701812   -1.612264   -1.160268
     13          1           0       -0.158746   -0.718769    0.177956
     14          6           0        1.954600    0.004747   -0.087364
     15          6           0        3.183030   -0.304335   -0.943667
     16          1           0        4.028257    0.308893   -0.611334
     17          1           0        3.458364   -1.359685   -0.853842
     18          1           0        2.982253   -0.081281   -1.996099
     19          6           0        2.239667   -0.338898    1.369668
     20          1           0        3.084559    0.245790    1.750142
     21          1           0        1.368400   -0.117841    1.996954
     22          1           0        2.479060   -1.402744    1.470288
     23          6           0        1.574506    1.473964   -0.229326
     24          1           0        1.367445    1.710460   -1.278879
     25          1           0        0.679242    1.696712    0.361741
     26          1           0        2.385312    2.123746    0.119371
     27          8           0        0.947184   -0.826581   -0.609519
 ---------------------------------------------------------------------
```

TS3

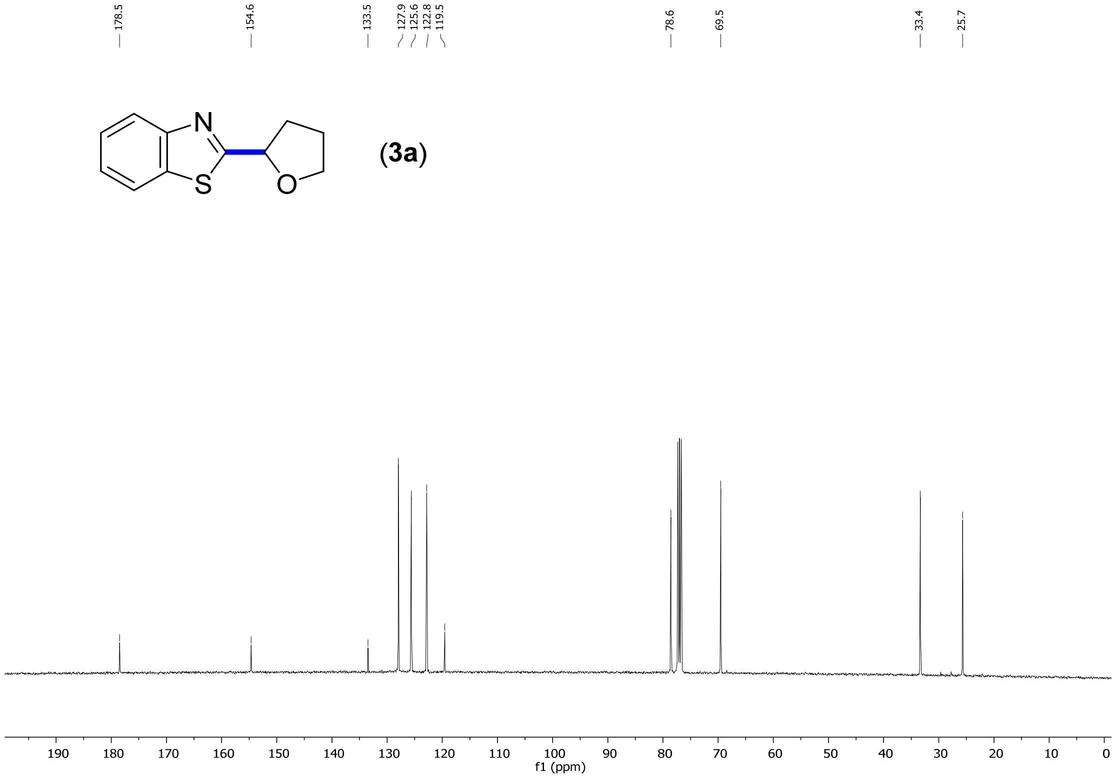
```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          1           0        3.994737    0.834543    0.015359
      2          1           0        2.010582    2.312628    0.010151
      3          1           0       -3.031978   -0.358889   -0.007508
      4         16           0       -0.950919    1.403143   -0.005244
      5          1           0        3.729957   -1.624035    0.007109
```

```
     6          8           0       -4.321125   -0.479490    0.011916
     7          1           0        1.460627   -2.643377   -0.006202
     8          6           0        0.623245    0.656691   -0.000937
     9          6           0        1.891119    1.233401    0.006524
    10          6           0        1.589268   -1.564552   -0.002710
    11          6           0       -1.725513   -0.229028   -0.012892
    12          7           0       -0.850433   -1.186796   -0.011871
    13          6           0        0.459913   -0.743044   -0.005404
    14          6           0        2.848112   -0.990195    0.004743
    15          6           0        2.998957    0.400882    0.009405
    16          1           0       -4.537789   -1.412595    0.060385
 ---------------------------------------------------------------------
```

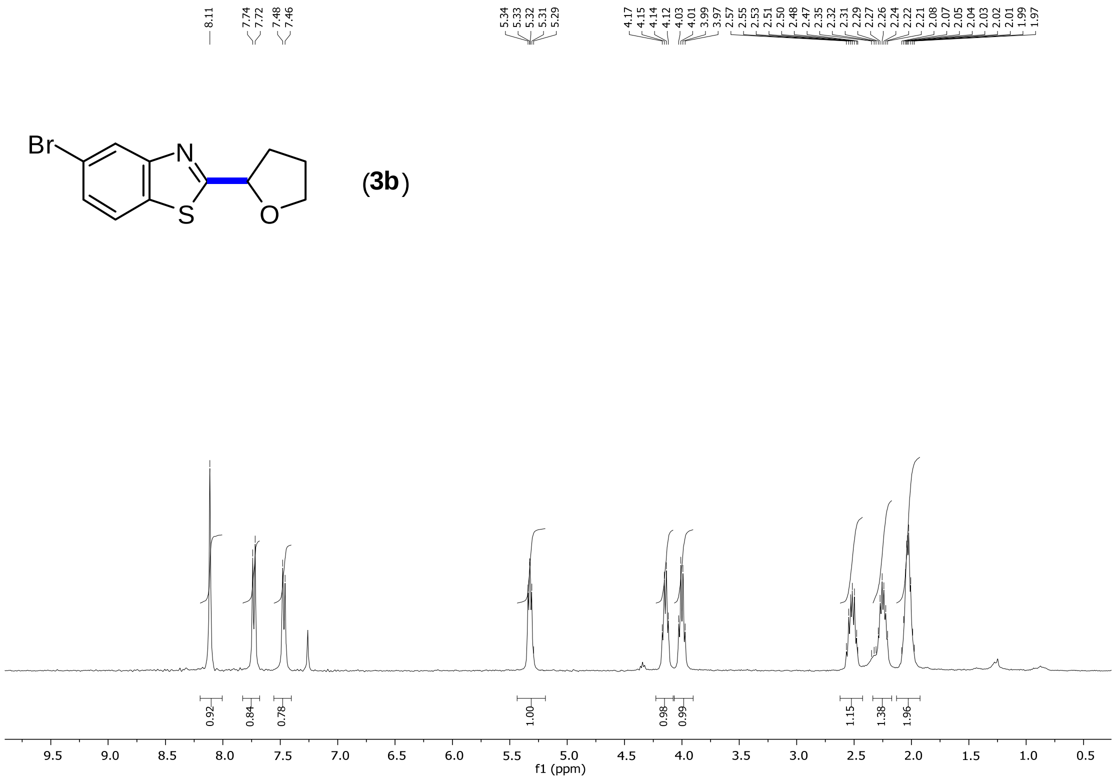
^{1}H NMR and ^{13}C NMR Spectra



(**3a**)



(**3a**)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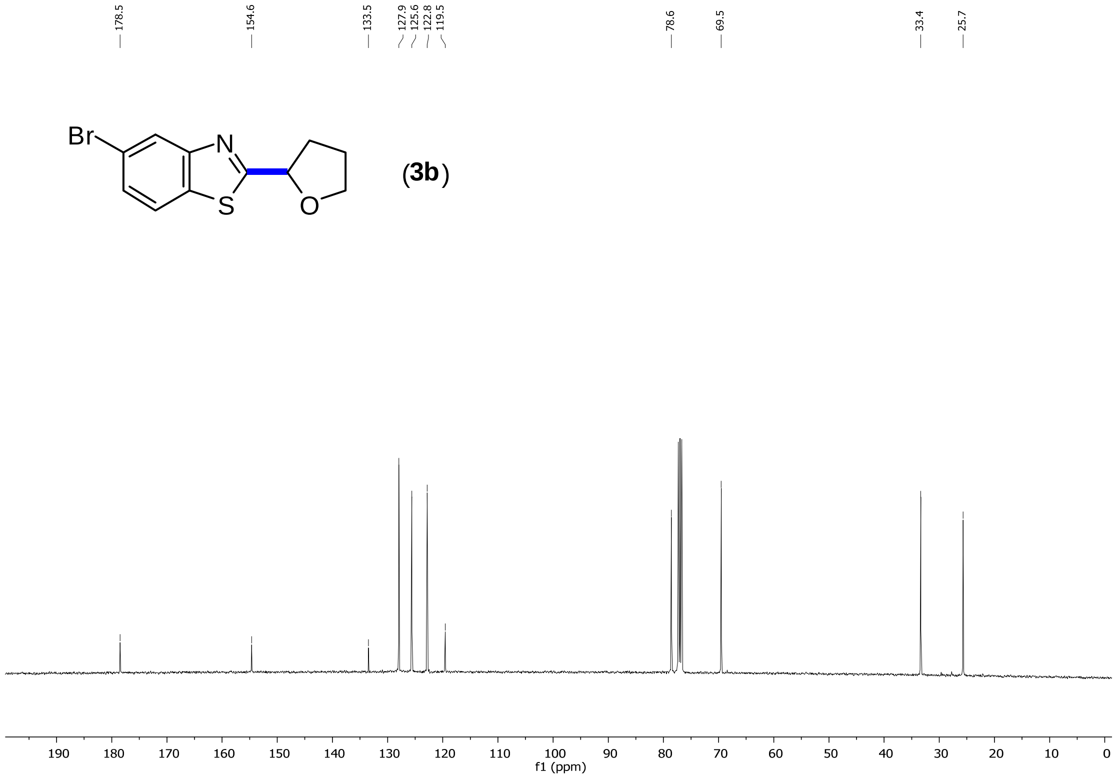
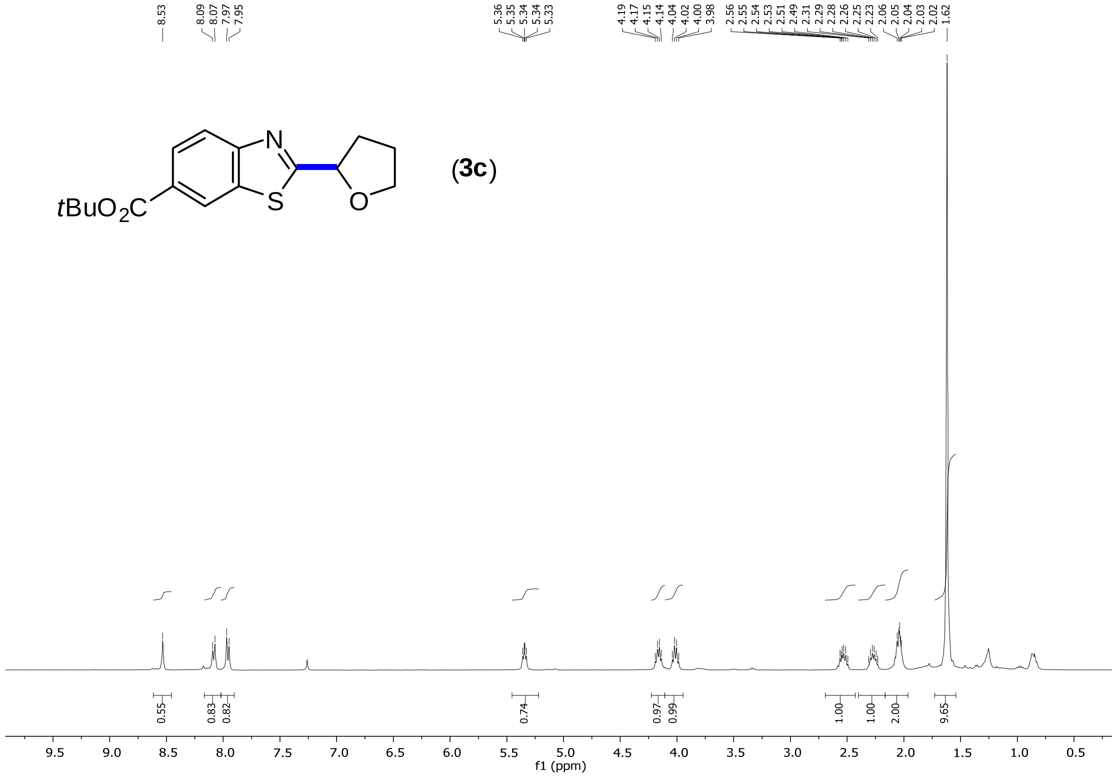
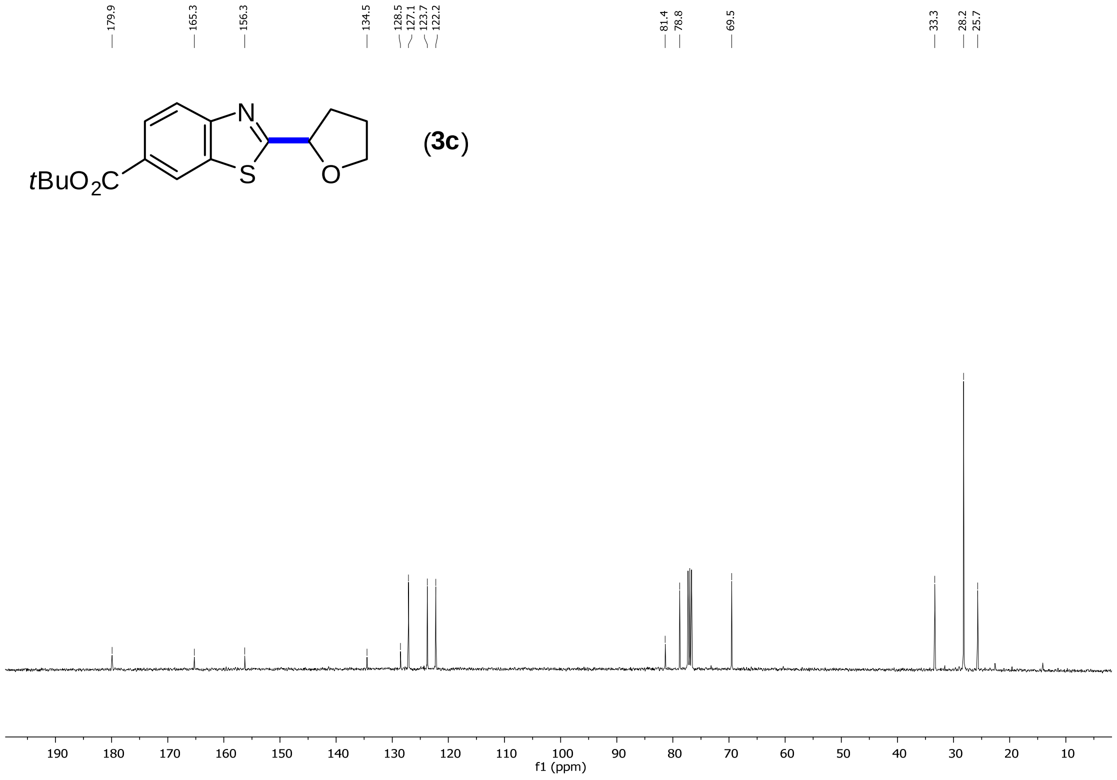
7.74
7.72
7.48
7.46
5.34
5.33
5.32
5.31
5.29
4.17
4.15
4.14
4.12
4.03
4.01
3.99
3.97
2.57
2.55
2.53
2.51
2.50
2.48
2.47
2.35
2.32
2.31
2.29
2.27
2.26
2.24
2.22
2.21
2.08
2.07
2.05
2.04
2.03
2.02
2.01
1.99
1.97
Br
N
S
O
0.92
0.84
0.78
1.00
0.98
0.99
1.15
1.38
1.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

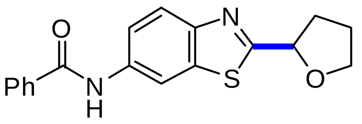
(**3b**)


178.5
154.6
133.5
127.9
125.6
122.8
119.5
78.6
69.5
33.4
25.7
Br
N
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

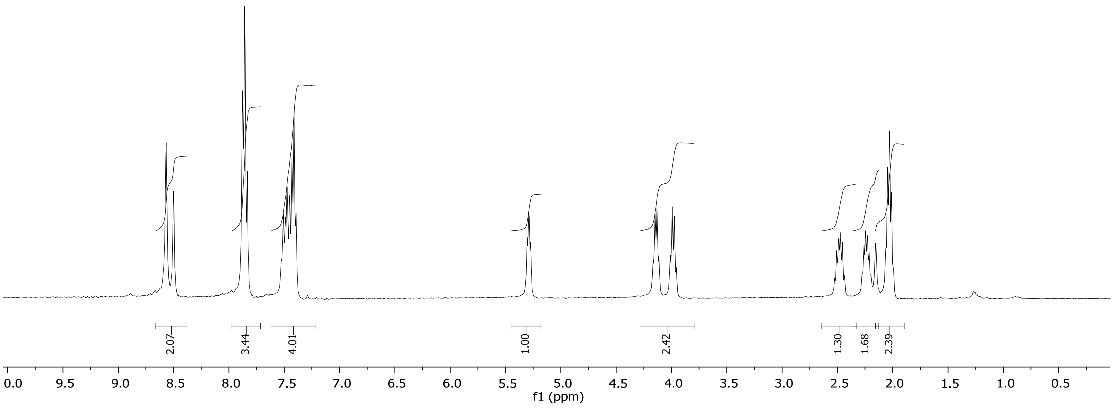
(**3b**)


8.53
8.09
8.07
7.97
7.95
5.36
5.35
5.34
5.34
5.33
4.19
4.17
4.15
4.14
4.04
4.02
4.00
3.98
2.56
2.55
2.54
2.53
2.51
2.49
2.31
2.29
2.28
2.26
2.25
2.23
2.06
2.05
2.04
2.03
2.02
1.62
N
S
O
*t*BuO$_2$C
(**3c**)
0.55
0.83
0.82
0.74
0.97
0.99
1.00
1.00
2.00
9.65
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
f1 (ppm)

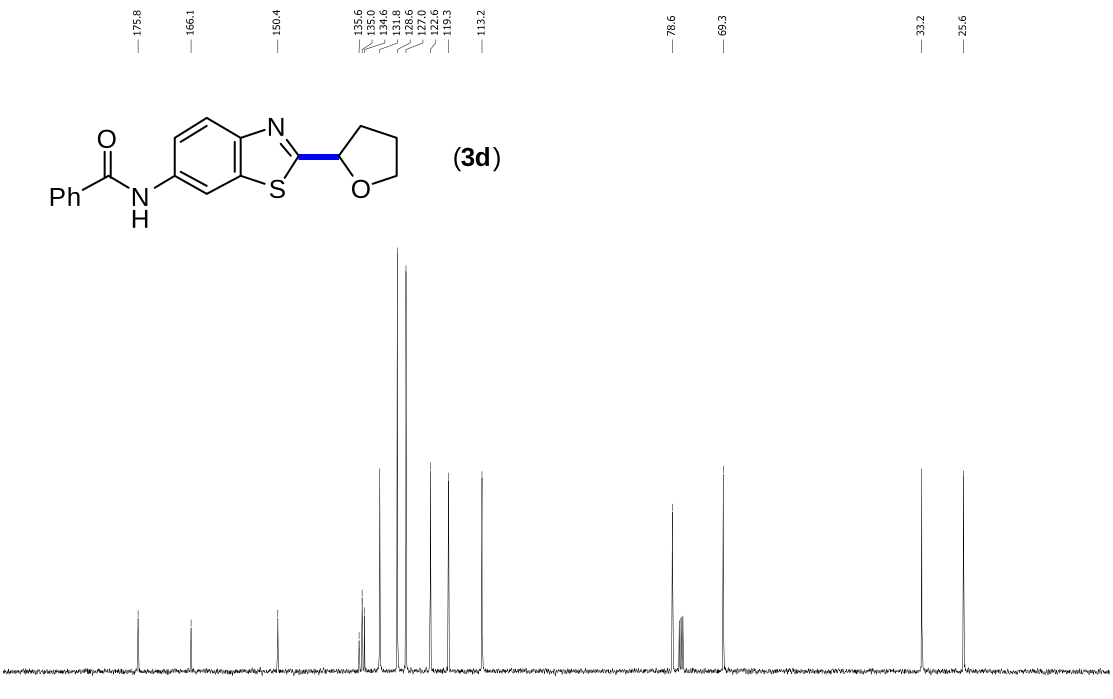

179.9
165.3
156.3
134.5
128.5
127.1
123.7
122.2
81.4
78.8
69.5
33.3
28.2
25.7
N
S
O
*t*BuO$_2$C
(**3c**)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

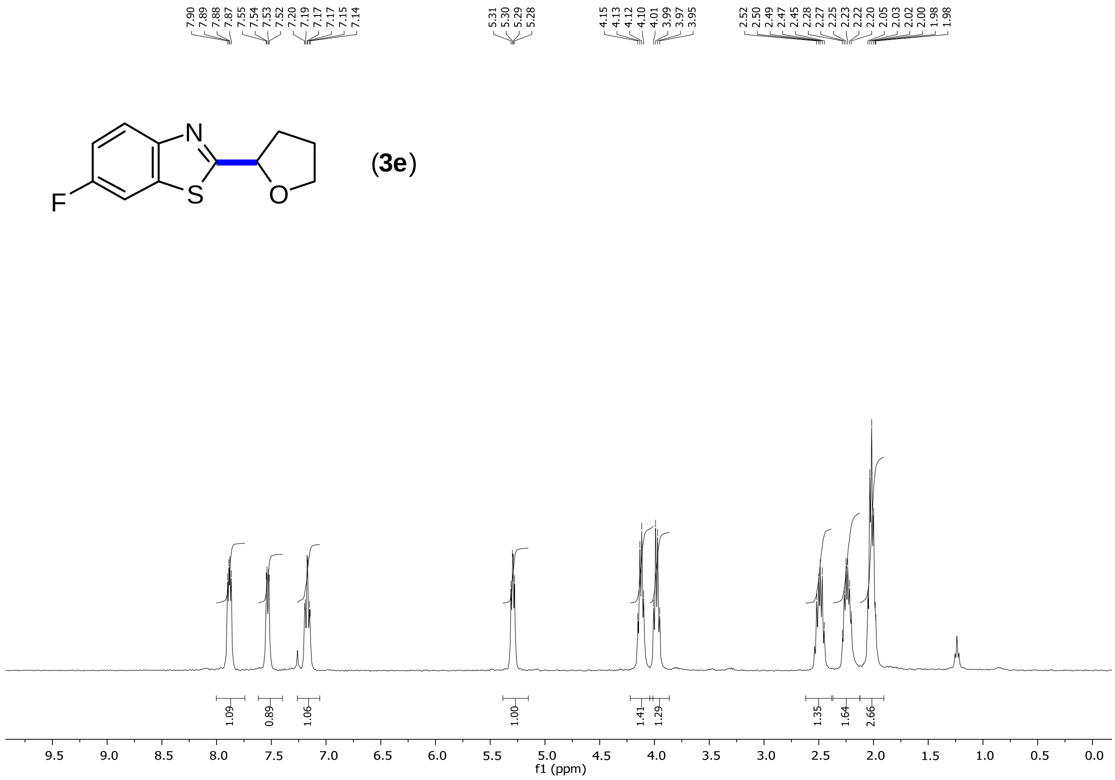

O
Ph
N
H
N
S
O

(**3d**)

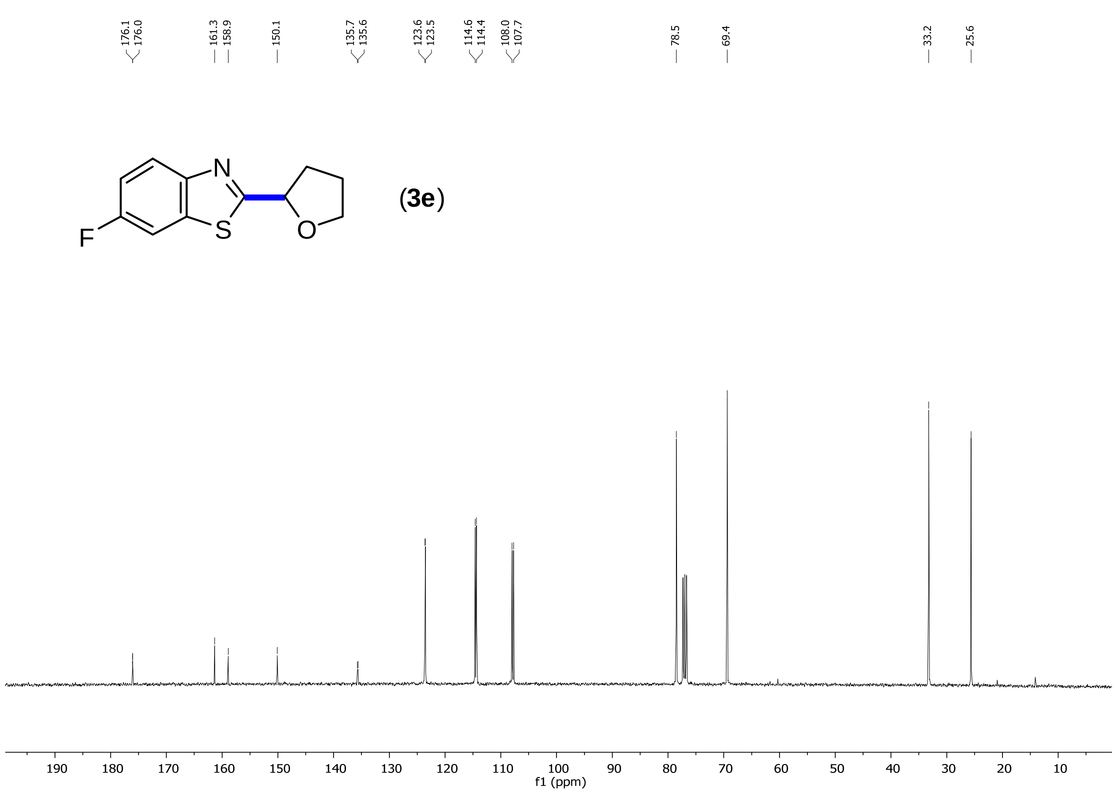

2.07
3.44
4.01
1.00
2.42
1.30
1.68
2.39
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

(**3d**)

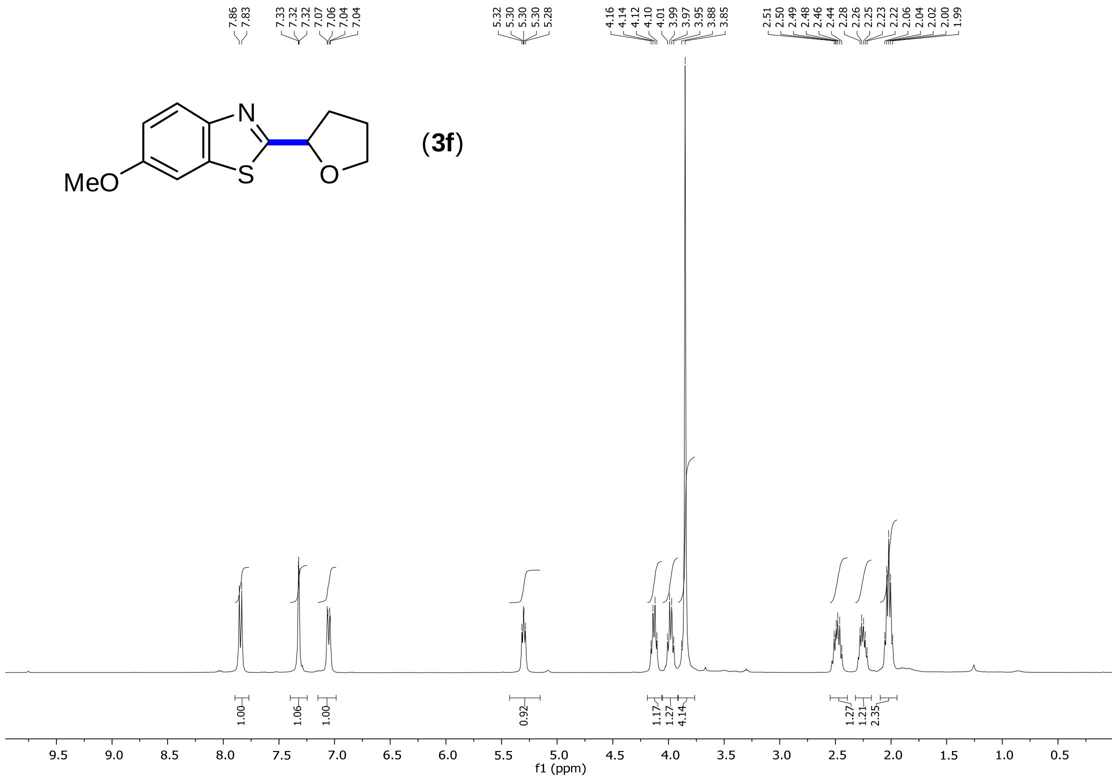

175.8
166.1
150.4
135.6
135.0
134.6
131.8
128.6
127.0
122.6
119.3
113.2
78.6
69.3
33.2
25.6
O
Ph
N
H
N
S
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.90
7.89
7.88
7.87
7.55
7.54
7.53
7.52
7.20
7.19
7.17
7.17
7.15
7.14
5.31
5.30
5.29
5.28
4.15
4.13
4.12
4.10
4.01
3.99
3.97
3.95
2.52
2.50
2.49
2.47
2.45
2.28
2.27
2.25
2.23
2.22
2.20
2.05
2.03
2.02
2.00
1.98
1.98
N
S
O
F
1.09
0.89
1.06
1.00
1.41
1.29
1.35
1.64
2.66
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
f1 (ppm)

(**3e**)

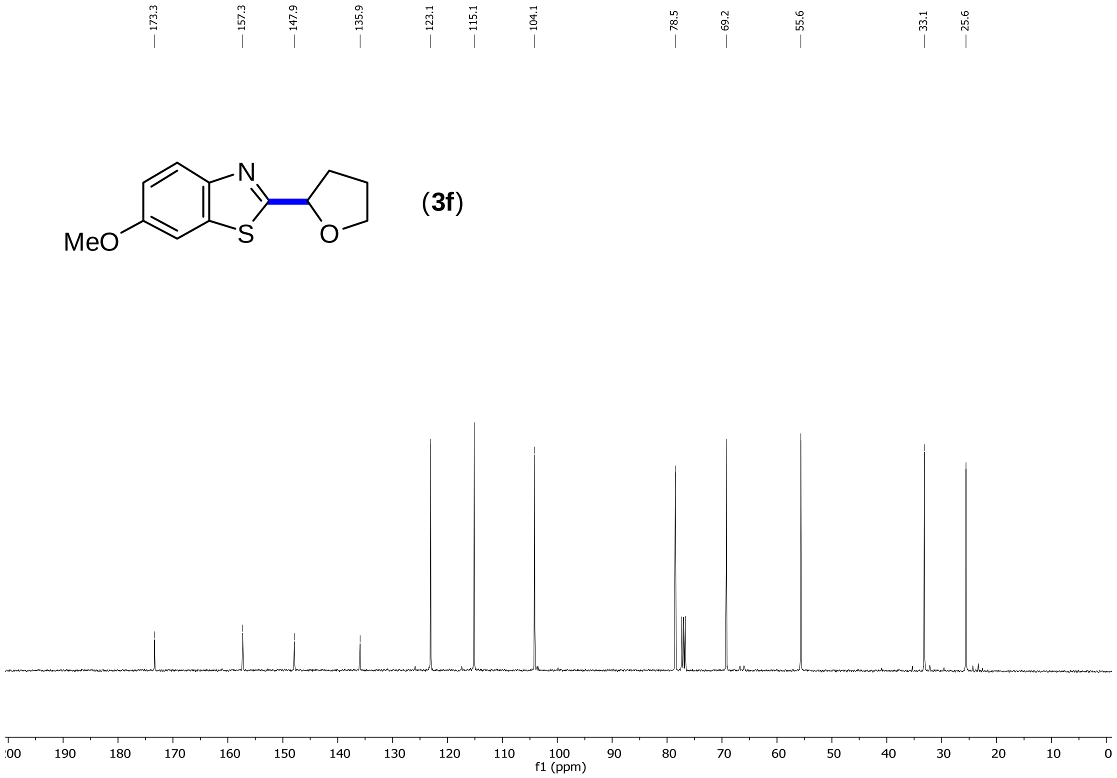

176.1
176.0
161.3
158.9
150.1
135.7
135.6
123.6
123.5
114.6
114.4
108.0
107.7
78.5
69.4
33.2
25.6
N
S
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(**3e**)



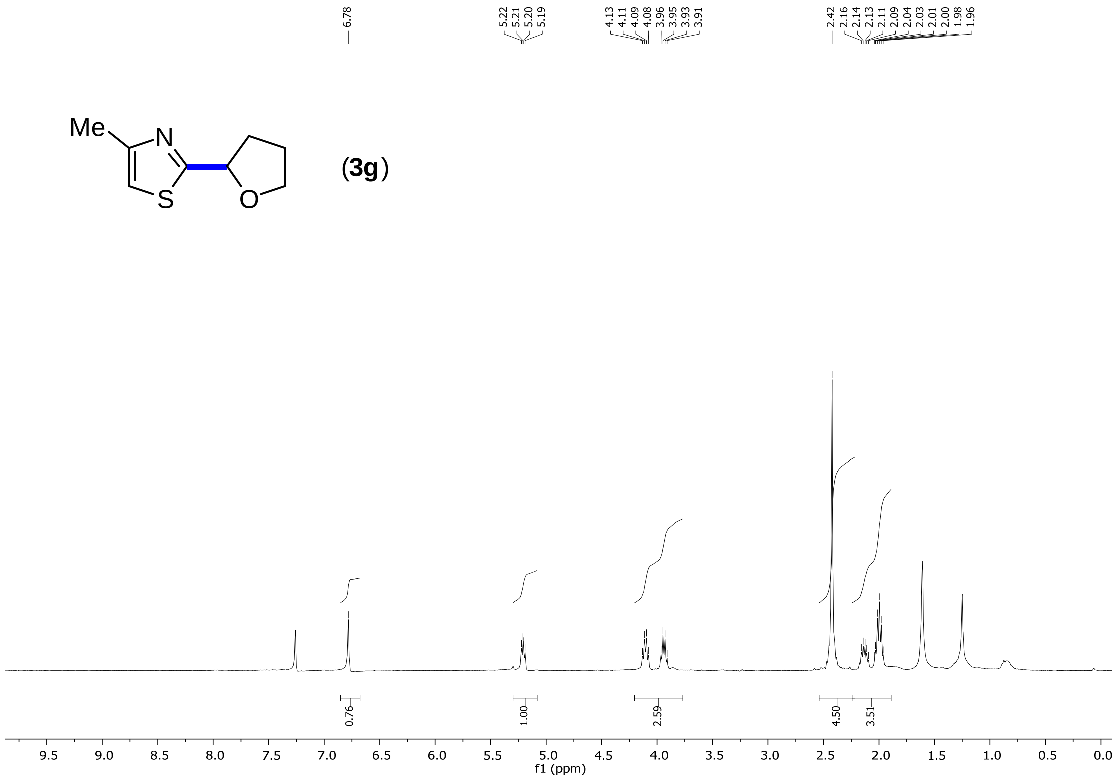
7.86
7.83
7.33
7.32
7.32
7.07
7.06
7.04
7.04
5.32
5.30
5.30
5.30
5.28
4.16
4.14
4.12
4.10
4.01
3.99
3.97
3.95
3.88
3.85
2.51
2.50
2.49
2.48
2.46
2.44
2.28
2.26
2.25
2.23
2.22
2.06
2.04
2.02
2.00
1.99
N
S
O
MeO
1.00
1.06
1.00
0.92
1.17
1.27
4.14
1.27
1.21
2.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

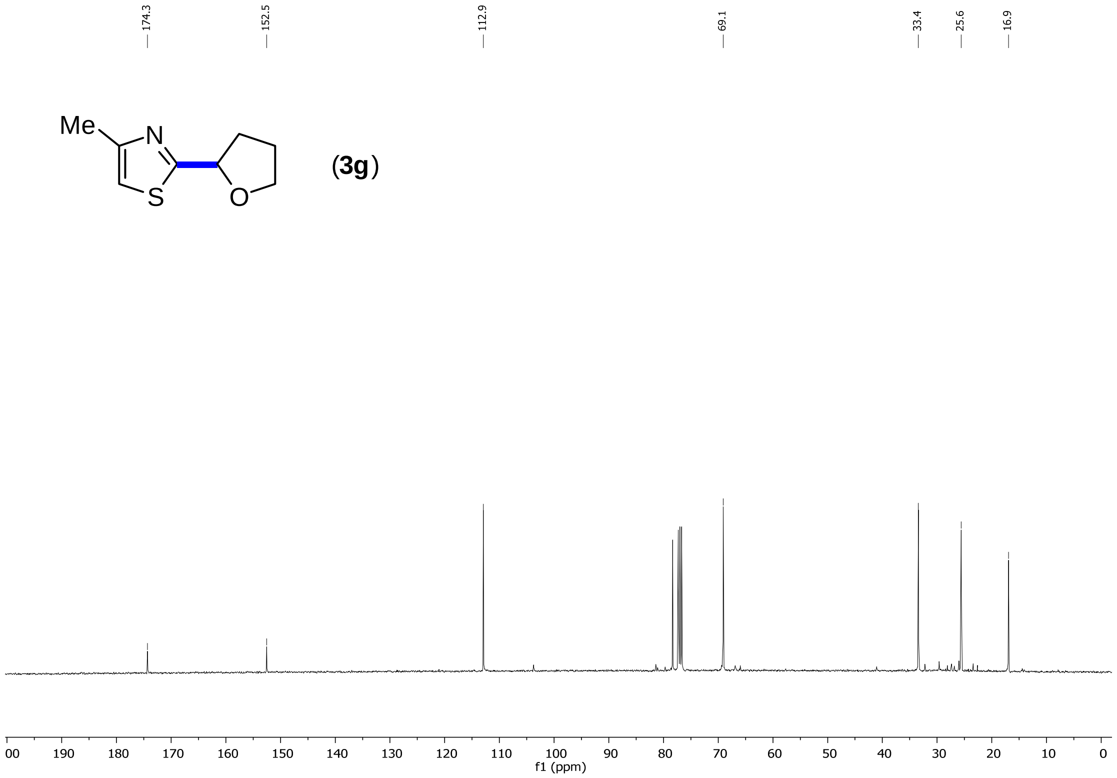
(**3f**)

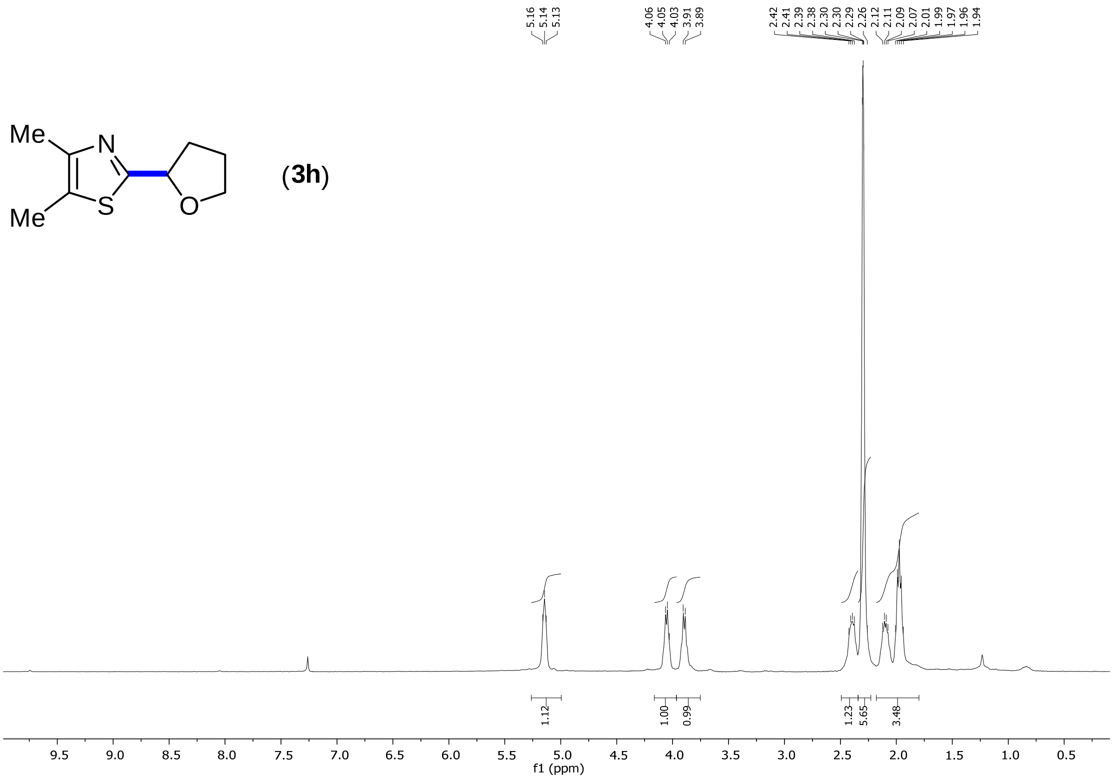


173.3
157.3
147.9
135.9
123.1
115.1
104.1
78.5
69.2
55.6
33.1
25.6
N
S
O
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

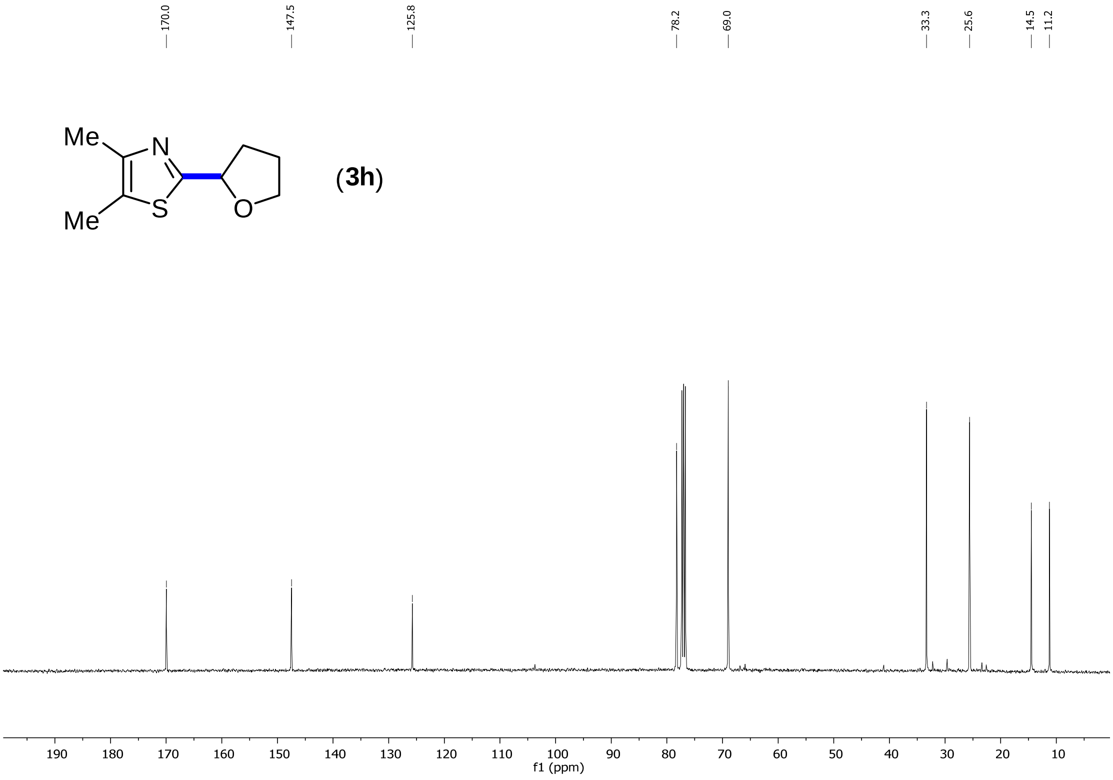
(**3f**)


6.78
5.22
5.21
5.20
5.19
4.13
4.11
4.09
4.08
3.96
3.95
3.93
3.91
2.42
2.16
2.14
2.13
2.11
2.09
2.04
2.03
2.01
2.00
1.98
1.96
Me
N
S
O
(3g)
0.76
1.00
2.59
4.50
3.51
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
f1 (ppm)

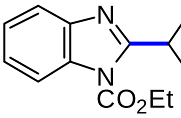

174.3
152.5
112.9
69.1
33.4
25.6
16.9
Me
N
S
O
(3g)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(**3h**)

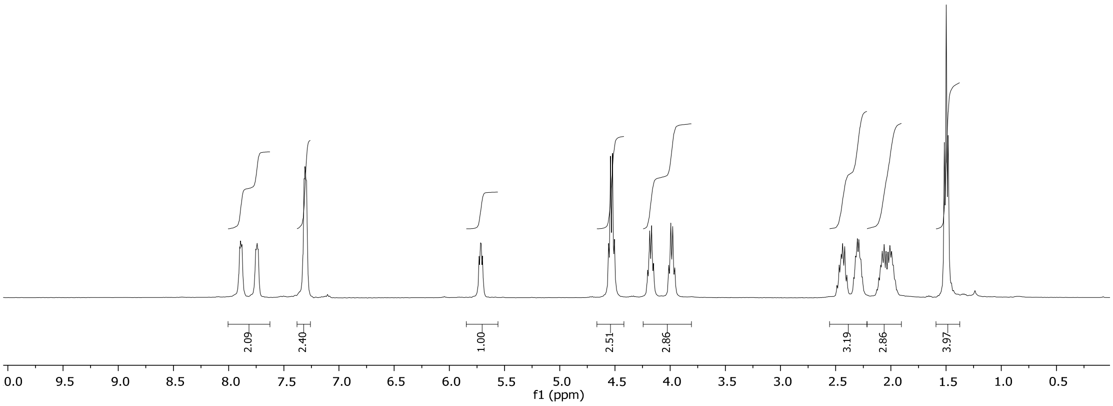
5.16
5.14
5.13
4.06
4.05
4.03
3.91
3.89
2.42
2.41
2.39
2.38
2.30
2.30
2.29
2.26
2.12
2.11
2.09
2.07
2.01
1.99
1.97
1.96
1.94
Me
N
S
O
Me
1.12
1.00
0.99
1.23
5.65
3.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

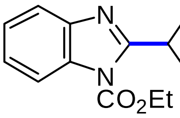

(**3h**)

170.0
147.5
125.8
78.2
69.0
33.3
25.6
14.5
11.2
Me
N
S
O
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

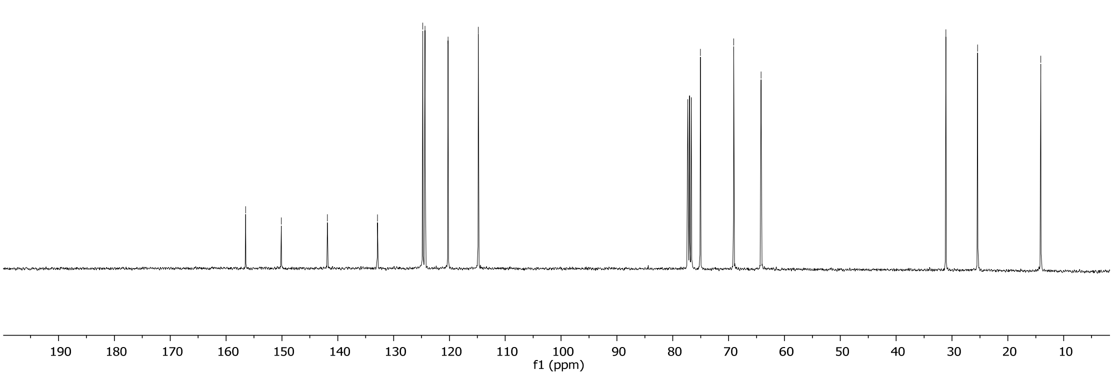

N
N
O
CO2Et

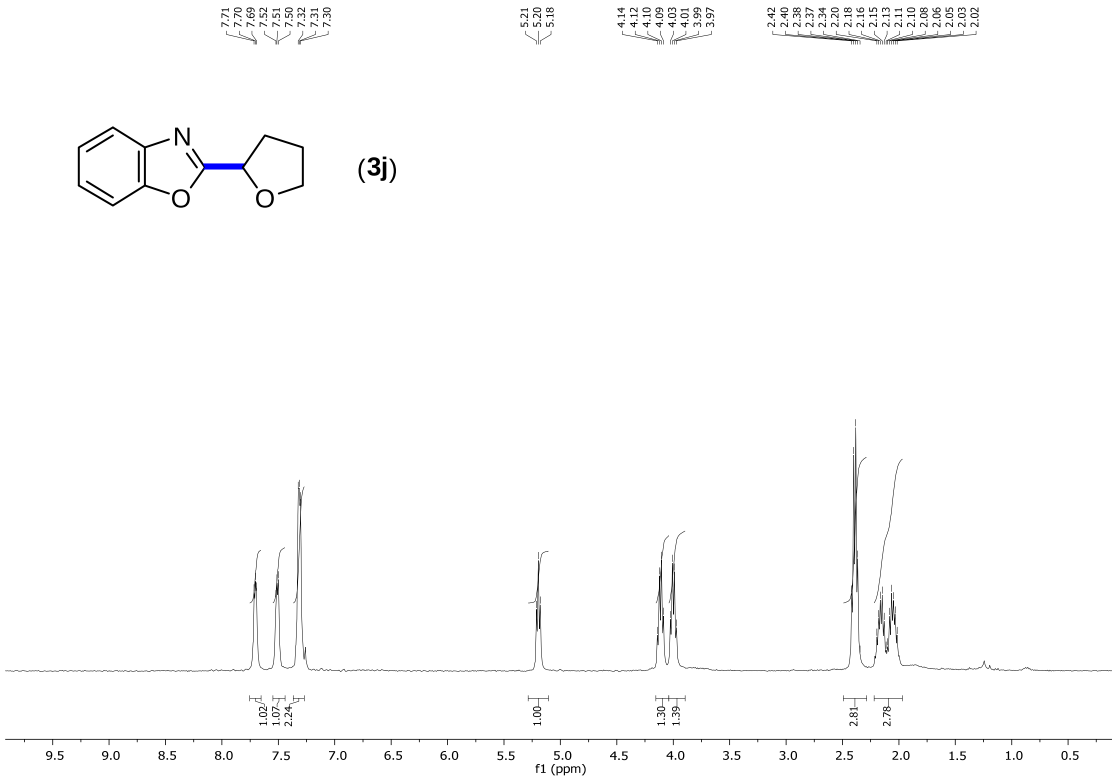
(**3i**)

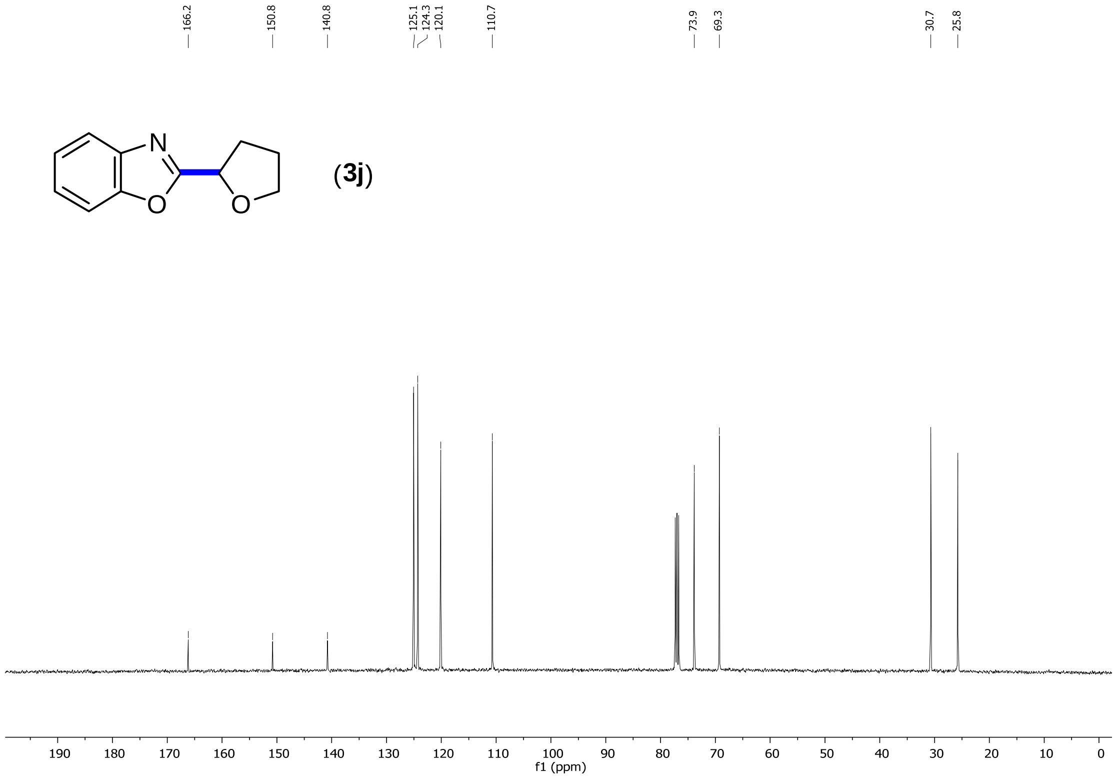

2.09
2.40
1.00
2.51
2.86
3.19
2.86
3.97
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

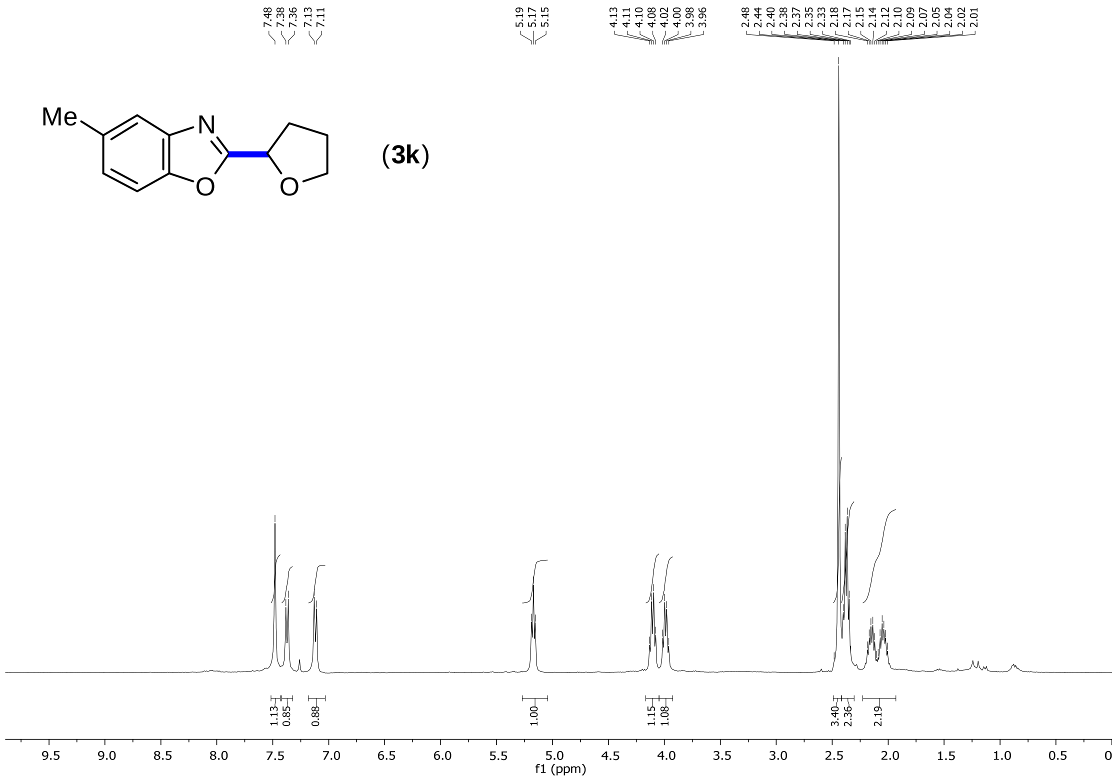

N
N
O
CO2Et

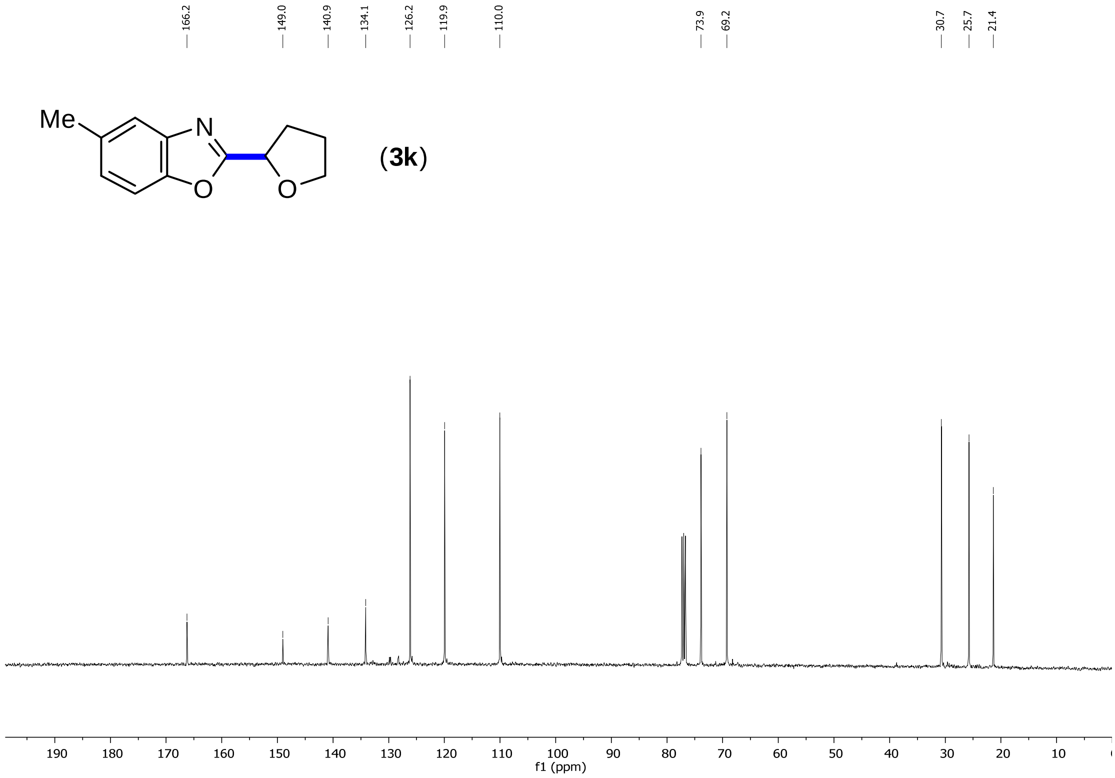
(**3i**)

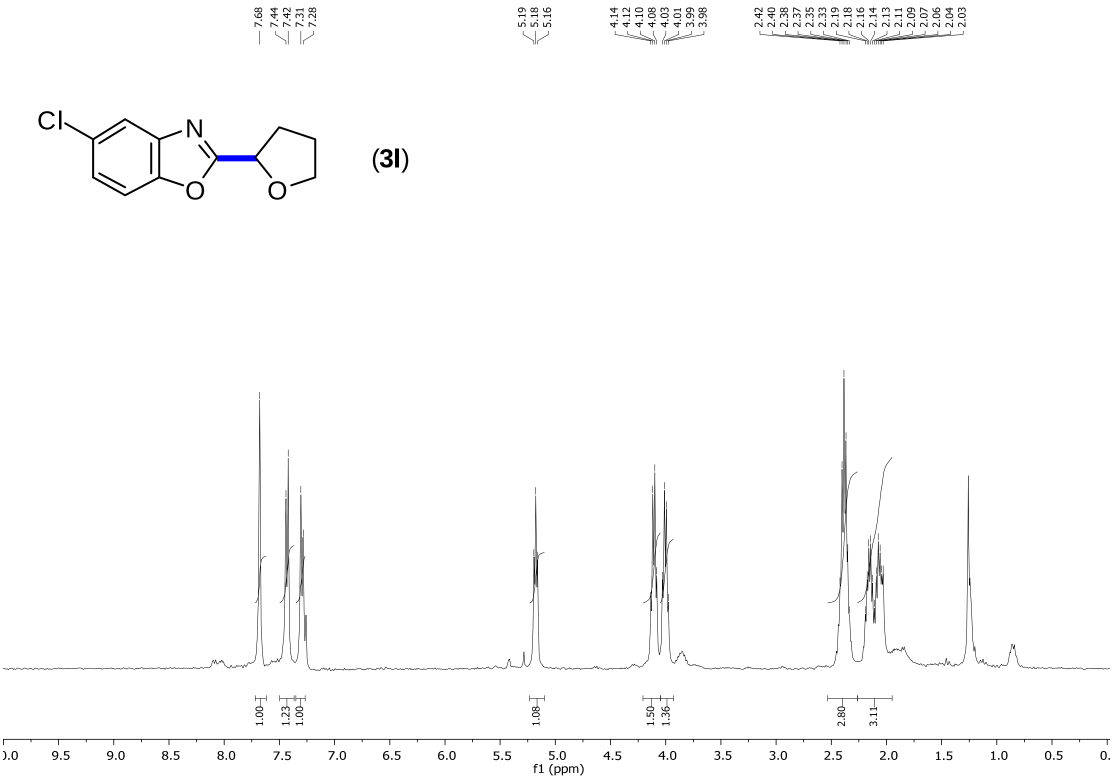

156.5
150.1
141.8
132.9
124.8
124.4
120.2
114.8
75.1
69.1
64.2
31.1
25.4
14.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


(3j)
7.71
7.70
7.69
7.52
7.51
7.50
7.32
7.31
7.30
5.21
5.20
5.18
4.14
4.12
4.10
4.09
4.03
4.01
3.99
3.97
2.42
2.40
2.38
2.37
2.34
2.20
2.18
2.16
2.15
2.13
2.11
2.10
2.08
2.06
2.05
2.03
2.02
N
O
O
1.02
1.07
2.24
1.00
1.30
1.39
2.81
2.78
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
f1 (ppm)

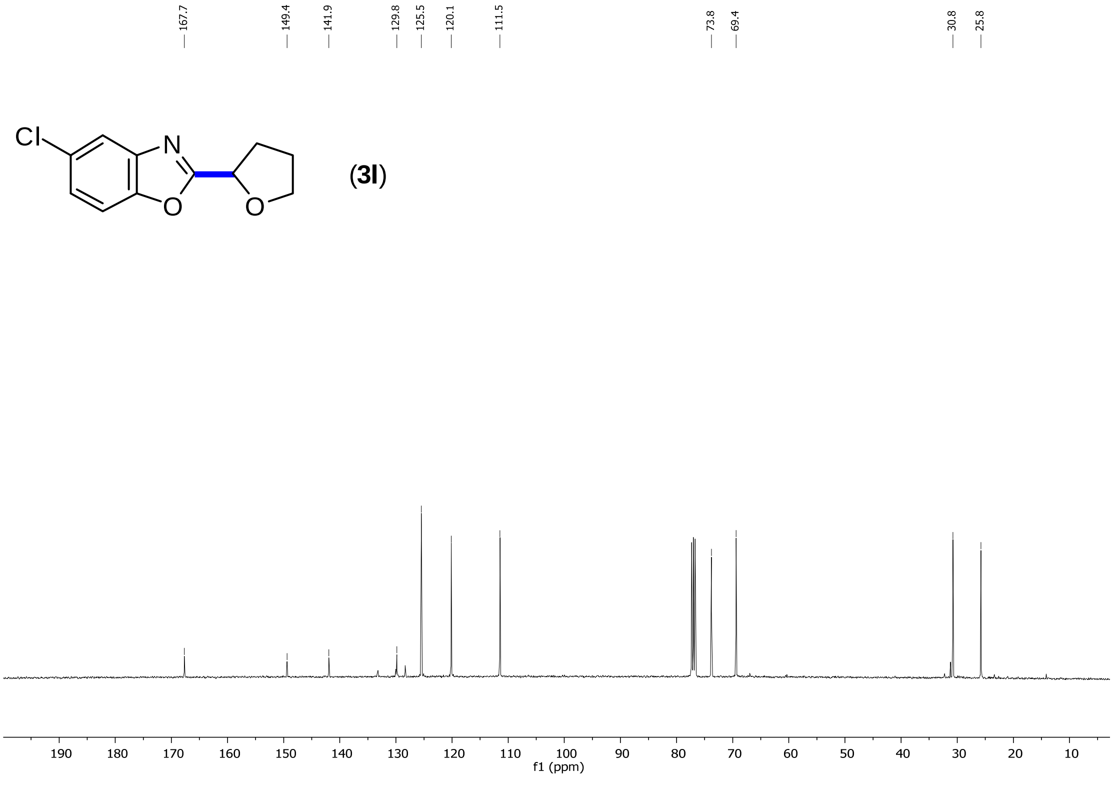

(3j)
166.2
150.8
140.8
125.1
124.3
120.1
110.7
73.9
69.3
30.7
25.8
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.48
7.38
7.36
7.13
7.11
5.19
5.17
5.15
4.13
4.11
4.10
4.08
4.02
4.00
3.98
3.96
2.48
2.44
2.40
2.38
2.37
2.35
2.33
2.18
2.17
2.15
2.14
2.12
2.10
2.09
2.07
2.05
2.04
2.02
2.01
Me
N
O
O
(3k)
1.13
0.85
0.88
1.00
1.15
1.08
3.40
2.36
2.19
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
f1 (ppm)

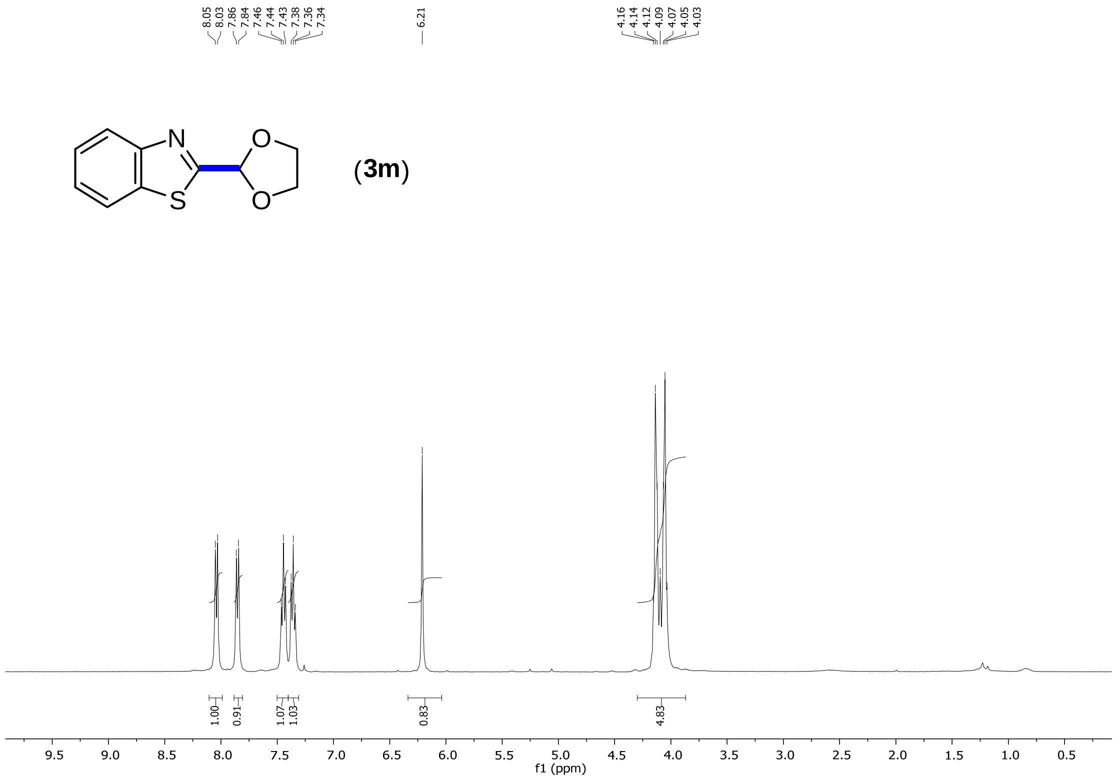

166.2
149.0
140.9
134.1
126.2
119.9
110.0
73.9
69.2
30.7
25.7
21.4
Me
N
O
O
(3k)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

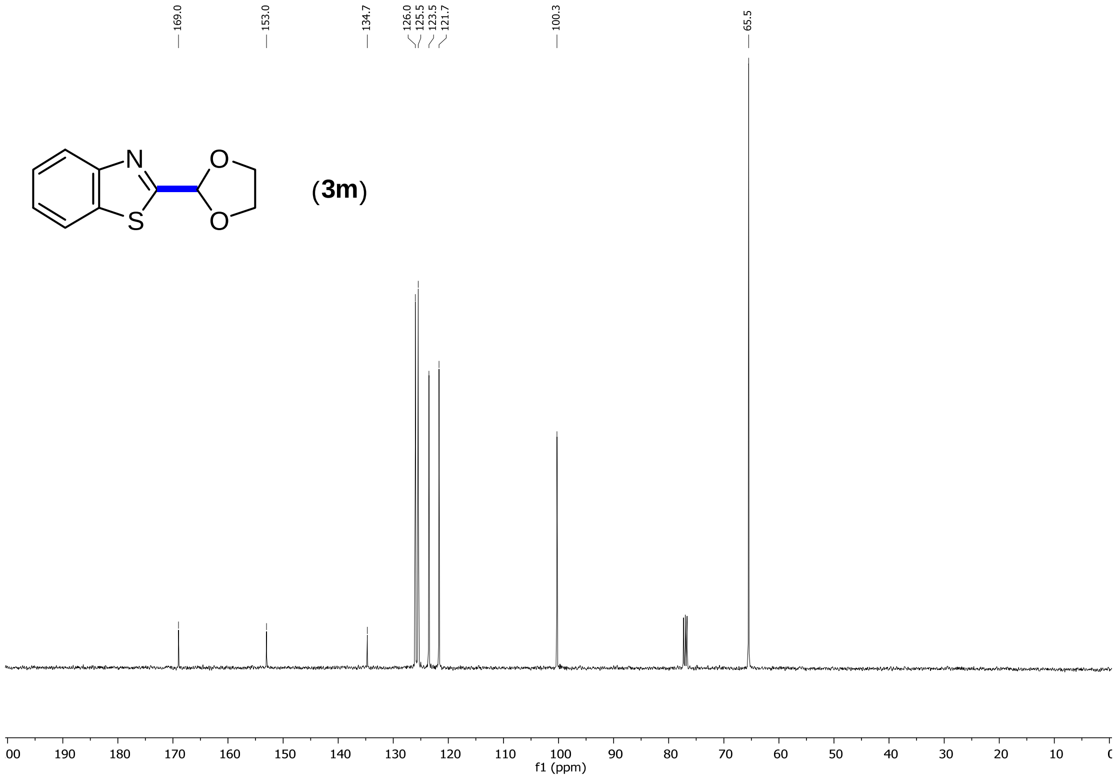

7.68
7.44
7.42
7.31
7.28
5.19
5.18
5.16
4.14
4.12
4.10
4.08
4.03
4.01
3.99
3.98
2.42
2.40
2.38
2.37
2.35
2.33
2.19
2.18
2.16
2.14
2.13
2.11
2.09
2.07
2.06
2.04
2.03
Cl
N
O
O
1.00
1.23
1.00
1.08
1.50
1.36
2.80
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

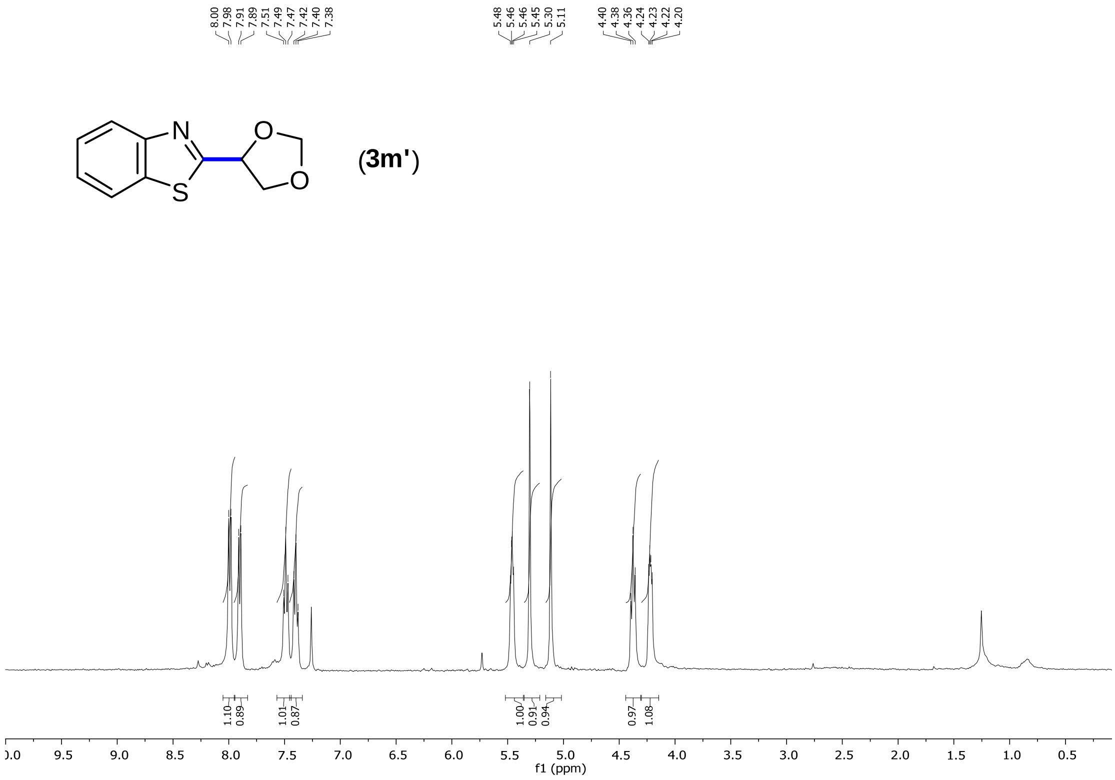
(**3l**)


167.7
149.4
141.9
129.8
125.5
120.1
111.5
73.8
69.4
30.8
25.8
Cl
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(**3l**)

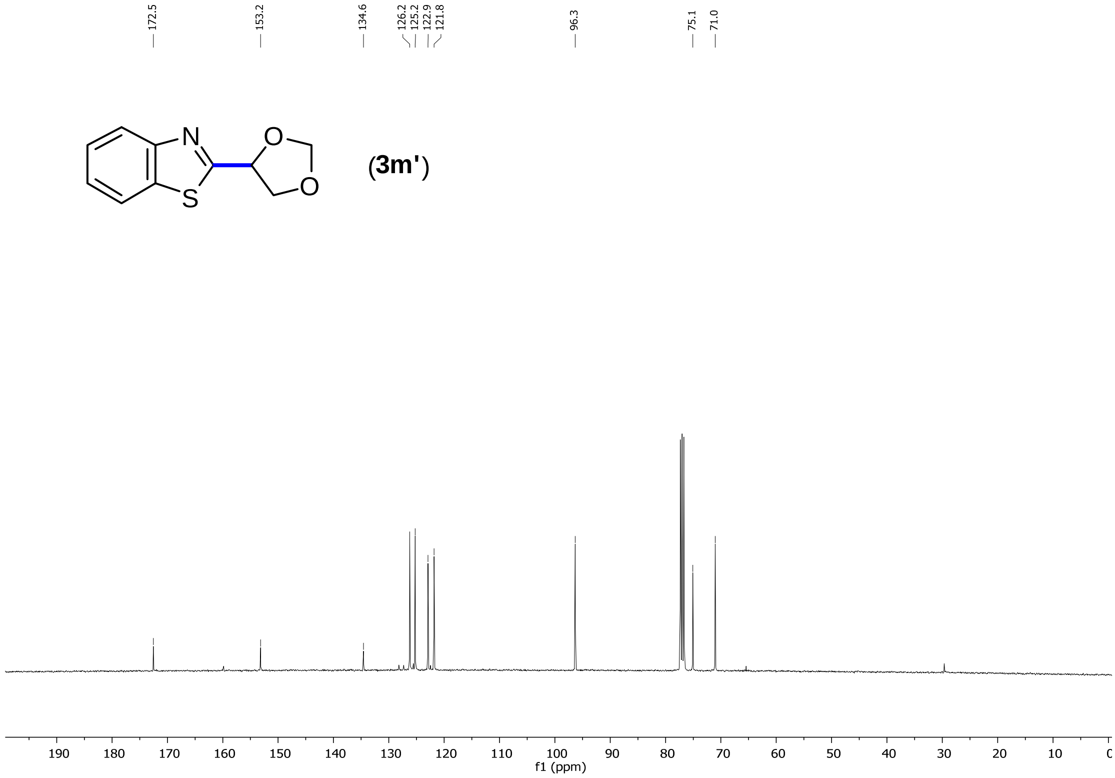

8.05
8.03
7.86
7.84
7.46
7.44
7.43
7.38
7.36
7.34
6.21
4.16
4.14
4.12
4.09
4.07
4.05
4.03
N
S
O
O
(3m)
1.00
0.91
1.07
1.03
0.83
4.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


169.0
153.0
134.7
126.0
125.5
123.5
121.7
100.3
65.5
N
S
O
O
(3m)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



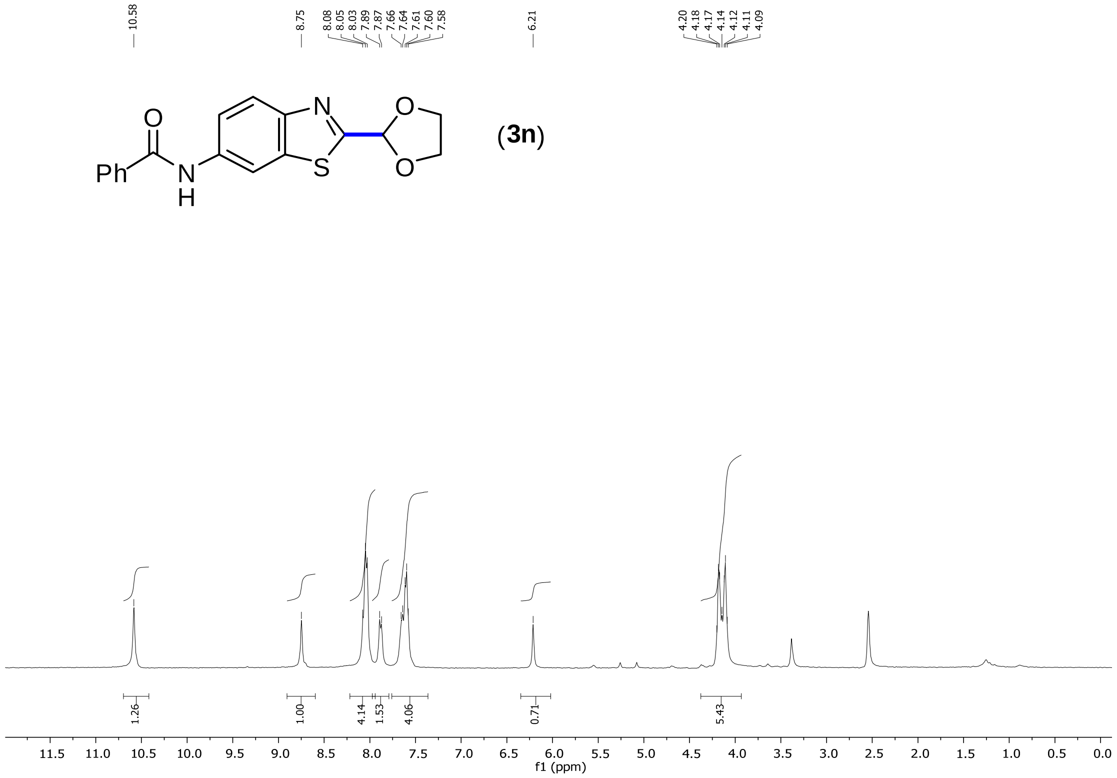
(3m')

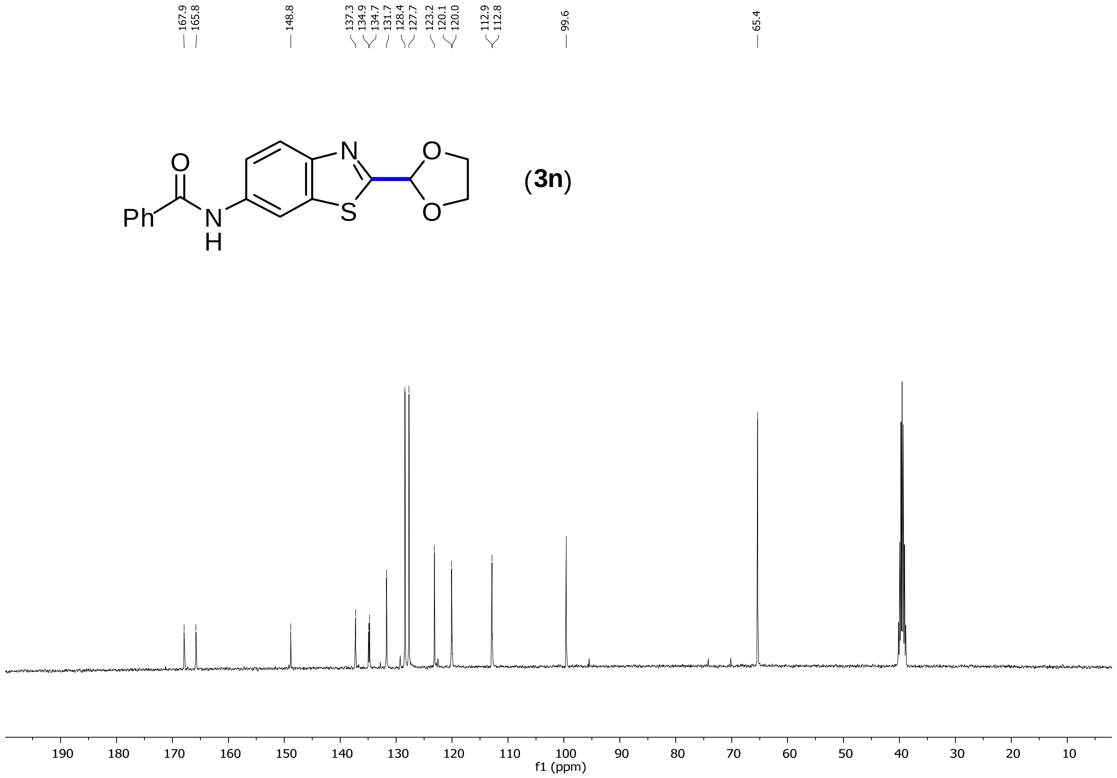
8.00
7.98
7.91
7.89
7.51
7.49
7.47
7.42
7.40
7.38
5.48
5.46
5.46
5.45
5.30
5.11
4.40
4.38
4.36
4.24
4.23
4.22
4.20
N
O
S
O
1.10
0.89
1.01
0.87
1.00
0.91
0.94
0.97
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

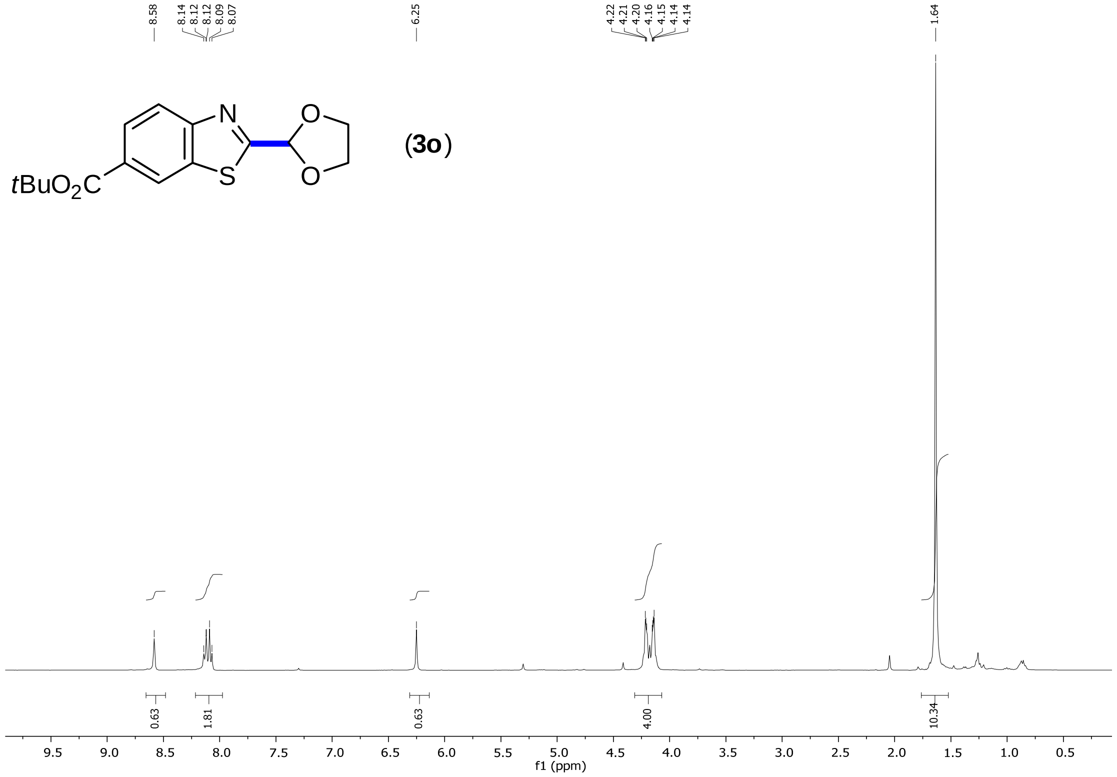


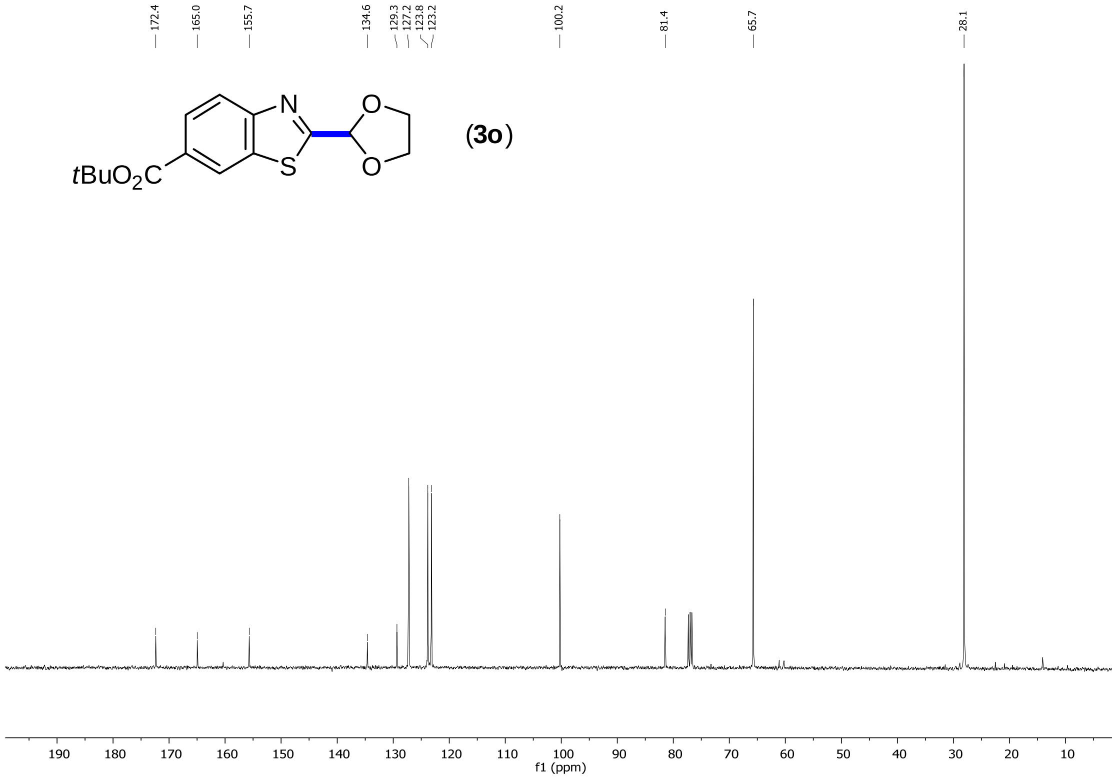
(3m')

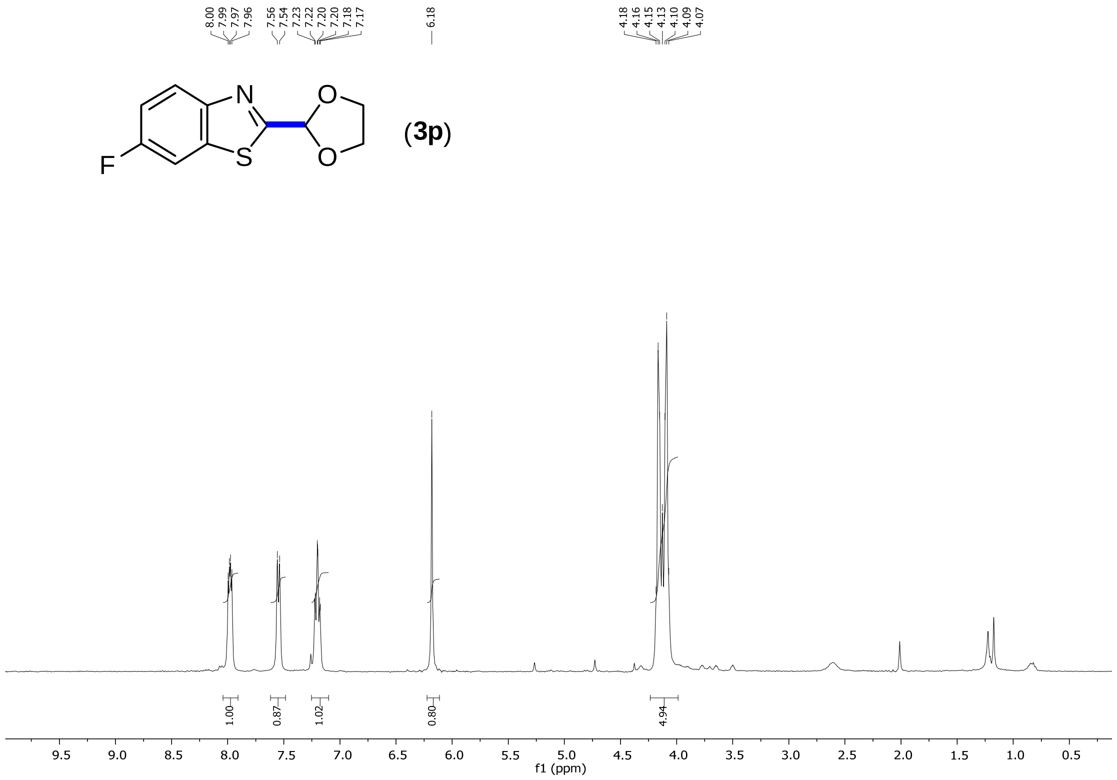
172.5
153.2
134.6
126.2
125.2
122.9
121.8
96.3
75.1
71.0
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.58
8.75
8.08
8.05
8.03
7.89
7.87
7.66
7.64
7.61
7.60
7.58
6.21
4.20
4.18
4.17
4.14
4.12
4.11
4.09
O
Ph
N
H
N
S
O
O
(3n)
1.26
1.00
4.14
1.53
4.06
0.71
5.43
11.5
11.0
10.5
10.0
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
f1 (ppm)

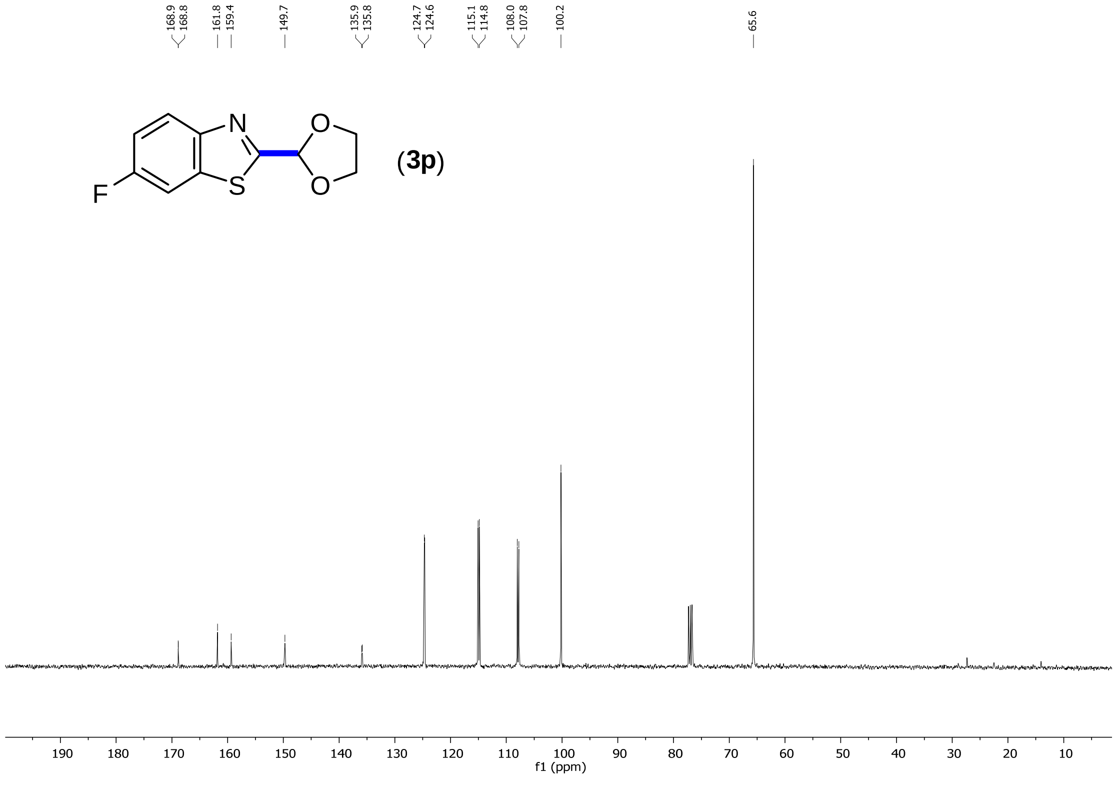

167.9
165.8
148.8
137.3
134.9
134.7
131.7
128.4
127.7
123.2
120.1
120.0
112.9
112.8
99.6
65.4
O
Ph
N
H
N
S
O
O
(3n)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.58
8.14
8.12
8.12
8.09
8.07
6.25
4.22
4.21
4.20
4.16
4.15
4.14
4.14
1.64
tBuO2C
N
S
O
O
(3o)
0.63
1.81
0.63
4.00
10.34
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
f1 (ppm)

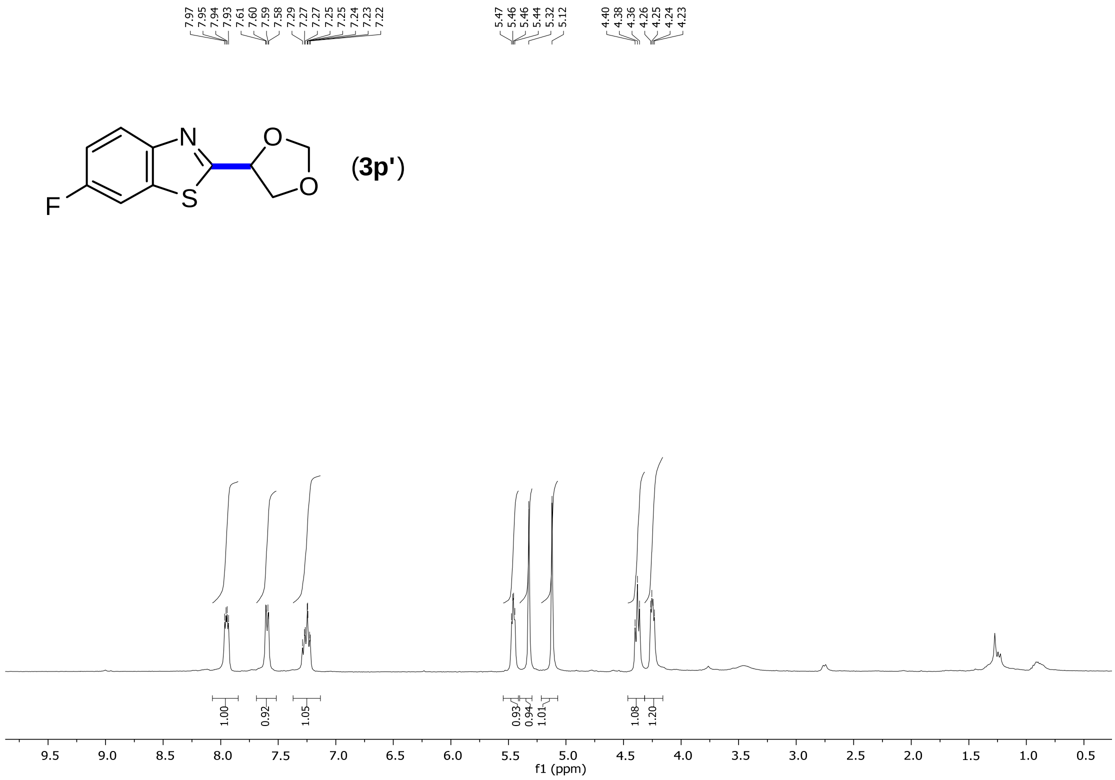

172.4
165.0
155.7
134.6
129.3
127.2
123.8
123.2
100.2
81.4
65.7
28.1
tBuO2C
N
S
O
O
(3o)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.00
7.99
7.97
7.96
7.56
7.54
7.23
7.22
7.20
7.20
7.18
7.17
6.18
4.18
4.16
4.15
4.13
4.10
4.09
4.07
N
S
O
O
F
1.00
0.87
1.02
0.80
4.94
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
f1 (ppm)

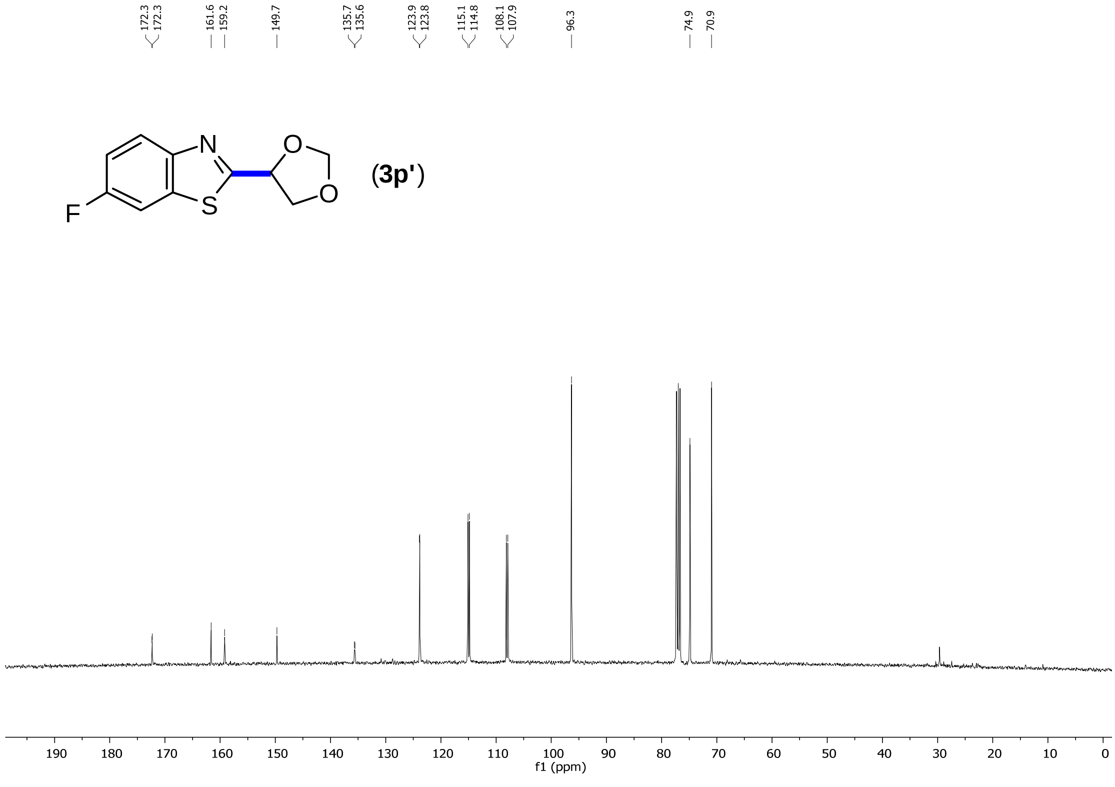
(**3p**)


168.9
168.8
161.8
159.4
149.7
135.9
135.8
124.7
124.6
115.1
114.8
108.0
107.8
100.2
65.6
N
S
O
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

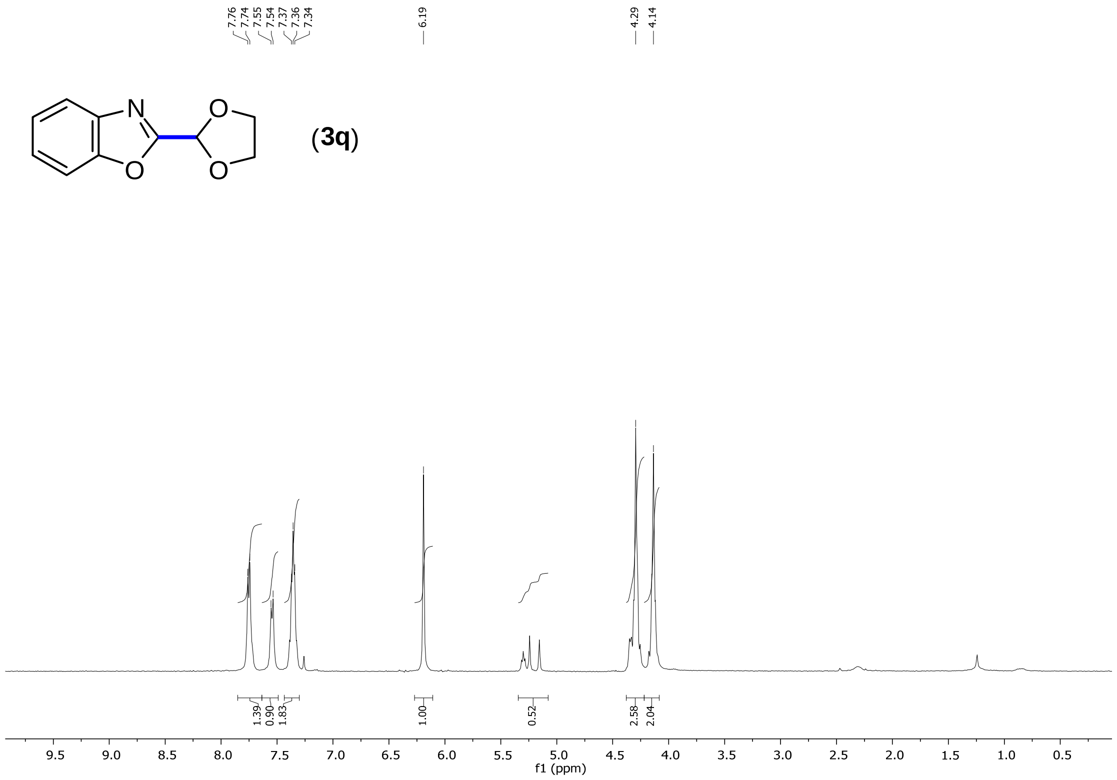
(**3p**)


7.97
7.95
7.94
7.93
7.61
7.60
7.59
7.58
7.29
7.27
7.27
7.25
7.25
7.24
7.23
7.22
5.47
5.46
5.46
5.44
5.32
5.12
4.40
4.38
4.36
4.26
4.25
4.24
4.23
N
O
O
S
F
1.00
0.92
1.05
0.93
0.94
1.01
1.08
1.20
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
f1 (ppm)

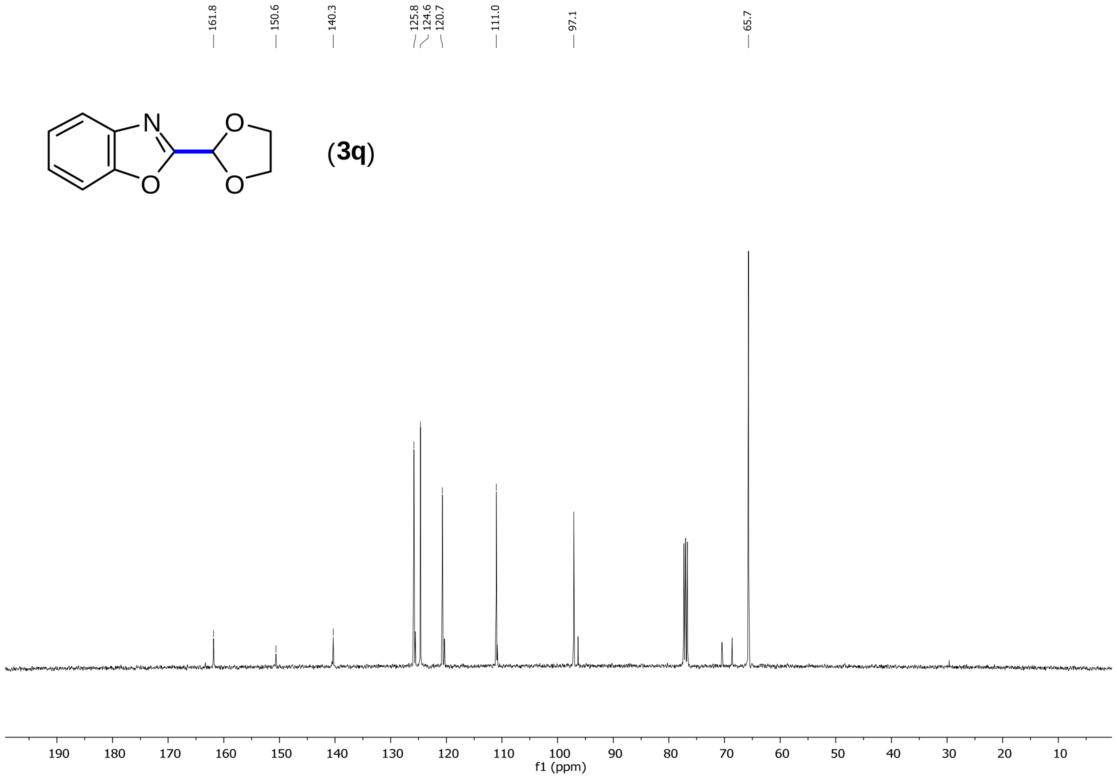
(**3p'**)


172.3
172.3
161.6
159.2
149.7
135.7
135.6
123.9
123.8
115.1
114.8
108.1
107.9
96.3
74.9
70.9
N
O
O
S
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

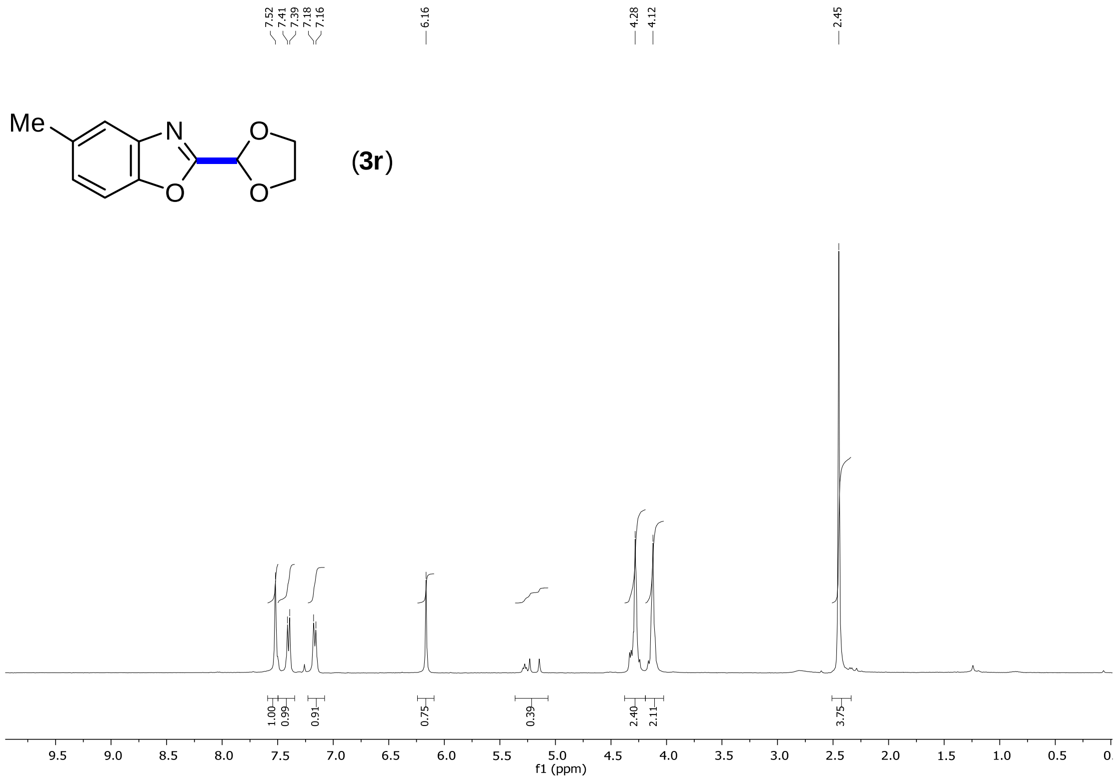
(**3p'**)


7.76
7.74
7.55
7.54
7.37
7.36
7.34
6.19
4.29
4.14
N
O
O
O
1.39
0.90
1.83
1.00
0.52
2.58
2.04
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
f1 (ppm)

(**3q**)

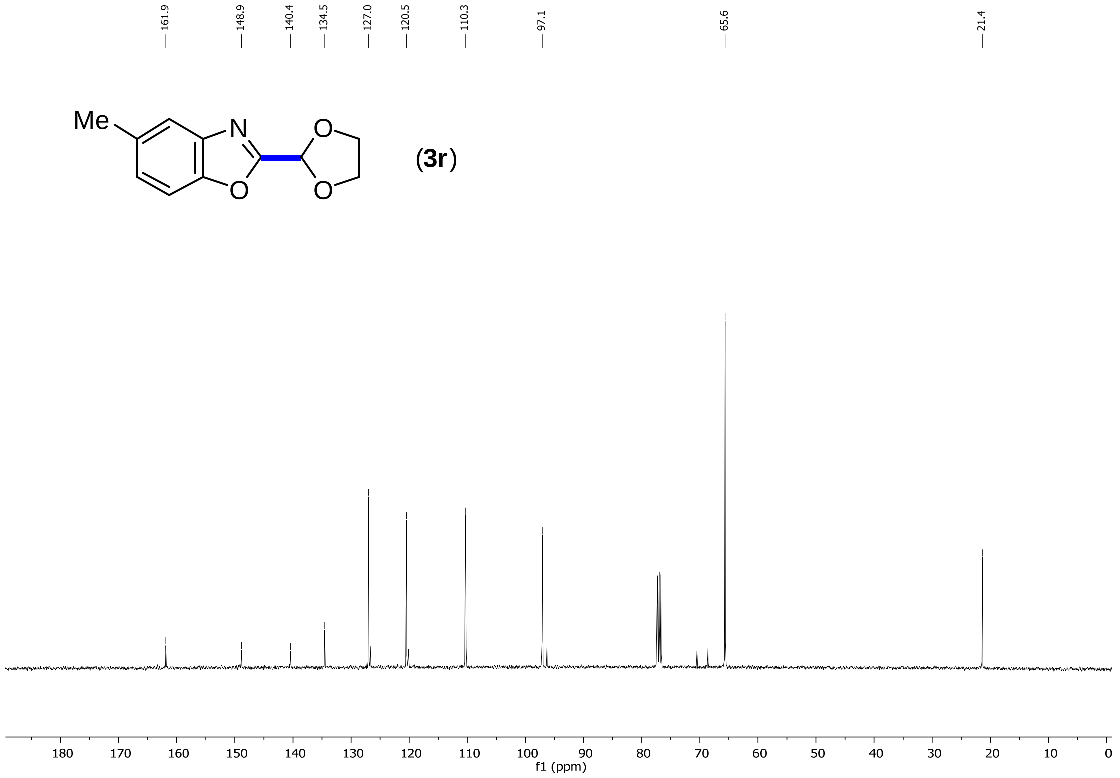

161.8
150.6
140.3
125.8
124.6
120.7
111.0
97.1
65.7
N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(**3q**)



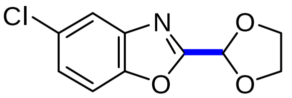
(3r)

Me
N
O
O
O
7.52
7.41
7.39
7.18
7.16
6.16
4.28
4.12
2.45
1.00
0.99
0.91
0.75
0.39
2.40
2.11
3.75
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
f1 (ppm)

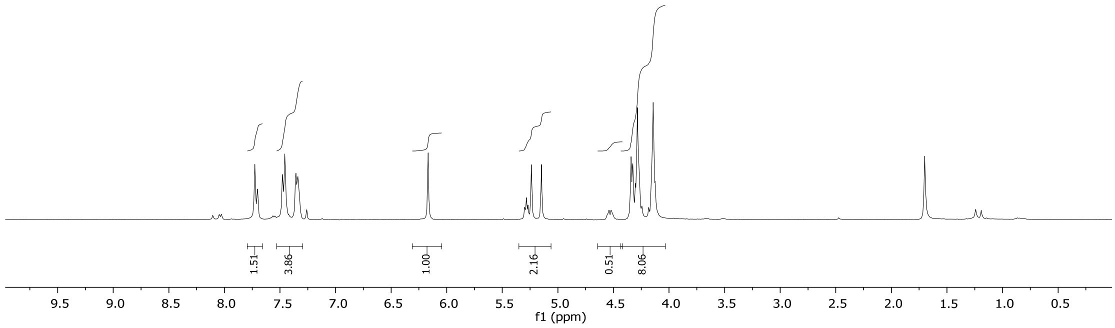


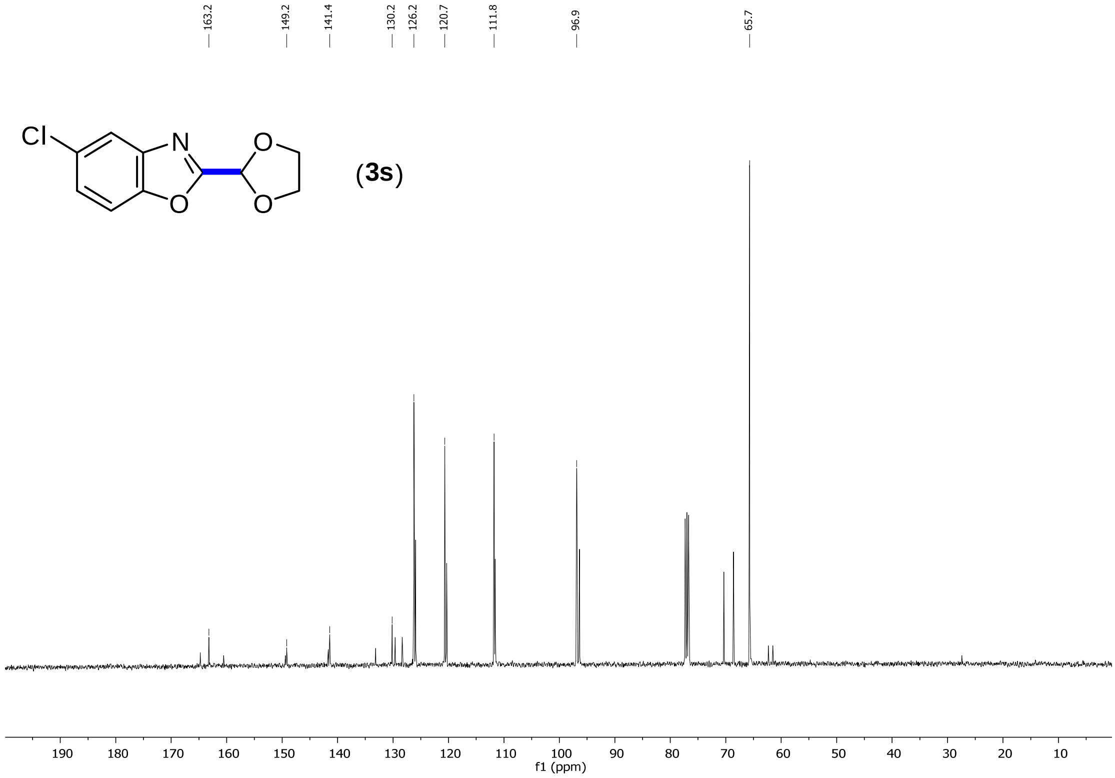
(3r)

Me
N
O
O
O
161.9
148.9
140.4
134.5
127.0
120.5
110.3
97.1
65.6
21.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

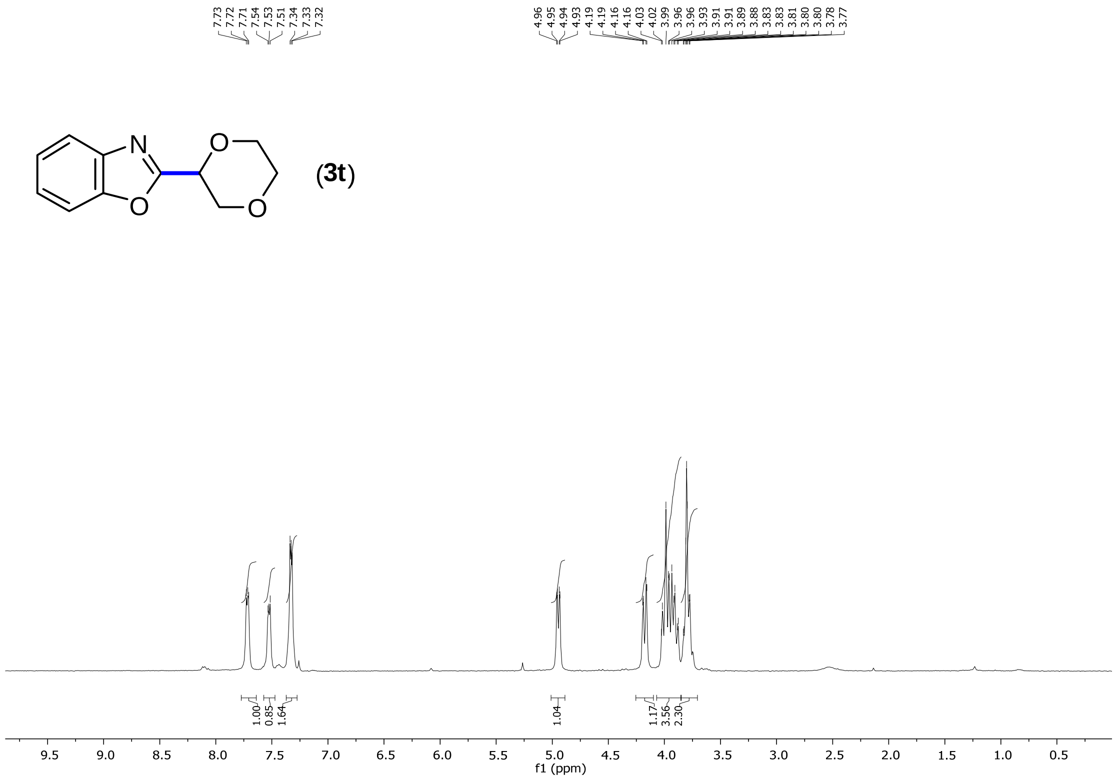

Cl
N
O
O
O

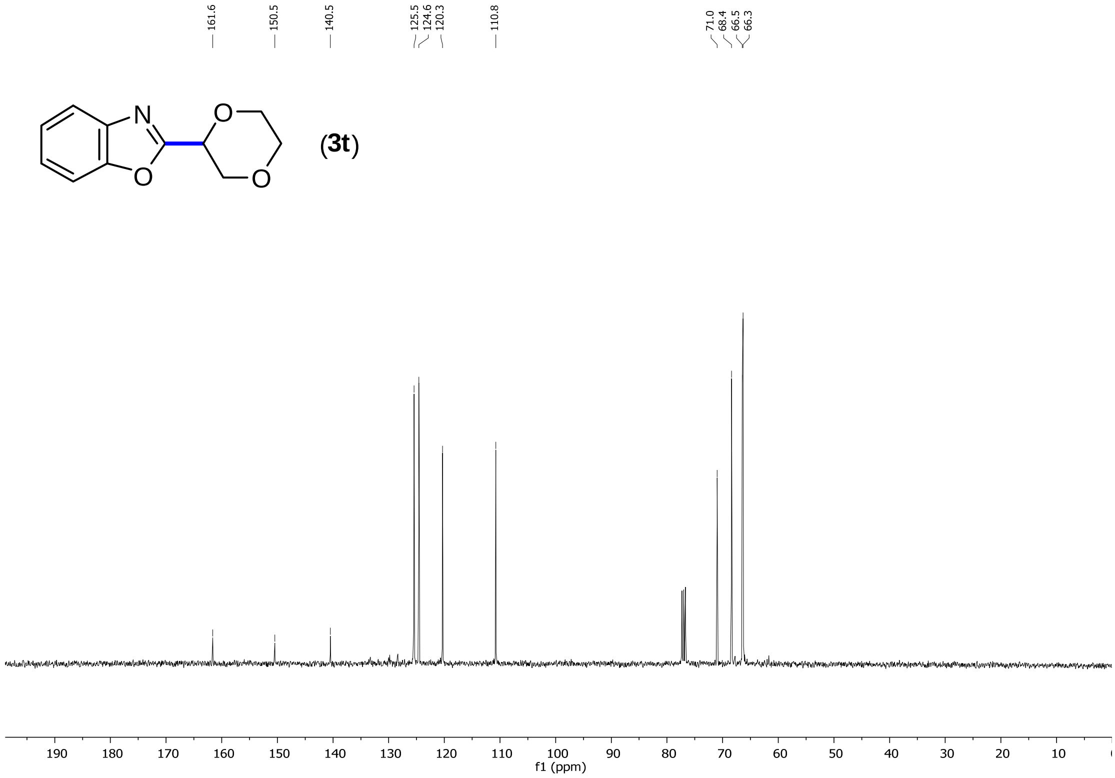
(**3s**)

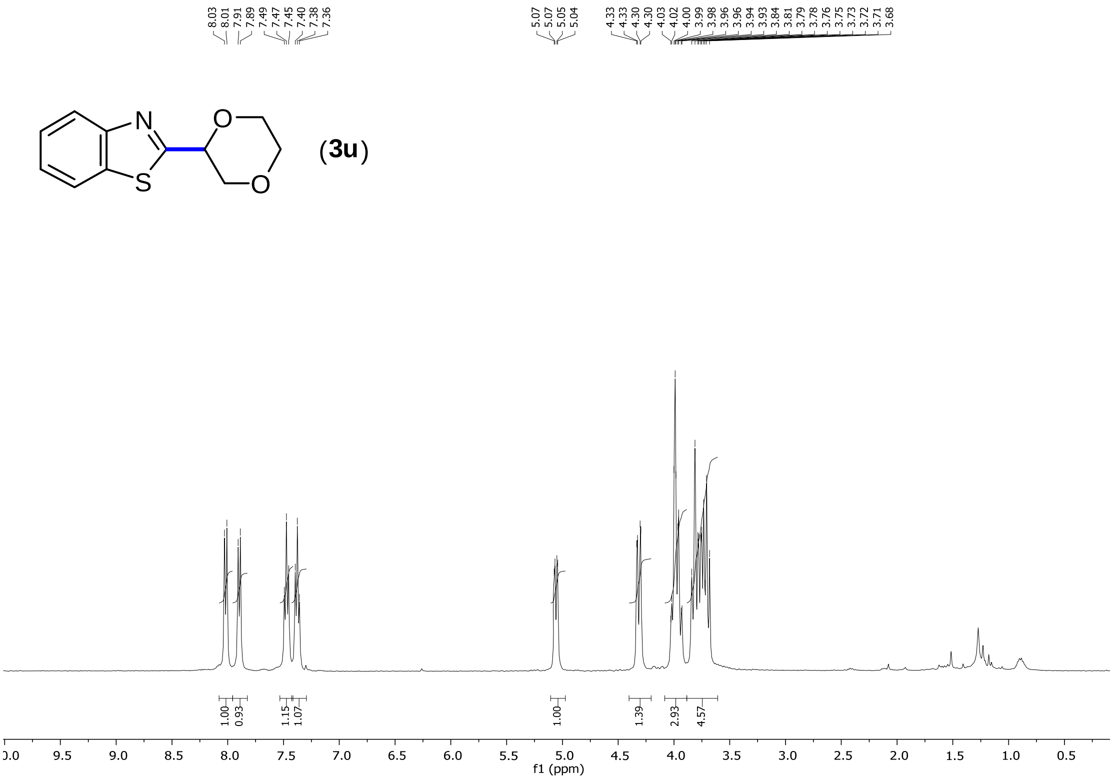

1.51
3.86
1.00
2.16
0.51
8.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


163.2
149.2
141.4
130.2
126.2
120.7
111.8
96.9
65.7
Cl
N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

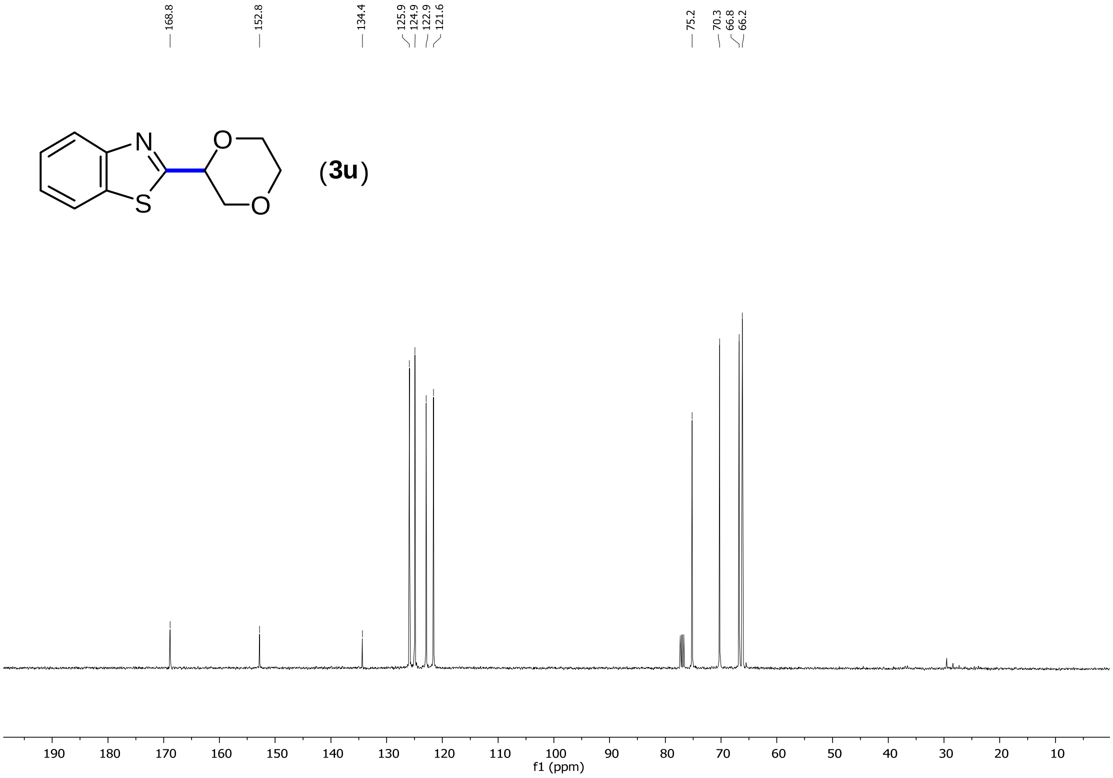
(**3s**)


(3t)
7.73
7.72
7.71
7.54
7.53
7.51
7.34
7.33
7.32
4.96
4.95
4.94
4.93
4.19
4.19
4.16
4.16
4.03
4.02
3.99
3.96
3.96
3.93
3.91
3.91
3.89
3.88
3.83
3.83
3.81
3.80
3.80
3.78
3.77
N
O
O
O
1.00
0.85
1.64
1.04
1.17
3.56
2.30
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
f1 (ppm)

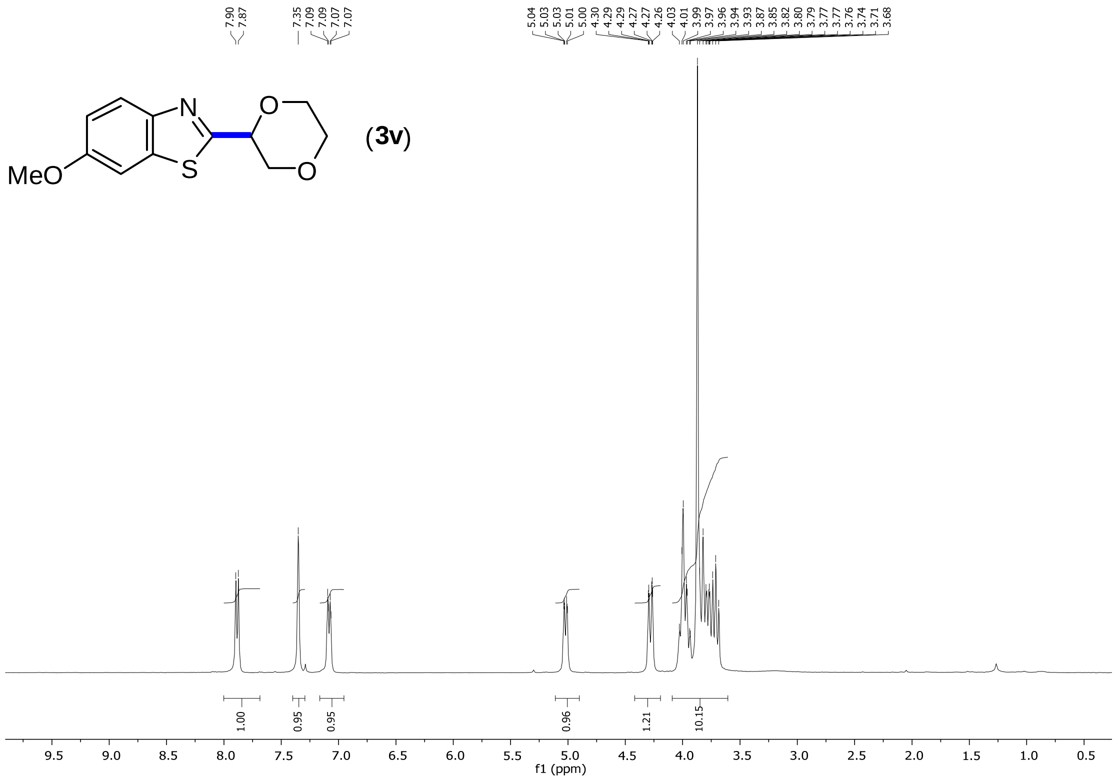

(3t)
161.6
150.5
140.5
125.5
124.6
120.3
110.8
71.0
68.4
66.5
66.3
N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.03
8.01
7.91
7.89
7.49
7.47
7.45
7.40
7.38
7.36
5.07
5.07
5.05
5.04
4.33
4.33
4.30
4.30
4.03
4.02
4.00
3.99
3.98
3.96
3.96
3.94
3.93
3.84
3.81
3.79
3.78
3.76
3.75
3.73
3.72
3.71
3.68
N
O
S
O
1.00
0.93
1.15
1.07
1.00
1.39
2.93
4.57
.0
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
f1 (ppm)

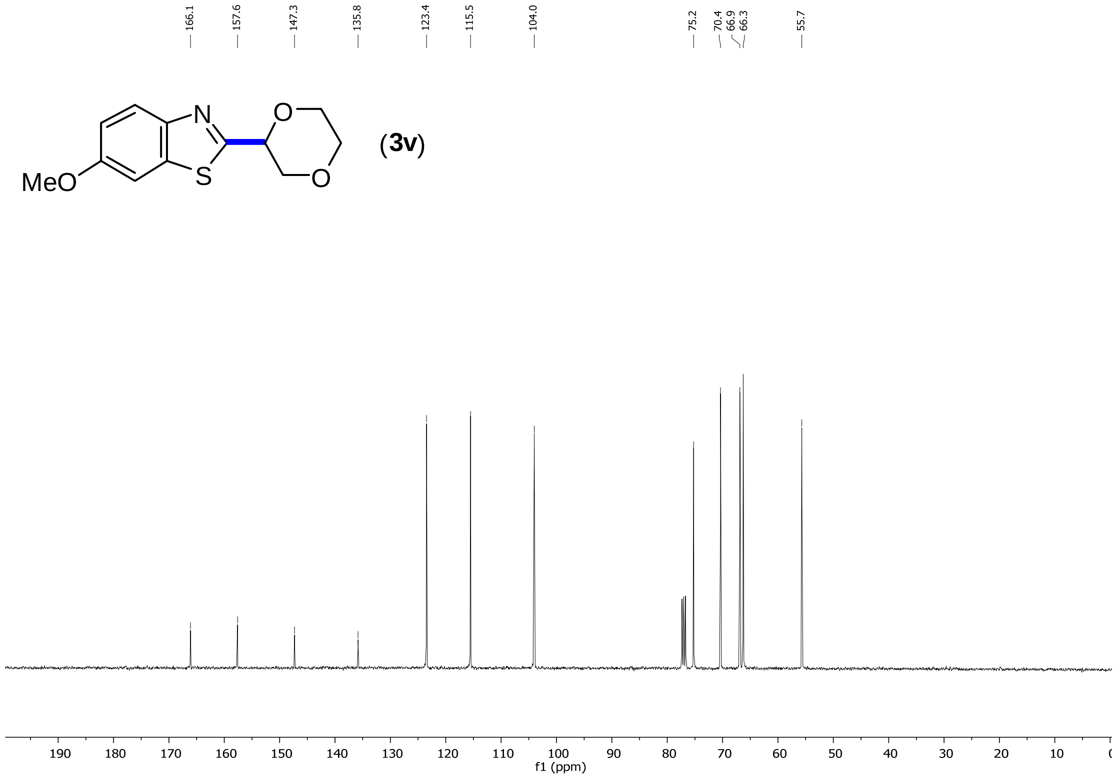
(**3u**)


168.8
152.8
134.4
125.9
124.9
122.9
121.6
75.2
70.3
66.8
66.2
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

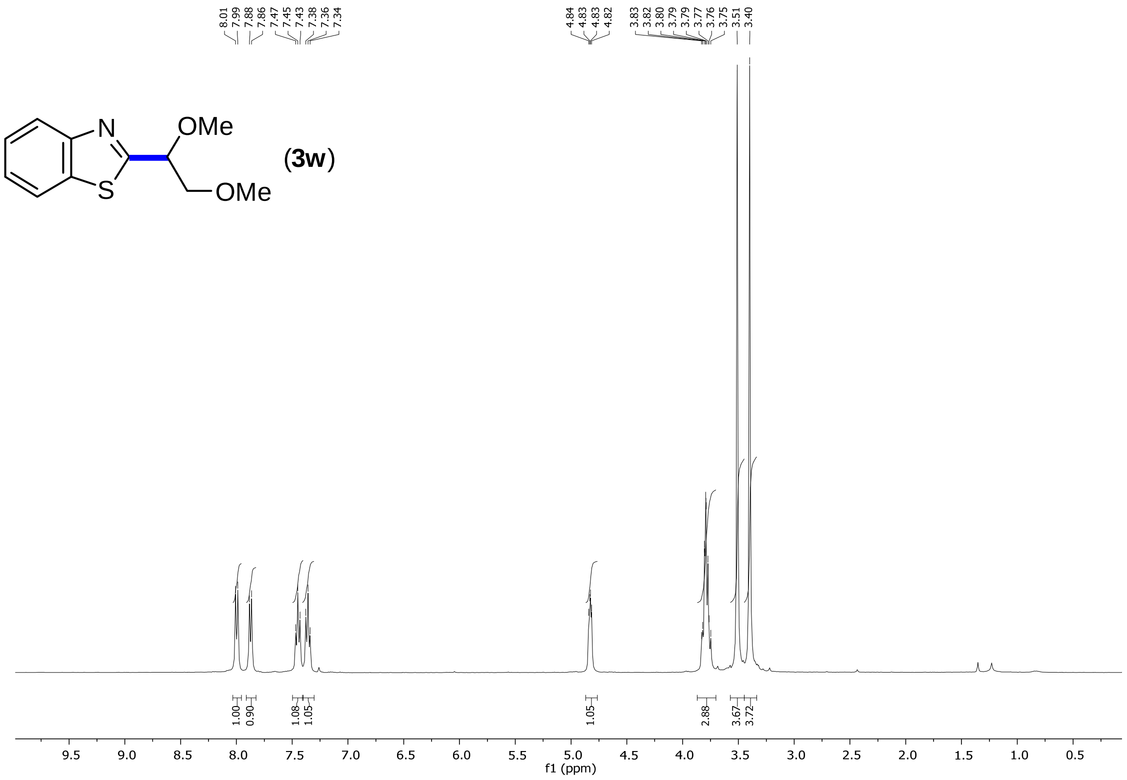
(**3u**)

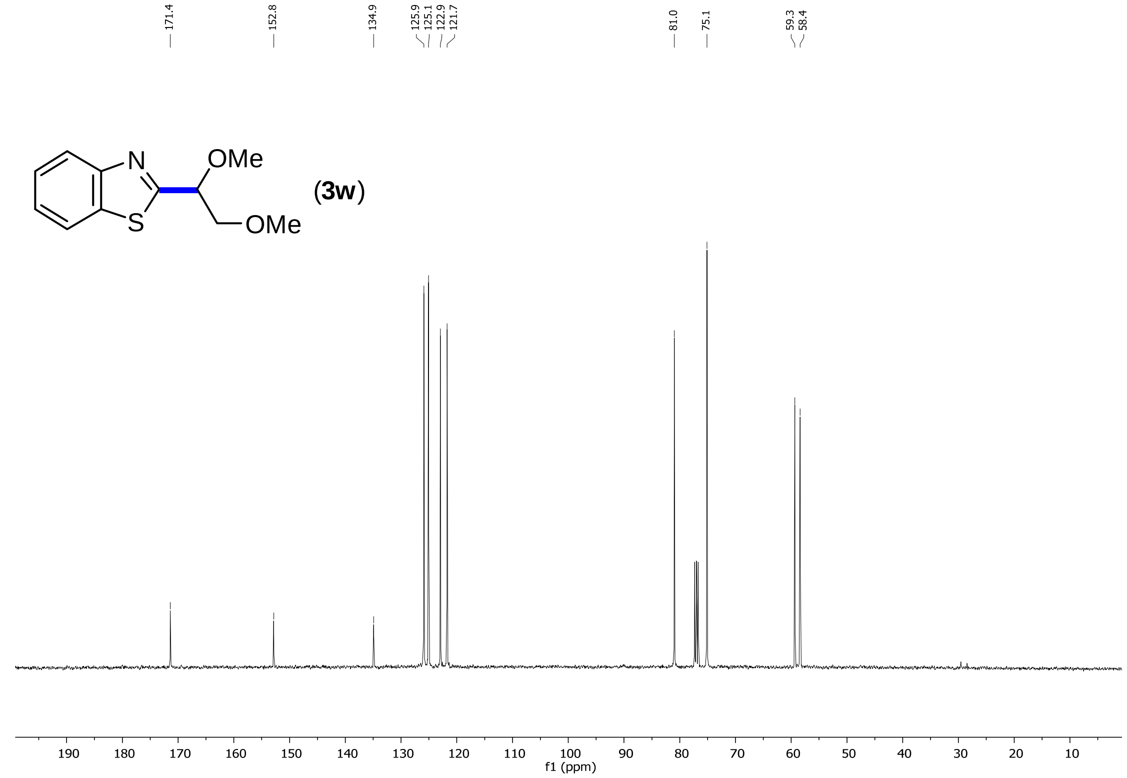

7.90
7.87
7.35
7.09
7.09
7.07
7.07
5.04
5.03
5.03
5.01
5.00
4.30
4.29
4.29
4.27
4.27
4.26
4.03
4.01
3.99
3.97
3.96
3.94
3.93
3.87
3.85
3.82
3.80
3.79
3.77
3.77
3.76
3.74
3.71
3.68
MeO
N
S
O
O
1.00
0.95
0.95
0.96
1.21
10.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

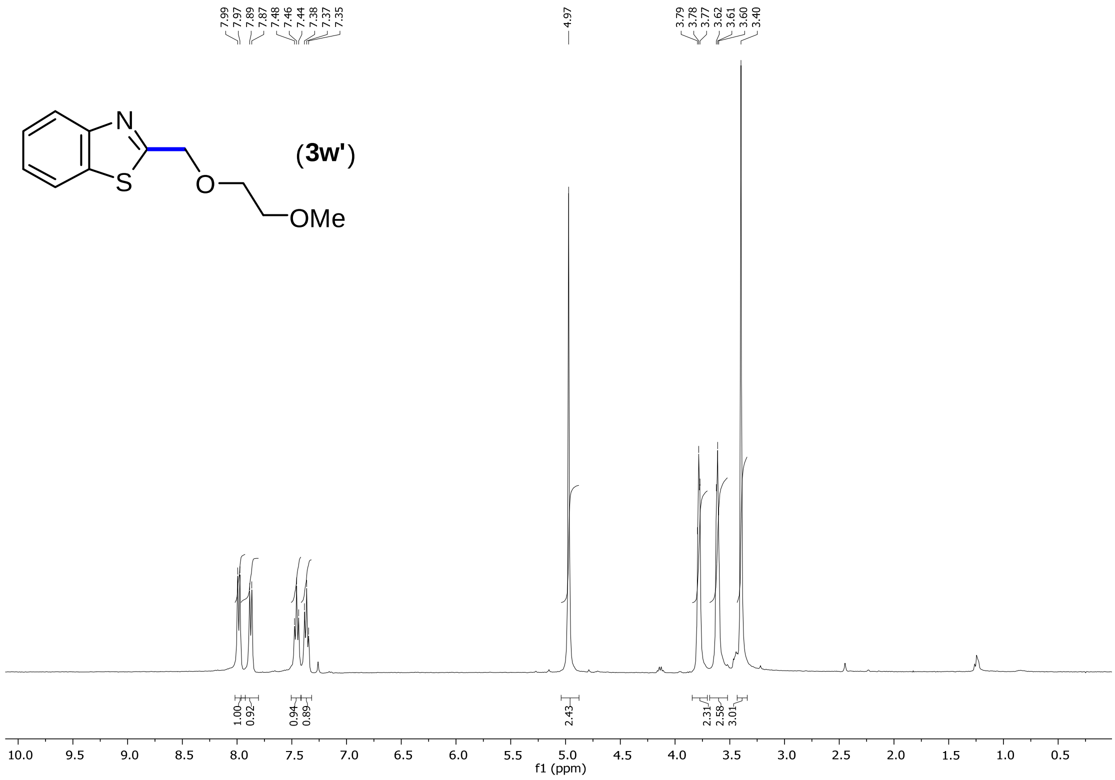
(**3v**)

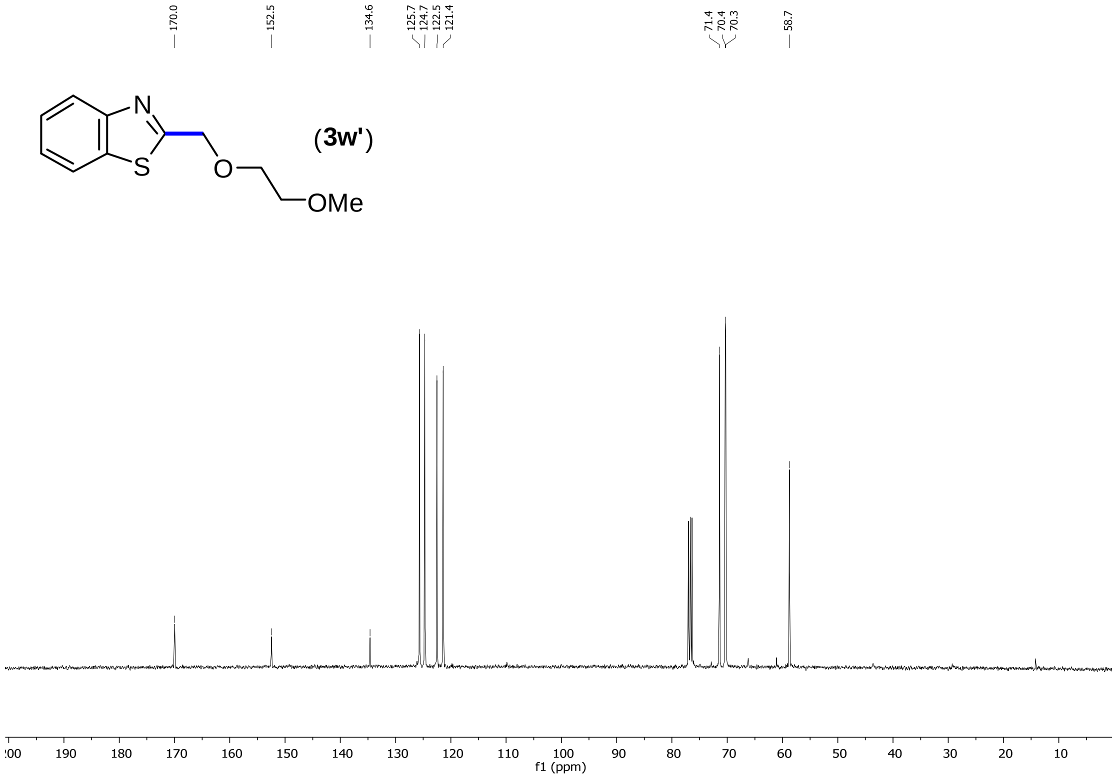

166.1
157.6
147.3
135.8
123.4
115.5
104.0
75.2
70.4
66.9
66.3
55.7
MeO
N
S
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

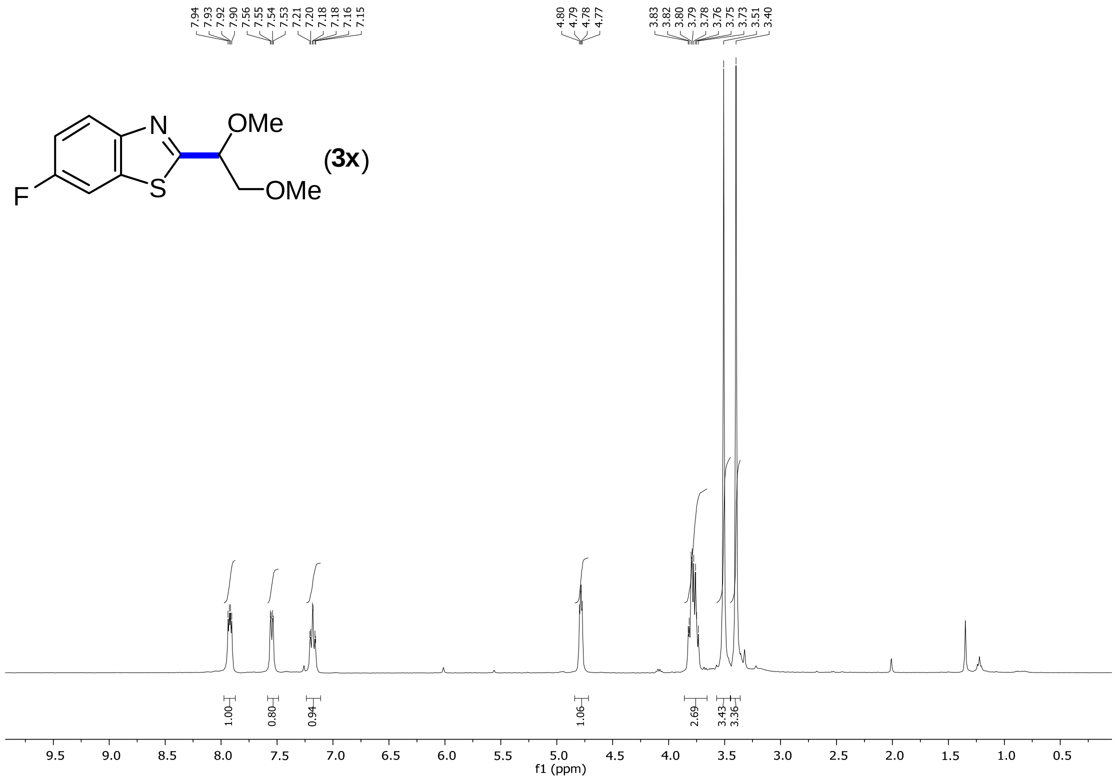
(**3v**)

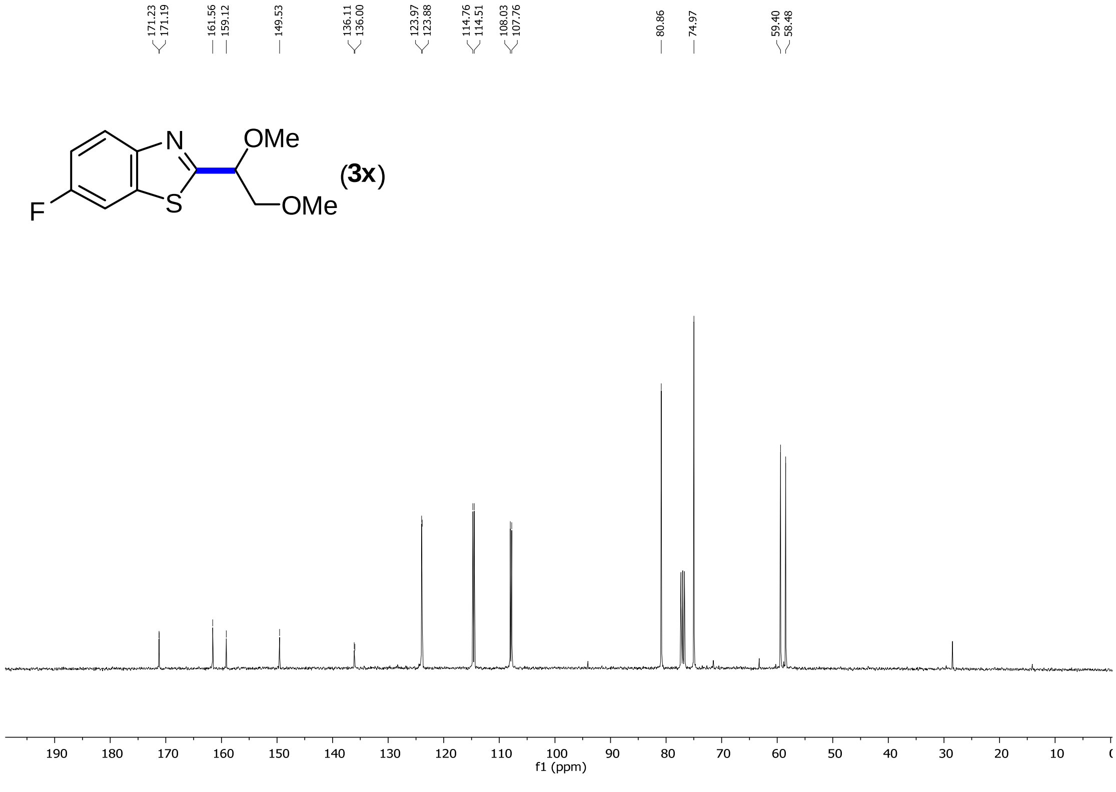

8.01
7.99
7.88
7.86
7.47
7.45
7.43
7.38
7.36
7.34
4.84
4.83
4.83
4.82
3.83
3.82
3.80
3.79
3.79
3.77
3.76
3.75
3.51
3.40
N
S
OMe
OMe
(3w)
1.00
0.90
1.08
1.05
1.05
2.88
3.67
3.72
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

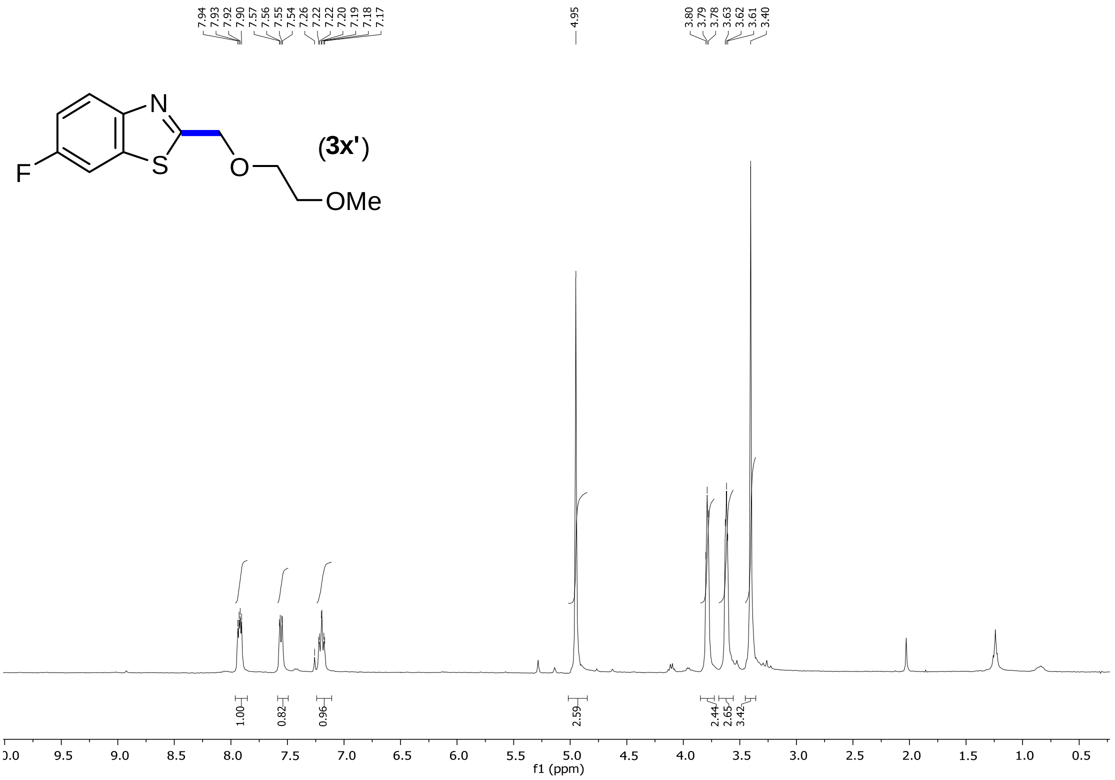

171.4
152.8
134.9
125.9
125.1
122.9
121.7
81.0
75.1
59.3
58.4
N
S
OMe
OMe
(3w)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

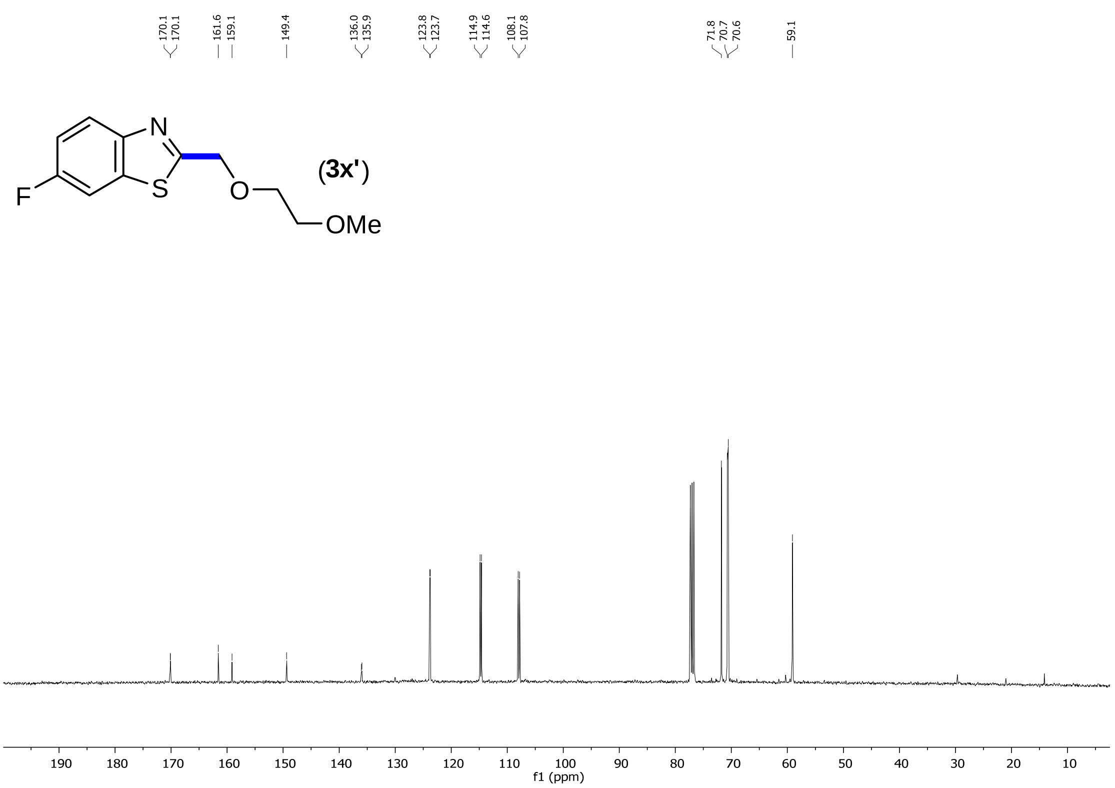

7.99
7.97
7.89
7.87
7.48
7.46
7.44
7.38
7.37
7.35
4.97
3.79
3.78
3.77
3.62
3.61
3.60
3.40
N
S
O
OMe
(3w')
1.00
0.92
0.94
0.89
2.43
2.31
2.58
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

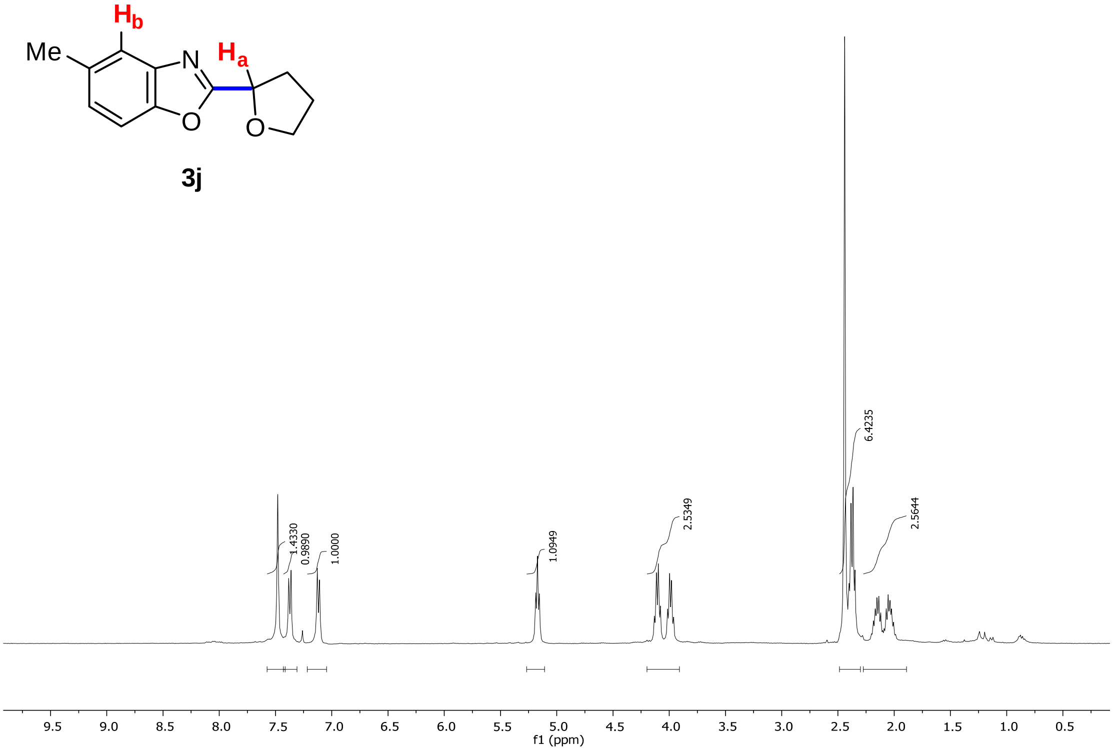

170.0
152.5
134.6
125.7
124.7
122.5
121.4
71.4
70.4
70.3
58.7
N
S
O
OMe
(3w')
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.94
7.93
7.92
7.90
7.56
7.55
7.54
7.53
7.21
7.20
7.18
7.18
7.16
7.15
4.80
4.79
4.78
4.77
3.83
3.82
3.80
3.79
3.78
3.76
3.75
3.73
3.51
3.40
N
OMe
F
S
OMe
(3x)
1.00
0.80
0.94
1.06
2.69
3.43
3.36
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
f1 (ppm)

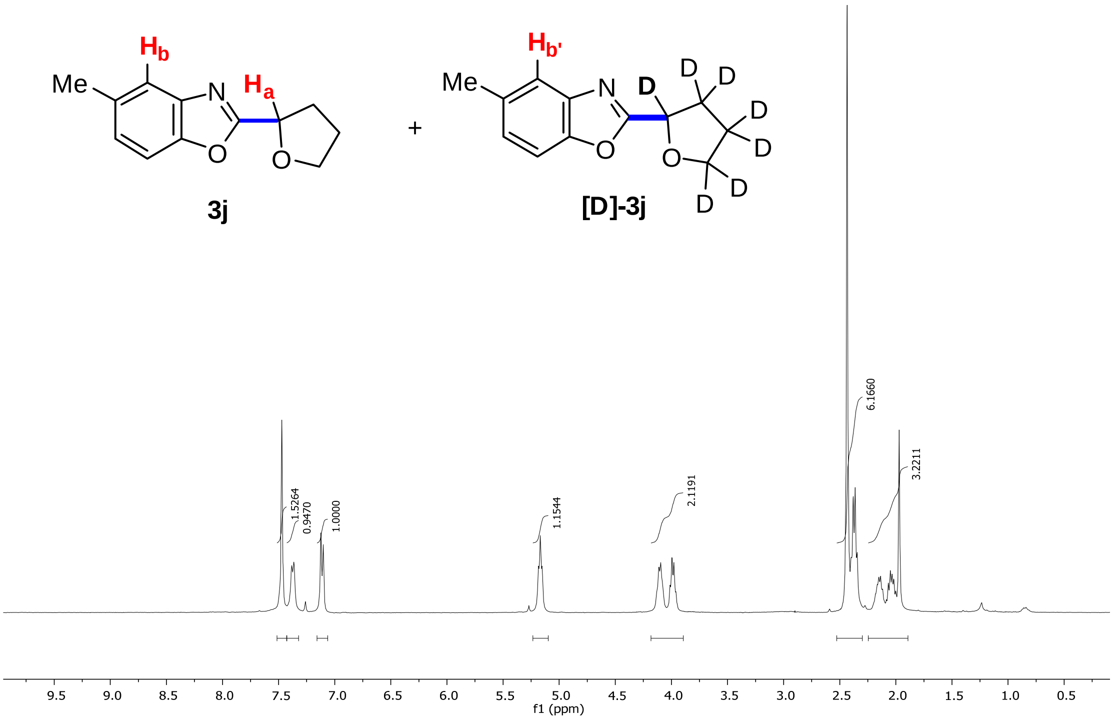

171.23
171.19
161.56
159.12
149.53
136.11
136.00
123.97
123.88
114.76
114.51
108.03
107.76
80.86
74.97
59.40
58.48
N
OMe
F
S
OMe
(3x)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.94
7.93
7.92
7.90
7.57
7.56
7.55
7.54
7.26
7.22
7.22
7.20
7.19
7.18
7.17
4.95
3.80
3.79
3.78
3.63
3.62
3.61
3.40
N
S
F
O
OMe
(3x')
1.00
0.82
0.96
2.59
2.44
2.65
3.42
0.0
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
f1 (ppm)

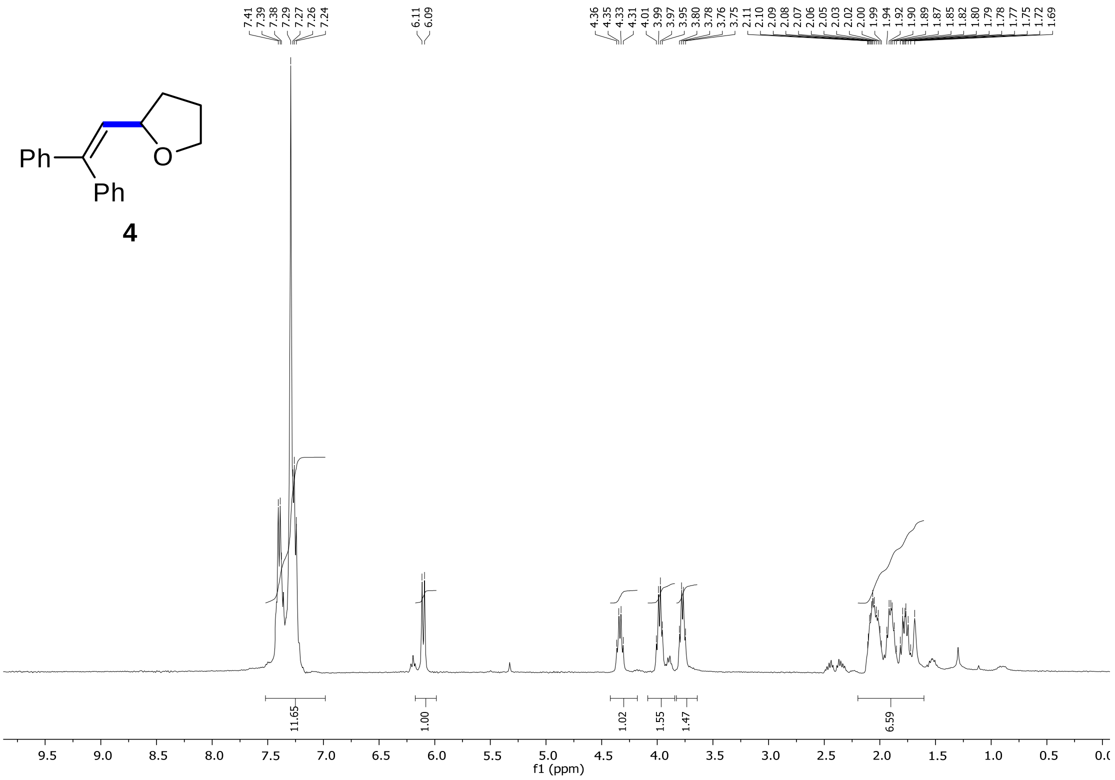

170.1
170.1
161.6
159.1
149.4
136.0
135.9
123.8
123.7
114.9
114.6
108.1
107.8
71.8
70.7
70.6
59.1
N
S
F
O
OMe
(3x')
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

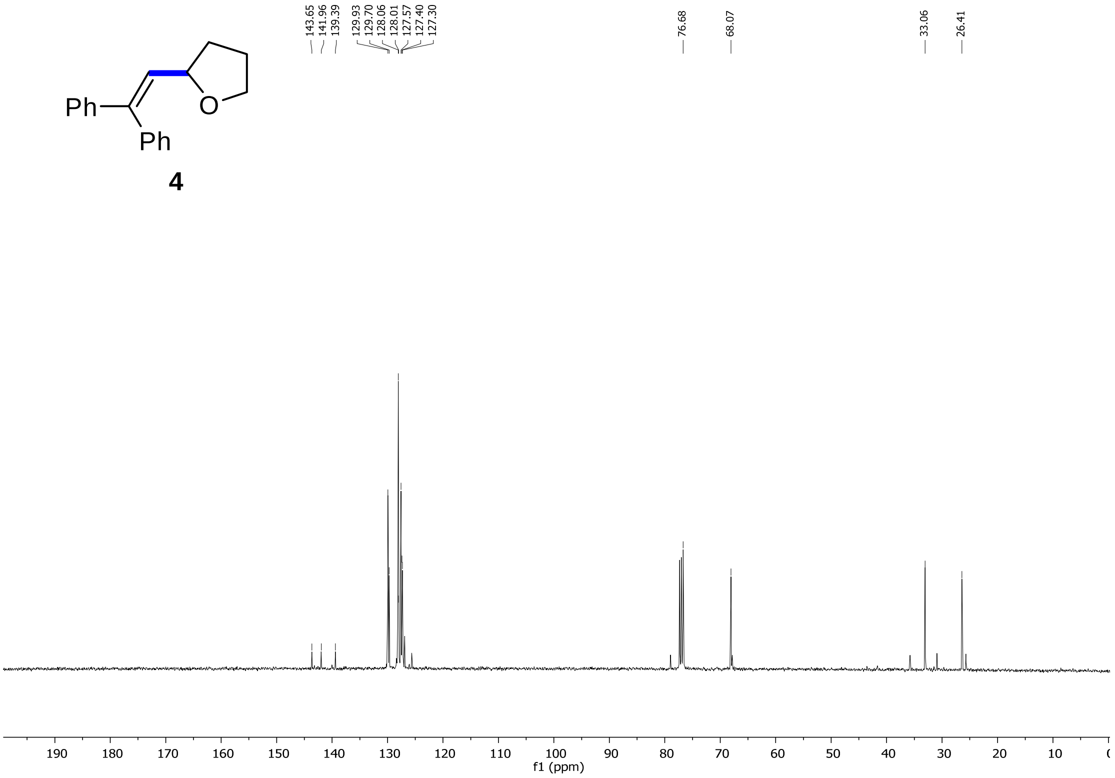


H_b
Me
N
H_a
O
O
3j
1.4330
0.9890
1.0000
1.0949
2.5349
6.4235
2.5644
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



H_b
Me
N
H_a
O
O
3j
+
H_b'
Me
N
D
D
D
D
D
O
O
D
D
[D]-3j
D
1.5264
0.9470
1.0000
1.1544
2.1191
6.1660
3.2211
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
f1 (ppm)


7.41
7.39
7.38
7.29
7.27
7.26
7.24
6.11
6.09
4.36
4.35
4.33
4.31
4.01
3.99
3.97
3.95
3.80
3.78
3.76
3.75
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.03
2.02
2.00
1.99
1.94
1.92
1.90
1.89
1.87
1.85
1.82
1.80
1.79
1.78
1.77
1.75
1.72
1.69
Ph
O
Ph
4
11.65
1.00
1.02
1.55
1.47
6.59
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
f1 (ppm)


143.65
141.96
139.39
129.93
129.70
128.06
128.01
127.57
127.40
127.30
76.68
68.07
33.06
26.41
Ph
O
Ph
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)