Supporting Information

Phosphine-Catalyzed Regio- and Stereoselective Hydroboration of Ynamides to (*Z*)-β-borylenamides

Swetha Jos,[1] Christine Tan,[1] Pierre Thilmany,[2] Alaâ Saadane,[2] Carla Slebodnick, [1] Gwilherm Evano, [2] Webster L. Santos[1]*

[1]Department of Chemistry, Virginia Tech, Blacksburg, Virginia, United States

[2]Université Libre de Bruxelles, Laboratoire de Chimie Organique, Brussels, Belgium

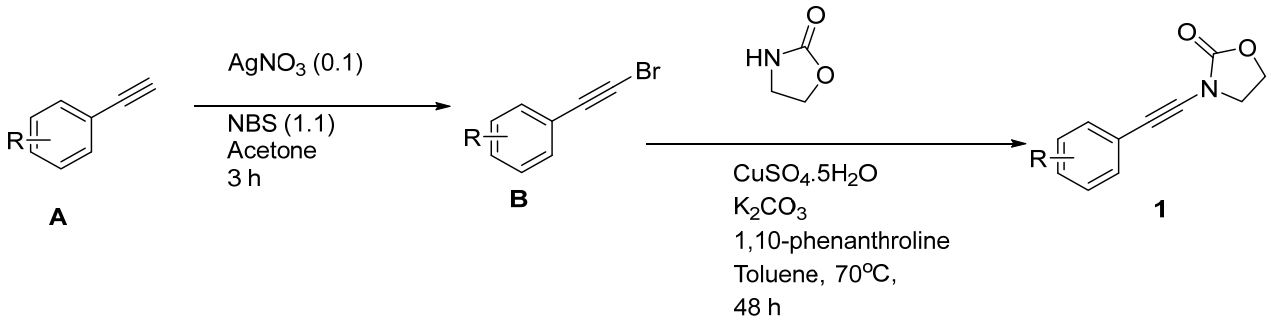
Table of Contents

I General Experimental Methods:

Reactions were performed using the Schlenk technique under Argon or Nitrogen atmosphere. All glassware used was flame-dried or oven-dried overnight. Chemicals were obtained from commercial sources unless otherwise noted. THF, toluene, MeCN, and DCM were dried using the Innovative Technology Pure SolvMD solvent purification system. Column chromatography was performed using SiliaFlash P60 40-63 μm, 60 Å. TLC analyses were performed using Silicycle aluminum-backed silica gel F-254 plates and visualized by UV light or $KMnO_4$ stain. Silica gel column chromatography was performed using SiliaFlash P60 40-63 μm, 60 A silica from SiliCycle Inc. ^{1}H, ^{13}C, ^{11}B, ^{31}P and ^{19}F spectra were recorded using an Agilent 400-MR 400 MHz, an Agilent U4-DD2 400 Hz, or a Bruker Avance II 500 MHz spectrometer. Chemical shifts are reported in δ ppm, and ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR are referenced to an internal standard ($CDCl_3$, CD_2Cl_2, CD_3CN, or TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constants (Hz), and integration. GC−MS experiments were performed using an Agilent 7890 Series GC system coupled to an HP 5975 mass selective detector. ESI mass spectra were acquired with an Agilent 6220 LC-ESI-TOF or a Thermo Scientific Q-Exactive Orbitrap.

II Synthesis of substrates

All the ynamides (**1a-1t**) were synthesized according to the reported procedure [1] and were compared with previous literature except **1f** and **1j**.



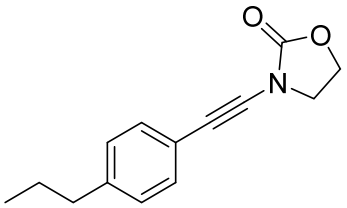
To a 100 mL round bottom flask containing the **A** dissolved in acetone, NBS was added slowly. To this $AgNO_3$ was added and stirred under argon atmosphere for 3 h. After the completion of the reaction, the solvent was evaporated, and the crude mixture purified by flash column chromatography (1-10% EtOAc/hexanes) to yield **B**.

A 15 mL pressure tube was charged with the oxazolidinone (4.0 mmol), potassium carbonate (8 mmol), $CuSO_4.5H_2O$ (0.8 mmol), 1,10-phenanthroline (3.0 mmol) and the bromoalkyne (4.0 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times. Dry toluene (4 mL) was next added, the rubber septum was replaced by a Teflon-coated screw cap and the mixture was stirred at 70 °C for 48 hours. The reaction mixture was then cooled to room temperature, filtered over a plug of silica (washed with EtOAc) and concentrated under reduced pressure. The crude residue was finally purified by flash column chromatography over silica gel.

Substrate (R)		Reference
H	**1a**	Chen, M.; Sun, N.; Chen, H.; Liu, Y., *Chem. Commun.* **2016,** *52*, 6324-6327.
2-Me	**1b**	Jin, X.; Yamaguchi, K.; Mizuno, N., *Chem. Commun.* **2012,** *48*, 4974-4976.
3-Me	**1c**	Jin, X.; Yamaguchi, K.; Mizuno, N., *Chem. Commun.* **2012,** *48*, 4974-4976.
4-Me	**1d**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
4-terbutyl	**1e**	Dubovtsev, A. Y.; Shcherbakov, N. V.; Dar'in, D. V.; Kukushkin, V. Y., *Adv. Synth. Catal.* **2020,** *362*, 2672-2682.
4- OMe	**1g**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
3-OMe	**1h**	Jin, X.; Yamaguchi, K.; Mizuno, N., *Chem. Commun.* **2012,** *48*, 4974-4976.
2-OMe	**1i**	Singh, H.; Sahoo, T.; Sen, C.; Galani, S. M.; Ghosh, S. C., *Catal. Sci.Technol.* **2019,** *9*, 1691-1698.
2-napthyl	**1k**	Dubovtsev, A. Y.; Shcherbakov, N. V.; Dar'in, D. V.; Kukushkin, V. Y., *Adv. Synth. Catal.* **2020,** *362*, 2672-2682.
4-Ph	**1l**	Gao, Y.; Wu, G.; Zhou, Q.; Wang, J., *Angew. Chem. Int. Ed.* **2018,** *57*, 2716-2720.
4-OPh	**1m**	Jouvin, K.; Couty, F.; Evano, G., *Org. Lett.* **2010,** *12*, 3272-3275.
4-F	**1n**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
4-Cl	**1o**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
3-Cl	**1p**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
2-Cl	**1q**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.
4-Br	**1r**	Singh, H.; Sahoo, T.; Sen, C.; Galani, S. M.; Ghosh, S. C., *Catalysis Science & Technology* **2019,** *9*, 1691-1698.
4-CF_3	**1s**	Cao, W.; Chen, P.; Wang, L.; Wen, H.; Liu, Y.; Wang, W.; Tang, Y., *Org. Lett.* **2018,** *20*, 4507-4511.

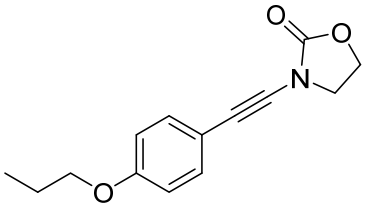
4-OCF_3	**1t**	Wang, L.; Lu, C.; Yue, Y.; Feng, C., *Org. Lett.* **2019,** *21*, 3514-3517.

3-((4-propylphenyl) ethynyl) oxazolidin-2-one (**1f**)



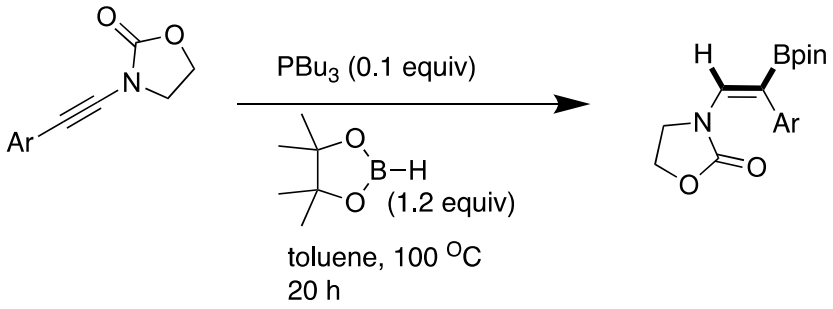
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.48 (t, *J* = 8.0 Hz, 2H), 4.00 (t, *J* = 8.0 Hz, 2H), 2.64 – 2.46 (m, 2H), 1.67 – 1.48 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.9, 143.1, 131.5, 128.4, 119.1, 78.2, 71.2, 62.9, 47.0, 37.8, 24.2, 13.7. **HRMS**: (ESI^+) m/z calcd for $C_{14}H_{15}NO_2$ $[M+H]^+$ 230.1181; Found: 230.1185.

3-((4-propoxyphenyl)ethynyl)oxazolidin-2-one (1j)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.48 (t, *J* = 8.0 Hz, 2H), 3.99 (t, *J* = 8.0 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.80 (h, *J* = 7.1 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 156.4, 133.8, 114.8, 114.1, 77.6, 71.4, 69.9, 63.3, 47.5, 22.9, 10.8. **HRMS**: (ESI^+) m/z calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$ 246.1130; Found: 246.1132.

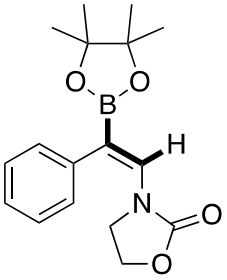
III Synthesis of *cis*-hydroborated ynamides:



To a 2-dram vial enabled with a septum under Schlenk line conditions, the ynamide (**1a**-**1t**) 0.25 mmol was added. To this, toluene (0.2 M) was added. Under argon atmosphere, the pinacol borane (0.3 mmol) and tri-*n*-butyl phosphine (0.025 mmol) was added. This mixture was stirred at 100 °C for 20 h. The reaction was monitored by GC-MS, and after the completion of the reaction, it was directly purified *via* flash chromatography (20% - 30% EtOAc/Hexanes).

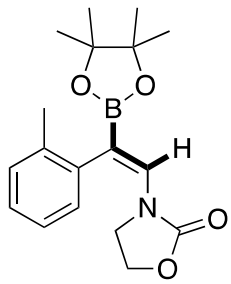
Note: The peak for the carbon directly attached to Bpin is missing in the ^{13}C NMR for each compound due to quadrupolar relaxation.

(*Z*)-3-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) vinyl) oxazolidin-2-one (**2a**)



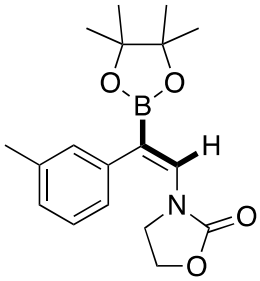
47 mg scale, White powdery solid, 48 mg, 60%. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.36 – 7.20 (m, 4H), 7.19 – 7.08 (m, 2H), 4.13 (t, *J* = 7.5 Hz, 2H), 3.11 (t, *J* = 7.5 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 157.4, 139.2, 135.3, 130.7, 128.3, 127.2, 84.5, 63.6, 45.3, 25.3. **^{11}B NMR** (128 MHz, CD_2Cl_2) δ 30.8. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BNO_4$ $[M+H]^+$ 316.1720; Found: 316.1717.

(*Z*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl) vinyl) oxazolidin-2-one (**2b**)



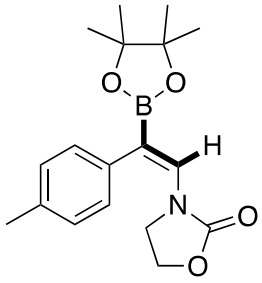
50 mg scale, White powdery solid, 30 mg, 37 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.23 – 6.92 (m, 4H), 4.12 (t, *J* = 8.1 Hz, 2H), 3.10 (q, *J* = 8.7 Hz, 1H), 2.90 (q, *J* = 8.7 Hz, 1H), 2.19 (s, 3H), 1.23 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 137.6, 136.5, 134.4, 130.1, 129.3, 126.8, 124.9, 83.4, 62.4, 43.8, 24.7, 24.4, 20.3.**^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.8. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{25}BNO_4$ $[M+H]^+$ 330.1877; Found : 330.1876.

(*Z*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*m*-tolyl)vinyl)oxazolidin-2-one (2c)



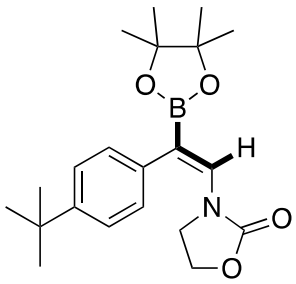
50 mg scale, White powdery solid, 41 mg, 51%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.19 – 7.15 (m, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.96 – 6.90 (m, 2H), 4.16 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8,137.9, 137.0, 134.6, 130.5, 127.4, 127.3, 126.9, 83.6, 62.7, 44.6, 24.7, 21.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.7. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{25}BNO_4$ $[M+H]^+$ 330.1877; Found: 330.1880.

(*Z*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)vinyl)oxazolidin-2-one (2d)



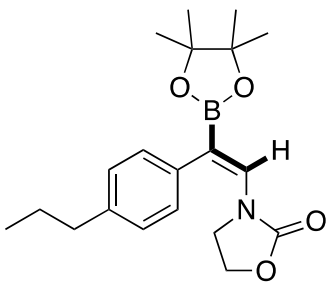
50 mg scale, White powdery solid, 41 mg, 51%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.16 (t, *J* = 8.0 Hz, 3H), 3.16 (t, *J* = 8.0 Hz, 3H), 2.33 (s, 1H), 1.24 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.7, 136.0, 134.9, 134.5, 129.6, 128.3, 83.5, 62.6, 44.6, 24.6, 21.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.7. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{25}BNO_4$ $[M+H]^+$ 330.1877; Found: 330.1870.

(*Z*)-3-(2-(4-(*tert*-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2e)



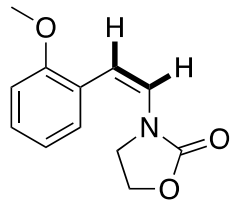
61 mg scale, White powdery solid, 48 mg, 52%. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.33 – 7.28 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.14 – 4.11 (t, *J* = 8.2 Hz, 2H), 3.12 (, *J* = 8.2 Hz, 2H), 1.32 (s, 9H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 156.6, 149.4, 135.0, 134.5, 129.5, 124.4, 83.6, 62.8, 44.4, 34.3, 31.1, 24.4. **^{11}B NMR** (128 MHz, CD_2Cl_2) δ 30.9. **HRMS**: (ESI^+) m/z calcd for $C_{21}H_{31}BNO_4$ $[M+H]^+$ 372.2346; Found: 372.2344.

(*Z*)-3-(2-(4-propylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2f)



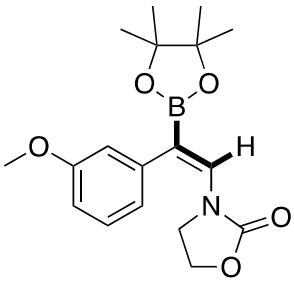
57 mg scale, White powdery solid, 40 mg, 45%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.16 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.63 – 2.53 (m, 2H), 1.67 – 1.59 (m, 2H), 1.25 (s, 12H) 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.8, 140.7, 135.0, 134.6, 129.5, 127.6, 83.5, 62.6, 44.5, 37.7, 24.6, 24.4, 13.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6. **HRMS**: (ESI^+) m/z calcd for $C_{20}H_{29}BNO_4$ $[M+H]^+$ 358.2190; Found: 358.2195.

(*Z*)-3-(2-(2-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2g)



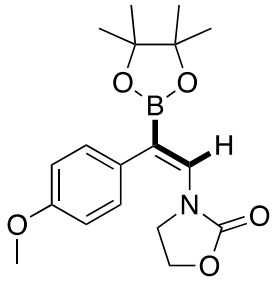
Observed *via* GC-MS (13% conversion)

(*Z*)-3-(2-(3-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2h)



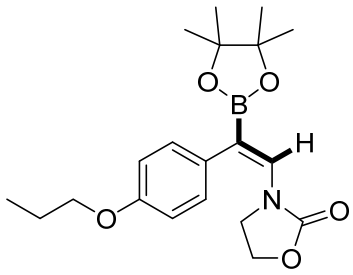
54 mg scale, White powdery solid, 35 mg, 40%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.80 – 6.64 (m, 3H), 4.17 (t, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.20 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 156.7, 139.6, 134.7, 128.5, 122.5, 115.7, 111.7, 83.6, 62.7, 55.1, 44.5, 24.7.**^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.8. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{24}BNO_5Na$ $[M+Na]^+$ 368.1645; Found: 368.1647.

(*Z*)-3-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2i)



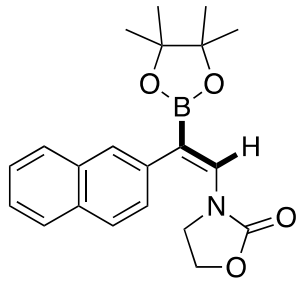
54 mg scale, White powdery solid, 53 mg, 62%. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.28 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.14 (t, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 158.5, 156.9, 134.7, 131.0, 130.4, 113.1, 83.8, 63.0, 55.4, 44.8, 24.6. **^{11}B NMR** (128 MHz, CD_2Cl_2) δ 30.6. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{25}BNO_5$ $[M+H]^+$ 346.1836; Found: 346.1829.

(*Z*)-3-(2-(4-propoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2j)



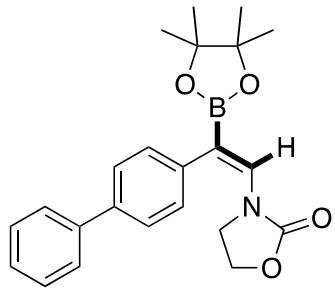
61 mg scale, White powdery solid, 51 mg, 55%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.02 - 7.00 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.20 – 4.13 (m, 2H), 3.90 (t, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 7.9 Hz, 2H), 1.83 – 1.78 (m ,2H), 1.25 (s, 12H), 1.04 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8, 134.6, 130.8, 129.9, 113.6, 83.6, 69.4, 62.7, 44.7, 24.7, 22.7, 10.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.5. **HRMS**: (ESI^+) m/z calcd for $C_{20}H_{29}BNO_5$ $[M+H]^+$ 374.2139; Found: 374.2142.

(*Z*)-3-(2-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2k)



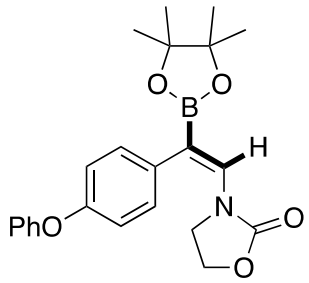
59 mg scale, White powdery solid, 48 mg, 52%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 3H), 7.57 – 7.42 (m, 4H), 7.31 – 7.29 (m, 1H), 4.09 (t, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.7, 135.9, 135.1, 132.8, 132.1, 128.5, 128.1, 127.8, 127.7, 127.1, 126.2, 125.7, 83.7, 62.7, 44.8, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.9. **HRMS**: (ESI^+) m/z calcd for $C_{21}H_{25}BNO_4$ $[M+H]^+$ 366.1877; Found: 366.1879.

(*Z*)-3-(2-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2l)



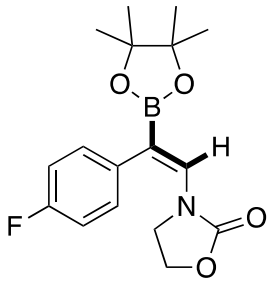
66 mg scale, White powdery solid, 47 mg, 47%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.45 – 7.42 (m, 2H), 7.35 – 7.32 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.18 (t, *J* = 8.0 Hz, 2H), 3.23 (t, *J* = 8.0 Hz, 2H), 1.27 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9, 140.8, 139.3, 137.3, 135.2, 130.4, 128.9, 127.4, 127.0, 126.4, 83.9, 62.9, 44.9, 24.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.7. **HRMS**: (ESI^+) m/z calcd for $C_{23}H_{27}BNO_4$ $[M+H]^+$ 392.2033; Found: 392.2025.

(*Z*)-3-(2-(4-phenoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) vinyl)oxazolidin-2-one (2m)



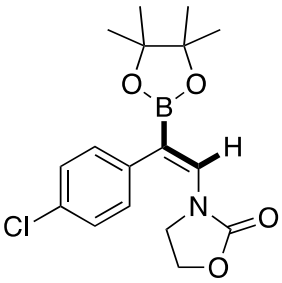
70 mg scale, White powdery solid, 55mg, 55%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.38 – 7.30 (m, 2H), 7.18 – 6.98 (m, 5H), 6.96 – 6.85 (m, 2H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 157.1, 156.4, 135.4, 133.1, 131.5, 130.2, 123.9, 119.7, 117.9, 84.1, 63.1, 45.1, 25.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.2. **HRMS**: (ESI^+) m/z calcd for $C_{23}H_{27}BNO_5$ $[M+H]^+$ 408.1982; Found: 408.1984.

(*Z*)-3-(2-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2n)



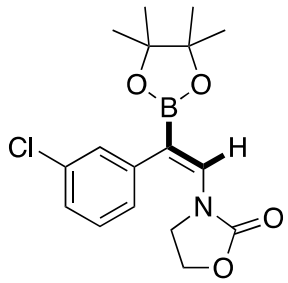
50 mg scale, White powdery solid, 20 mg, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.13 – 7.07 (m, 2H), 7.05 – 6.93 (m, 2H), 4.18 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.5 (d, *J* = 245.5 Hz), 156.6, 135.1, 133.8, 131.2 (d, *J* = 7.8 Hz), 114.5 (d, *J* = 21.2 Hz), 83.7, 62.6, 44.6, 24.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.12. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BFNO_4$ $[M+H]^+$ 334.1626; Found: 334.1615.

(*Z*)-3-(2-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2o)



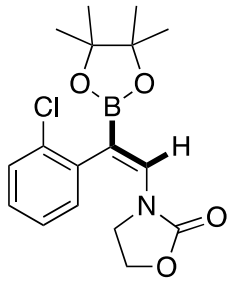
55 mg scale, White powdery solid, 49 mg, 57%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H), 1.24 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 136.7, 135.2, 132.4, 131.1, 127.8, 83.8, 62.7, 44.8, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.0. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BClNO_4$ $[M+H]^+$ 350.1330; Found: 350.1324.

(*Z*)-3-(2-(3-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2p)



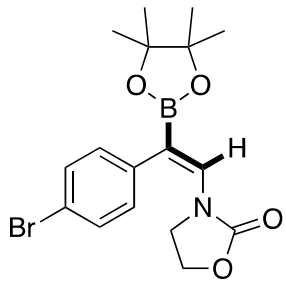
55 mg scale, White powdery solid, 41mg, 48%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.26 (s, 1H), 7.22 – 7.21 (s, 1H), 7.13 - 7.12 (m, 1H), 7.04 – 7.01 (m, 1H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.6, 140.1, 135.4, 133.5, 129.8, 128.8, 128.1, 126.7, 83.8, 62.7, 44.7, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.5. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BClNO_4$ $[M+H]^+$ 350.1330; Found: 350.1320.

(*Z*)-3-(2-(2-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2q)



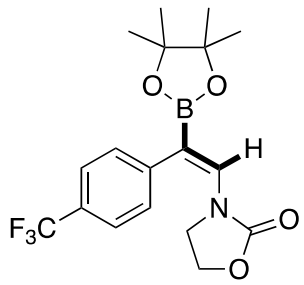
55 mg scale, White powdery solid, 48 mg, 56%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37 – 7.35 (m, 1H), 7.21 – 7.14 (m, 3H), 4.17 (t, *J* = 8.1 Hz, 2H), 3.11 (t, *J* = 8.1 Hz, 2H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.3, 137.3, 135.3, 134.3, 131.7, 129.0, 128.2, 126.0, 83.7, 62.5, 43.8, 24.9, 24.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.2. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BClNO_4$ $[M+H]^+$ 350.1330; Found: 350.1332.

(*Z*)-3-(2-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)oxazolidin-2-one (2r)



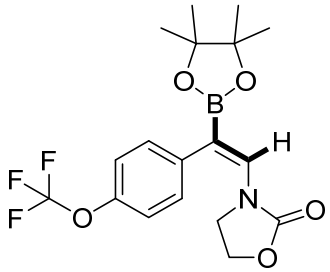
67 mg scale, White powdery solid, 41 mg, 43%. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 (s, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.16 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 157.1, 138.0, 135.6, 132.3, 131.2, 120.9, 84.4, 63.4, 45.3, 25.1. **^{11}B NMR** (128 MHz, CD_2Cl_2) δ 30.6. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{22}BBrNO_4$ $[M+H]^+$ 394.0825; Found: 394.0823.

(*Z*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)oxazolidin-2-one (2s)



64 mg scale, White powdery solid, 45 mg, 47%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.5, 142.3, 135.6, 130.1, 128.9 - 128.2 (q, *J* = 28.9 Hz), 127.4 – 120.9 (q, *J* = 270.8 Hz), 124.5 (q, *J* = 3.7 Hz), 83.9, 62.7, 44.8, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.5. **^{19}F NMR** (376 MHz $CDCl_3$) δ -62.38. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{22}BF_3NO_4$ $[M+H]^+$ 384.1594; Found: 384.1584.

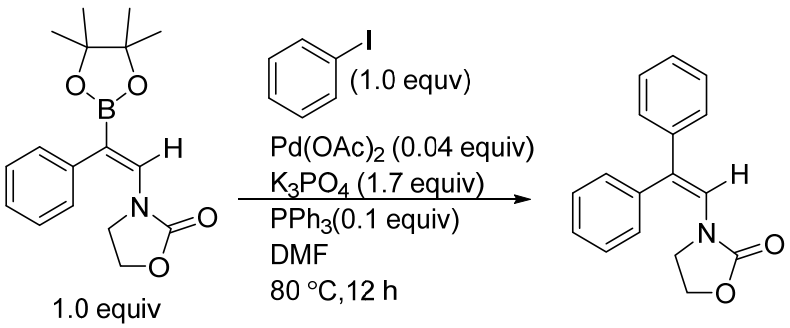
(*Z*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethoxy)phenyl) vinyl oxazolidin-2-one (2t)



68 mg scale, White powdery solid, 35 mg, 34%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.18 – 7.12 (m, 4H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8, 148.0, 137.0, 135.6, 131.3, 121.6, 123.7 – 117.3 (d, *J* = 252.5 Hz), 84.0, 62.8, 44.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.78. **HRMS**: (ESI^+) m/z calcd for $C_{18}H_{22}BF_3NO_5$ $[M+H]^+$ 400.1543; Found: 400.1545.

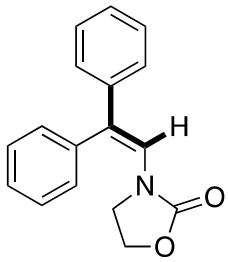
IV Applications

I Suzuki- Miyaura coupling reaction



0.3 mmol (130 mg) of **2a**, 0.3 mmol (70 mg) of iodobenzene, 0.03 mmol (9 mg) of triphenylphoshine, 0.60 mmol (130 mg) of potassium phosphate tribasic, and Pd $(OAc)_2$ (0.04 equiv, 4 mg) was heated at 80 ºC in DMF (1.5 mL) for 12 h. After the completion of the reaction, 10 mL of water was added. To this (2 x10 mL) of EtOAc was added and separated. The organic layer was dried under sodium sulfate and concentrated under a reduced vacuum. The resulting crude mixture was purified under column chromatography with EtOAc/Hexanes gradient with a yield of 91% (85 mg).

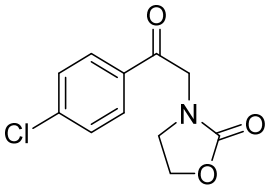
3-(2,2-diphenylvinyl) oxazolidin-2-one (3a)



Yellow powder, 85 mg, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 11H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.2, 140.8, 137.9, 130.8, 128.2, 128.2, 127.8, 127.0, 126.0, 122.3, 62.6, 44.8. **HRMS**: (ESI^+) m/z calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.1181; Found: 266.1177.

II Oxidation Reaction

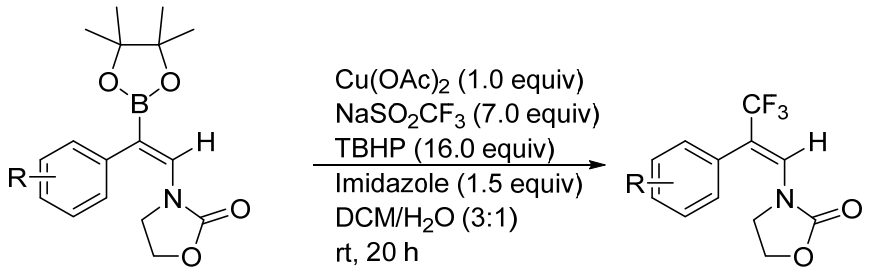
1o (25 mg, 0.072 mmol) was dissolved in THF (0.5 mL) at room temperature. To this NaOH (14 mg, 0.36 mmol) and 30% TBHP (37 µL, 0.36 mmol) was added at room temperature for 2h. After the completion of the reaction, monitored by TLC, 10 mL of water was added. This was extracted with EtOAc (2 x 10 mL). The organic layer was combined, dried over sodium sulfate, and concentrated under reduced vacuum. Purification was performed via column chromatograpy using hexanes/EtOAc gradient to yield **3b**.



3-(2-(4-chlorophenyl)-2-oxoethyl) oxazolidin-2-one (3b)

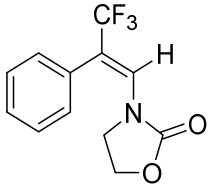
Pale yellow powder, 12 mg, 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 4.69 (s, 2H), 4.45 (t, *J* = 8.0 Hz, 2H), 3.85 – 3.64 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.7, 159.3, 141.1, 133.3, 129.8, 129.7, 62.7, 50.6, 45.5. **HRMS**: (ESI^+) m/z calcd for $C_{11}H_{11}ClNO_3$ 240.0427; Found: 240.0430.

II Trifluoromethylation Reaction [2]



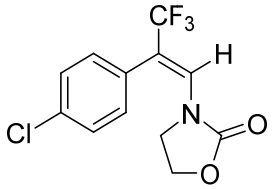
To a 1-dram vial with a septum and stir-bar was added the borylated alkenyl amide (1.0 equiv, 0.079 mmol), imidazole (1.5 equiv), Cu $(OAc)_2$ (1.0 equiv), and $NaSO_2CF_3$ (7.0 equiv) at room temperature. To the resulting mixture, 3:1 DCM/H_2O was added. The reaction was stirred for 2 min prior to the addition of TBHP (16.0 equiv) in portions. The septum was pierced a small-tip needle and the reaction mixture was stirred for 20 h at room temperature and quenched with a saturated solution of $NaHCO_3$. The mixture was extracted with DCM. The combined organic

layers were dried over sodium sulfate then concentrated in vacuo to afford a liquid that was purified by column chromatography.



(E)-3-(3,3,3-trifluoro-2-phenylprop-1-en-1-yl)oxazolidin-2-one (3c)

25 mg scale, White powdery solid, 20 mg, 58%, ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.44 – 7.29 (m, 5H), 4.20 (t, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.2, 131.5, 130.2, 129.3, 128.1, 127.7 (q, *J* = 6.9 Hz), 127.1 - 121.0 (q, *J* = 271.4 Hz), 111.8 (q, *J* = 30.9 Hz), 62.7, 44.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.12 (d, *J* = 1.7 Hz). **HRMS**: (ESI^+) m/z calcd for $C_{12}H_{11}F_3NO_2$ $[M+H]^+$ 258.0742; Found: 258.0746.

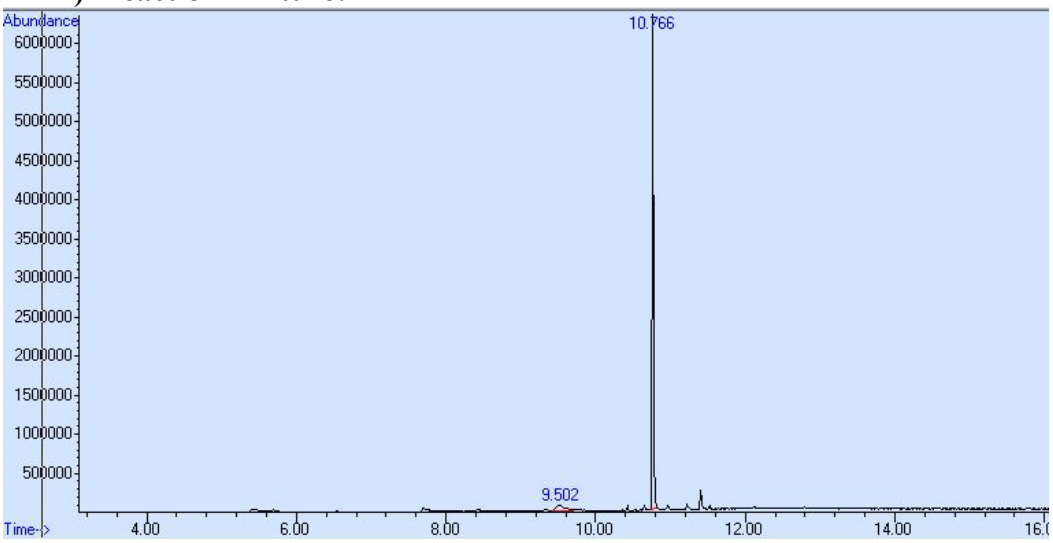


(E)-3-(2-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)oxazolidin-2-one (3d)

28 mg scale, White powdery solid, 40%, ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.19 (m, 2H), 4.24 (t, *J* = 7.9 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 136.0, 133.2, 129.0, 128.9, 128.7 (q, *J* = 6.8 Hz), 127.6 – 121.1 (q, *J* = 271.5 Hz), 110.8 (q, *J* = 31.2 Hz), 63.1, 44.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.08. **HRMS**: (ESI^+) m/z calcd for $C_{12}H_{10}ClF_3NO_2$ $[M+H]^+$ 292.0352; Found: 292.0385.

V GC-MS Phenyl substituent (2a)

A) Reaction mixture:



2a – GC-MS

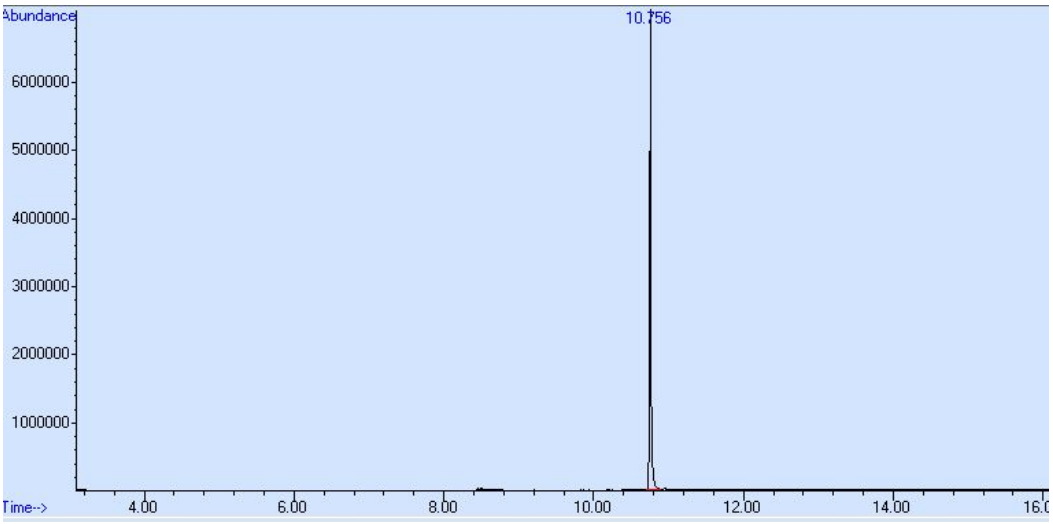


Figure 1 : a) Reaction mixture b) 2a alone

VI References:

[1] P. Thilmany, G. Evano, *Angew. Chem.Int.l Ed.* **2020**, *59*, 242-246.

[2] S. Jos, W. L. Santos, *Adv. Syn. Catal.* **2021**, *363*, 425-430.

[3] B. Sundararaju, A. Fürstner, *Angew. Chem. Int. Ed*. 2013, 52, 14050-14054.

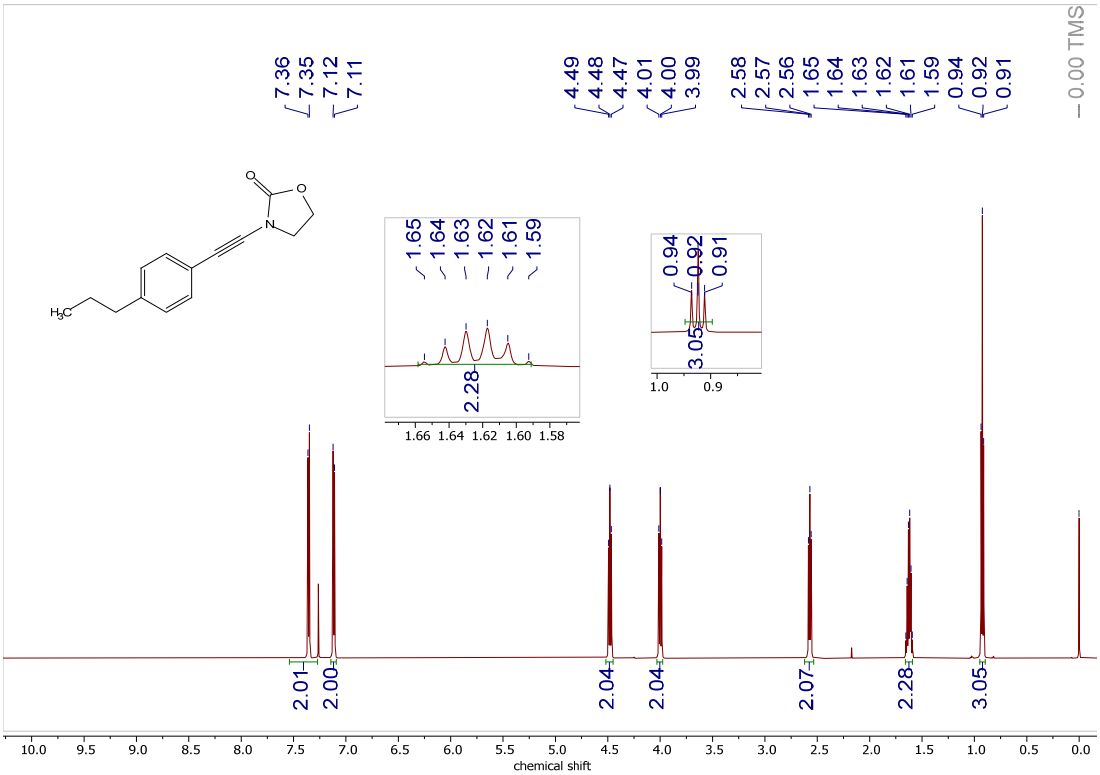
VIII X- Ray Crystallography- Experimental

2a (A colorless plate (0.05 x 0.13 x 0.15 mm^3)) 2n (A colorless prism (0.17 x 0.18 x 0.26 mm^3) and 3c (a colorless plate (0.05 × 0.23 × 0.31 mm^3)) was centered on the goniometer of a Rigaku Oxford Diffraction Synergy-S diffractometer equipped with a HyPix6000HE detector and operating with MoKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[1] The Laue was consistent with the tricilinc space groups P1 and P-1. The centrosymmetric space group, P-1, was chosen. The structure was solved using SHELXT[2] and refined using SHELXL[3] via Olex2.[4] The compound crystallizes with two molecules in the asymmetric unit. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. Olex2[5] AND/OR Mercury[6] was used for molecular graphics generation.

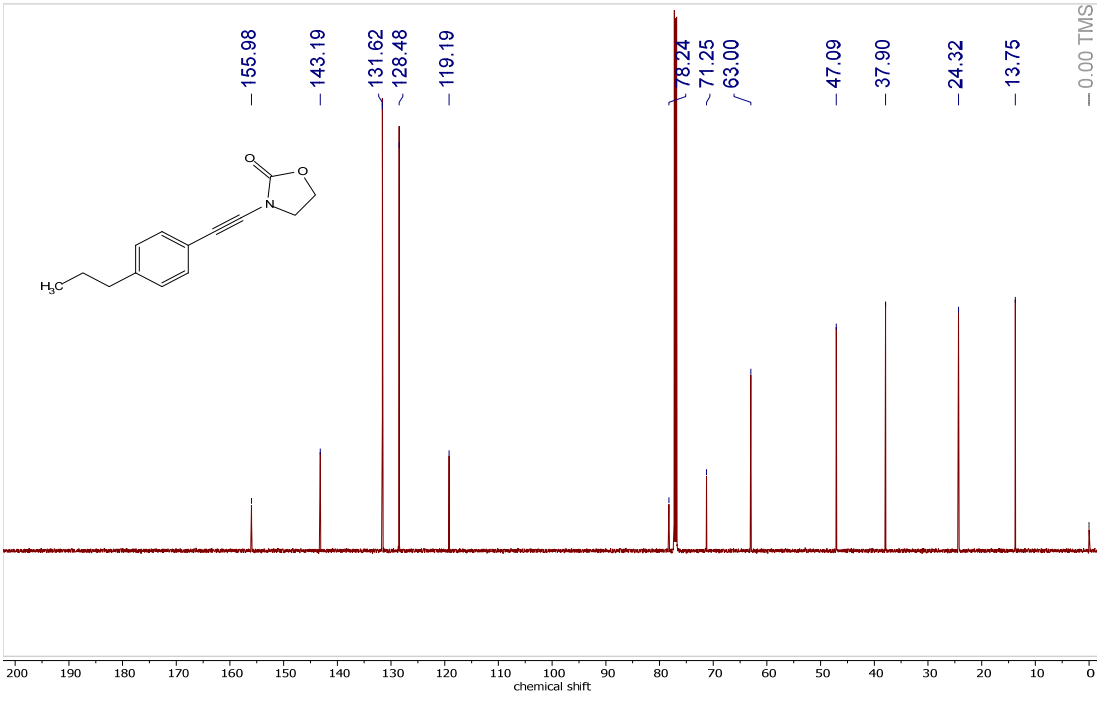
(1) CrysAlisPro Software System, v1.171.41.105a, Rigaku Oxford Diffraction, **2021**, Rigaku Corporation, Oxford, UK.
(2) Sheldrick, G. M. "SHELXT – Integrated space-group and crystal structure determination." *Acta Cryst*. **2015**, *A71*, 3–8.
(3) Sheldrick, G. M. "Crystal structure refinement with SHELXL." *Acta Cryst.* **2015**, *C71*, 3-8.
(4) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, ***42***, 339–341.
(5) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, ***42***, 339–341.
(6) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler M.; Wood, P. A. *J. Appl. Cryst.* **2020**, *53*, 226-235. [DOI: 10.1107/S1600576719014092].

VIII NMR spectra

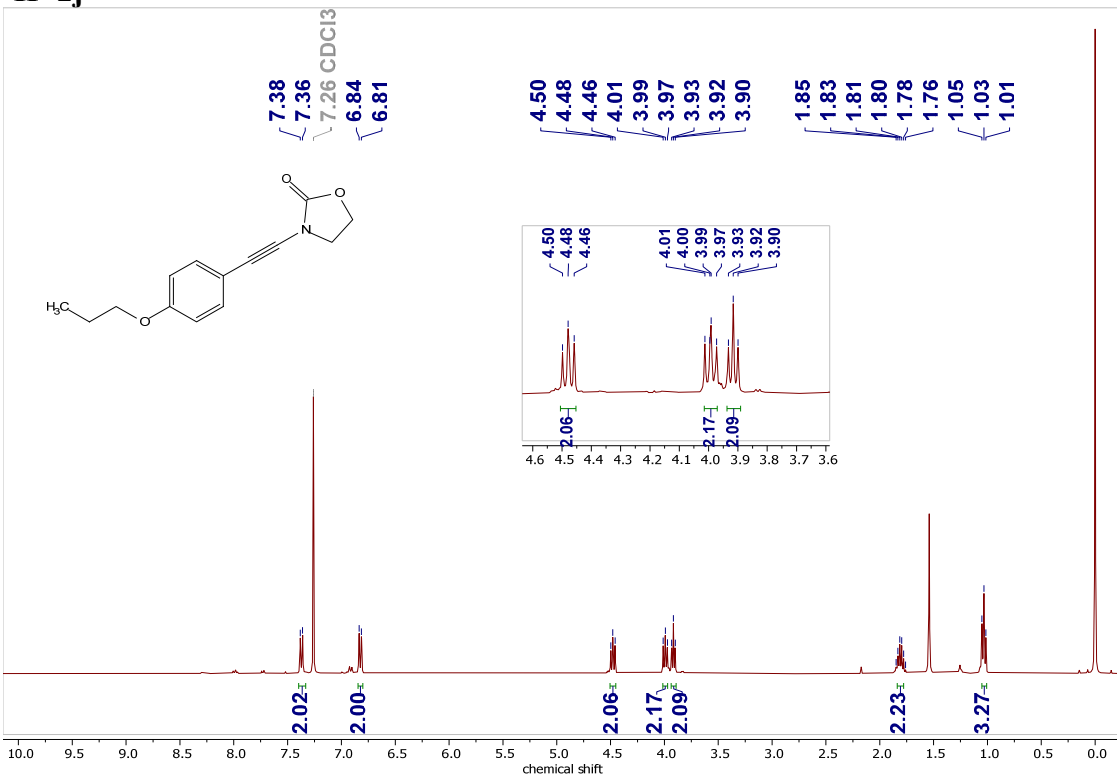
^{1}H-1f



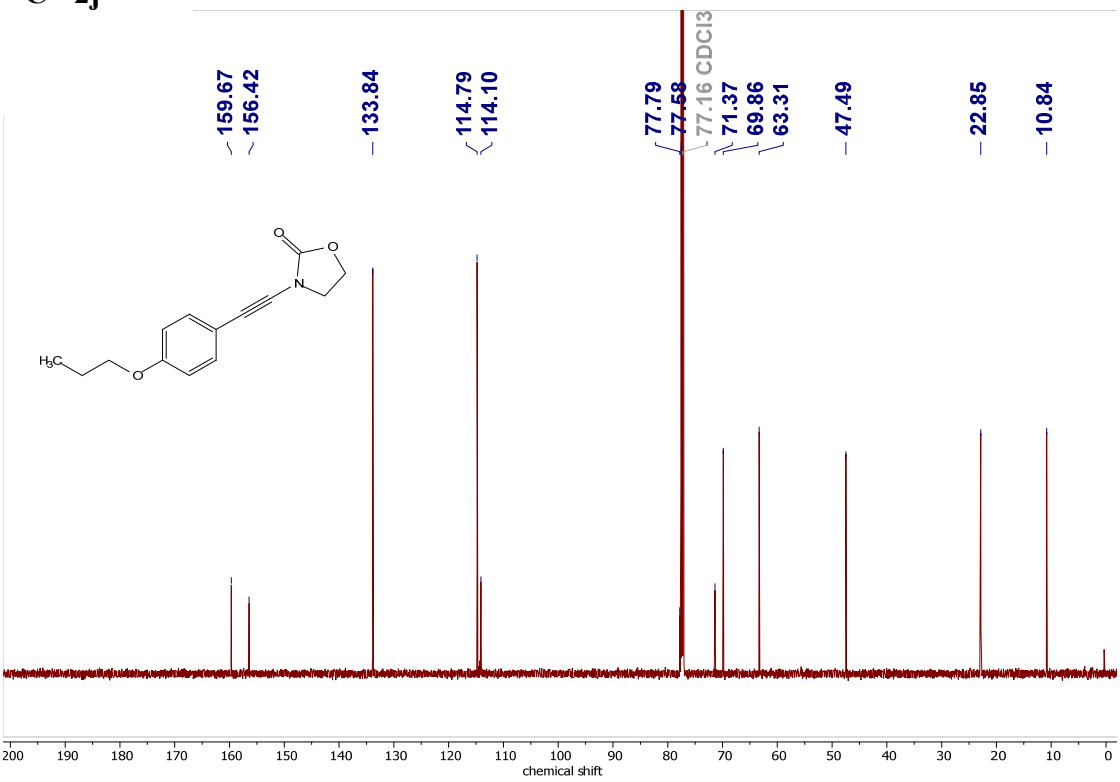
^{13}C-1f



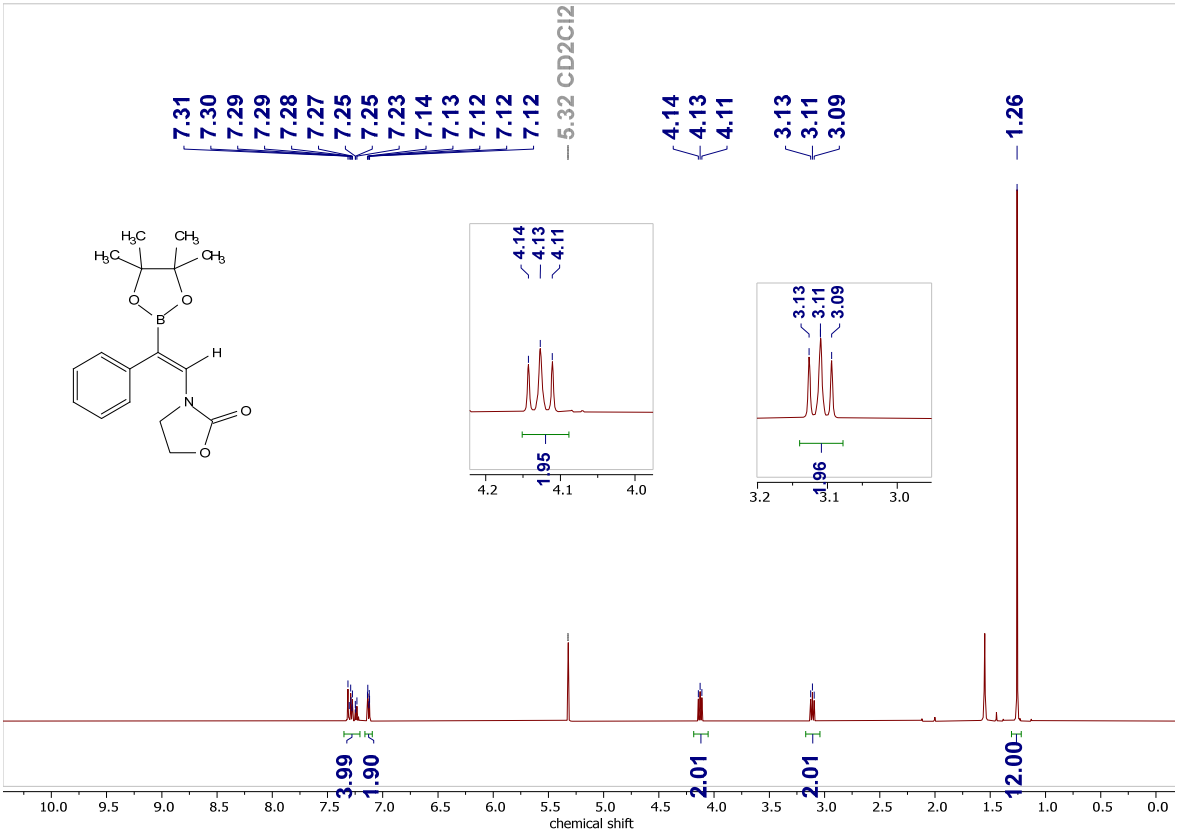
^{1}H- 2j


7.38
7.36
7.26 CDCl3
6.84
6.81
4.50
4.48
4.46
4.01
3.99
3.97
3.93
3.92
3.90
1.85
1.83
1.81
1.80
1.78
1.76
1.05
1.03
1.01
2.02
2.00
2.06
2.17
2.09
2.23
3.27
chemical shift

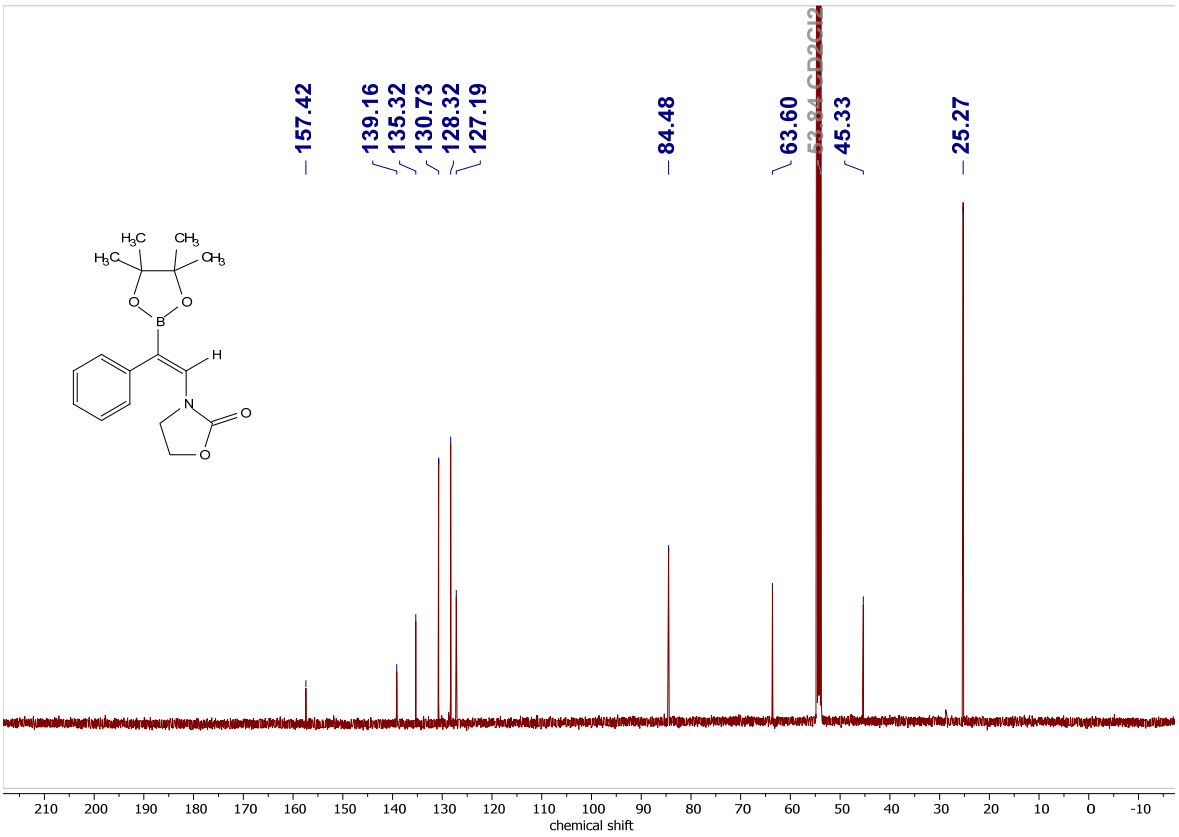
^{13}C - 2j


159.67
156.42
133.84
114.79
114.10
77.79
77.58
77.16 CDCl3
71.37
69.86
63.31
47.49
22.85
10.84
chemical shift

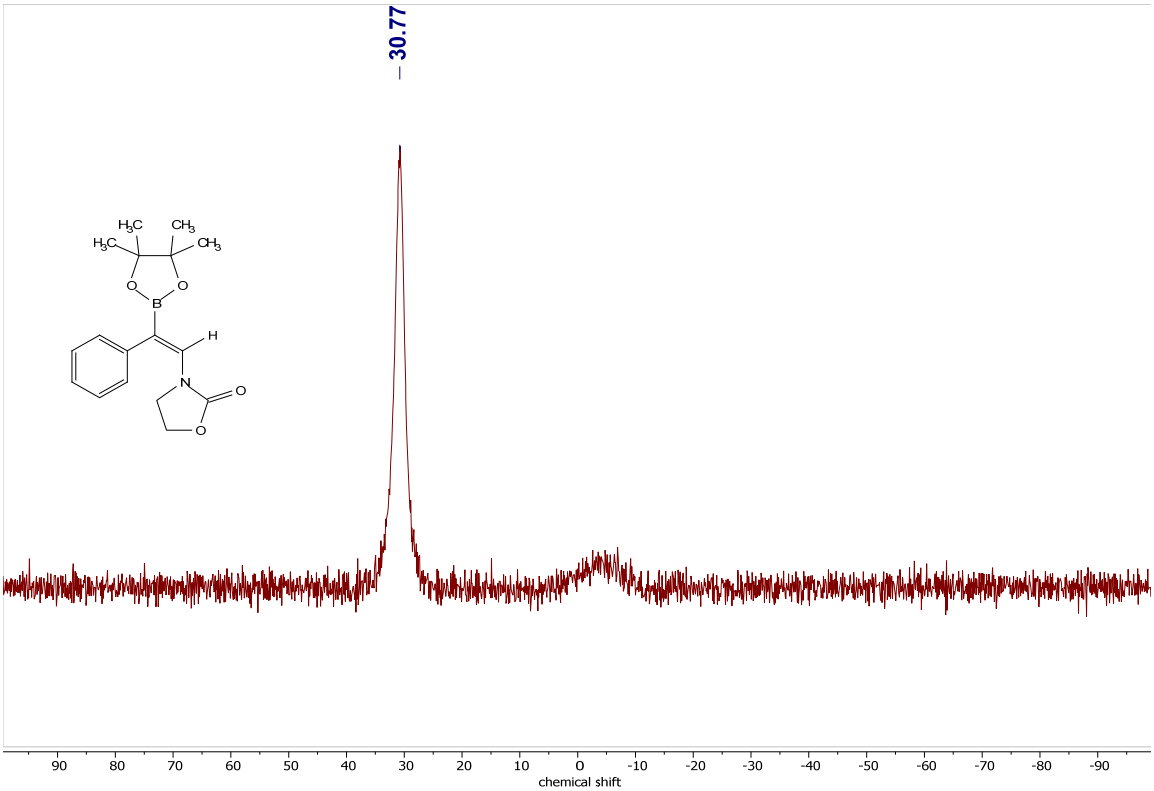
^{1}H-2a


7.31
7.30
7.29
7.29
7.28
7.27
7.25
7.25
7.23
7.14
7.13
7.12
7.12
7.12
5.32 CD2Cl2
4.14
4.13
4.11
3.13
3.11
3.09
1.26
H3C
CH3
H3C
CH3
O
O
B
H
N
O
O
1.95
1.96
3.99
1.90
2.01
2.01
12.00
chemical shift

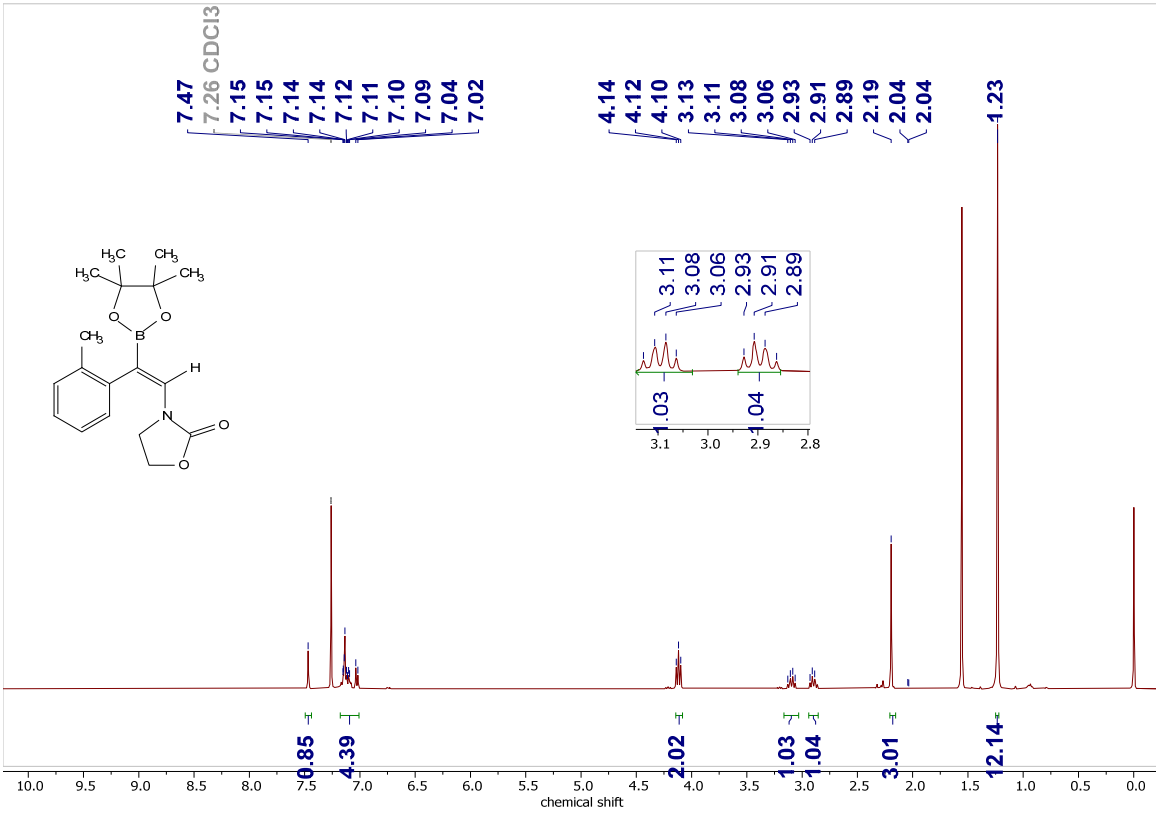
^{13}C-2a


157.42
139.16
135.32
130.73
128.32
127.19
84.48
63.60
53.84 CD2Cl2
45.33
25.27
chemical shift

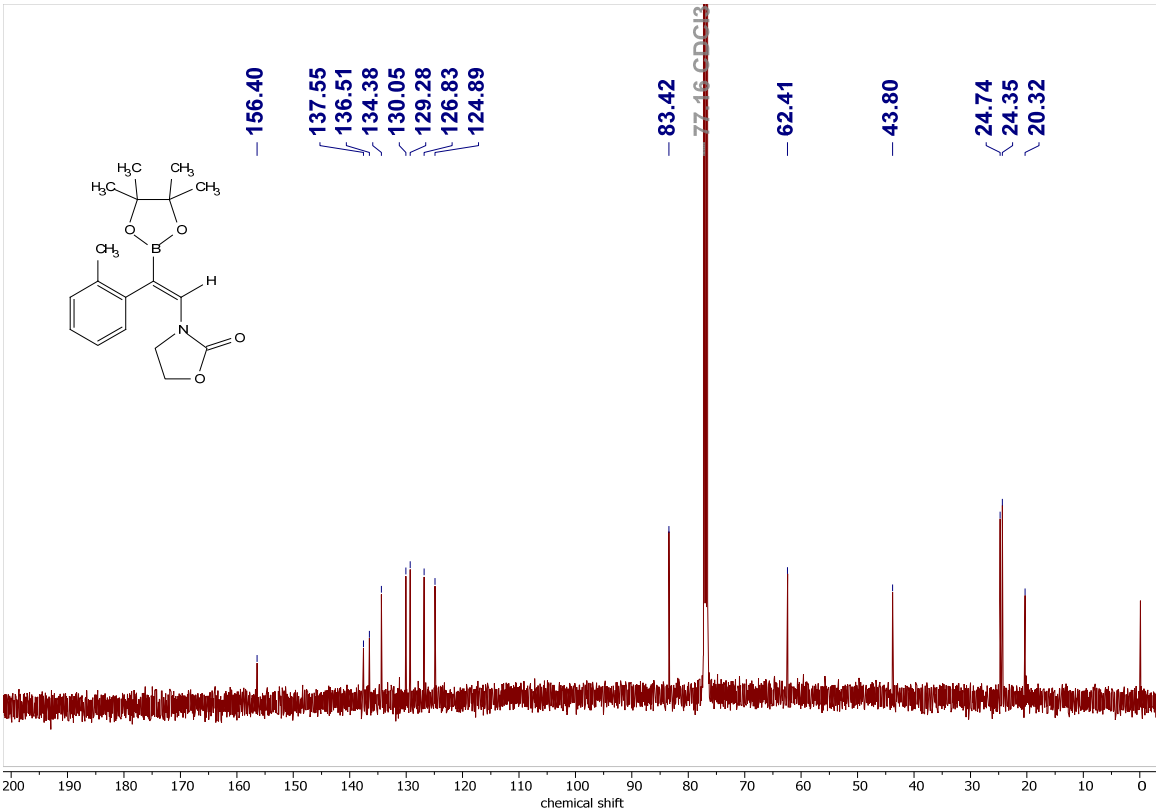
^{11}B-2a


30.77
chemical shift

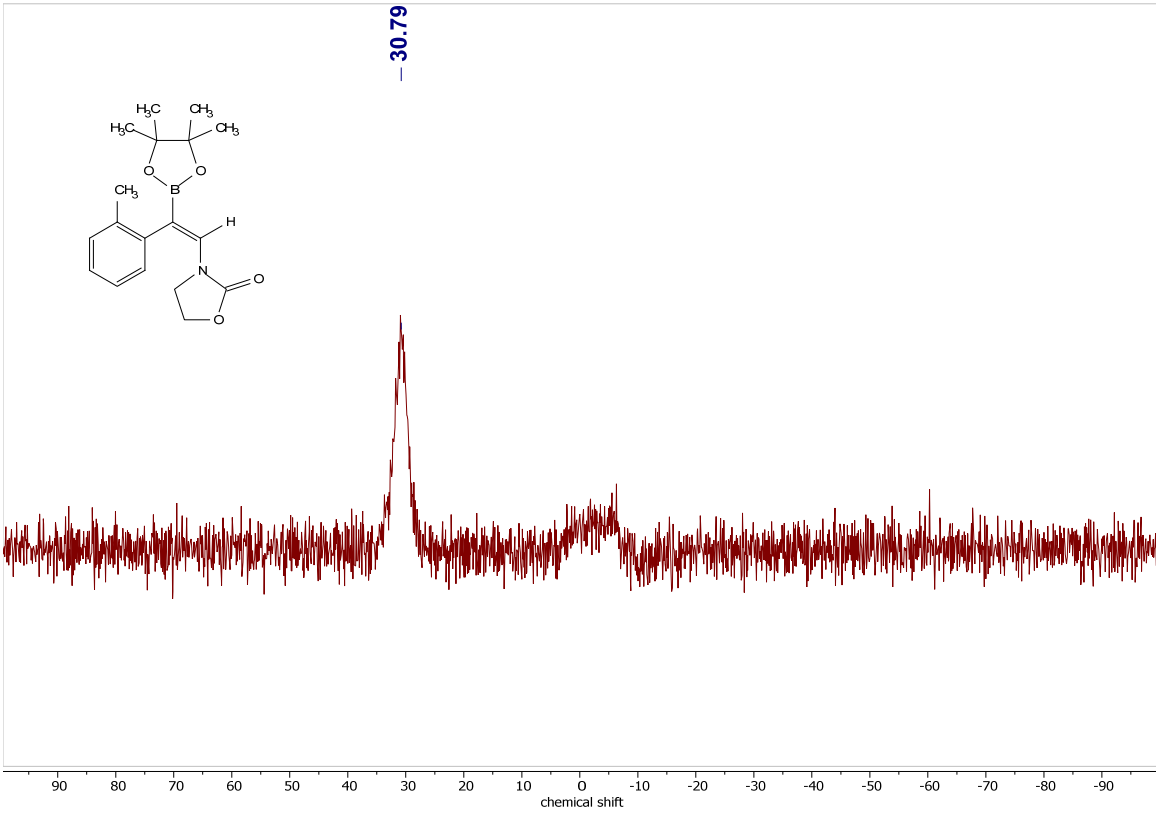
^{1}H- 2b


7.47
7.26 CDCl3
7.15
7.15
7.14
7.14
7.12
7.11
7.10
7.09
7.04
7.02
4.14
4.12
4.10
3.13
3.11
3.08
3.06
2.93
2.91
2.89
2.19
2.04
2.04
1.23
3.11
3.08
3.06
2.93
2.91
2.89
1.03
1.04
0.85
4.39
2.02
1.03
1.04
3.01
12.14
chemical shift

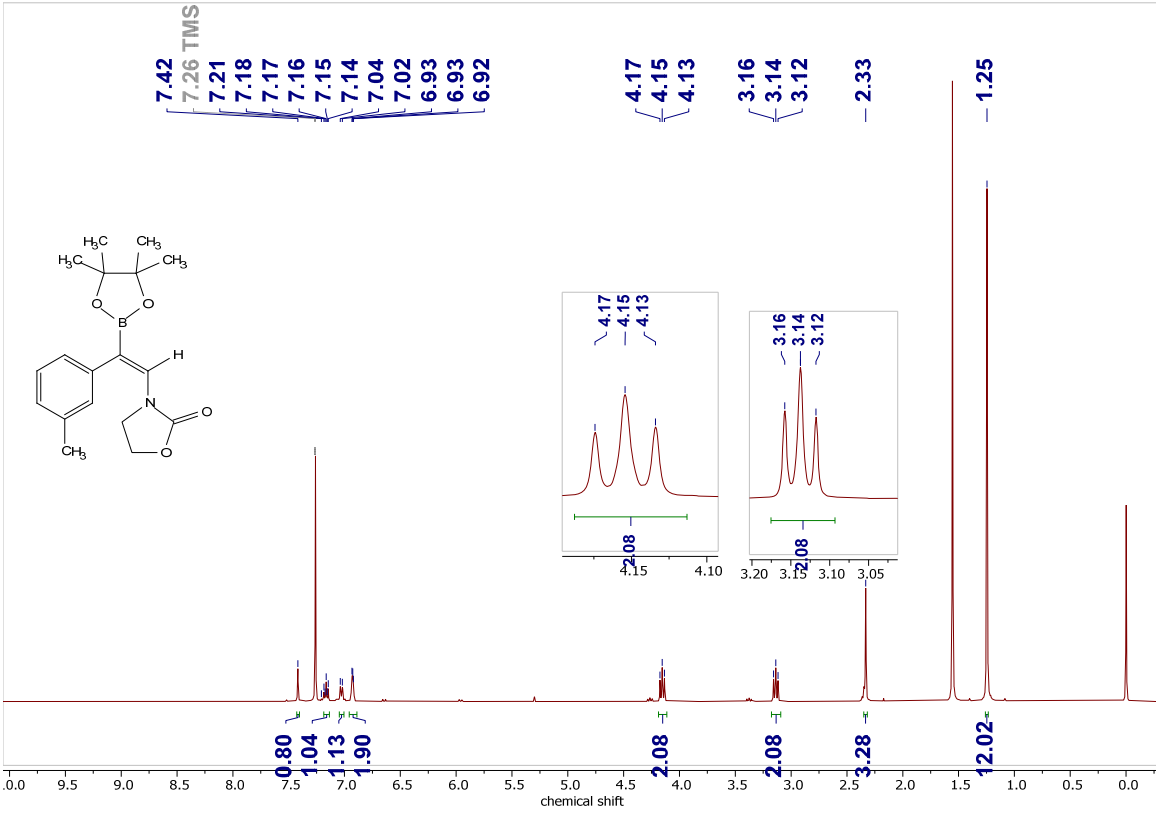
^{13}C-2b


156.40
137.55
136.51
134.38
130.05
129.28
126.83
124.89
83.42
77.16 CDCl3
62.41
43.80
24.74
24.35
20.32
chemical shift

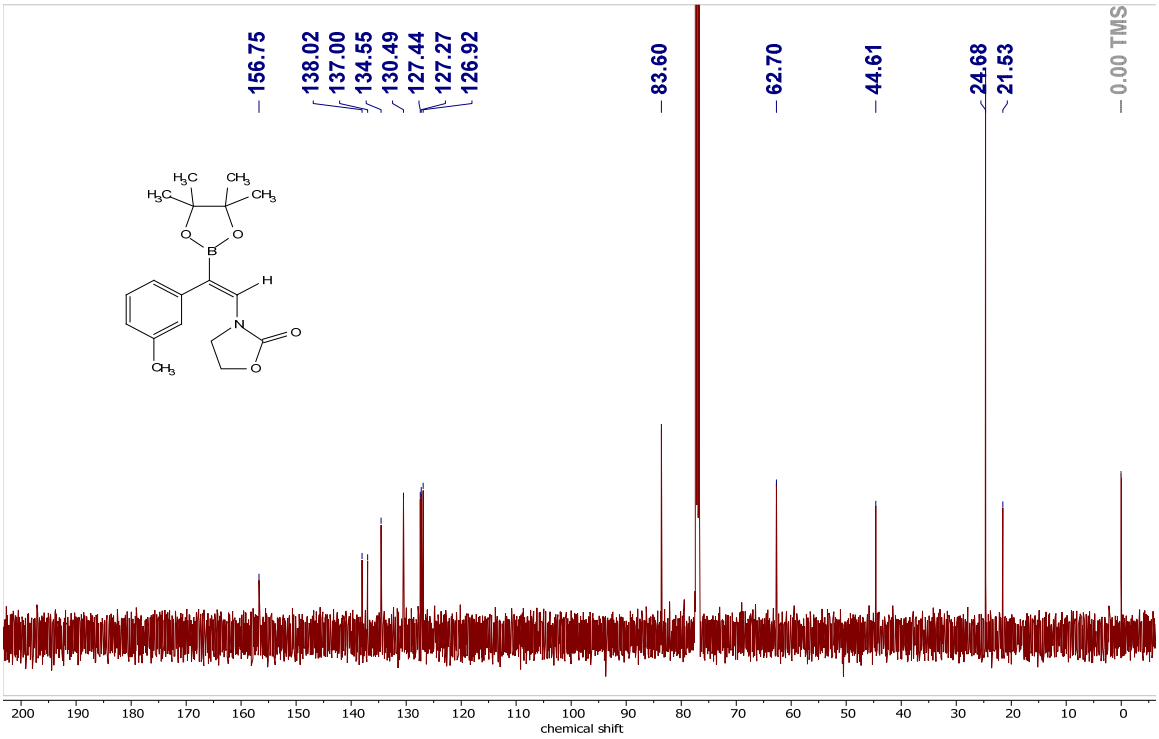
^{11}B-2b


30.79
chemical shift

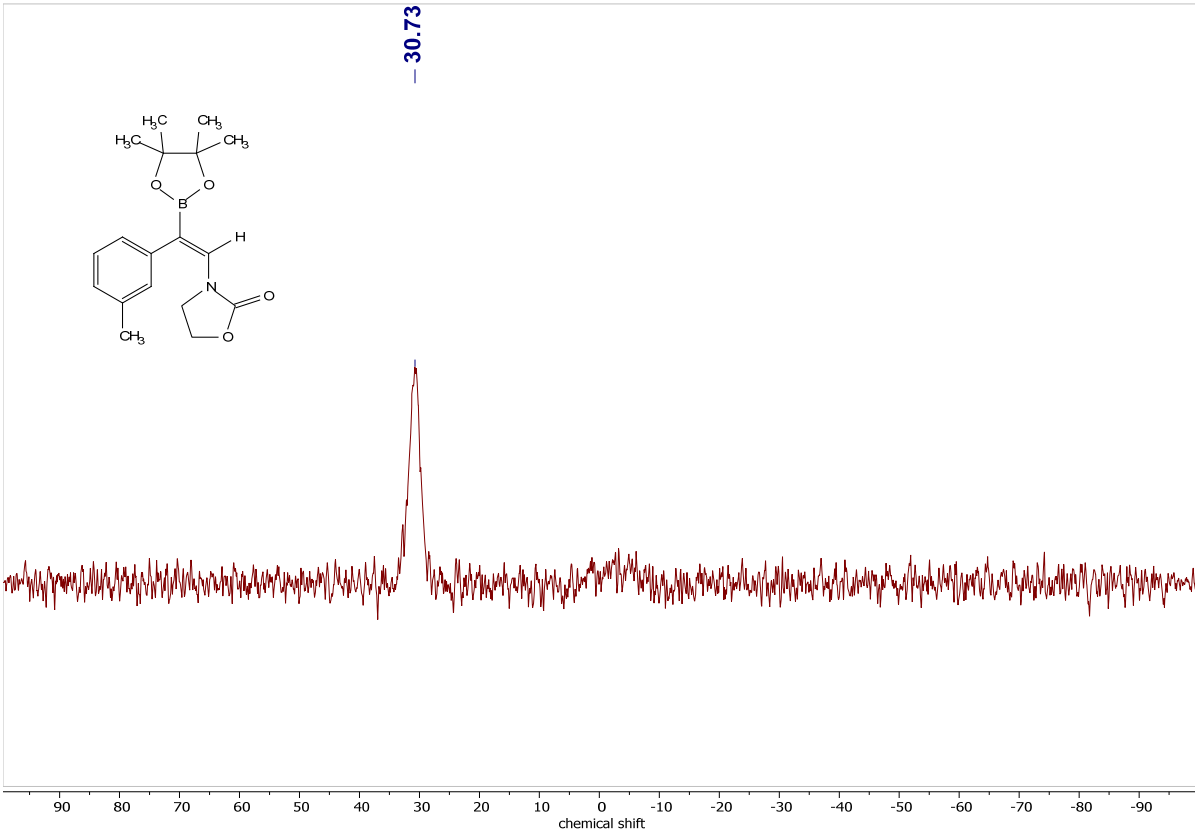
^{1}H- 2c


7.42
7.26 TMS
7.21
7.18
7.17
7.16
7.15
7.14
7.04
7.02
6.93
6.93
6.92
4.17
4.15
4.13
3.16
3.14
3.12
2.33
1.25
0.80
1.04
1.13
1.90
2.08
2.08
3.28
12.02
chemical shift

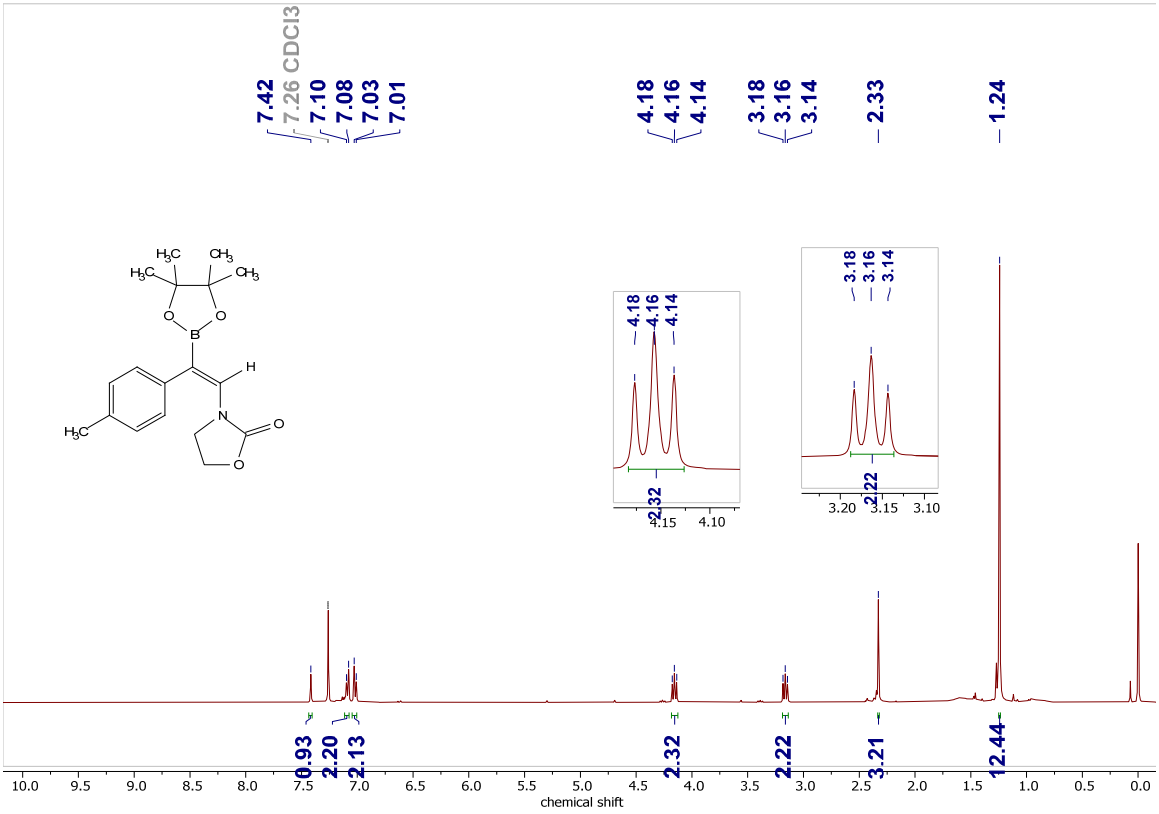
^{13}C-2c


156.75
138.02
137.00
134.55
130.49
127.44
127.27
126.92
83.60
62.70
44.61
24.68
21.53
0.00 TMS
chemical shift

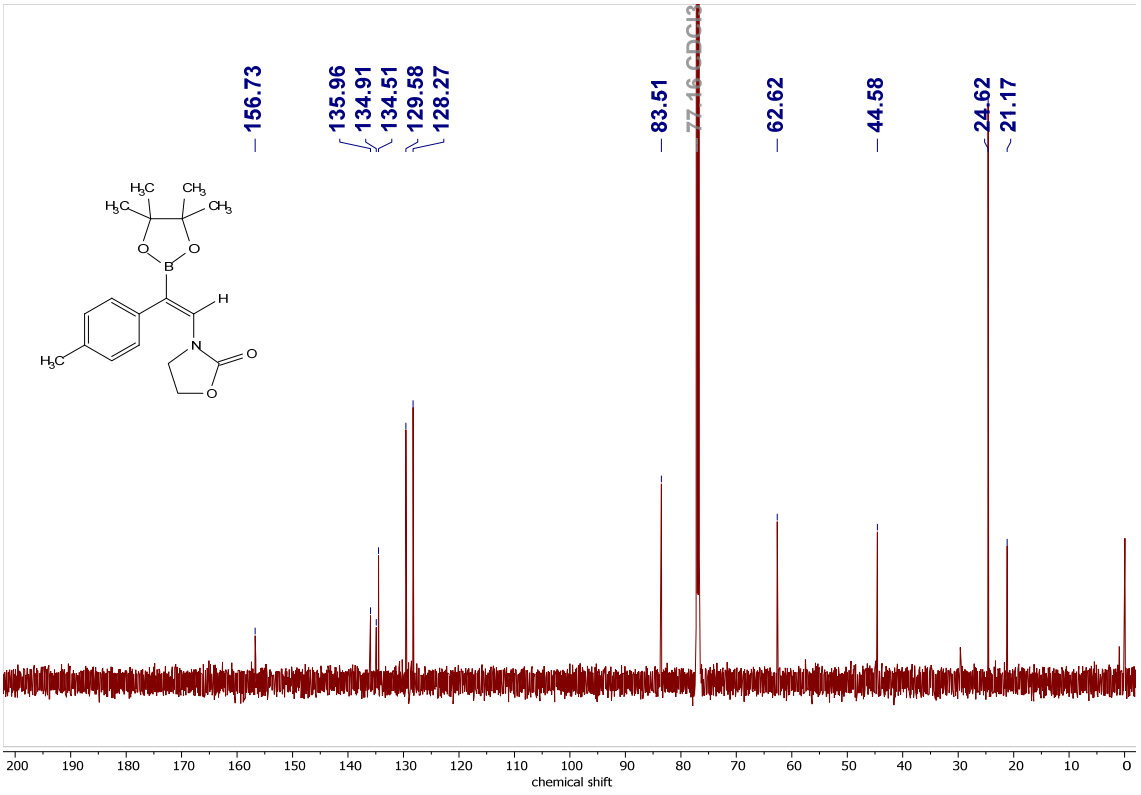
^{11}B-2c

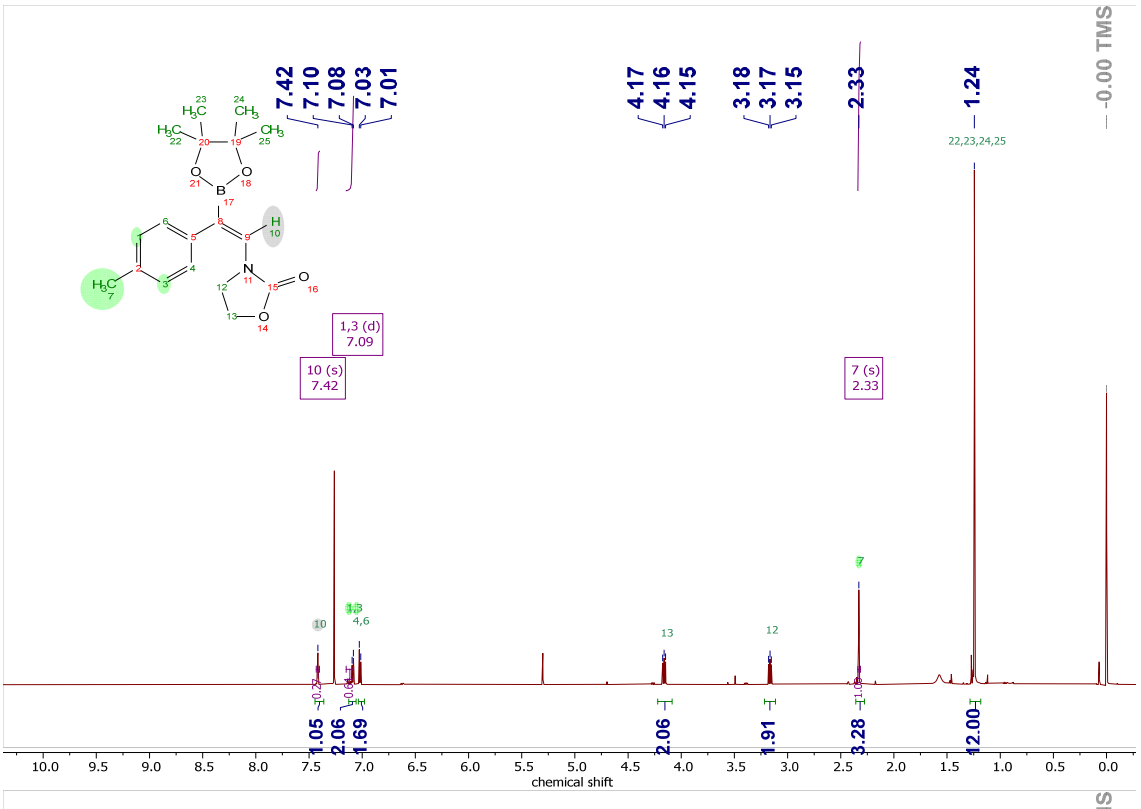

30.73
chemical shift

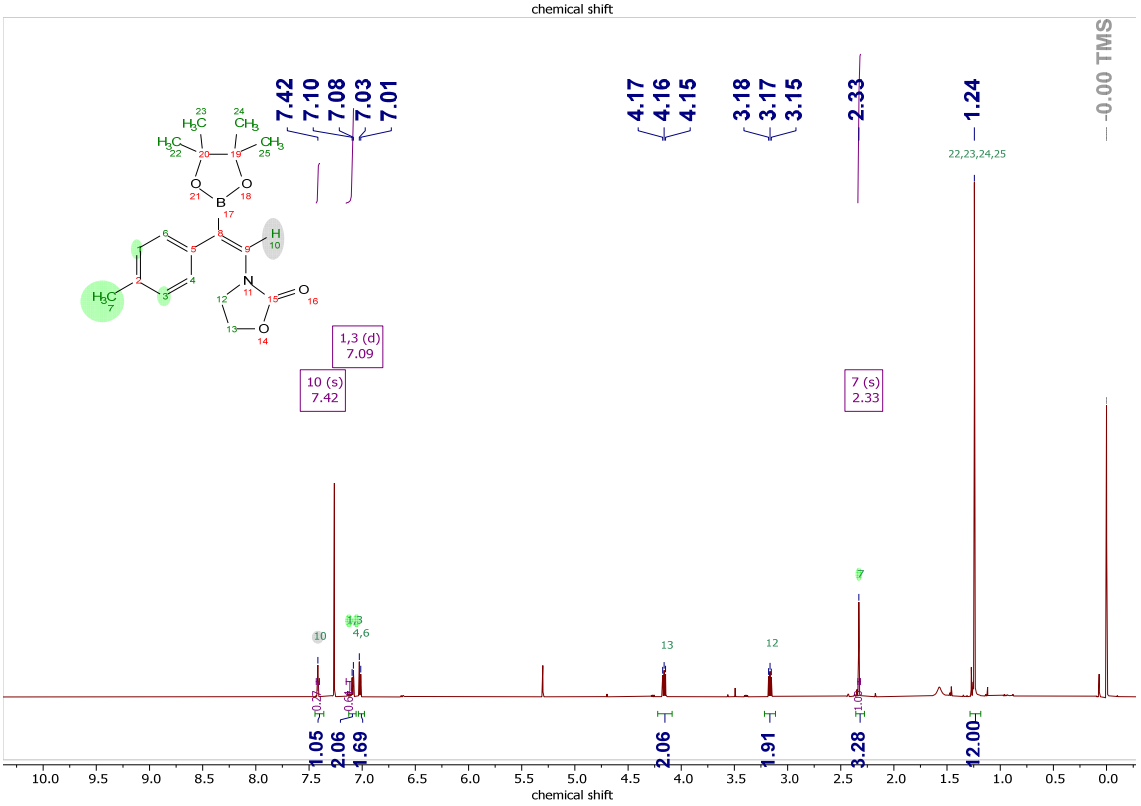
^{1}H-2d


7.42
7.26 CDCl3
7.10
7.08
7.03
7.01
4.18
4.16
4.14
3.18
3.16
3.14
2.33
1.24
0.93
2.20
2.13
2.32
2.22
3.21
12.44
chemical shift

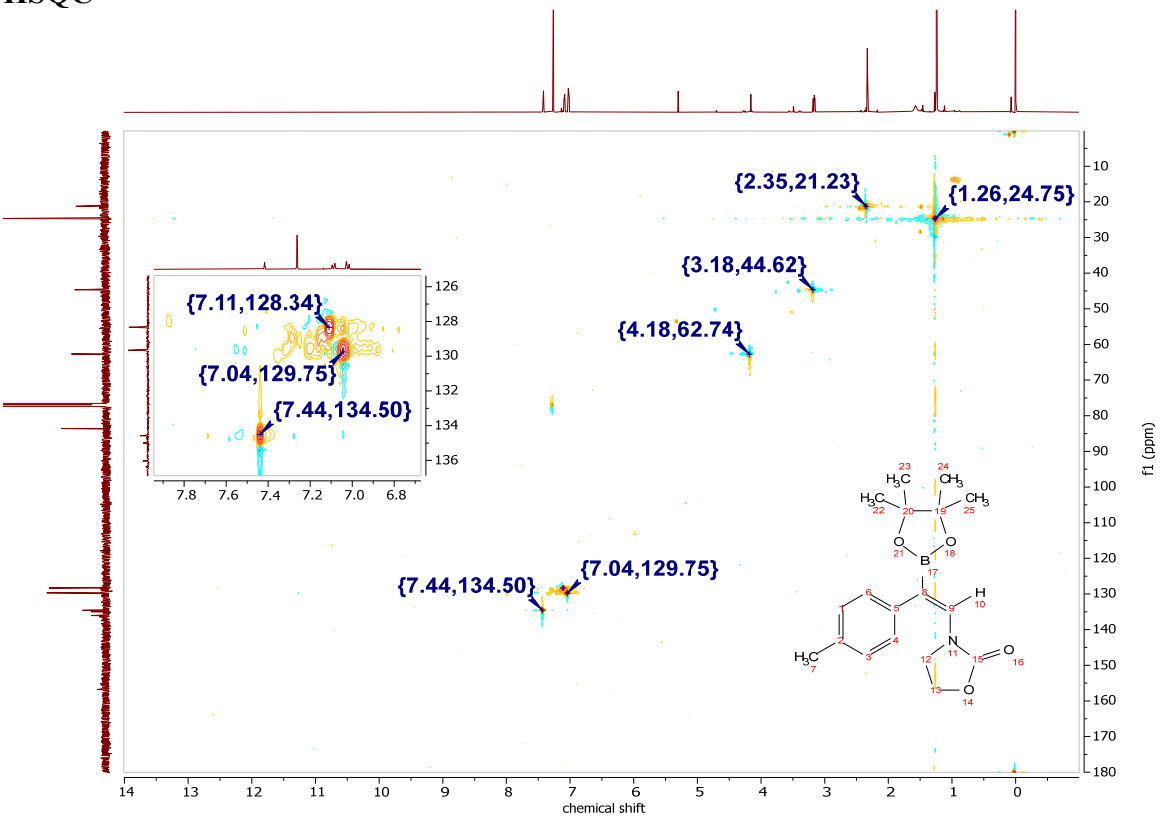
^{13}C-2d


156.73
135.96
134.91
134.51
129.58
128.27
83.51
77.16 CDCl3
62.62
44.58
24.62
21.17
chemical shift

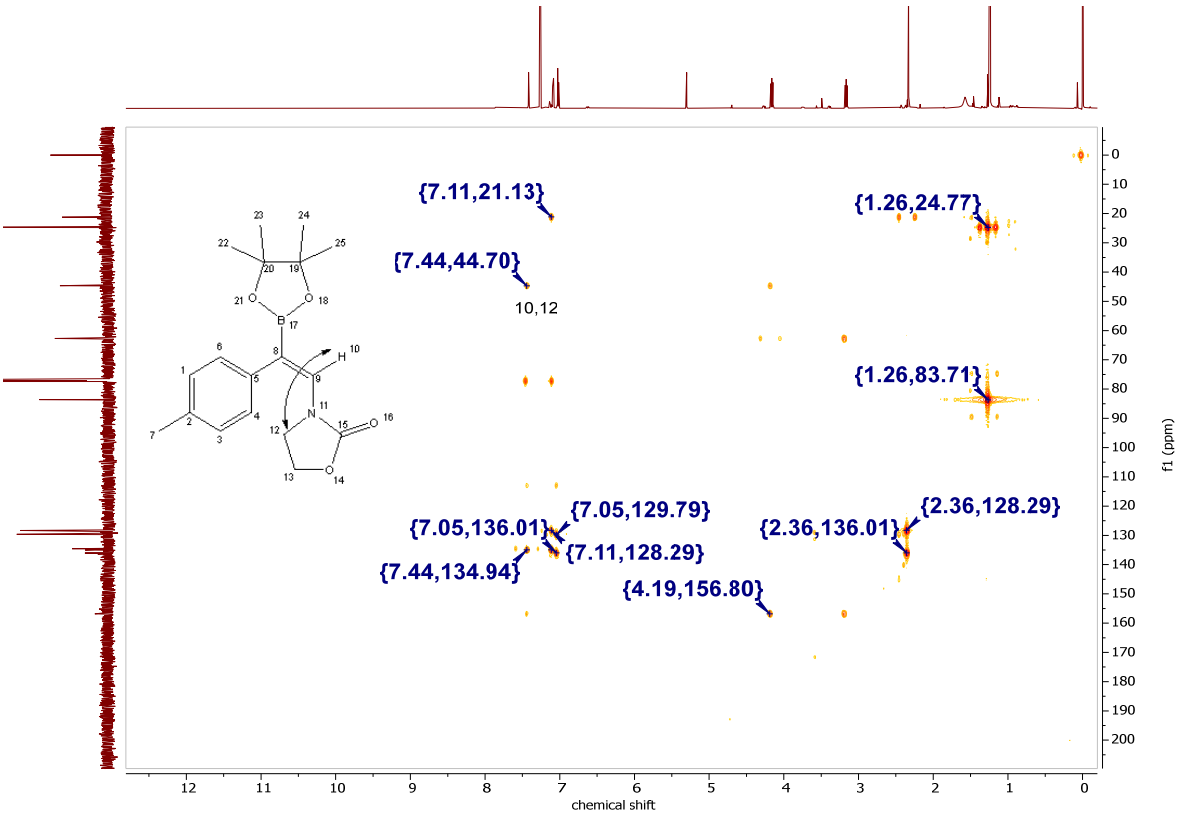

7.42
7.10
7.08
7.03
7.01
4.17
4.16
4.15
3.18
3.17
3.15
2.33
1.24
22,23,24,25
-0.00 TMS
1,3 (d)
7.09
10 (s)
7.42
7 (s)
2.33
1.05
2.06
1.69
2.06
1.91
3.28
12.00
chemical shift


7.42
7.10
7.08
7.03
7.01
4.17
4.16
4.15
3.18
3.17
3.15
2.33
1.24
22,23,24,25
-0.00 TMS
1,3 (d)
7.09
10 (s)
7.42
7 (s)
2.33
1.05
2.06
1.69
2.06
1.91
3.28
12.00
chemical shift

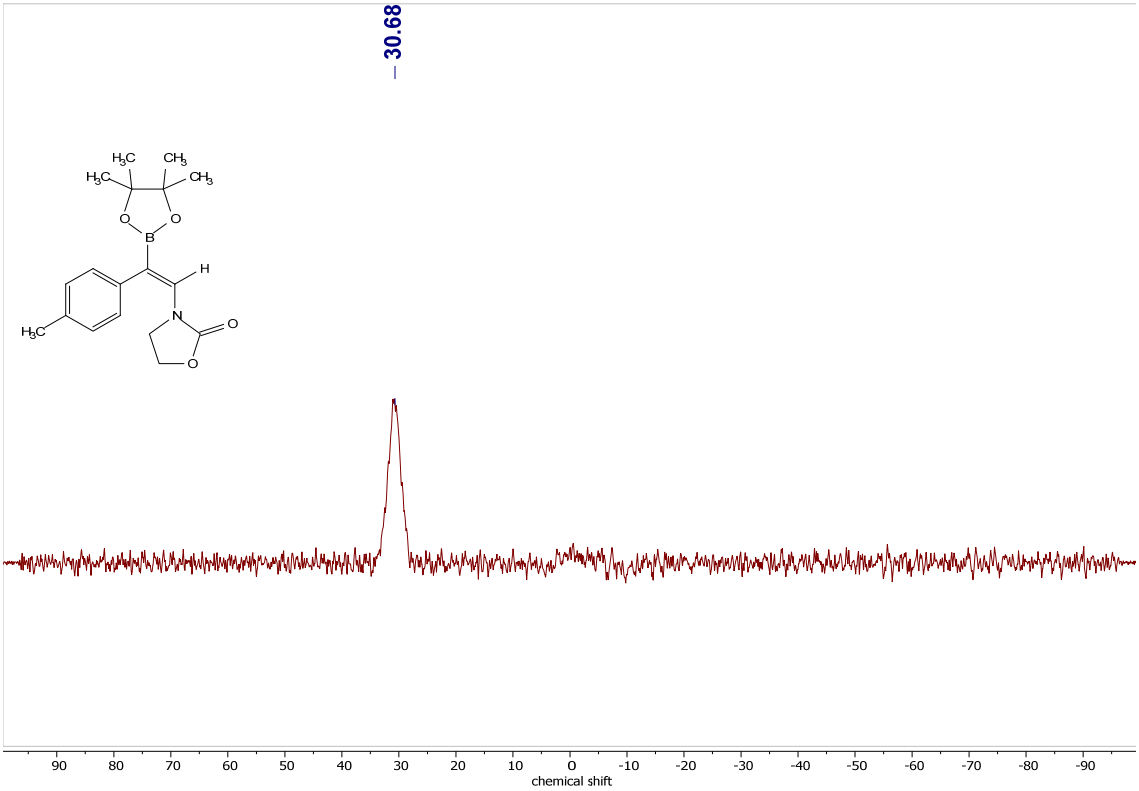
HSQC


{2.35,21.23}
{1.26,24.75}
{3.18,44.62}
{4.18,62.74}
{7.11,128.34}
{7.04,129.75}
{7.44,134.50}
{7.44,134.50}
{7.04,129.75}
chemical shift
f1 (ppm)

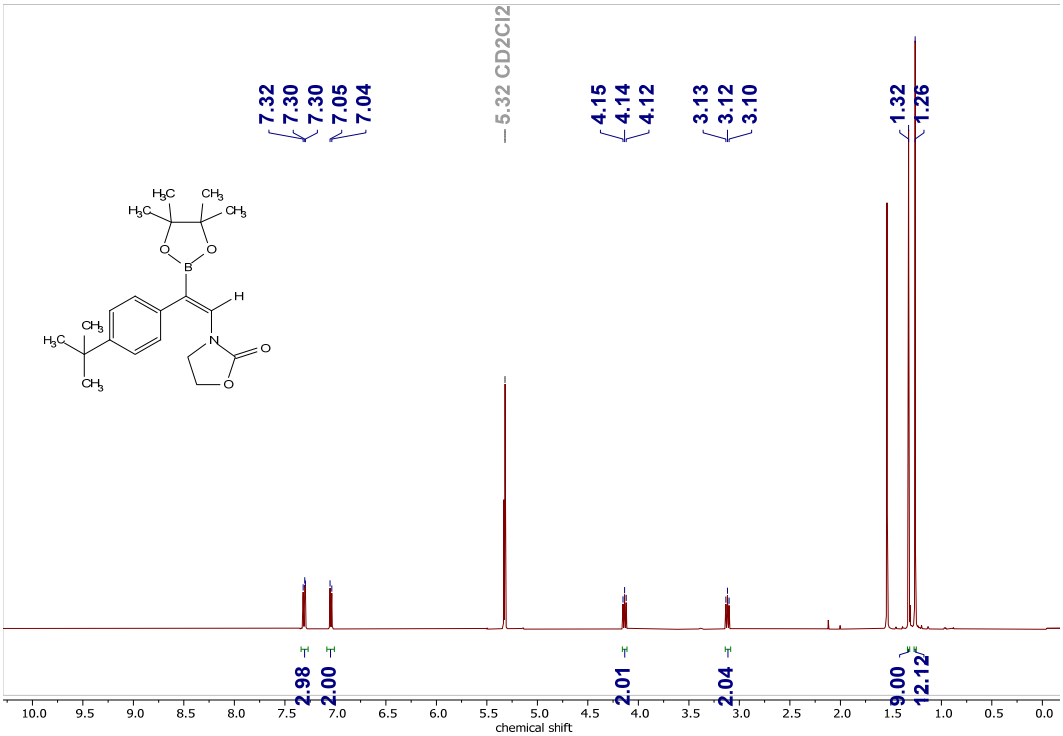
HMBC


{7.11,21.13}
{1.26,24.77}
{7.44,44.70}
10,12
{1.26,83.71}
{7.05,129.79}
{7.05,136.01}
{2.36,128.29}
{2.36,136.01}
{7.11,128.29}
{7.44,134.94}
{4.19,156.80}
chemical shift
f1 (ppm)

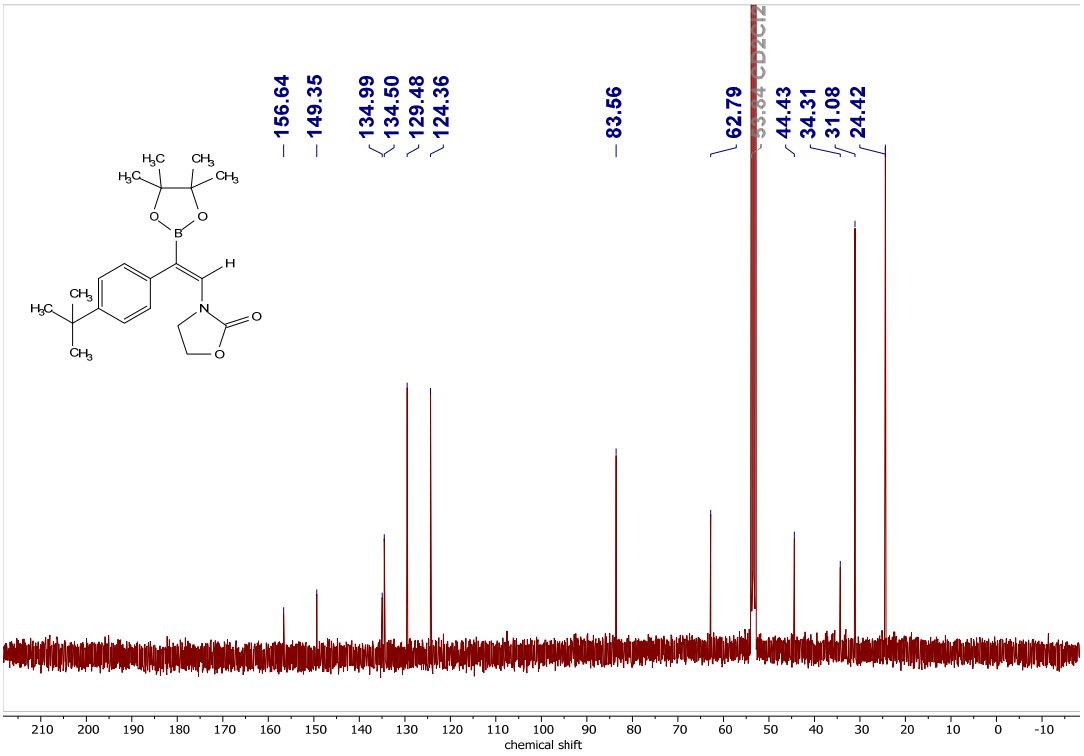
^{11}B-2d


30.68
chemical shift

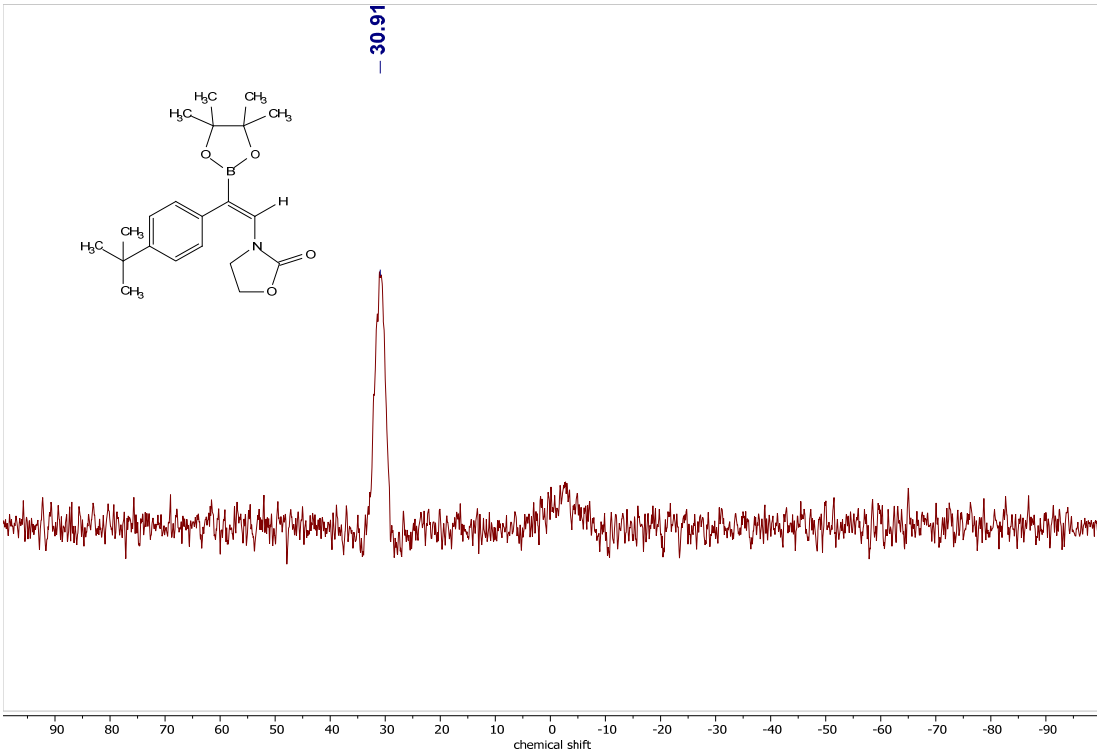
^{1}H-2e


7.32
7.30
7.30
7.05
7.04
5.32 CD2Cl2
4.15
4.14
4.12
3.13
3.12
3.10
1.32
1.26
2.98
2.00
2.01
2.04
9.00
12.12
chemical shift

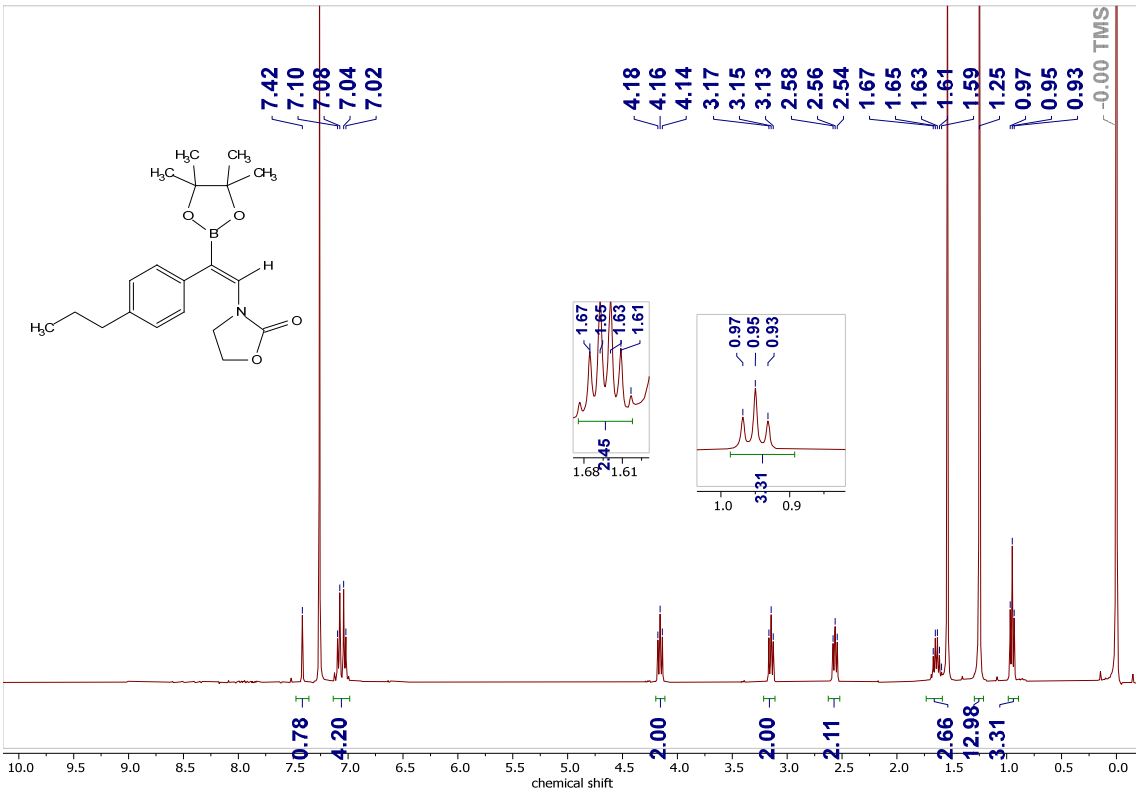
^{13}C-2e


156.64
149.35
134.99
134.50
129.48
124.36
83.56
62.79
44.43
34.31
31.08
24.42
chemical shift

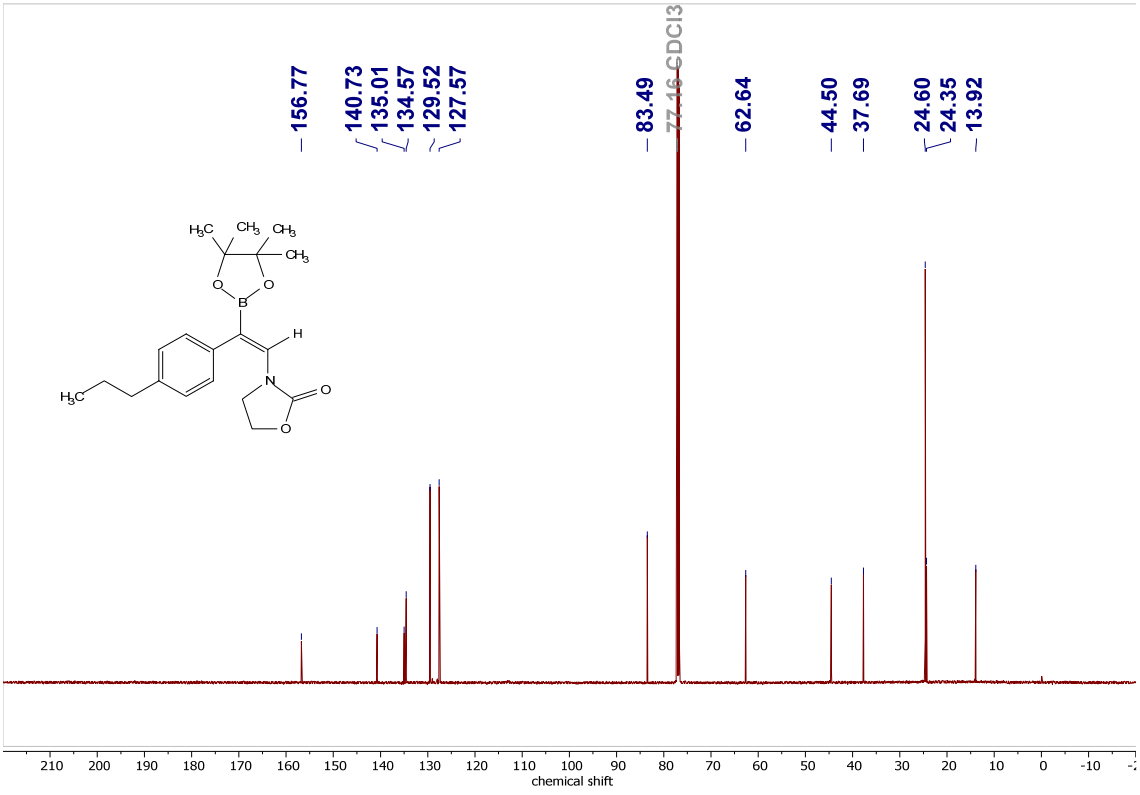
^{11}B-2e


30.91
chemical shift

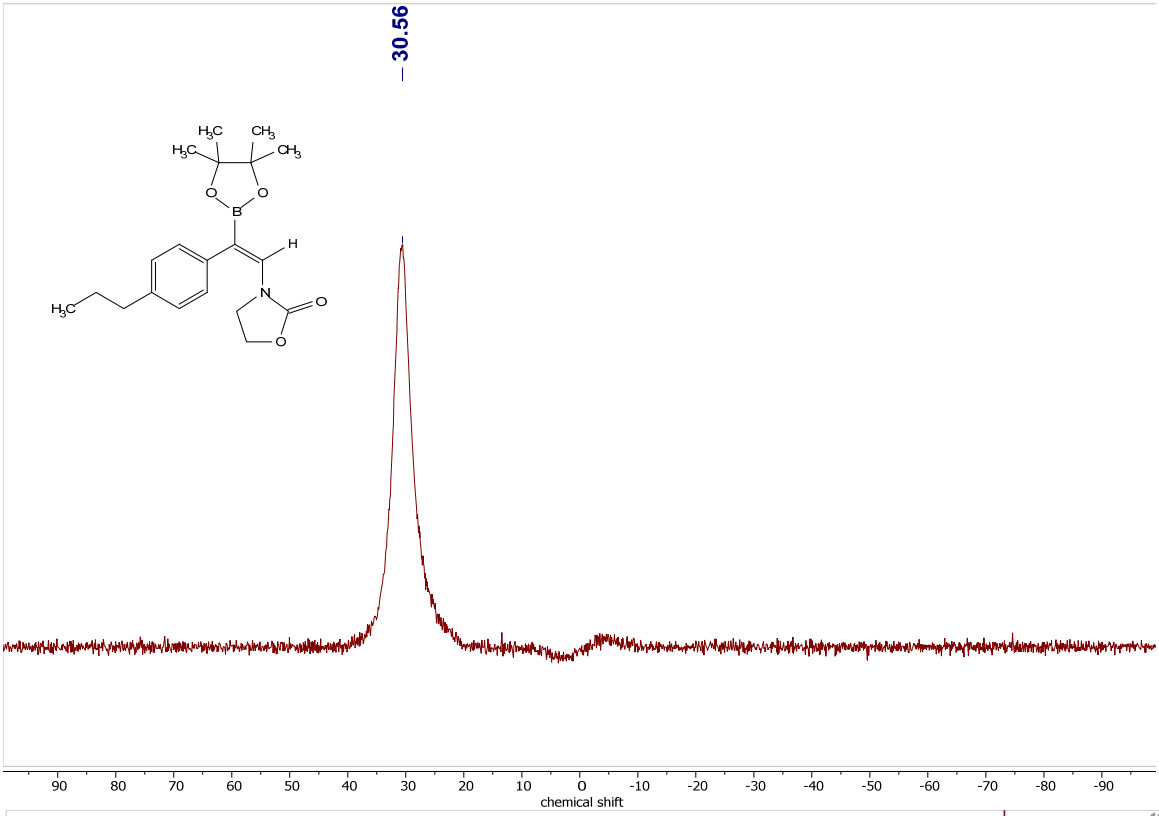
^{1}H-2f

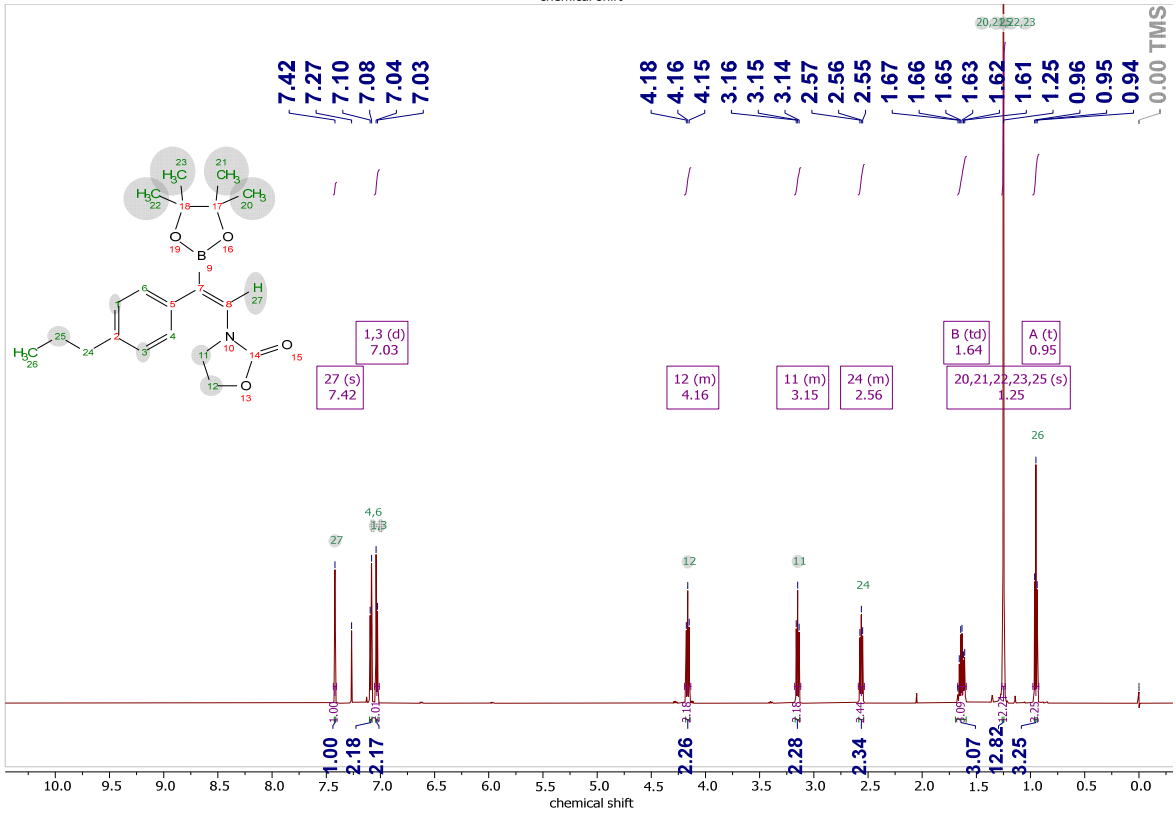

7.42
7.10
7.08
7.04
7.02
4.18
4.16
4.14
3.17
3.15
3.13
2.58
2.56
2.54
1.67
1.65
1.63
1.61
1.59
1.25
0.97
0.95
0.93
-0.00 TMS
0.78
4.20
2.00
2.00
2.11
2.66
12.98
3.31
chemical shift

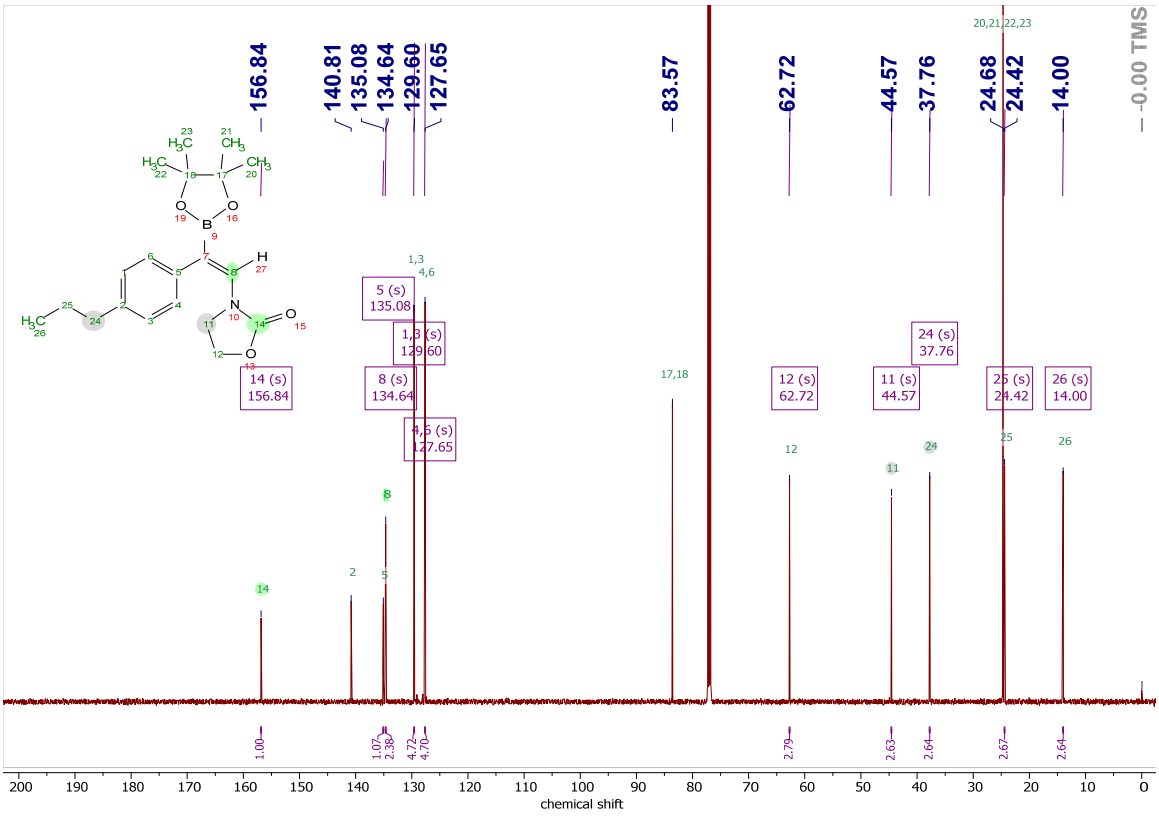
^{13}C-2f


156.77
140.73
135.01
134.57
129.52
127.57
83.49
77.16 CDCl3
62.64
44.50
37.69
24.60
24.35
13.92
chemical shift

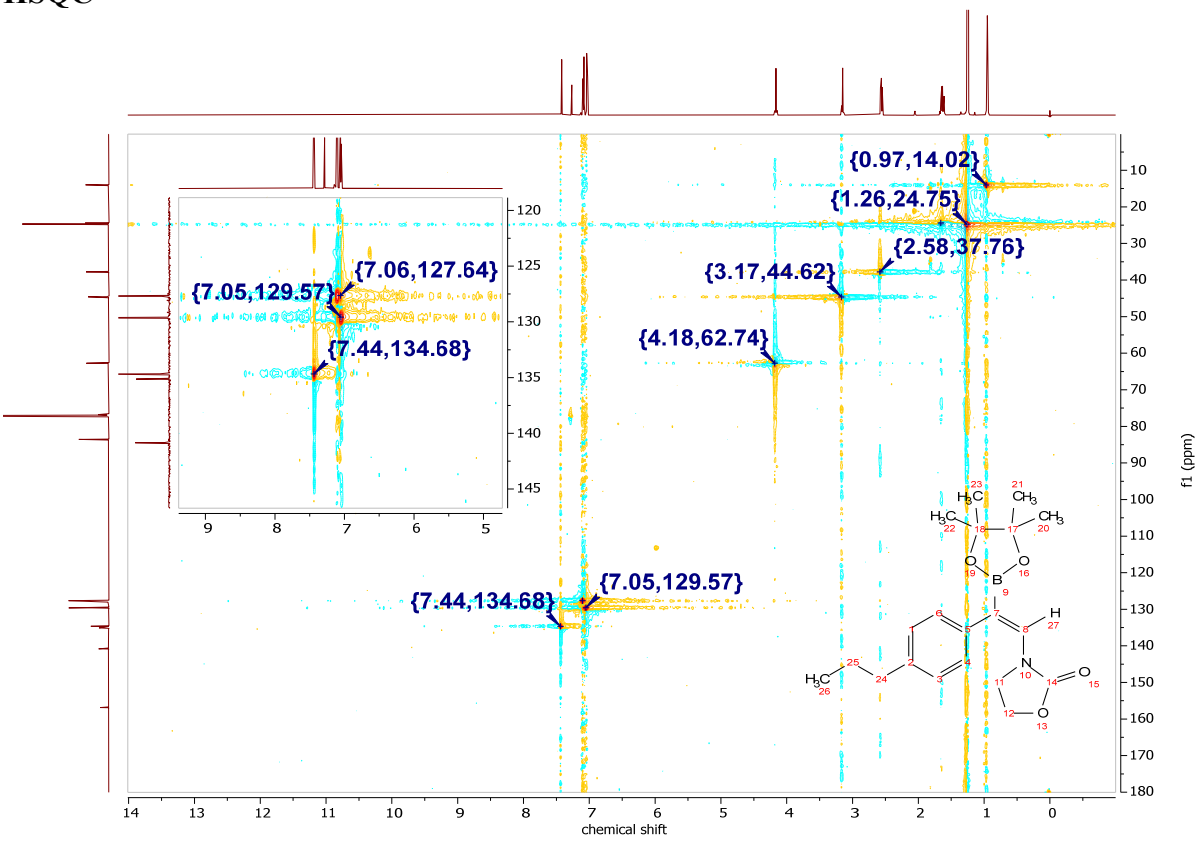
^{11}B-2f


30.56
chemical shift

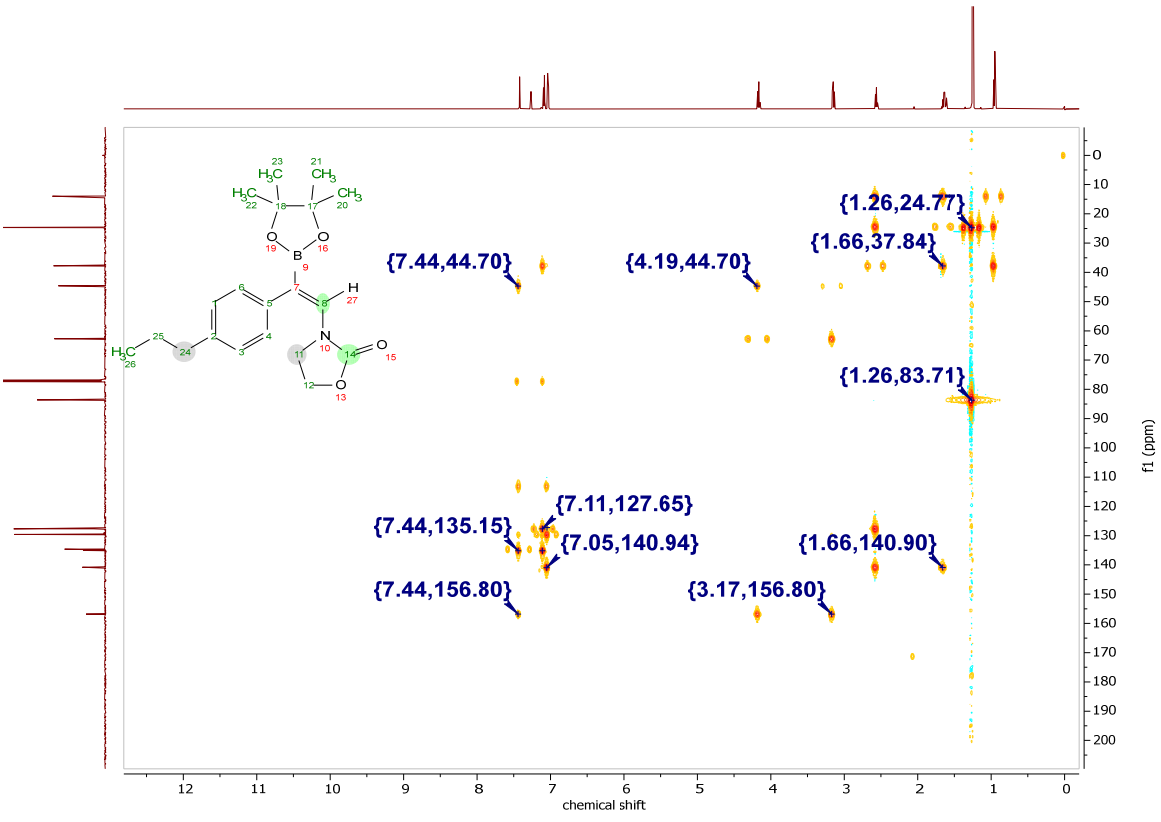

7.42
7.27
7.10
7.08
7.04
7.03
4.18
4.16
4.15
3.16
3.15
3.14
2.57
2.56
2.55
1.67
1.66
1.65
1.63
1.62
1.61
1.25
0.96
0.95
0.94
0.00 TMS
1,3 (d) 7.03
27 (s) 7.42
12 (m) 4.16
11 (m) 3.15
24 (m) 2.56
B (td) 1.64
A (t) 0.95
20,21,22,23,25 (s) 1.25
1.00
2.18
2.17
2.26
2.28
2.34
3.07
12.82
3.25
chemical shift


156.84
140.81
135.08
134.64
129.60
127.65
83.57
62.72
44.57
37.76
24.68
24.42
14.00
-0.00 TMS
20,21,22,23
14 (s)
156.84
5 (s)
135.08
1,3 (s)
129.60
8 (s)
134.64
4,6 (s)
127.65
12 (s)
62.72
11 (s)
44.57
24 (s)
37.76
25 (s)
24.42
26 (s)
14.00
17,18
chemical shift

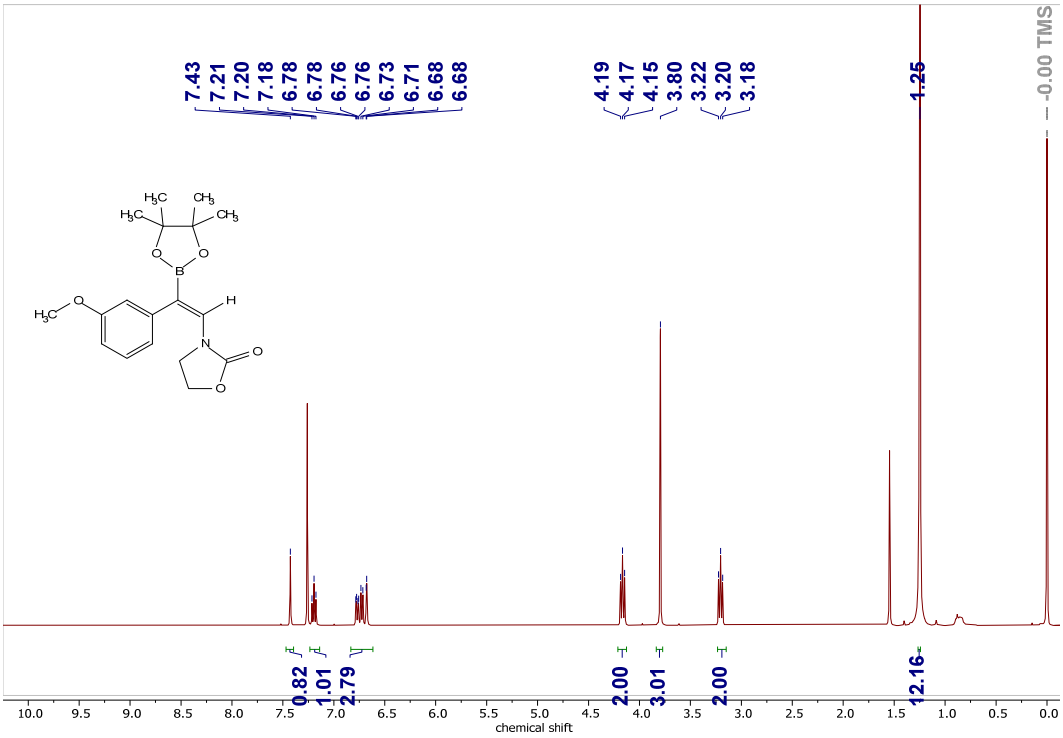
HSQC


{0.97,14.02}
{1.26,24.75}
{2.58,37.76}
{3.17,44.62}
{4.18,62.74}
{7.06,127.64}
{7.05,129.57}
{7.44,134.68}
{7.05,129.57}
{7.44,134.68}
chemical shift
f1 (ppm)

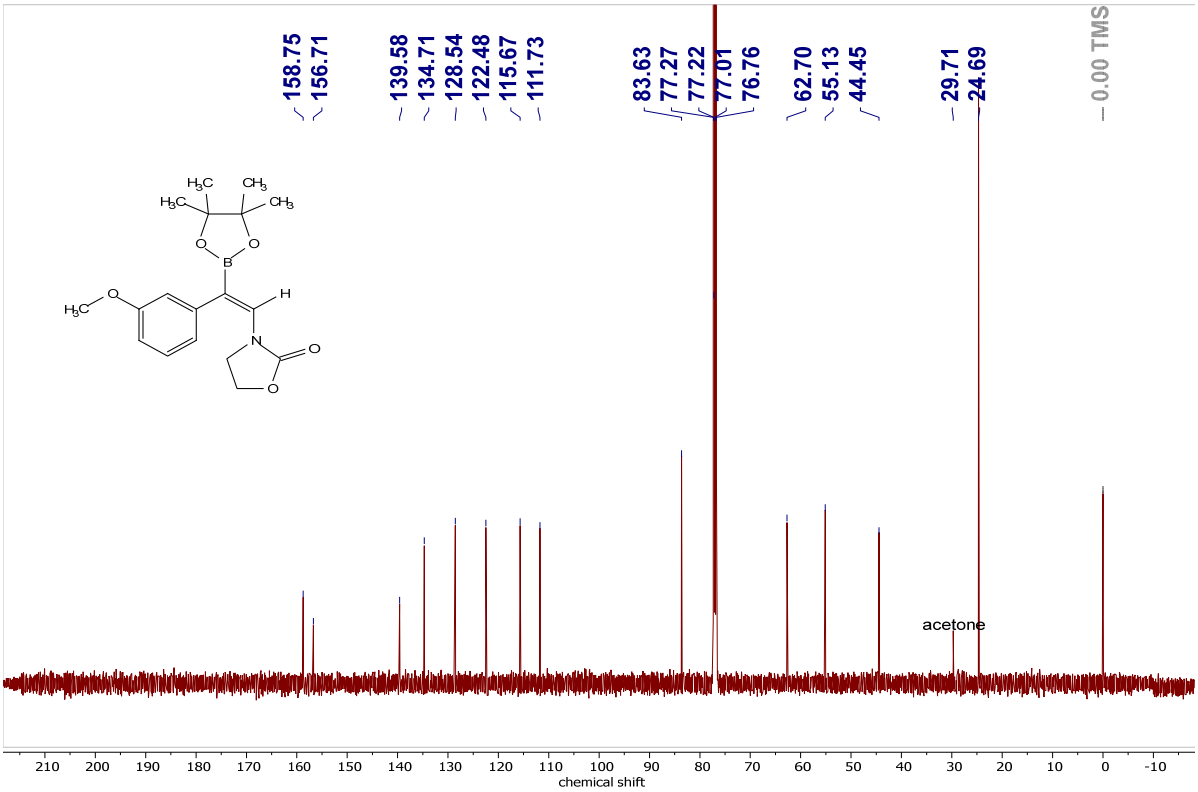
HMBC


{1.26,24.77}
{1.66,37.84}
{7.44,44.70}
{4.19,44.70}
{1.26,83.71}
{7.11,127.65}
{7.44,135.15}
{7.05,140.94}
{1.66,140.90}
{7.44,156.80}
{3.17,156.80}
chemical shift
f1 (ppm)

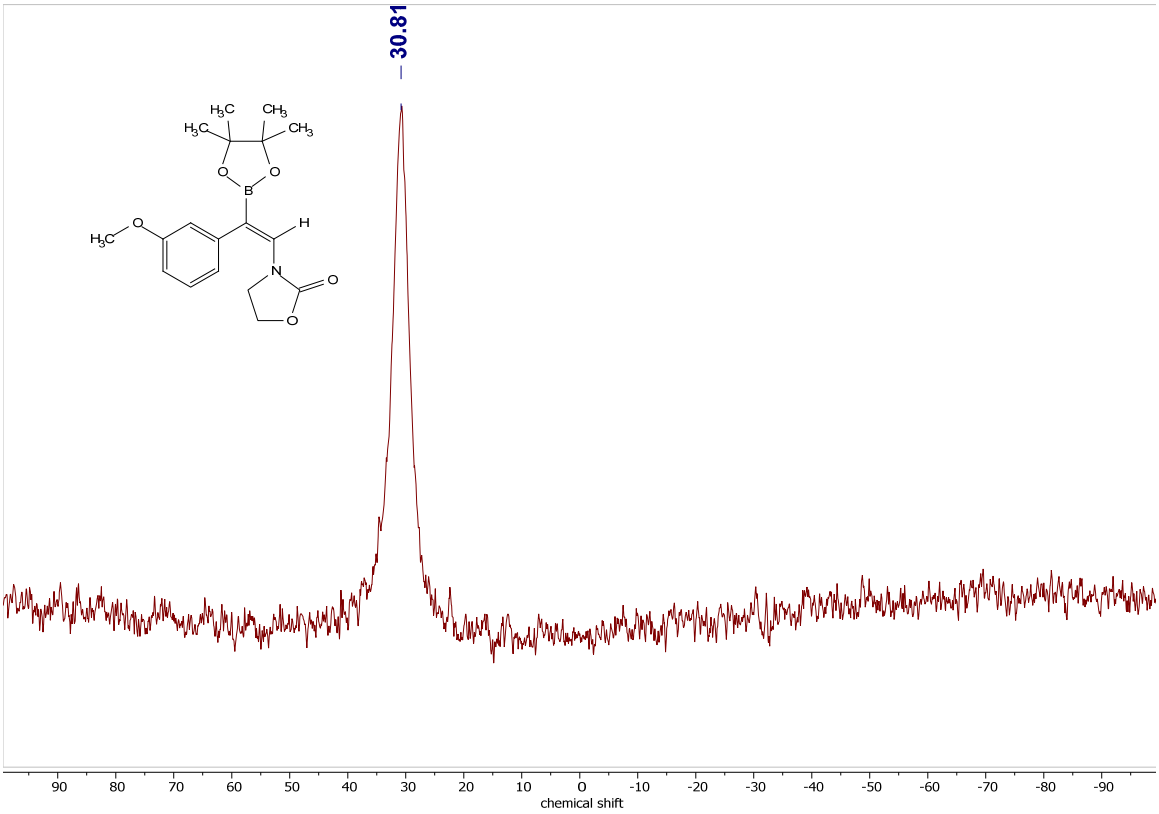
^{1}H-2h


7.43
7.21
7.20
7.18
6.78
6.78
6.76
6.76
6.73
6.71
6.68
6.68
4.19
4.17
4.15
3.80
3.22
3.20
3.18
1.25
-0.00 TMS
0.82
1.01
2.79
2.00
3.01
2.00
12.16
chemical shift

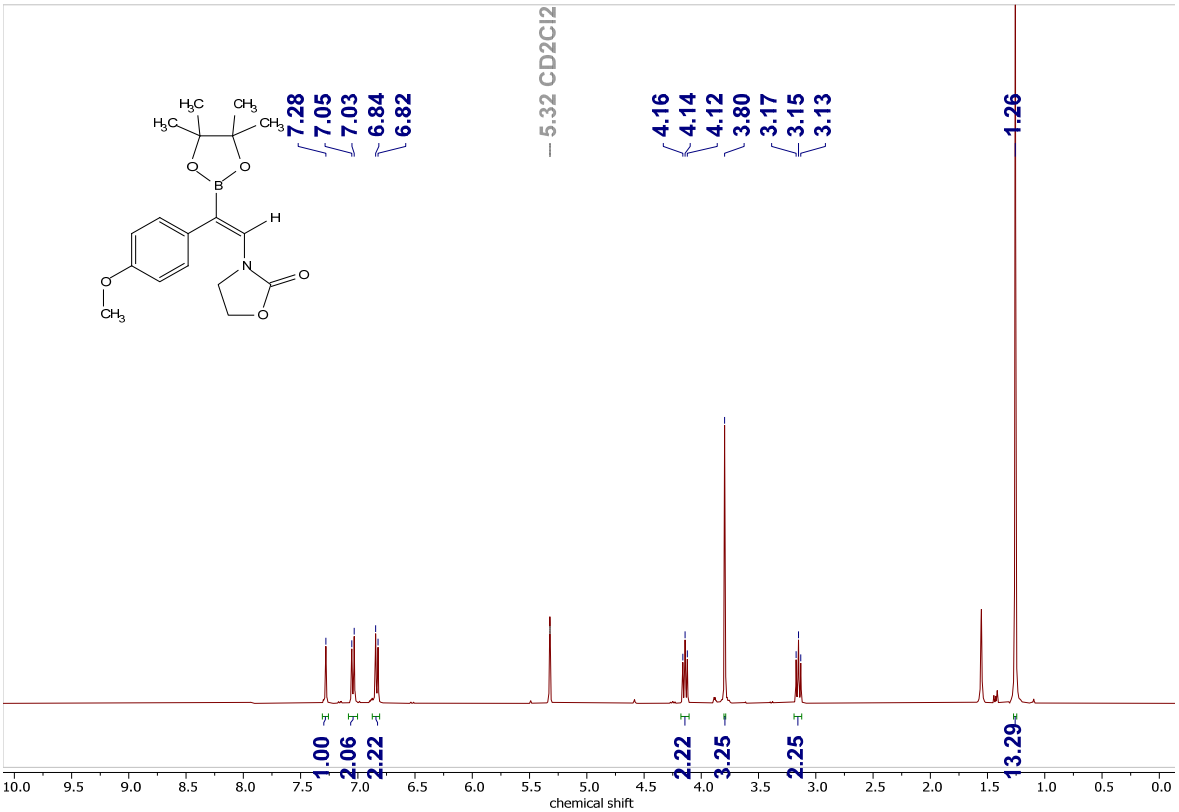
^{13}C-2h


158.75
156.71
139.58
134.71
128.54
122.48
115.67
111.73
83.63
77.27
77.22
77.01
76.76
62.70
55.13
44.45
29.71
24.69
-0.00 TMS
acetone
chemical shift

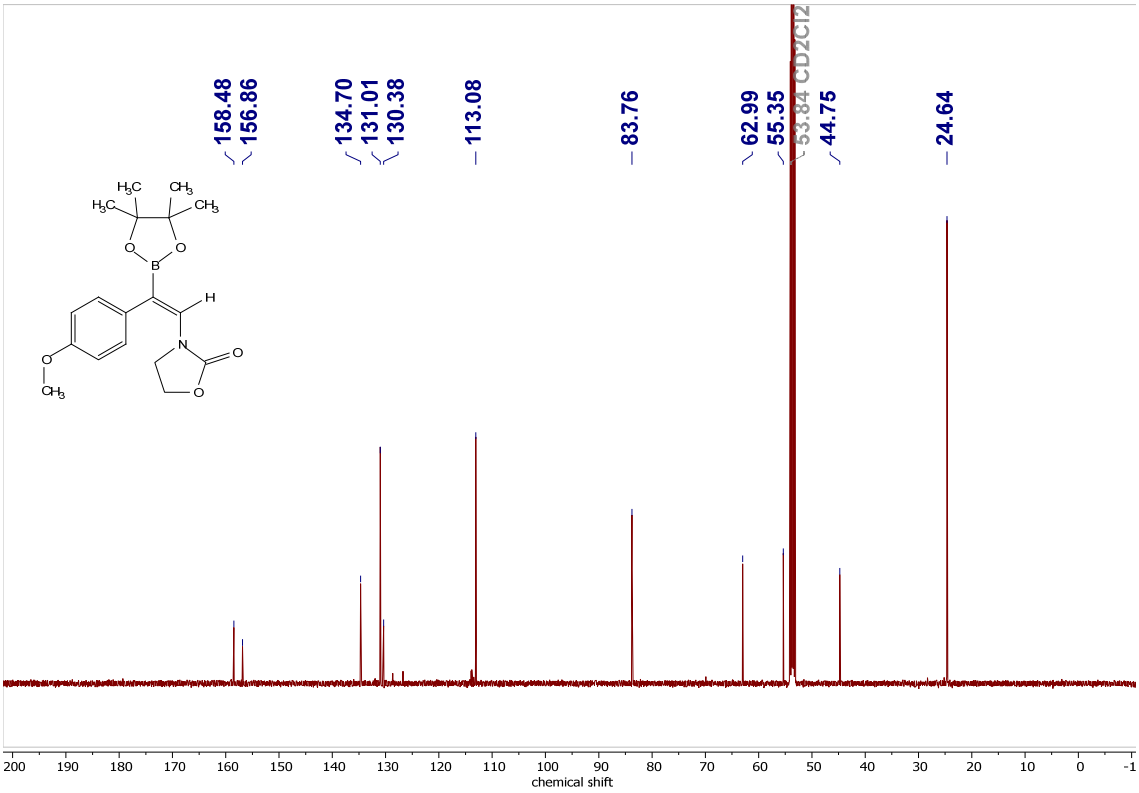
^{11}B-2h


30.81
chemical shift

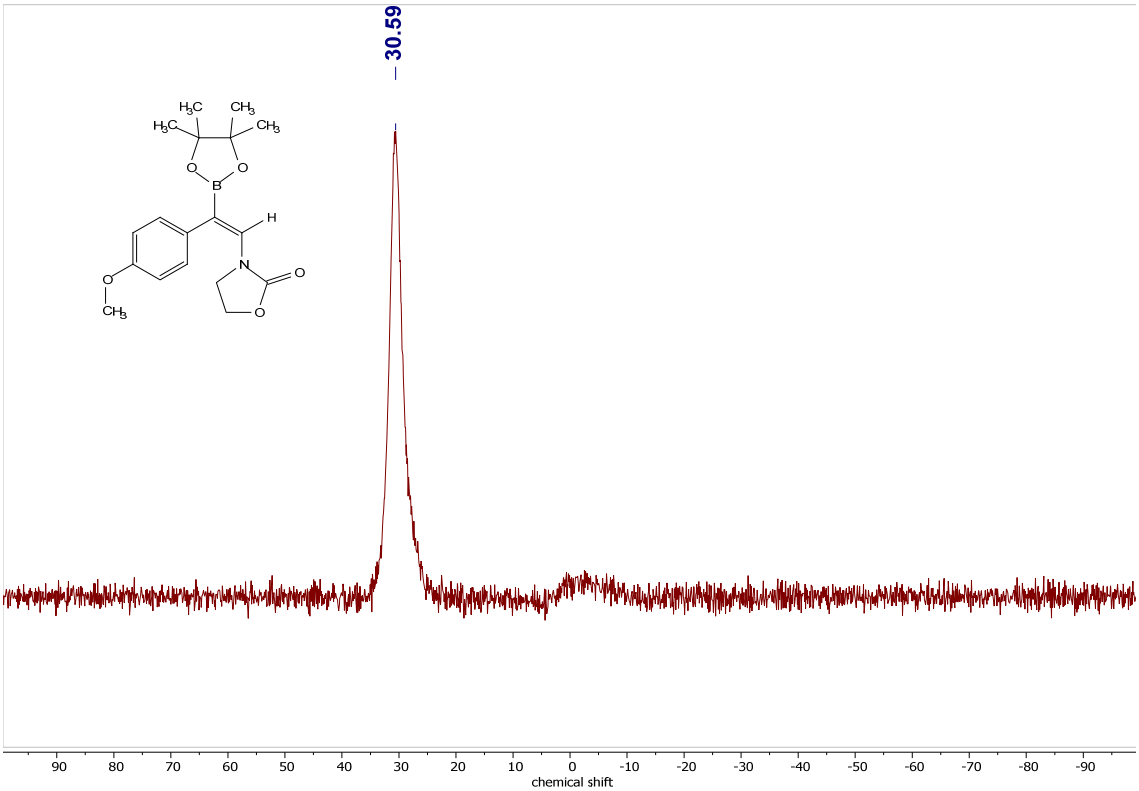
^{1}H-2i


7.28
7.05
7.03
6.84
6.82
5.32 CD2Cl2
4.16
4.14
4.12
3.80
3.17
3.15
3.13
1.26
1.00
2.06
2.22
2.22
3.25
2.25
3.29
chemical shift

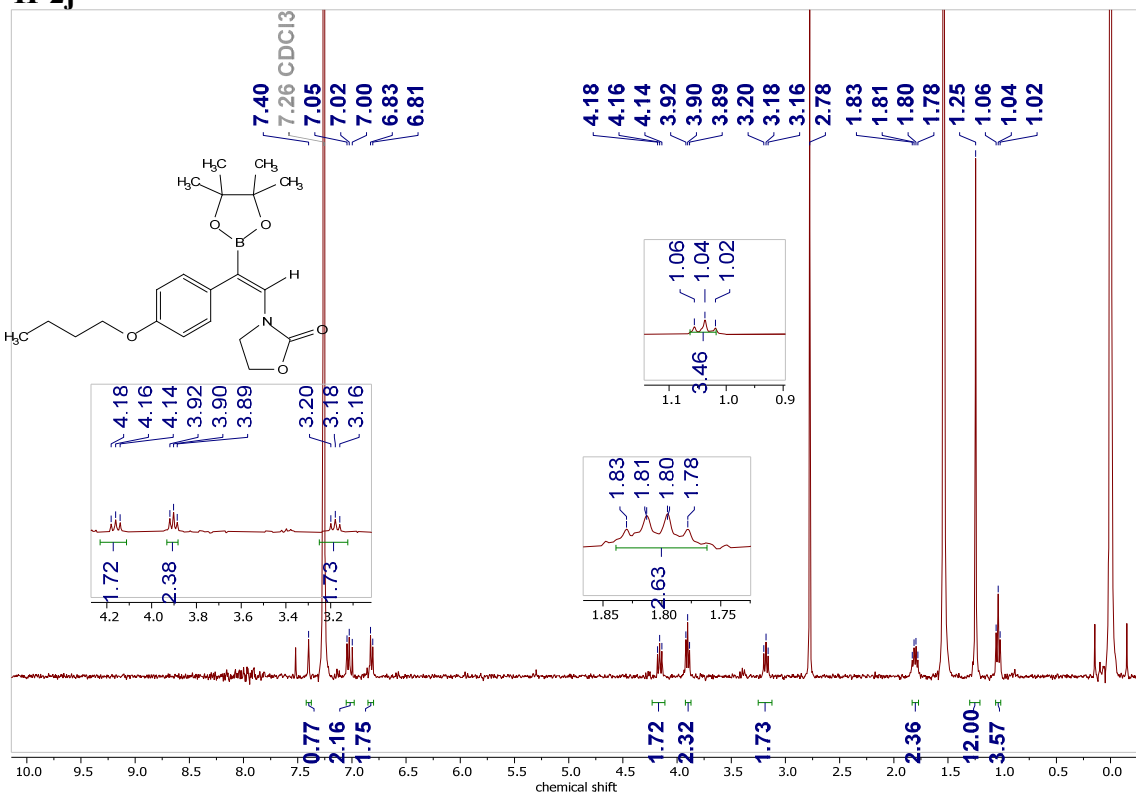
^{13}C-2i


158.48
156.86
134.70
131.01
130.38
113.08
83.76
62.99
55.35
53.84 CD2Cl2
44.75
24.64
chemical shift

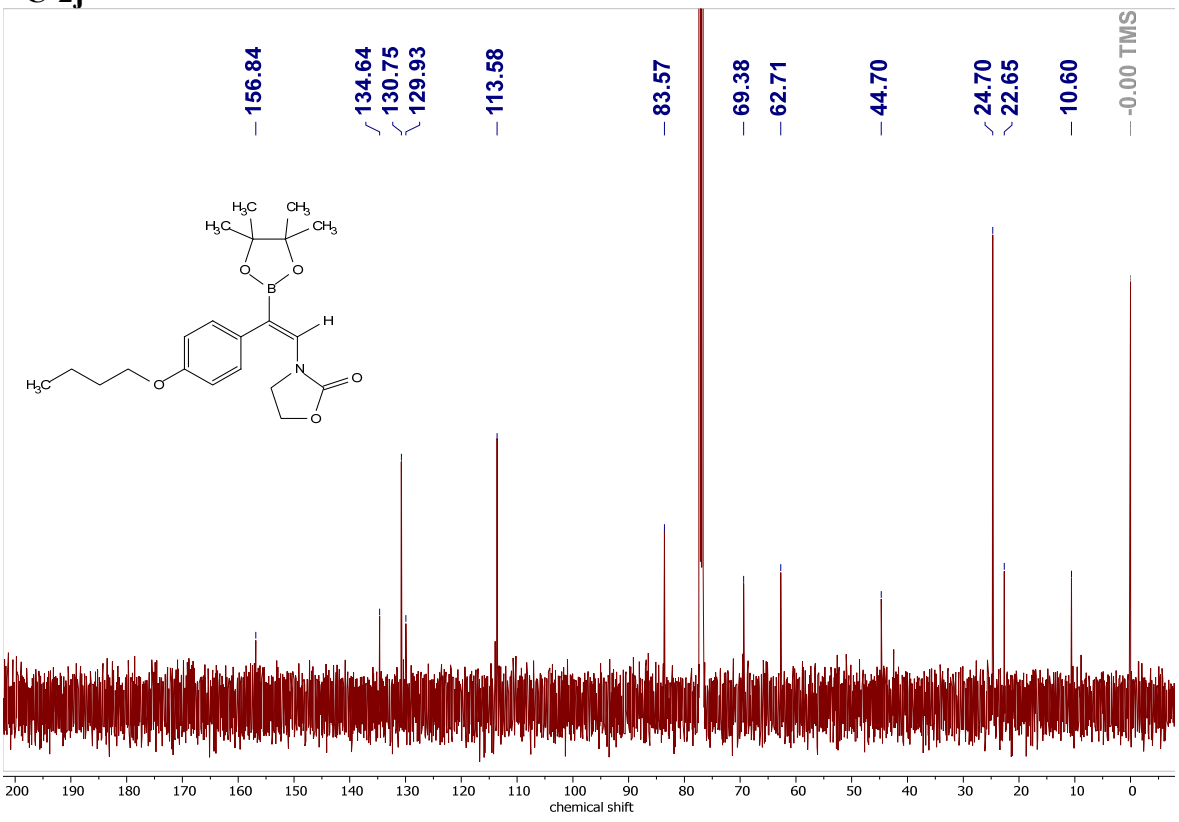
^{11}B-2i


30.59
chemical shift

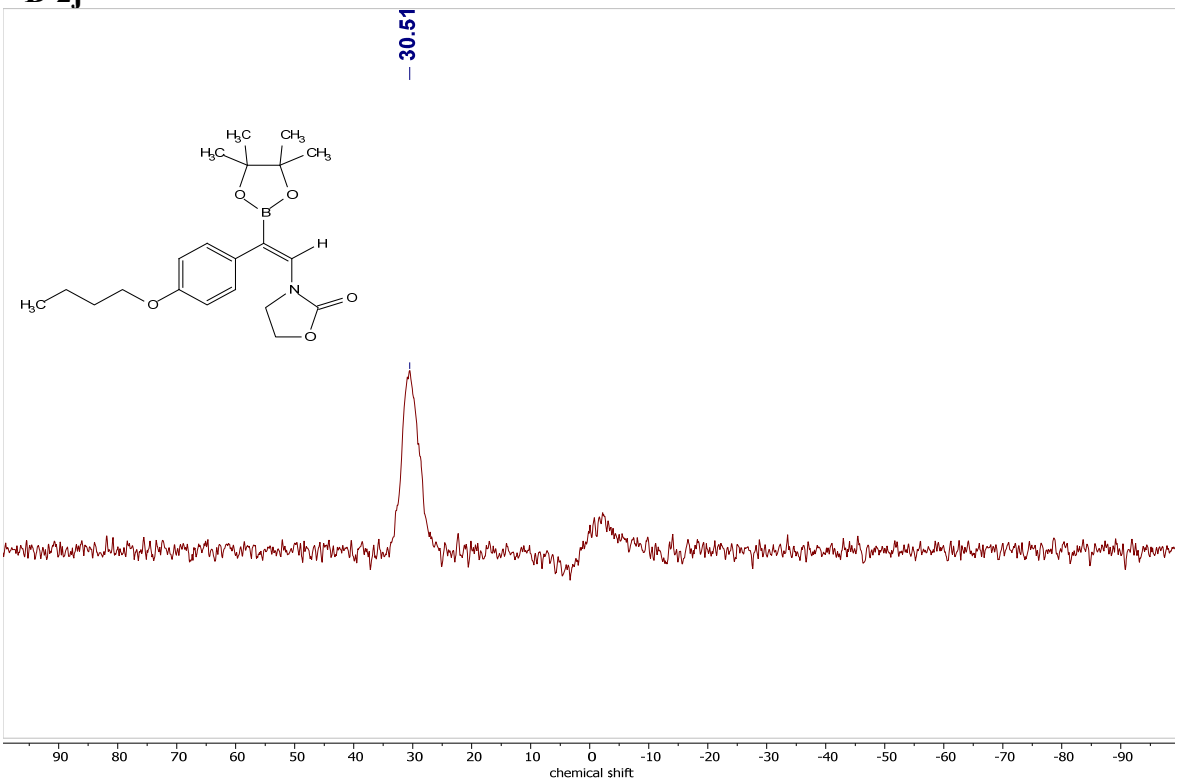
^{1}H-2j


7.40
7.26 CDCl3
7.05
7.02
7.00
6.83
6.81
4.18
4.16
4.14
3.92
3.90
3.89
3.20
3.18
3.16
2.78
1.83
1.81
1.80
1.78
1.25
1.06
1.04
1.02
0.77
2.16
1.75
1.72
2.32
1.73
2.36
12.00
3.57
chemical shift

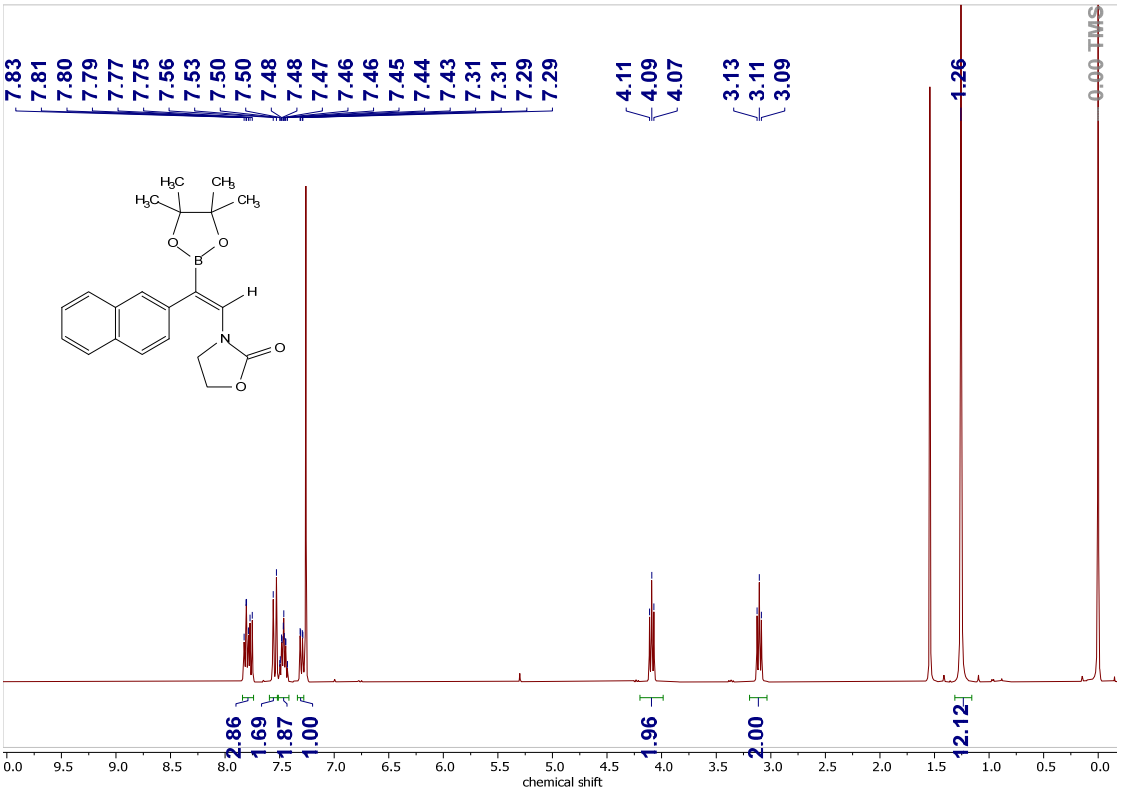
^{13}C-2j


156.84
134.64
130.75
129.93
113.58
83.57
69.38
62.71
44.70
24.70
22.65
10.60
-0.00 TMS
chemical shift

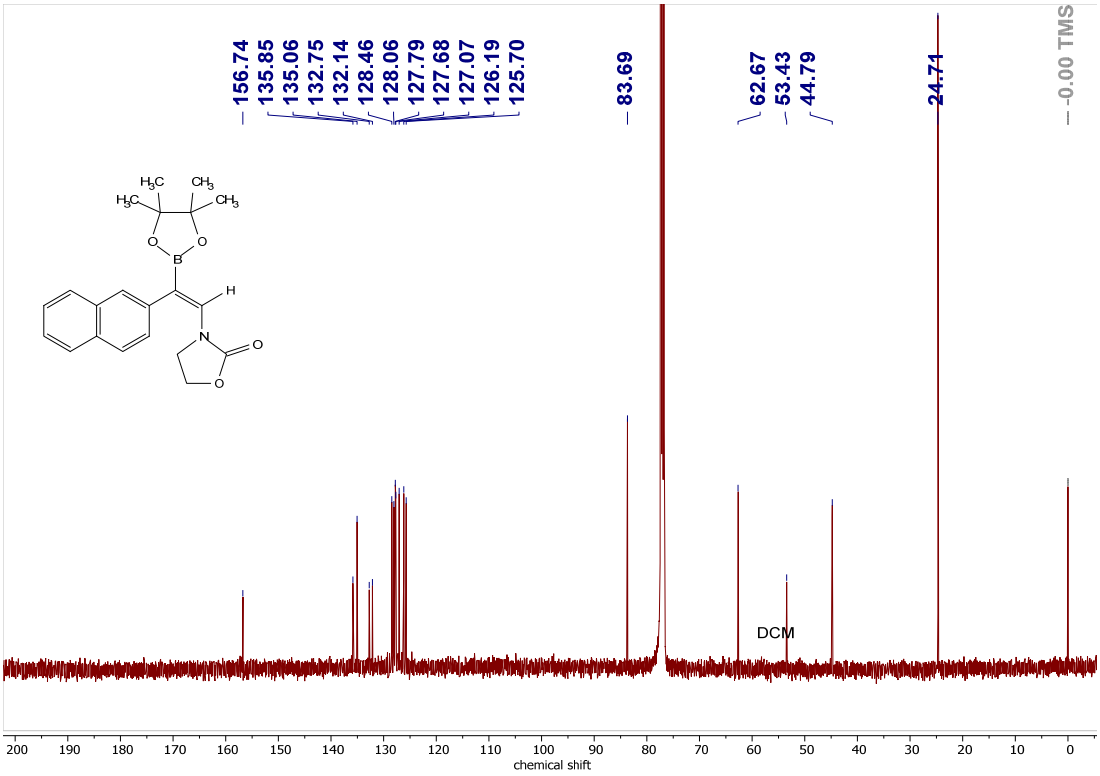
^{11}B-2j


30.51
chemical shift

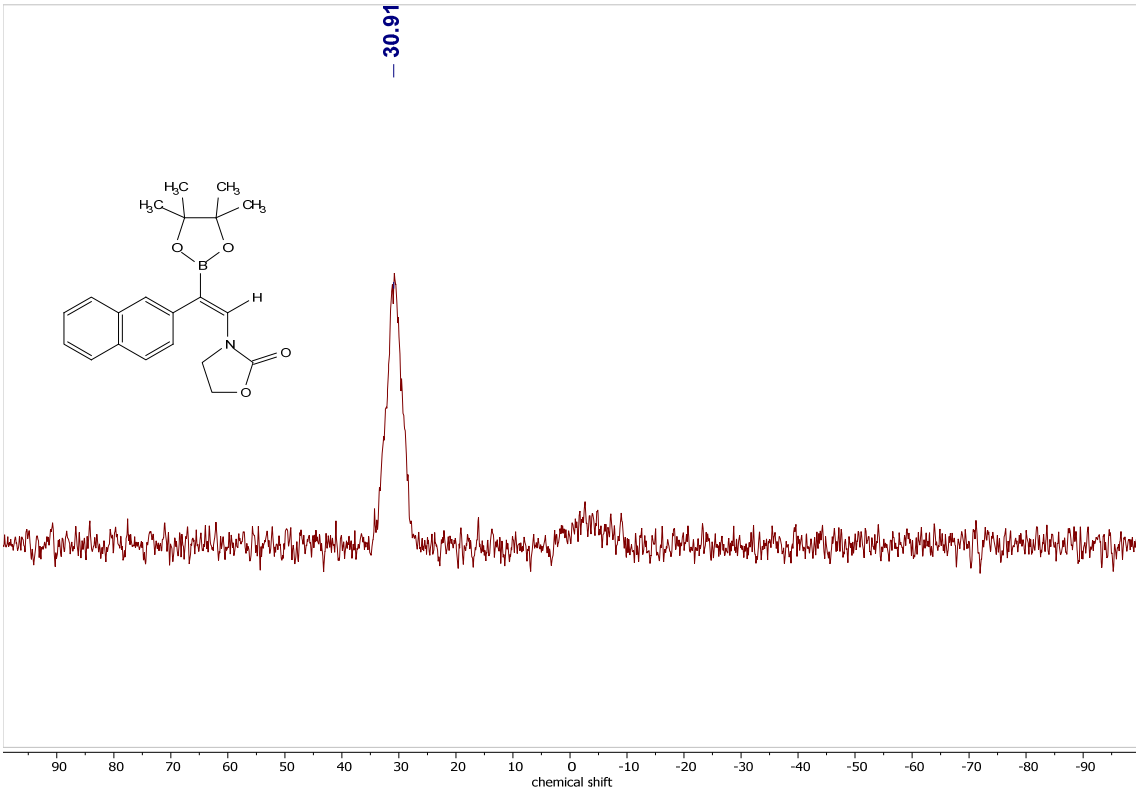
^{1}H-2k


7.83
7.81
7.80
7.79
7.77
7.75
7.56
7.53
7.50
7.50
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.31
7.31
7.29
7.29
4.11
4.09
4.07
3.13
3.11
3.09
1.26
0.00 TMS
2.86
1.69
1.87
1.00
1.96
2.00
12.12
chemical shift

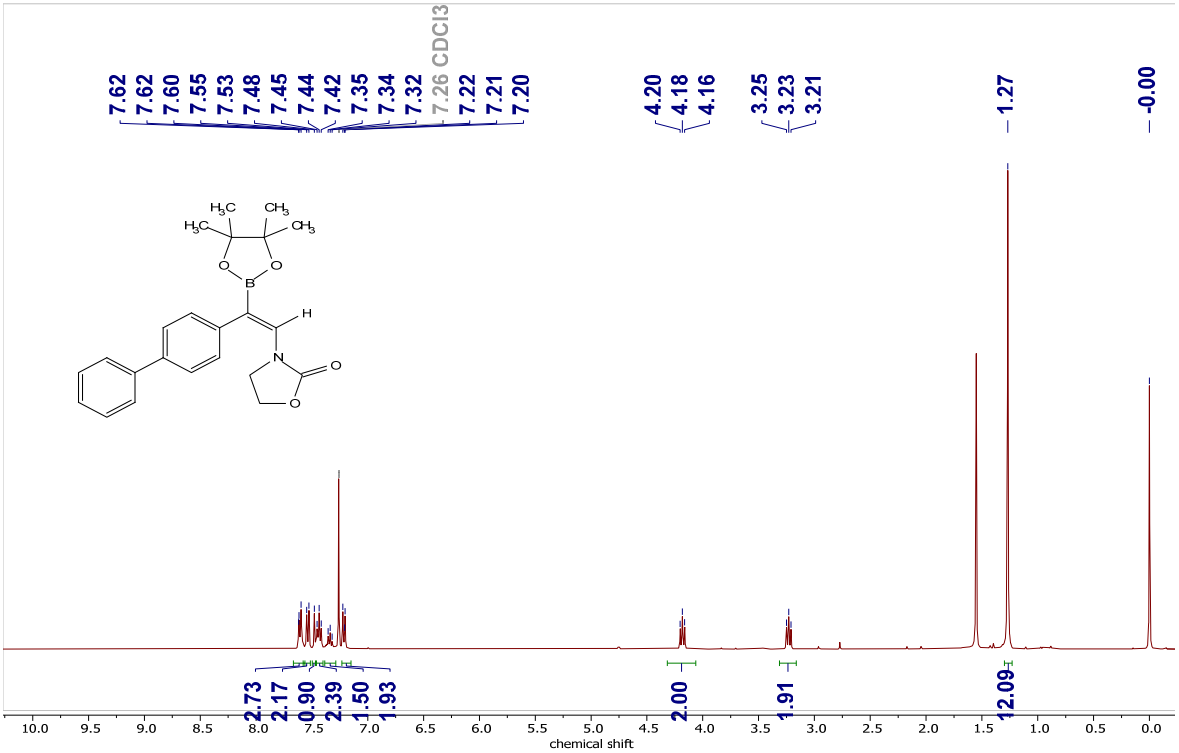
13C-2k


156.74
135.85
135.06
132.75
132.14
128.46
128.06
127.79
127.68
127.07
126.19
125.70
83.69
62.67
53.43
44.79
24.71
0.00 TMS
DCM
chemical shift

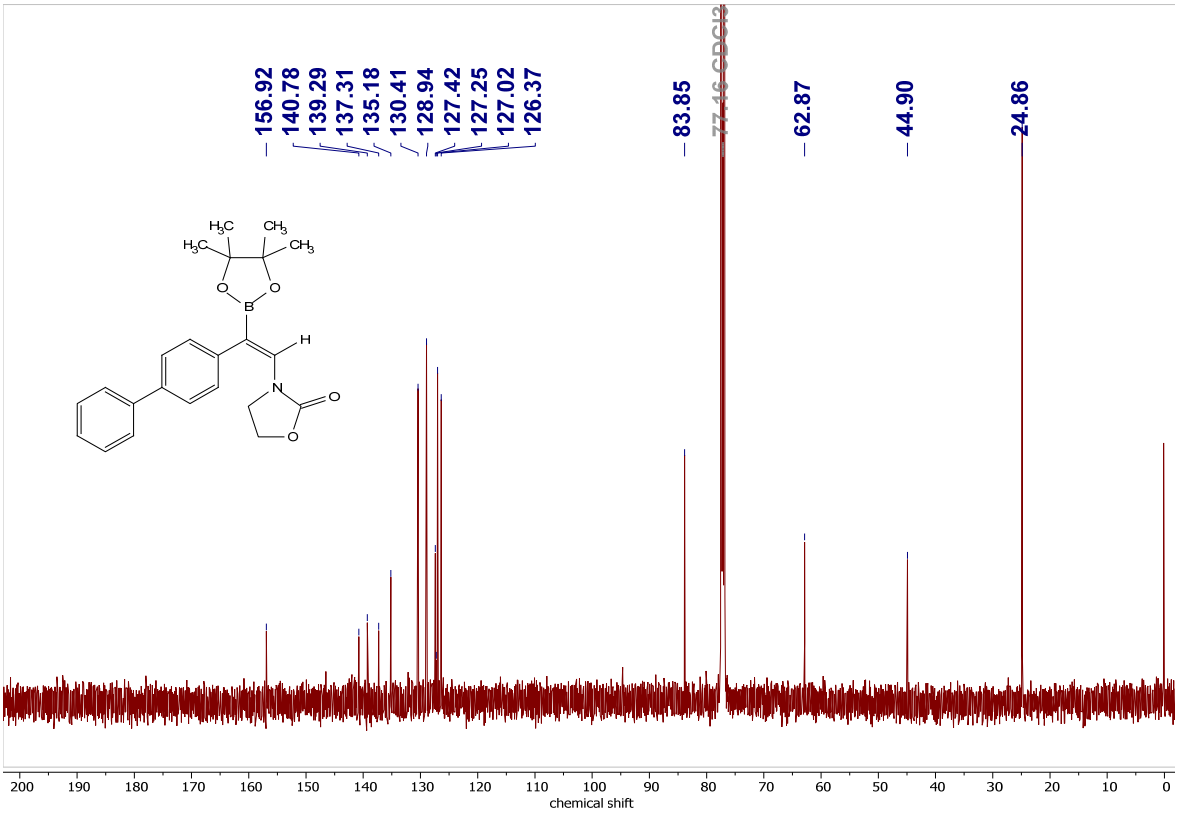
11B-2k


30.91
chemical shift

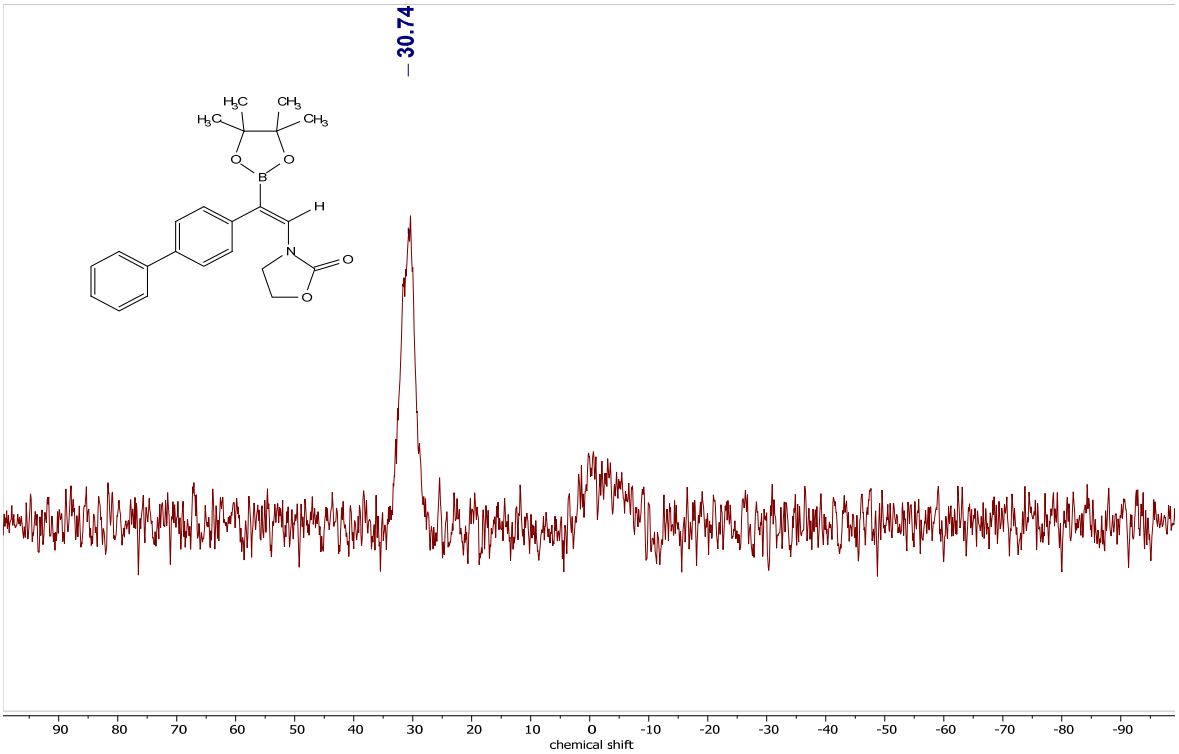
^{1}H-2l


7.62
7.62
7.60
7.55
7.53
7.48
7.45
7.44
7.42
7.35
7.34
7.32
7.26 CDCl3
7.22
7.21
7.20
4.20
4.18
4.16
3.25
3.23
3.21
1.27
-0.00
2.73
2.17
0.90
2.39
1.50
1.93
2.00
1.91
12.09
chemical shift

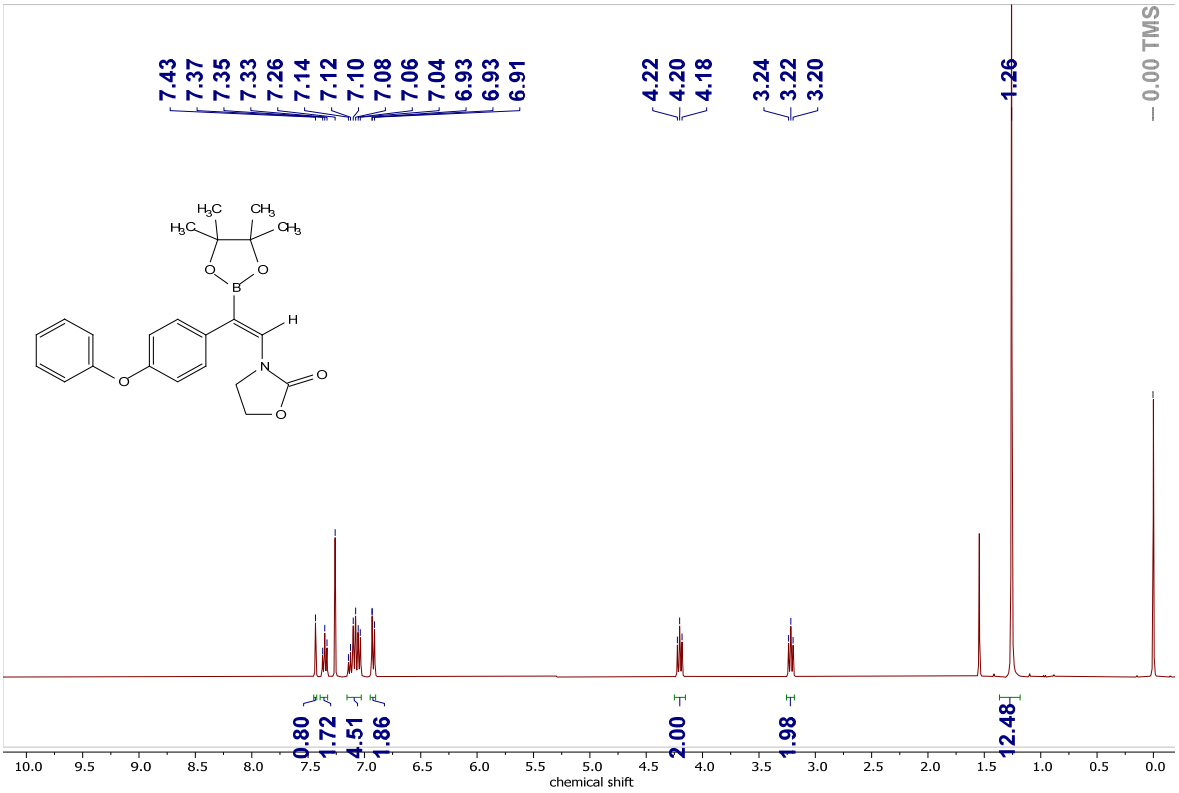
^{13}C-2l


156.92
140.78
139.29
137.31
135.18
130.41
128.94
127.42
127.25
127.02
126.37
83.85
77.16 CDCl3
62.87
44.90
24.86
chemical shift

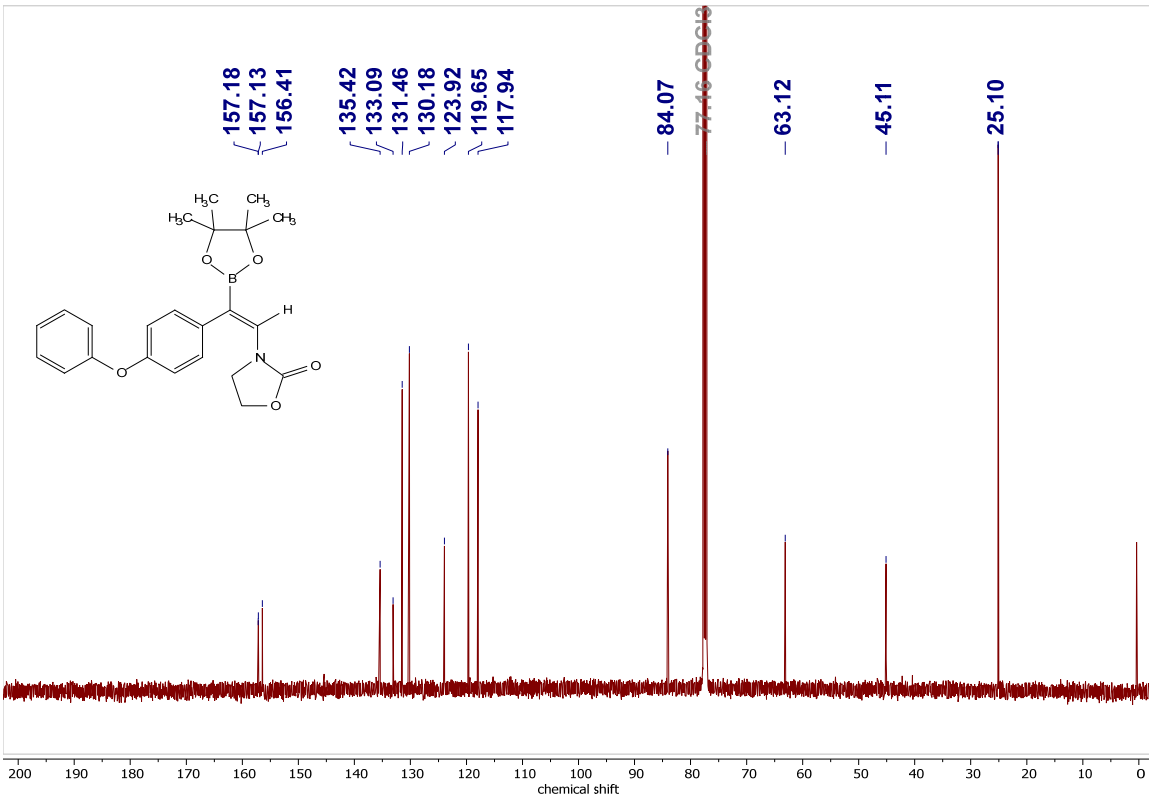
^{11}B-2l


30.74
chemical shift

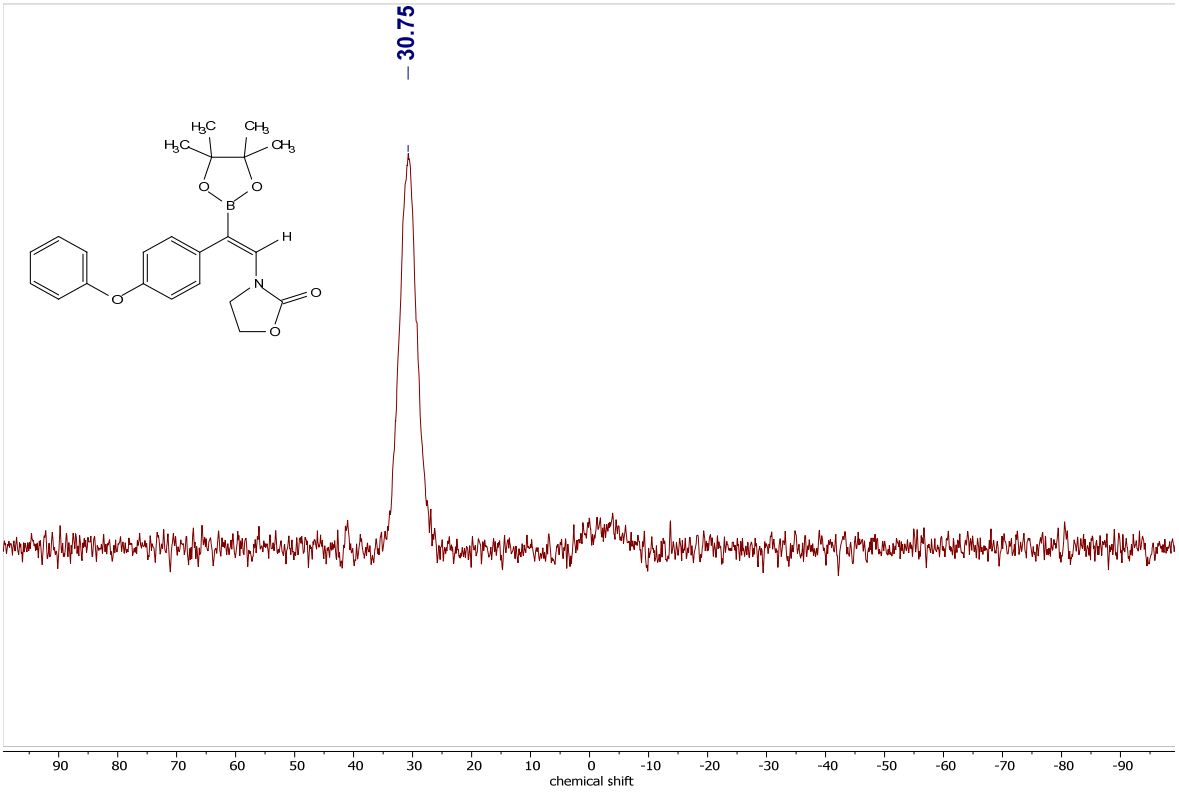
^{1}H-2m


7.43
7.37
7.35
7.33
7.26
7.14
7.12
7.10
7.08
7.06
7.04
6.93
6.93
6.91
4.22
4.20
4.18
3.24
3.22
3.20
1.26
0.00 TMS
0.80
1.72
4.51
1.86
2.00
1.98
12.48
chemical shift

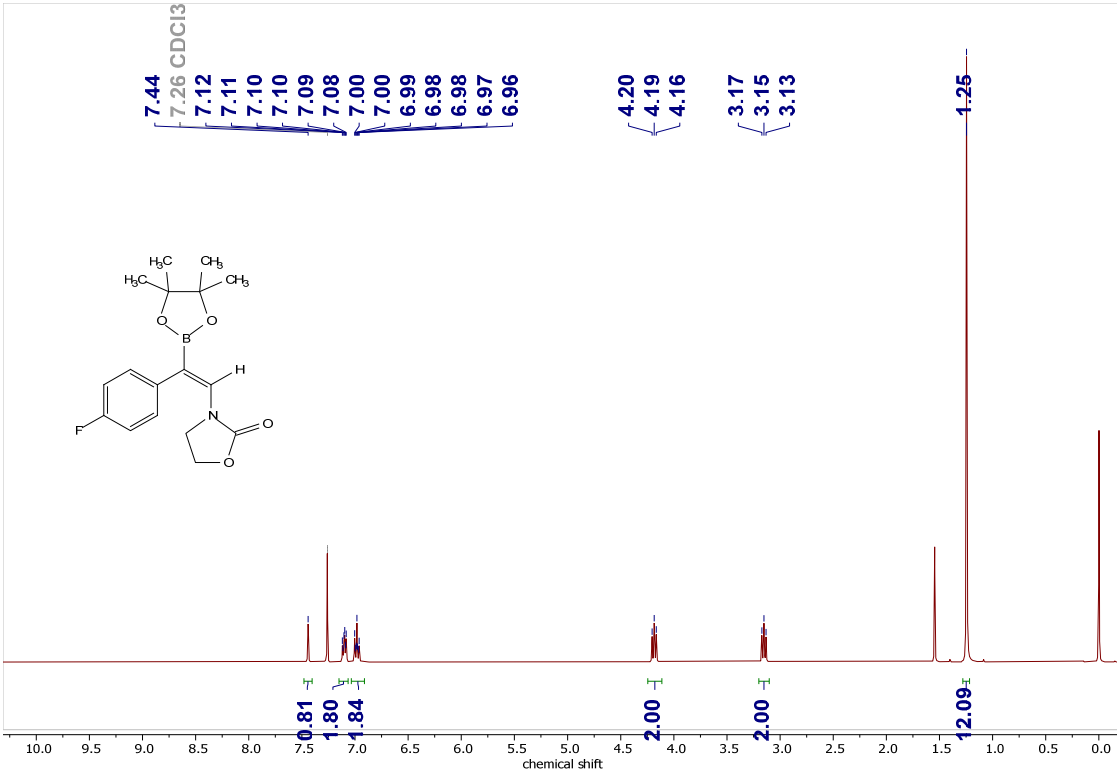
^{13}C-2m


157.18
157.13
156.41
135.42
133.09
131.46
130.18
123.92
119.65
117.94
84.07
77.16 CDCl3
63.12
45.11
25.10
chemical shift

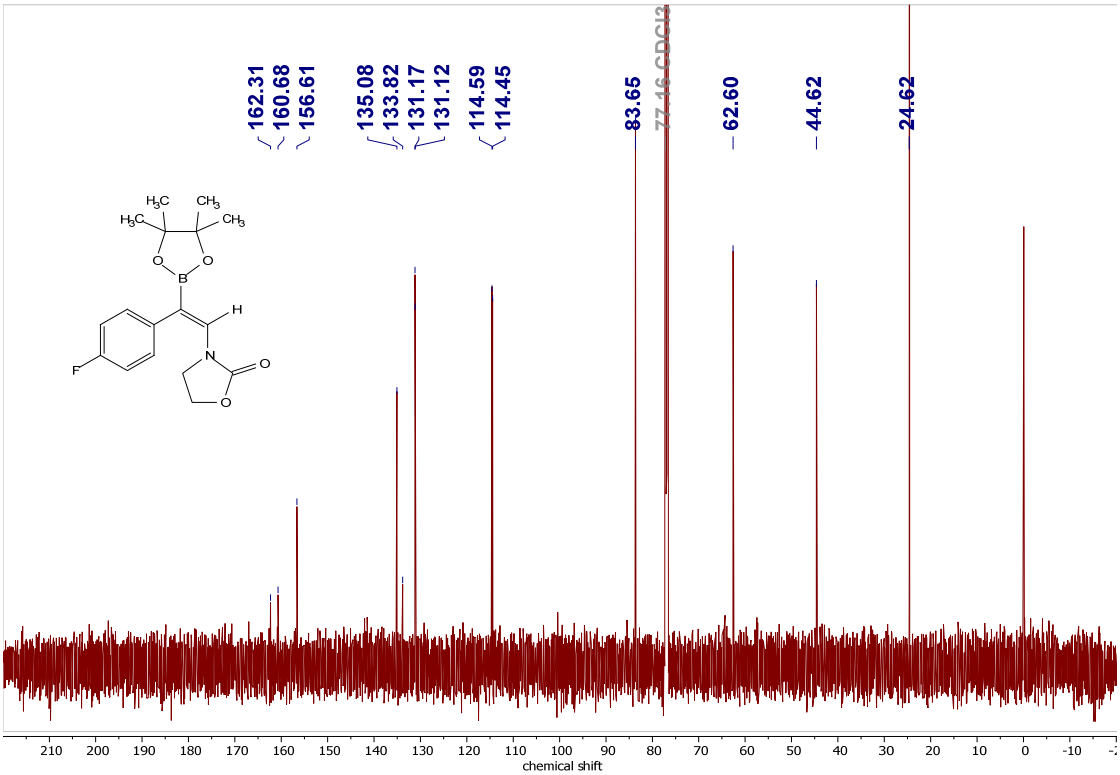
^{11}B-2m


30.75
chemical shift

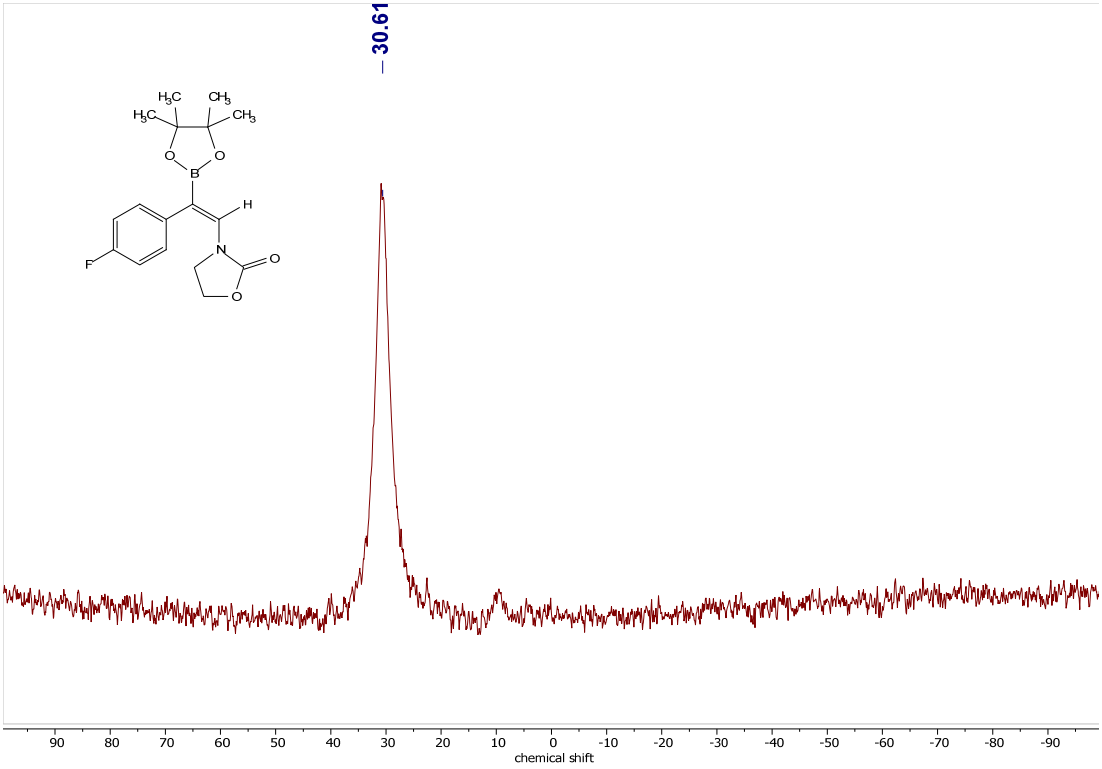
^{1}H-2n


7.44
7.26 CDCl3
7.12
7.11
7.10
7.10
7.09
7.08
7.00
7.00
6.99
6.98
6.98
6.97
6.96
4.20
4.19
4.16
3.17
3.15
3.13
1.25
0.81
1.80
1.84
2.00
2.00
12.09
chemical shift

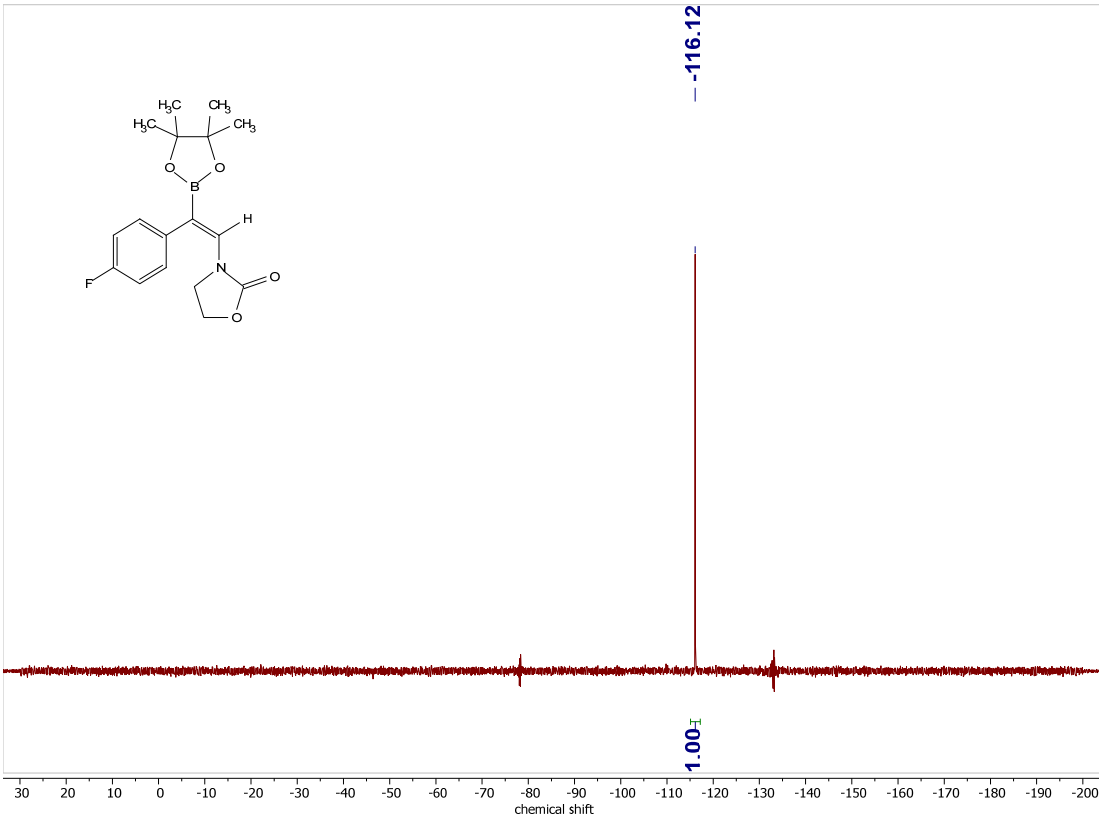
^{13}C-2n


162.31
160.68
156.61
135.08
133.82
131.17
131.12
114.59
114.45
83.65
77.16 CDCl3
62.60
44.62
24.62
chemical shift

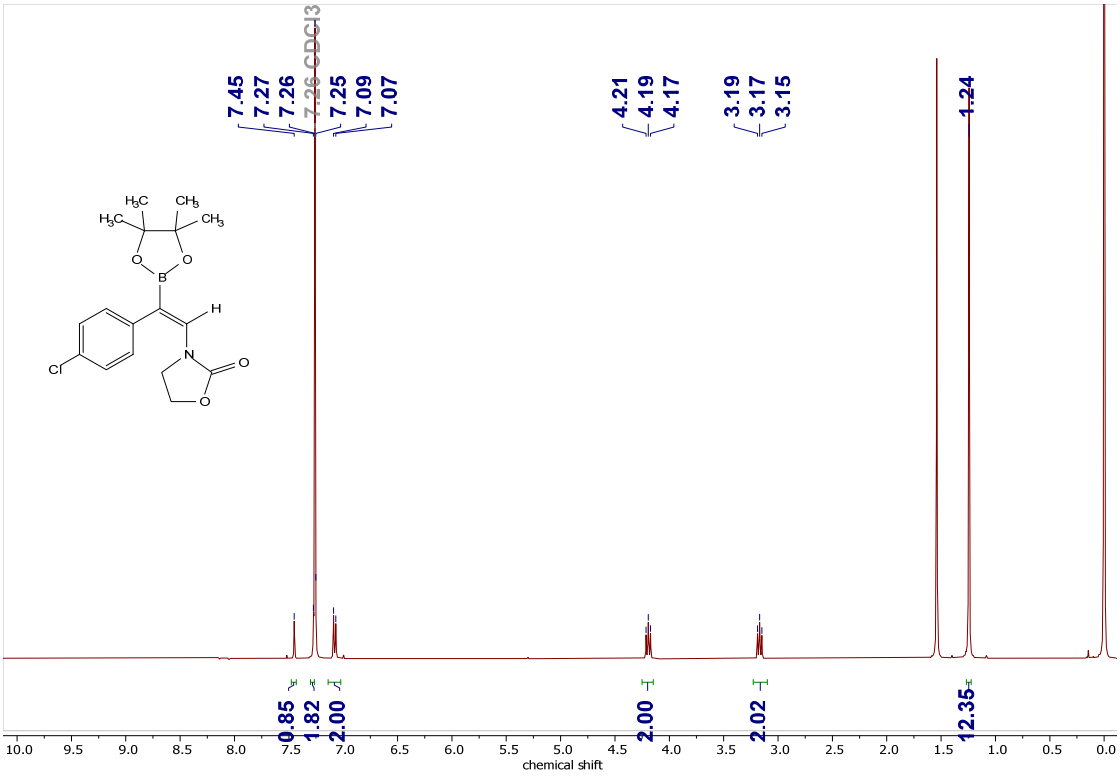
^{11}B-2n



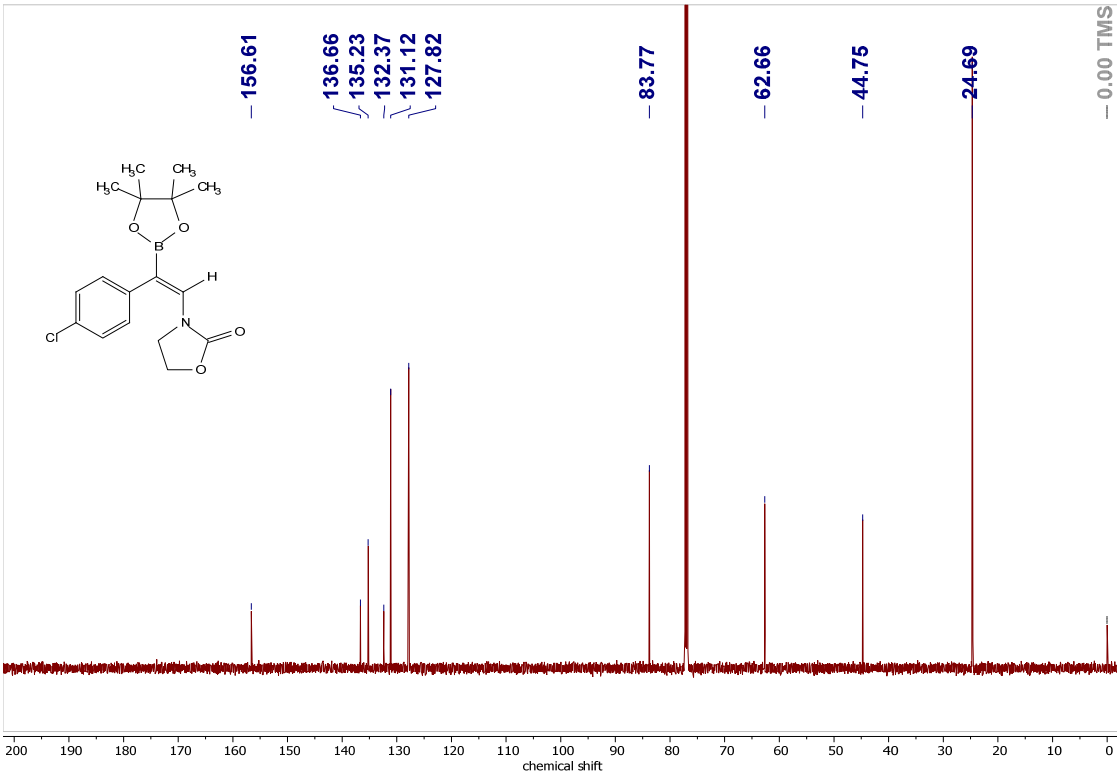
^{19}F-2n



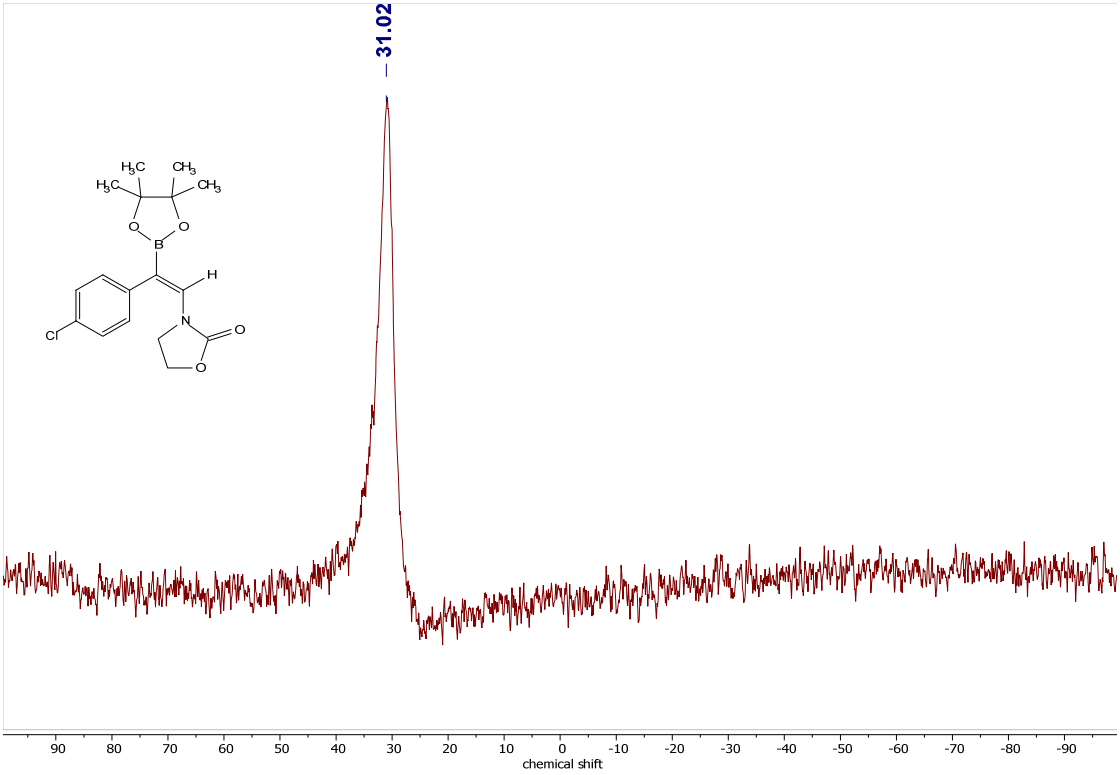
^{1}H-2o


7.45
7.27
7.26
7.26 CDCl3
7.25
7.09
7.07
4.21
4.19
4.17
3.19
3.17
3.15
1.24
0.85
1.82
2.00
2.00
2.02
12.35
chemical shift

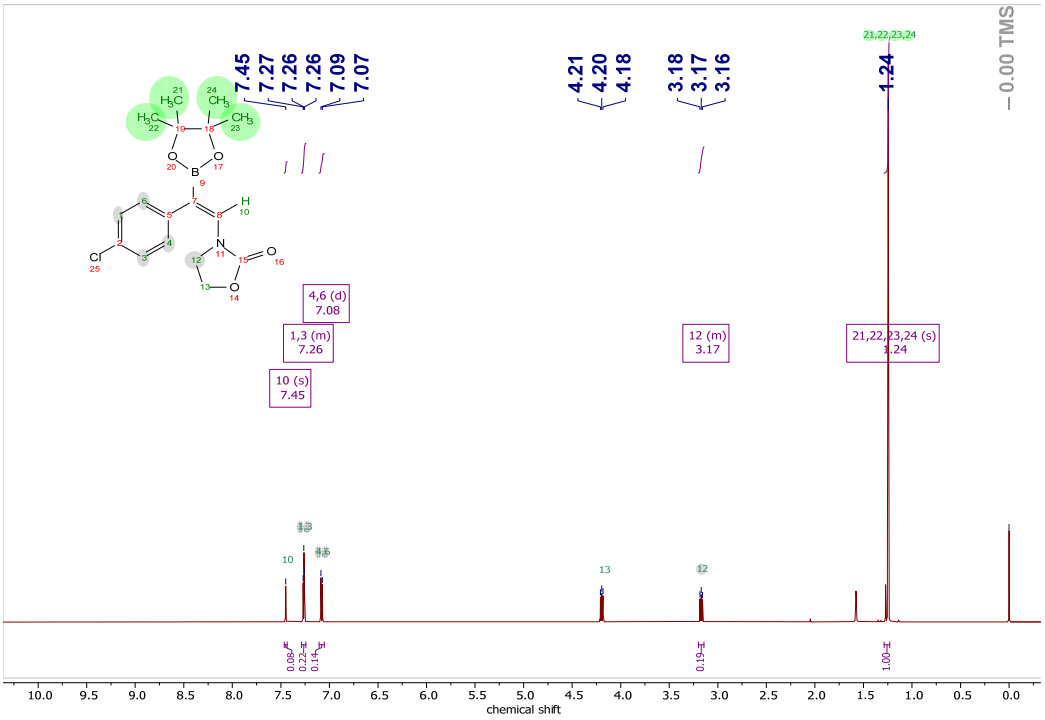
^{13}C-2o

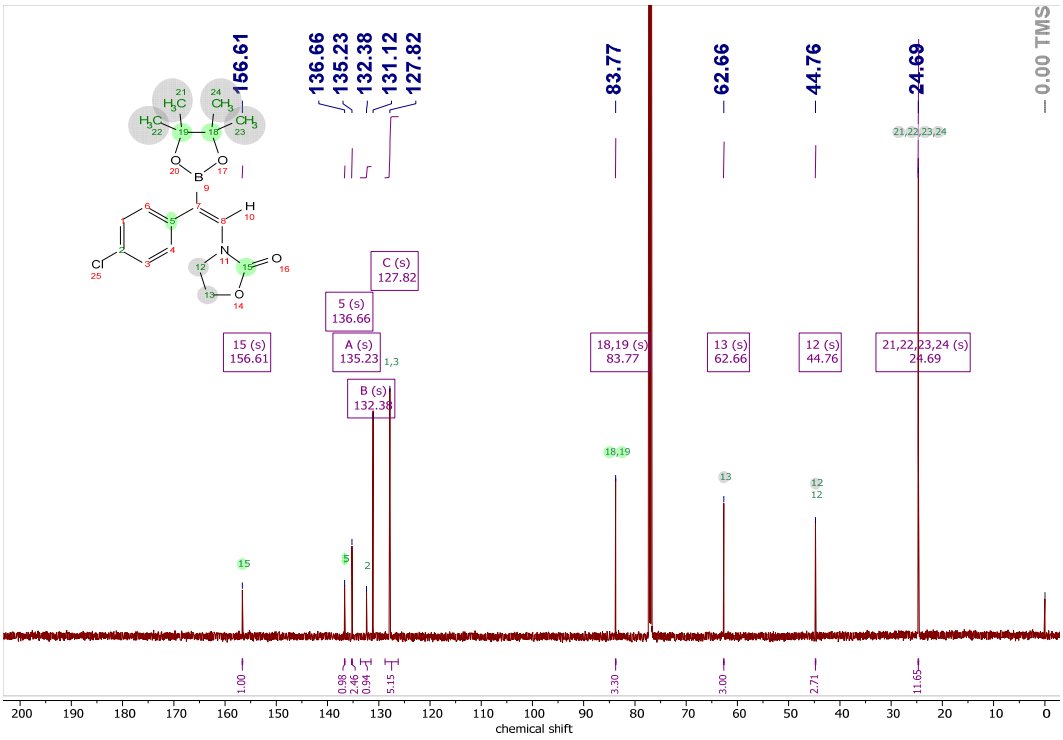

156.61
136.66
135.23
132.37
131.12
127.82
83.77
62.66
44.75
24.69
0.00 TMS
chemical shift

^{11}B-2o

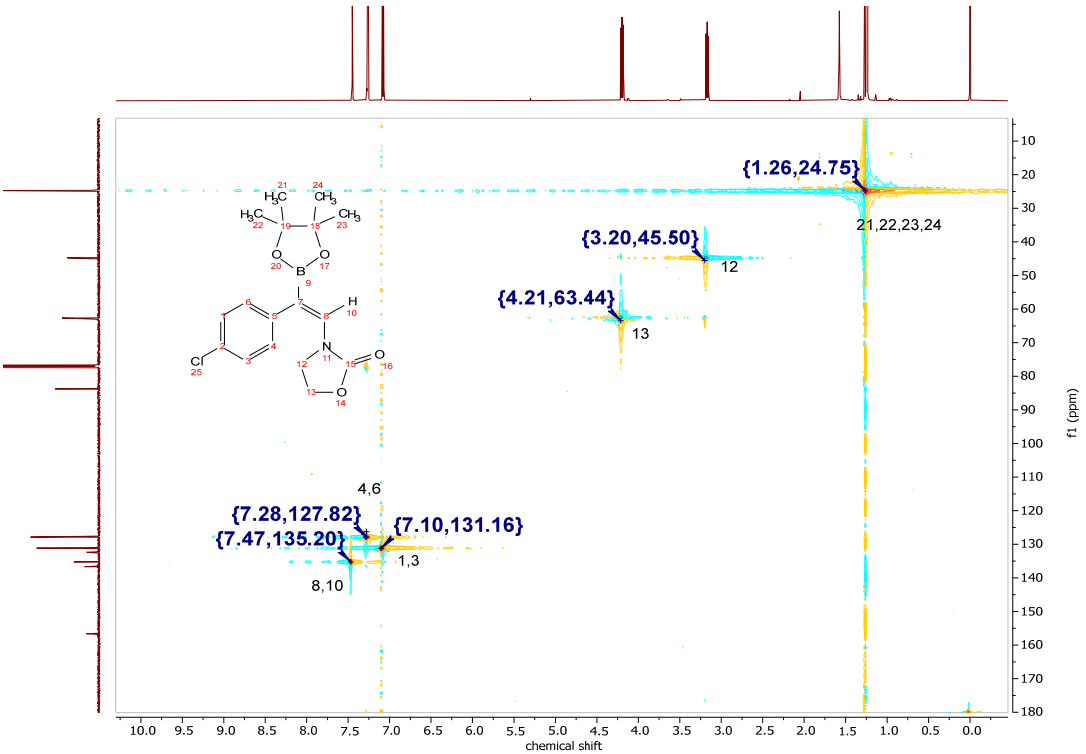

31.02
chemical shift

2D NMR

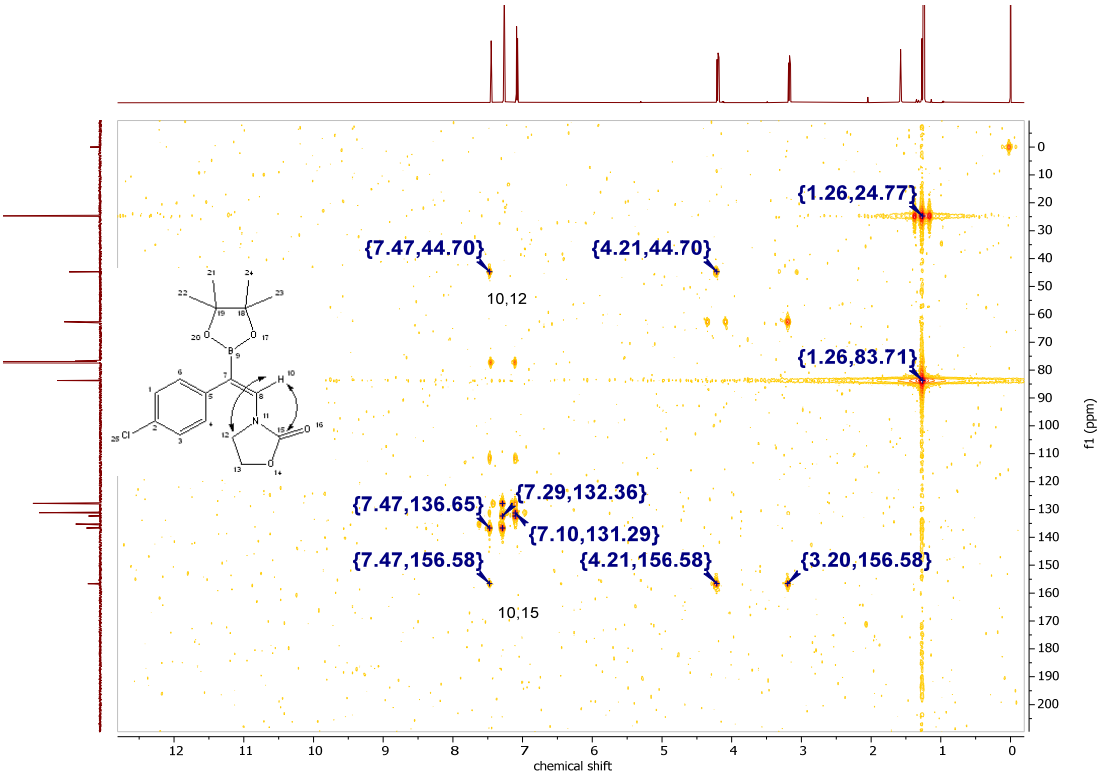

7.45
7.27
7.26
7.26
7.09
7.07
4.21
4.20
4.18
3.18
3.17
3.16
1.24
0.00 TMS
4,6 (d) 7.08
1,3 (m) 7.26
10 (s) 7.45
12 (m) 3.17
21,22,23,24 (s) 1.24
chemical shift


156.61
136.66
135.23
132.38
131.12
127.82
83.77
62.66
44.76
24.69
0.00 TMS
C (s) 127.82
5 (s) 136.66
15 (s) 156.61
A (s) 135.23
B (s) 132.38
18,19 (s) 83.77
13 (s) 62.66
12 (s) 44.76
21,22,23,24 (s) 24.69
chemical shift

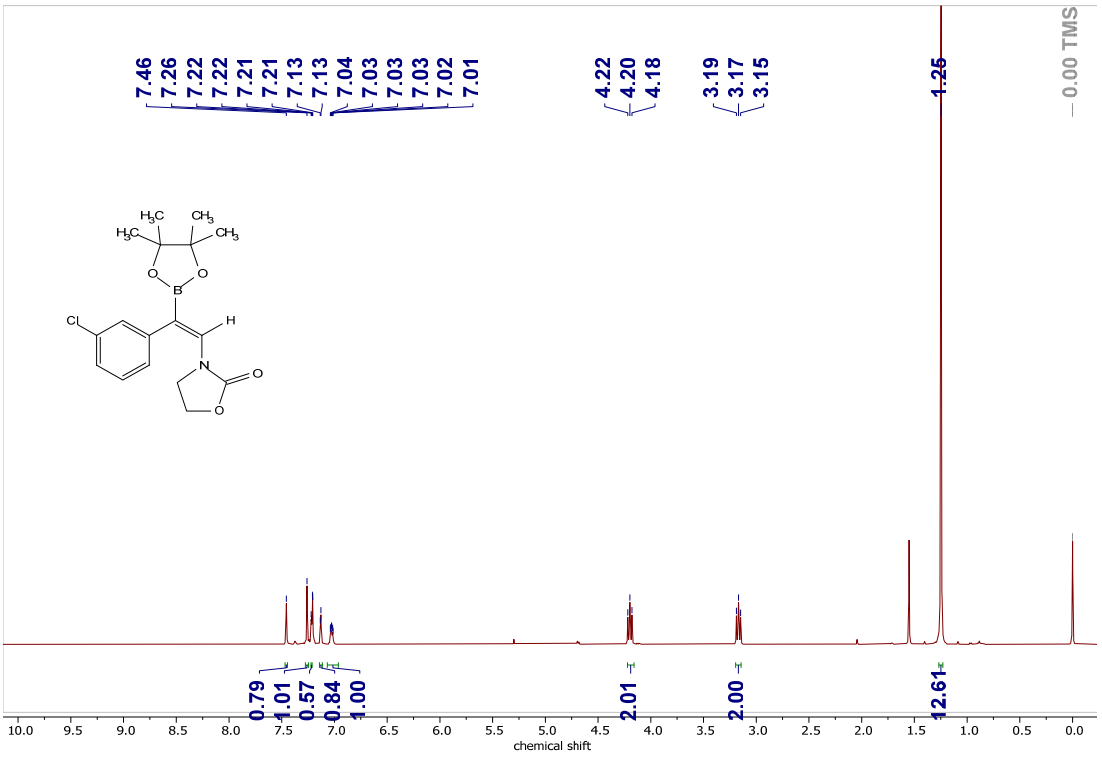
HSQC


{1.26,24.75}
21,22,23,24
{3.20,45.50}
12
{4.21,63.44}
13
{7.28,127.82}
{7.47,135.20}
{7.10,131.16}
4,6
8,10
1,3
f1 (ppm)
chemical shift

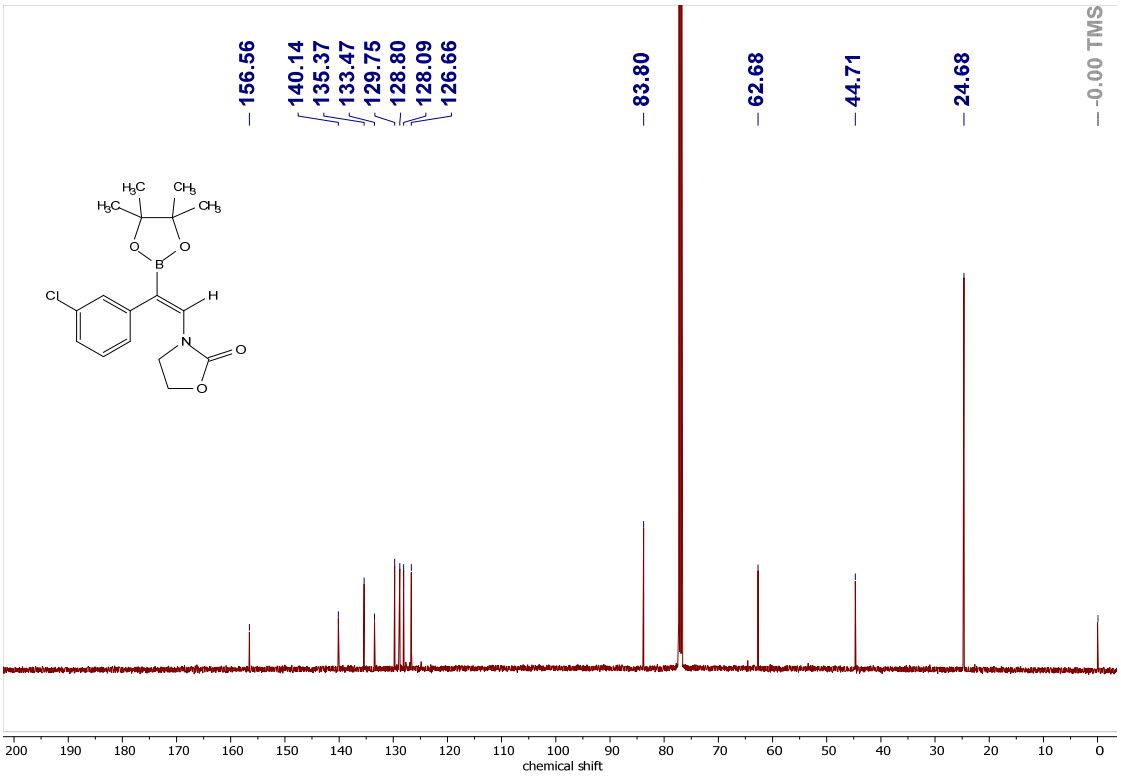
HMBC


{1.26,24.77}
{7.47,44.70}
{4.21,44.70}
10,12
{1.26,83.71}
{7.47,136.65}
{7.29,132.36}
{7.10,131.29}
{7.47,156.58}
{4.21,156.58}
{3.20,156.58}
10,15
f1 (ppm)
chemical shift

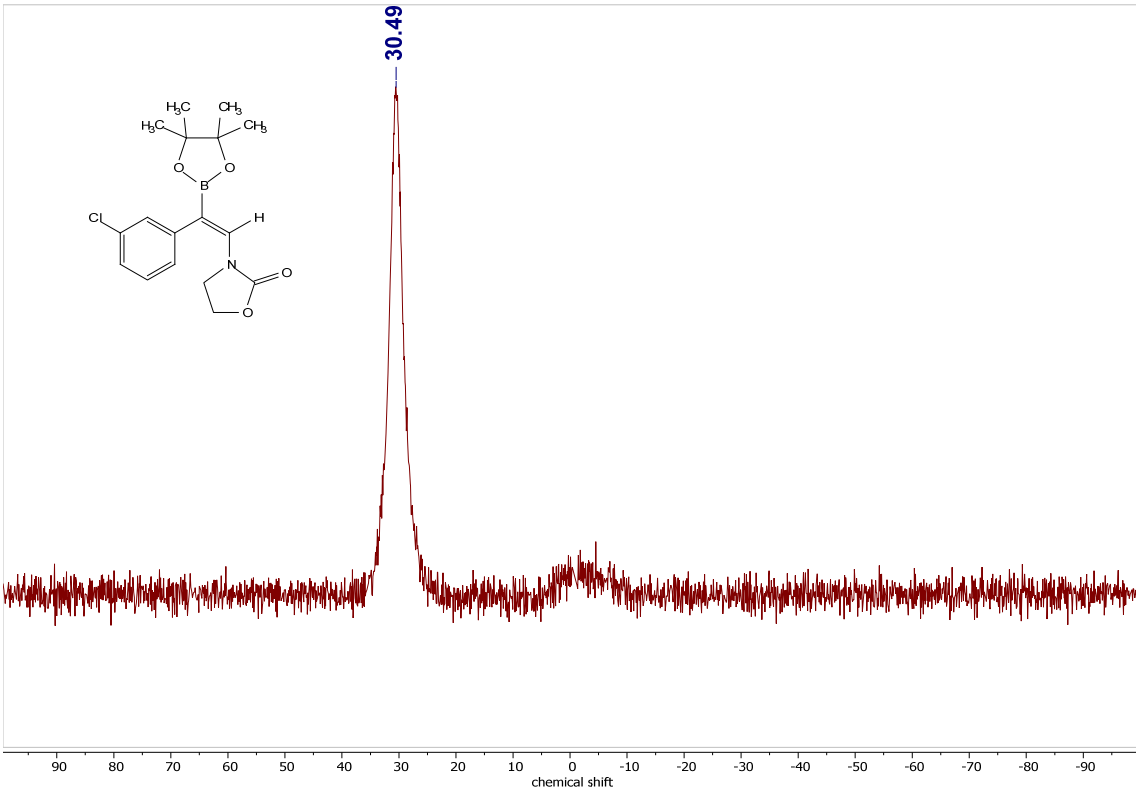
^{1}H-2p


7.46
7.26
7.22
7.22
7.21
7.21
7.13
7.13
7.04
7.03
7.03
7.03
7.02
7.01
4.22
4.20
4.18
3.19
3.17
3.15
1.26
0.00 TMS
0.79
1.01
0.57
0.84
1.00
2.01
2.00
12.61
chemical shift

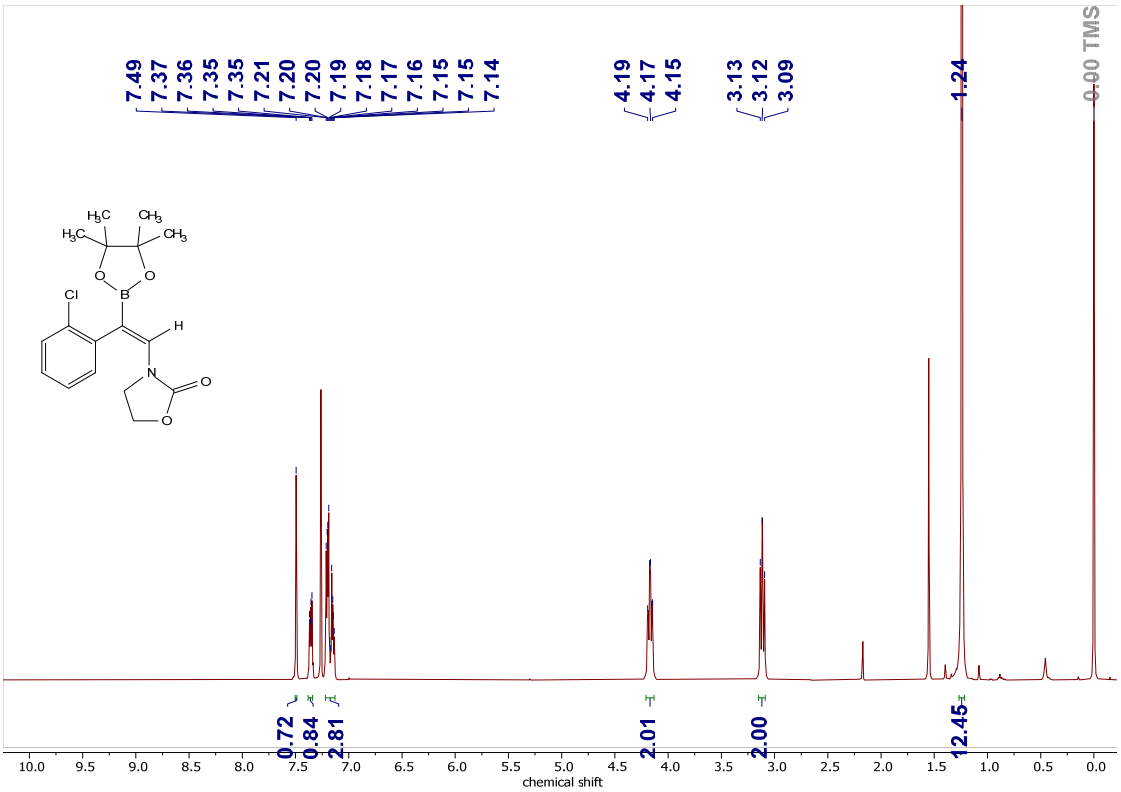
^{13}C-2p


156.56
140.14
135.37
133.47
129.75
128.80
128.09
126.66
83.80
62.68
44.71
24.68
-0.00 TMS
chemical shift

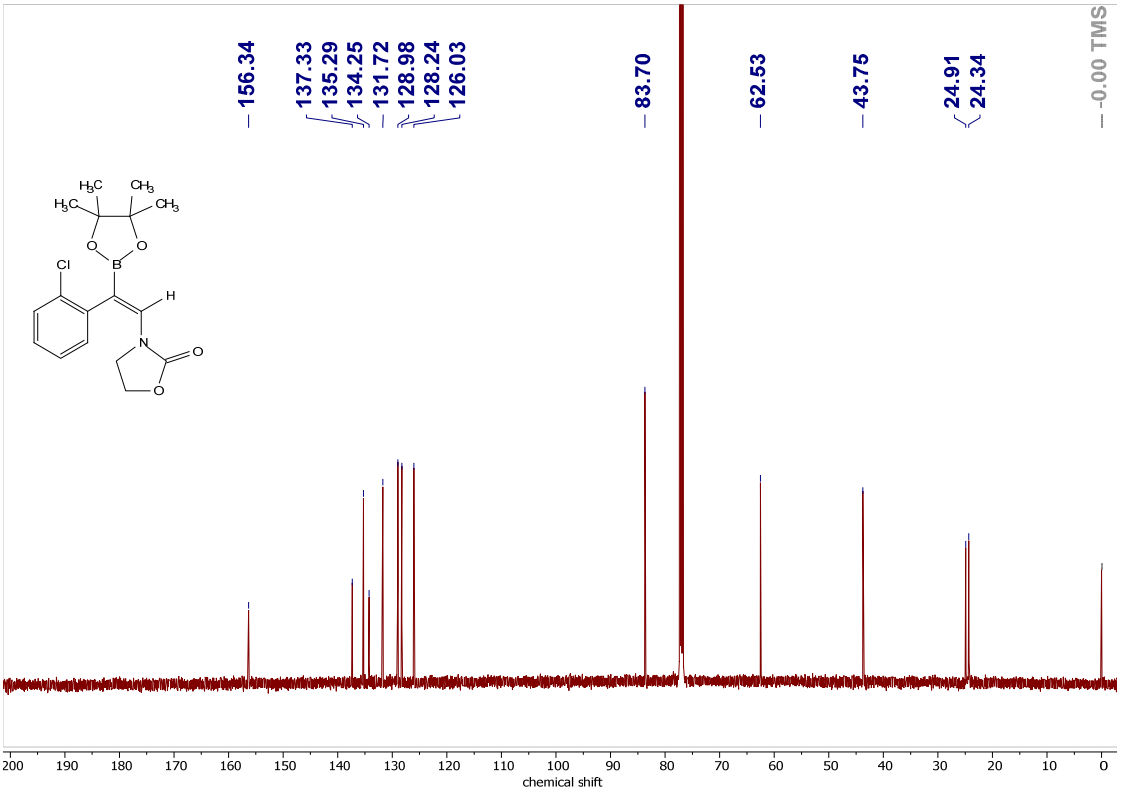
^{11}B-2p


30.49
chemical shift

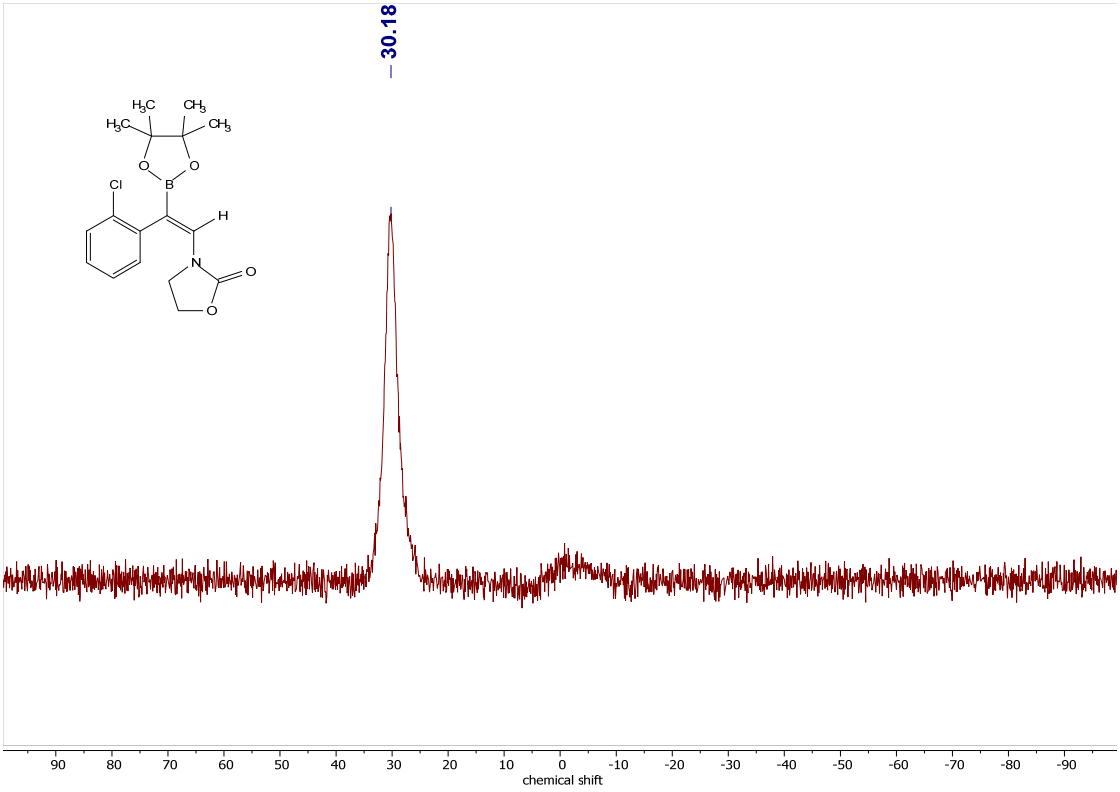
^{1}H-2q


7.49
7.37
7.36
7.35
7.35
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.15
7.15
7.14
4.19
4.17
4.15
3.13
3.12
3.09
1.24
0.00 TMS
0.72
0.84
2.81
2.01
2.00
12.45
chemical shift

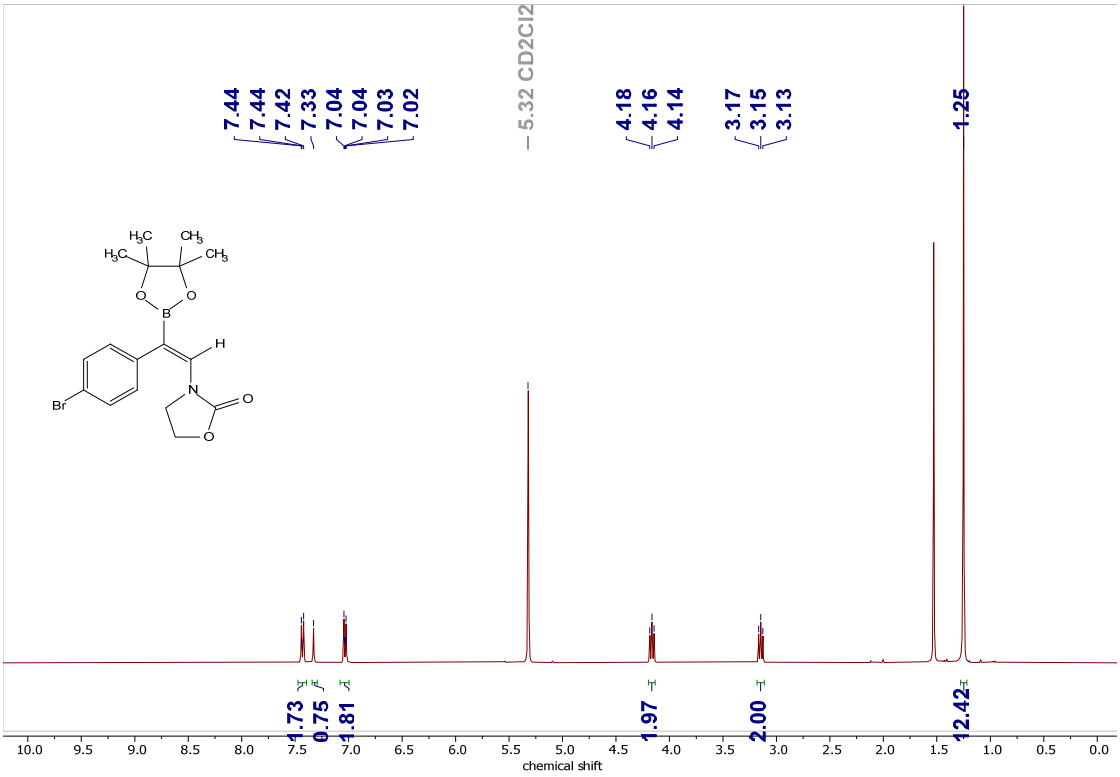
^{13}C-2q


156.34
137.33
135.29
134.25
131.72
128.98
128.24
126.03
83.70
62.53
43.75
24.91
24.34
-0.00 TMS
chemical shift

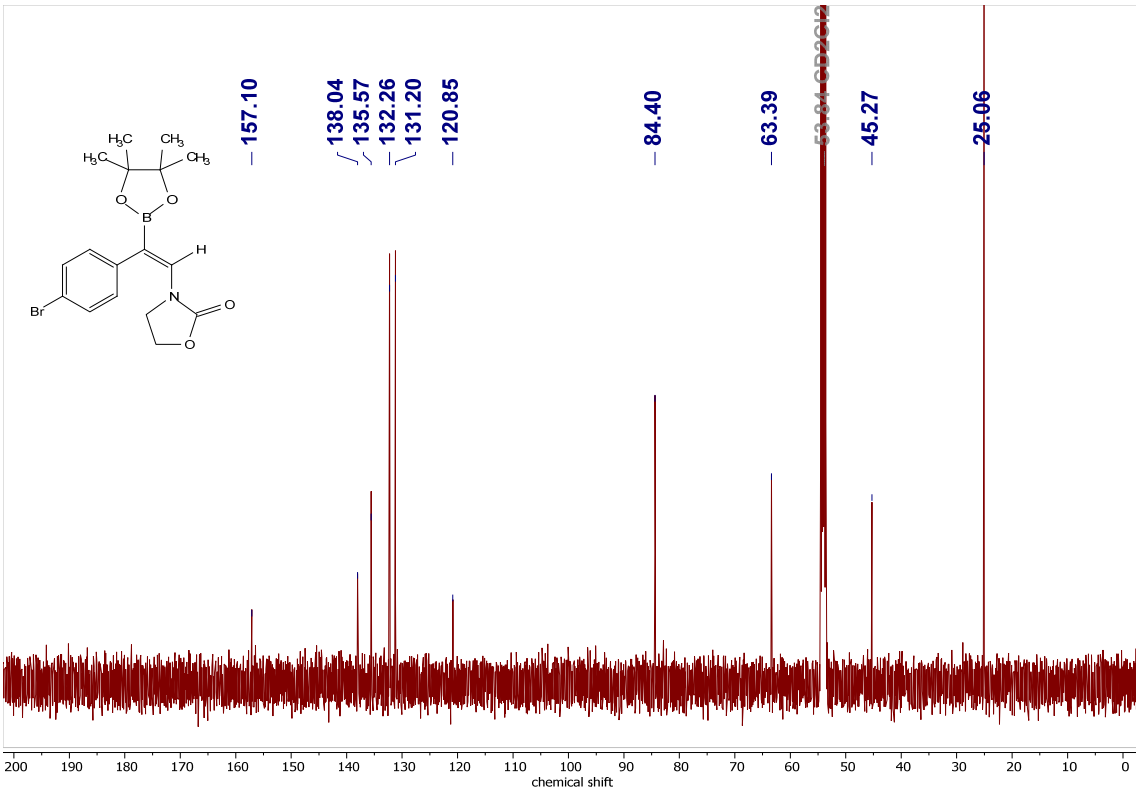
^{11}B-2q


30.18
chemical shift

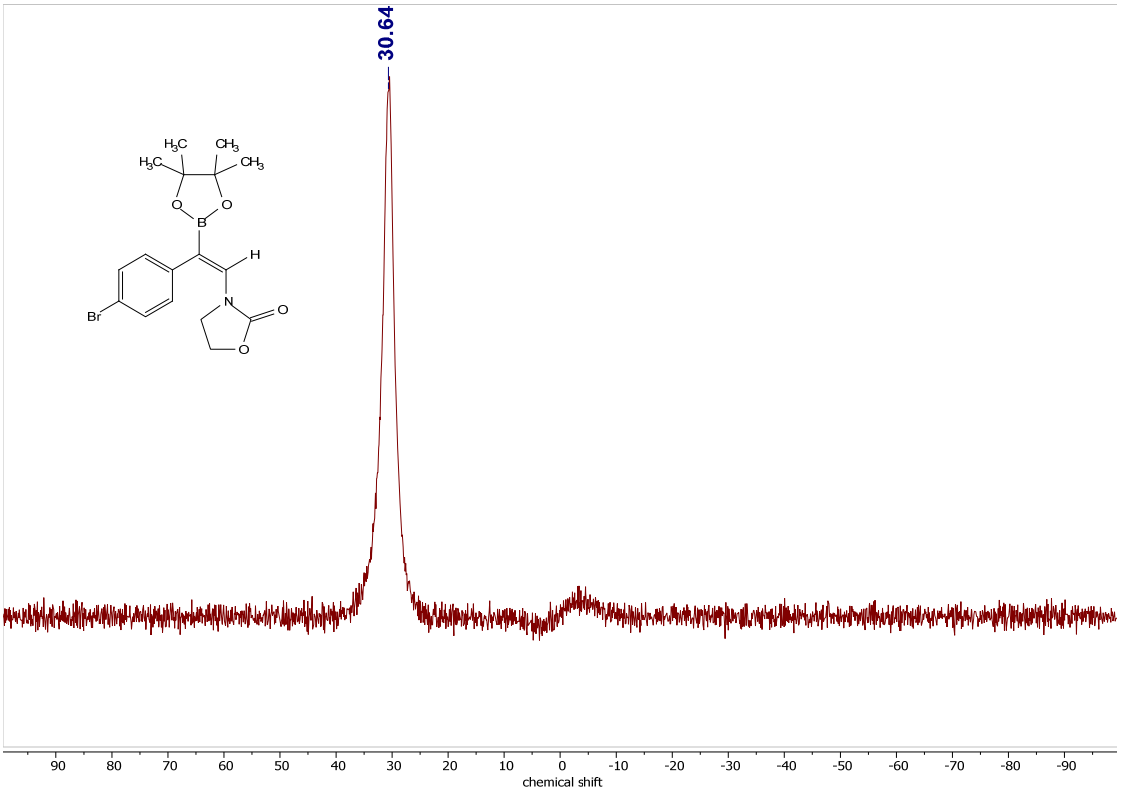
^{1}H-2r


7.44
7.44
7.42
7.33
7.04
7.04
7.03
7.02
5.32 CD2Cl2
4.18
4.16
4.14
3.17
3.15
3.13
1.25
1.73
0.75
1.81
1.97
2.00
12.42
chemical shift

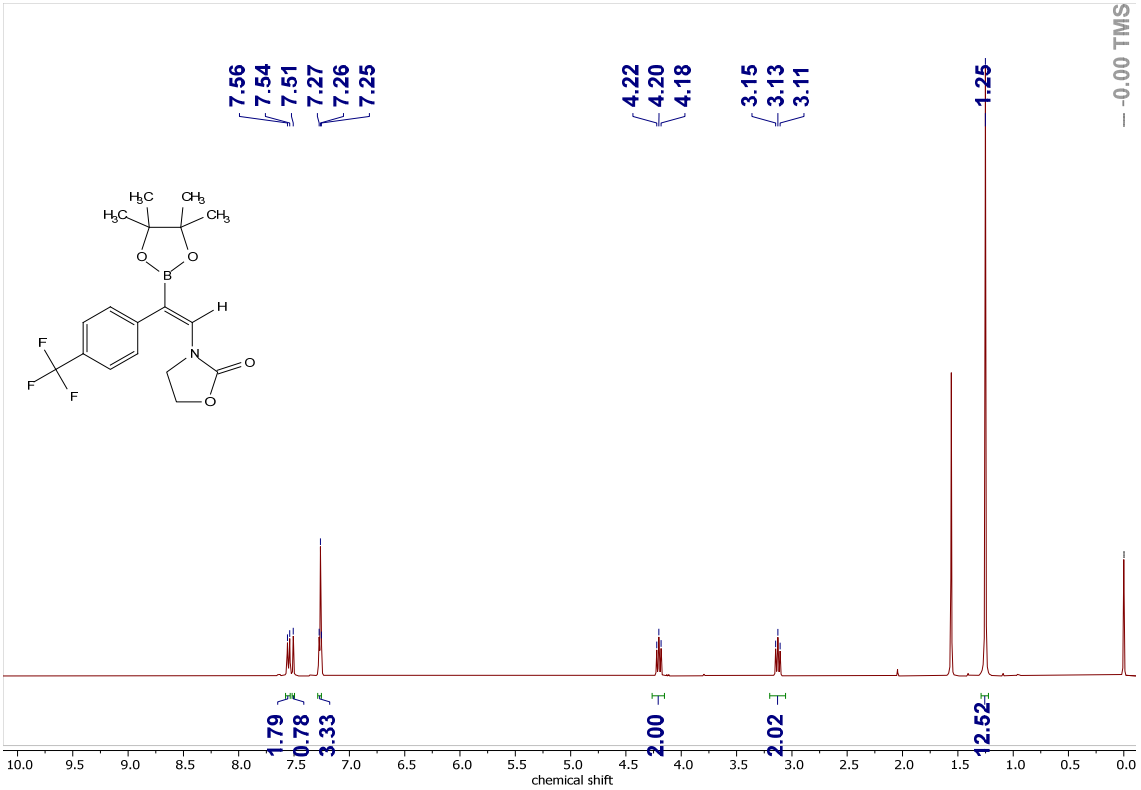
^{13}C-2r


157.10
138.04
135.57
132.26
131.20
120.85
84.40
63.39
53.04
45.27
25.06
chemical shift

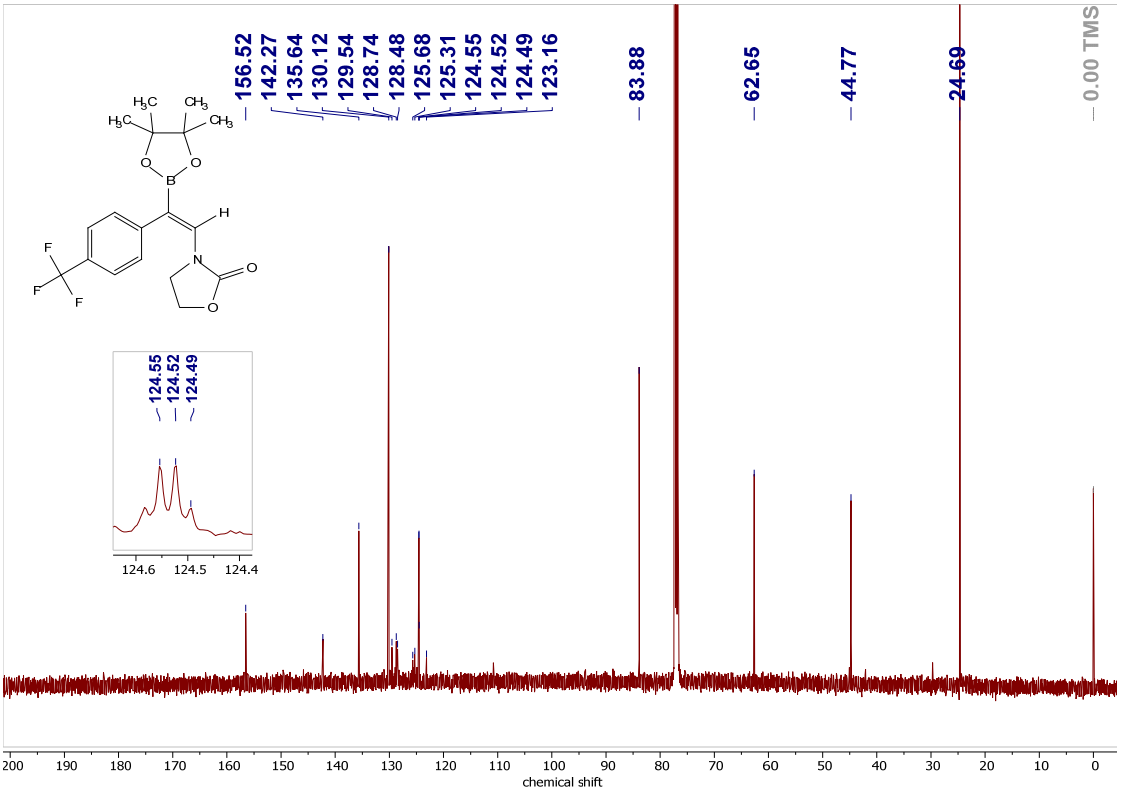
^{13}C-2r


30.64
chemical shift

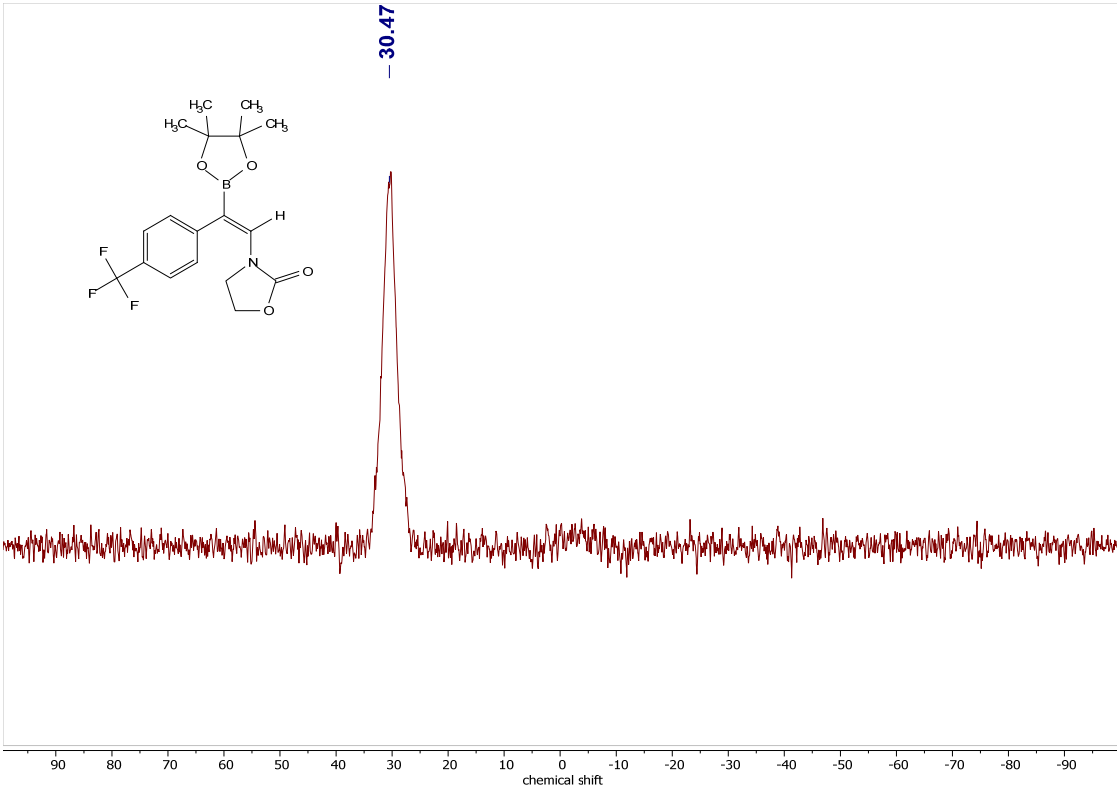
^{1}H-2s


7.56
7.54
7.51
7.27
7.26
7.25
4.22
4.20
4.18
3.15
3.13
3.11
1.25
-0.00 TMS
1.79
0.78
3.33
2.00
2.02
12.52
chemical shift

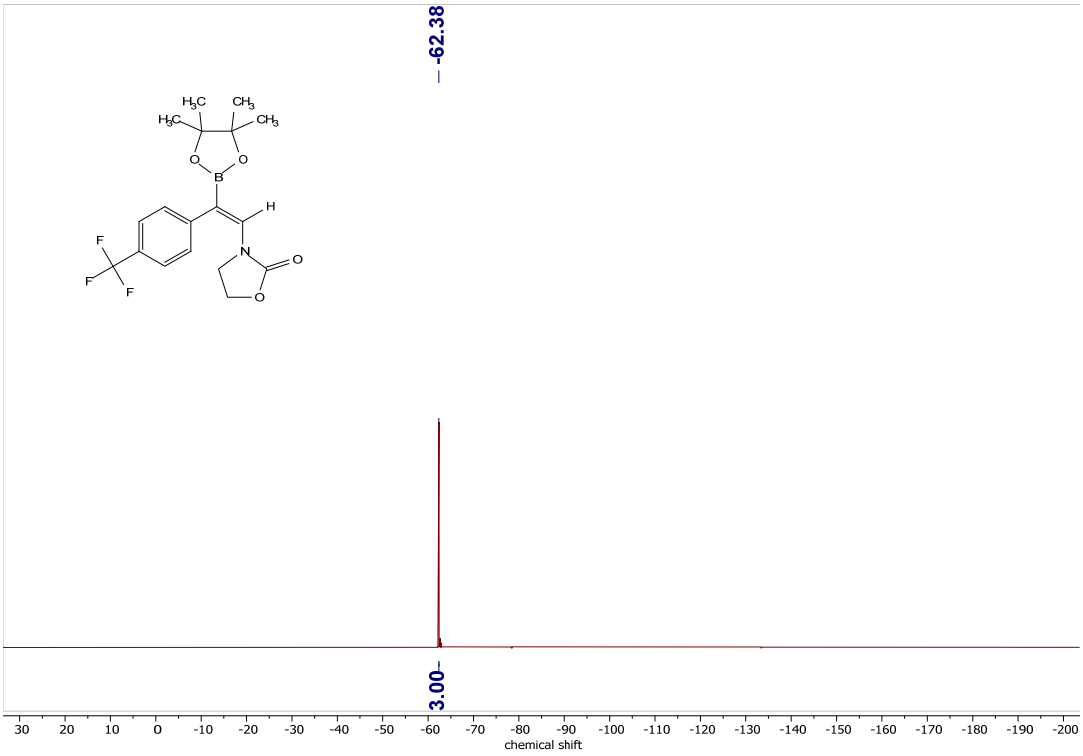
^{13}C-2s


156.52
142.27
135.64
130.12
129.54
128.74
128.48
125.68
125.31
124.55
124.52
124.49
123.16
83.88
62.65
44.77
24.69
0.00 TMS
124.55
124.52
124.49
chemical shift

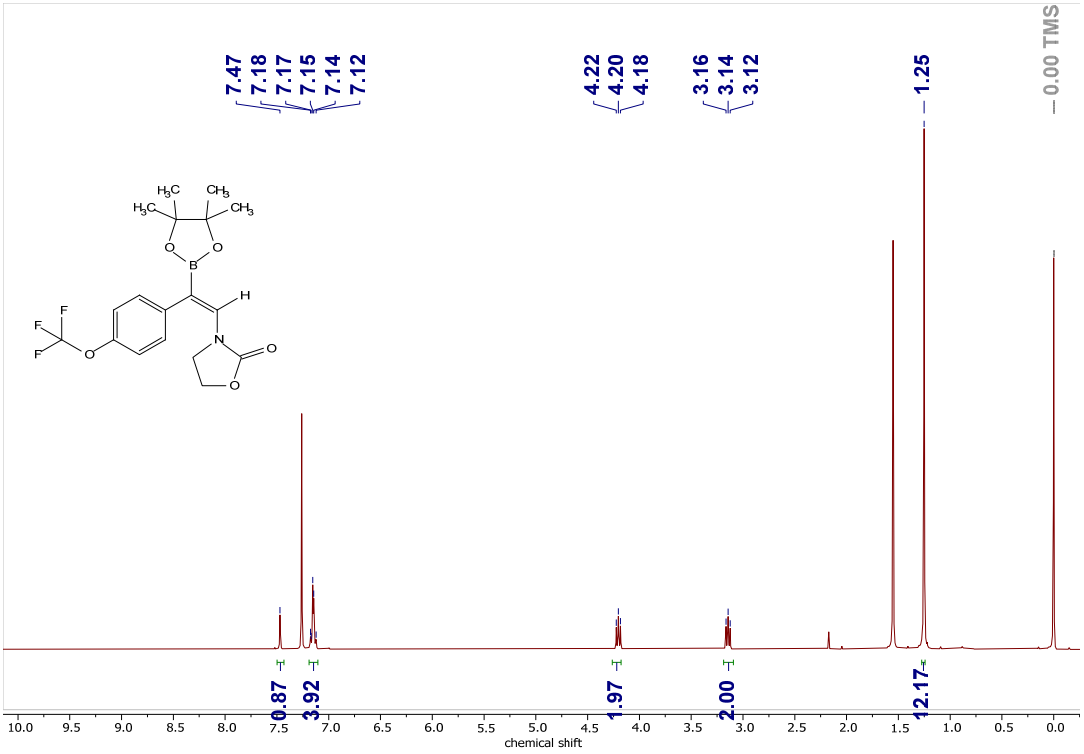
^{11}B-2s



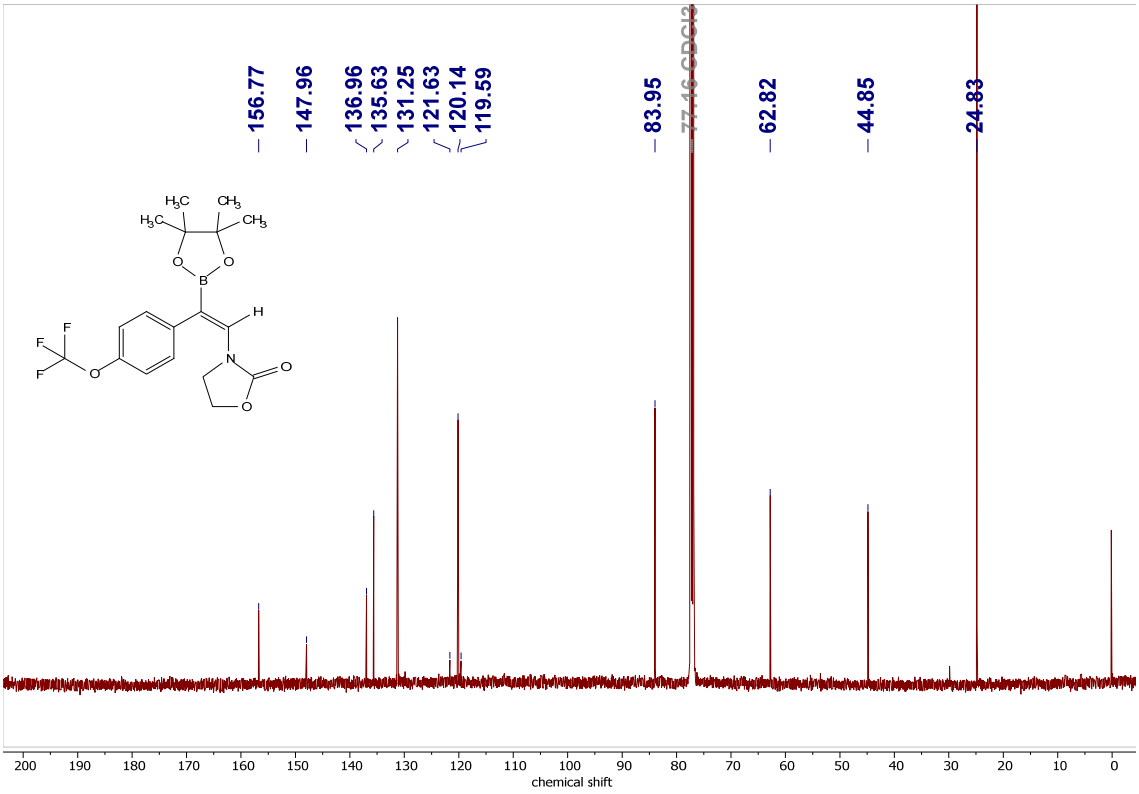
^{19}F-2s



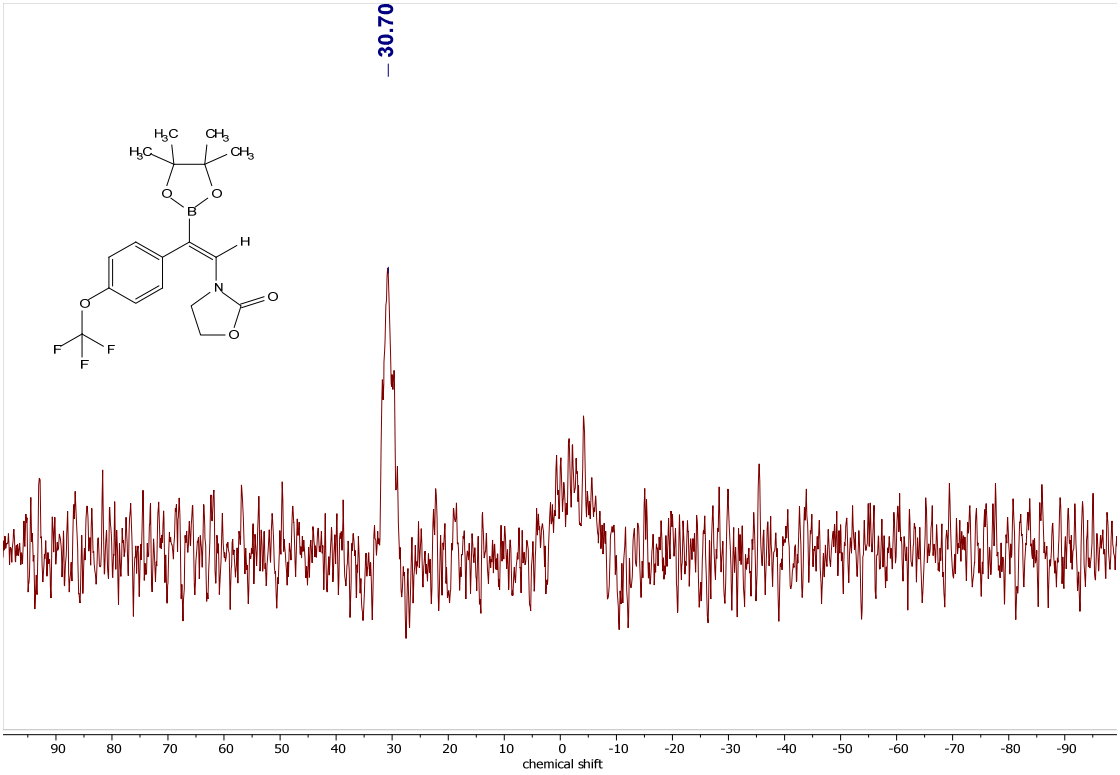
^{1}H-2t


7.47
7.18
7.17
7.15
7.14
7.12
4.22
4.20
4.18
3.16
3.14
3.12
1.25
0.00 TMS
0.87
3.92
1.97
2.00
12.17
chemical shift

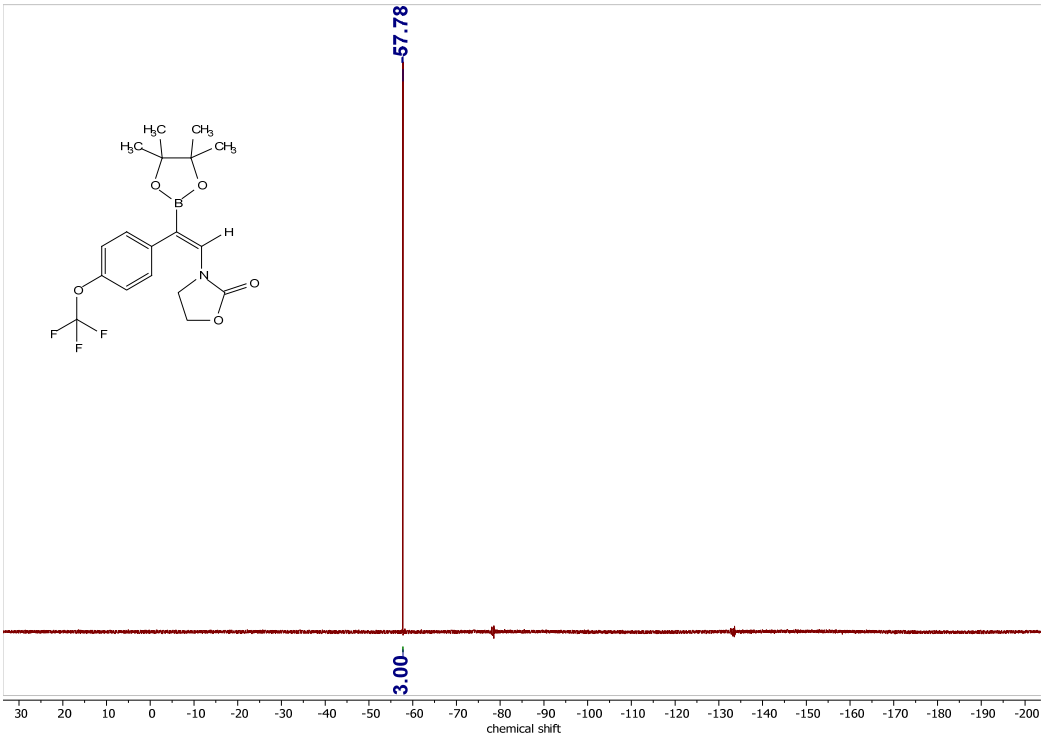
^{13}C-2t


156.77
147.96
136.96
135.63
131.25
121.63
120.14
119.59
83.95
77.16 CDCl3
62.82
44.85
24.83
chemical shift

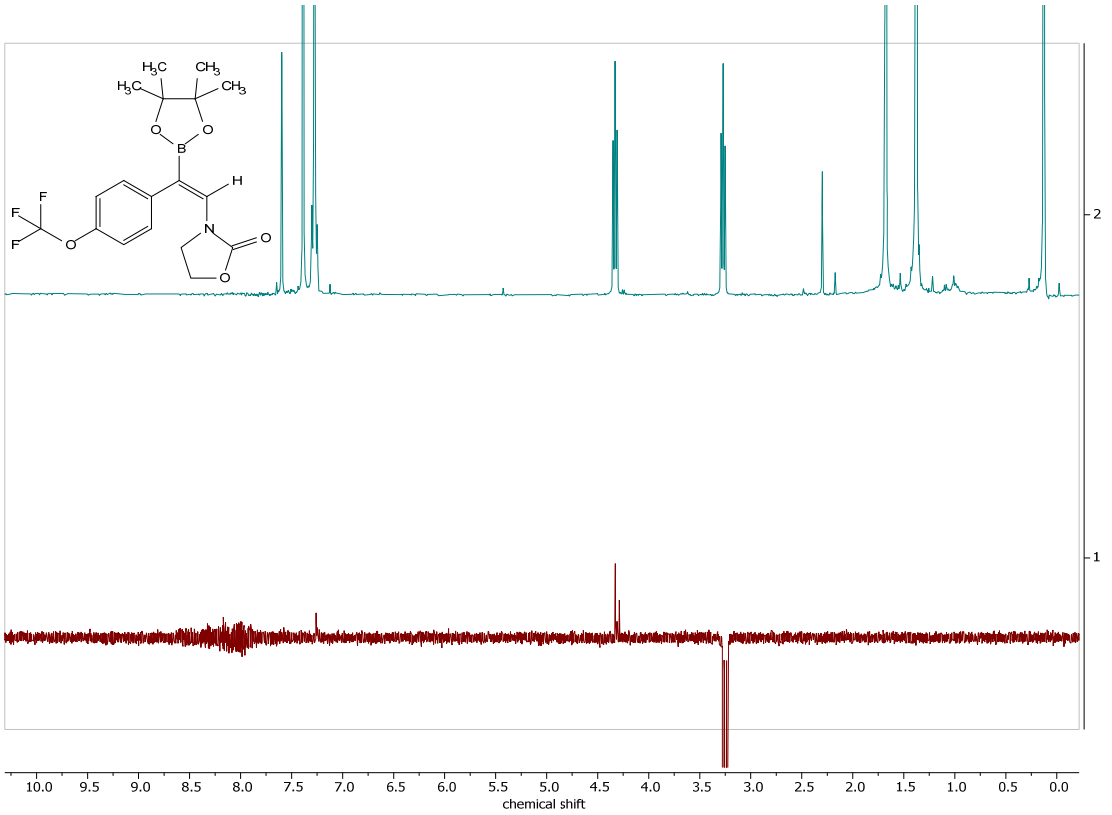
^{11}B-2t



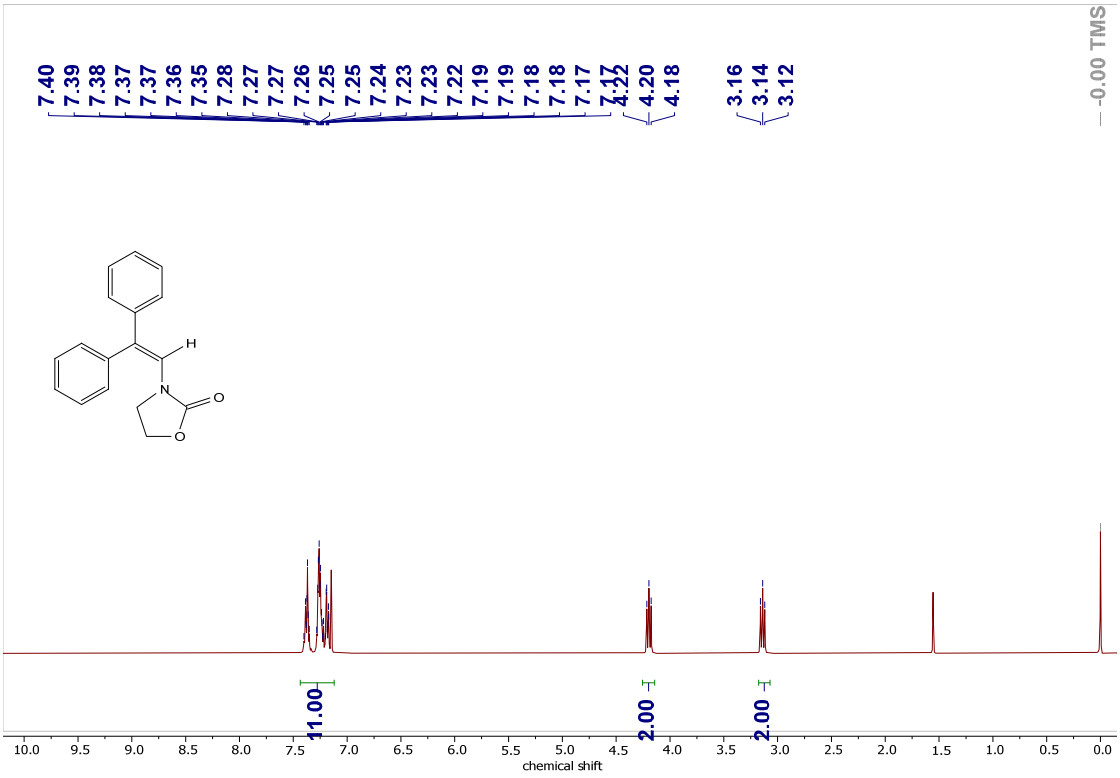
^{19}F-2t



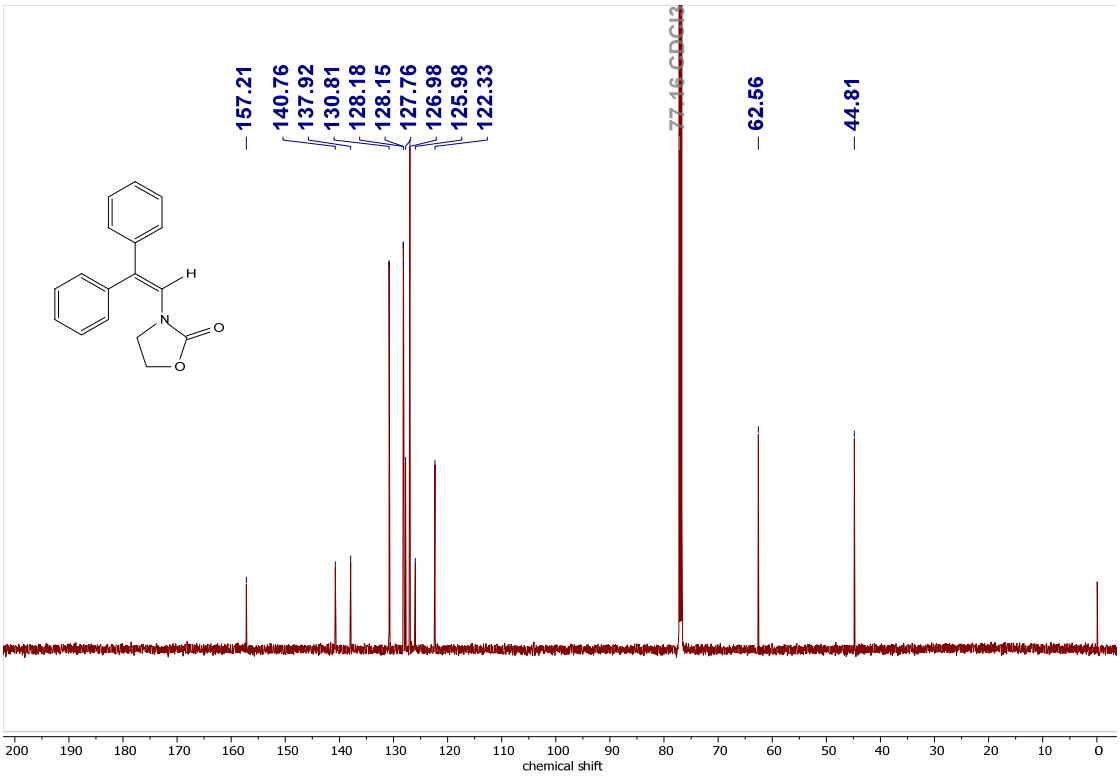
NOESY


2
1
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
chemical shift

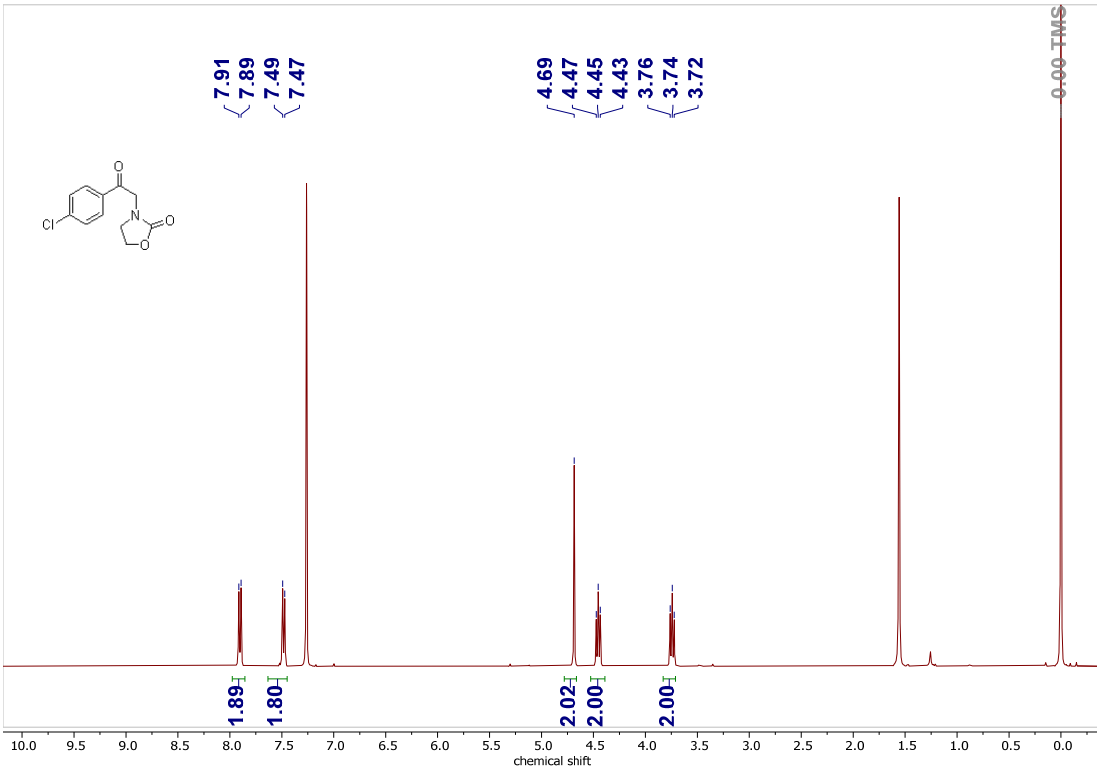
^{1}H-3a


7.40 7.39 7.38 7.37 7.37 7.36 7.35 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.19 7.19 7.18 7.18 7.17 7.17 4.22 4.20 4.18 3.16 3.14 3.12
0.00 TMS
11.00
2.00
2.00
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
chemical shift

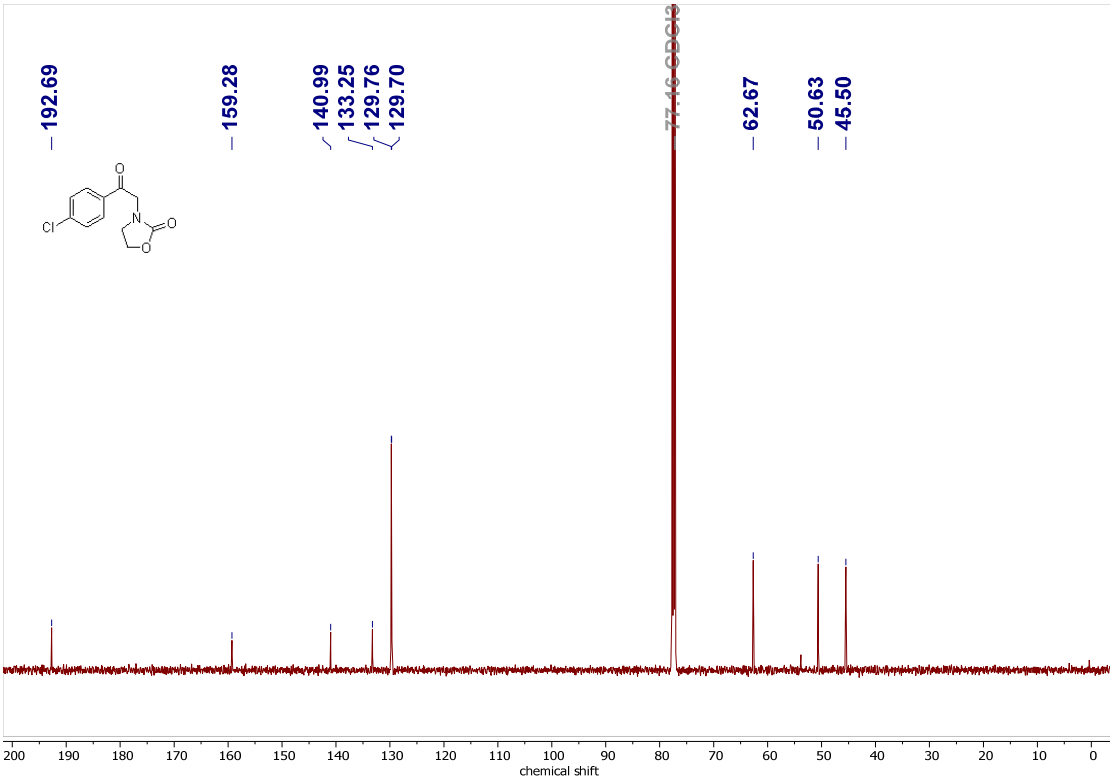
^{13}C-3a


157.21
140.76
137.92
130.81
128.18
128.15
127.76
126.98
125.98
122.33
77.16 CDCl3
62.56
44.81
chemical shift

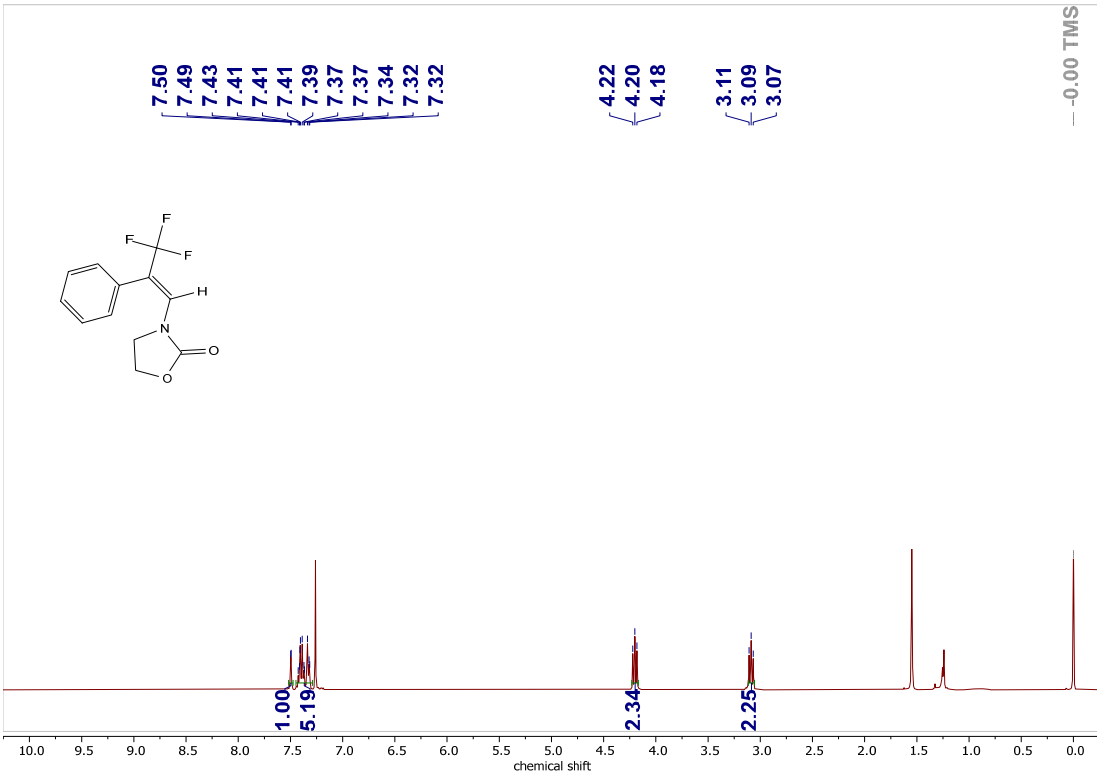
^{1}H-3b


7.91
7.89
7.49
7.47
4.69
4.47
4.45
4.43
3.76
3.74
3.72
0.00 TMS
1.89
1.80
2.02
2.00
2.00
chemical shift

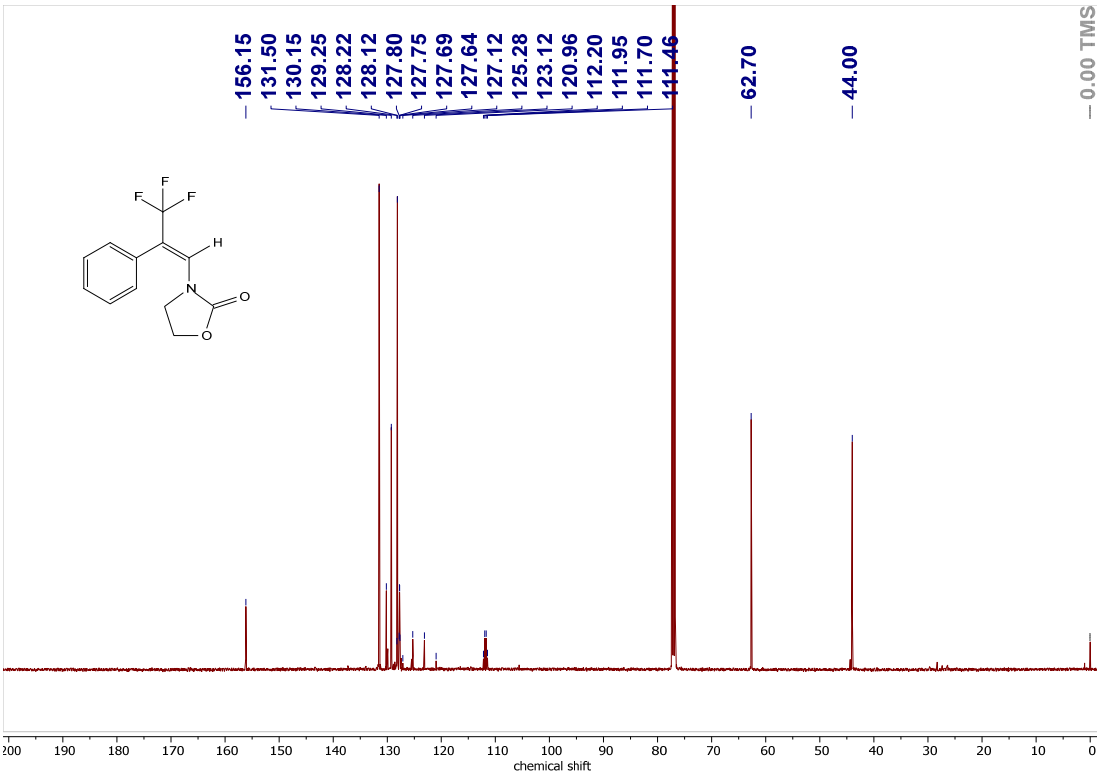
^{13}C-3b


192.69
159.28
140.99
133.25
129.76
129.70
77.46 CDCl3
62.67
50.63
45.50
chemical shift

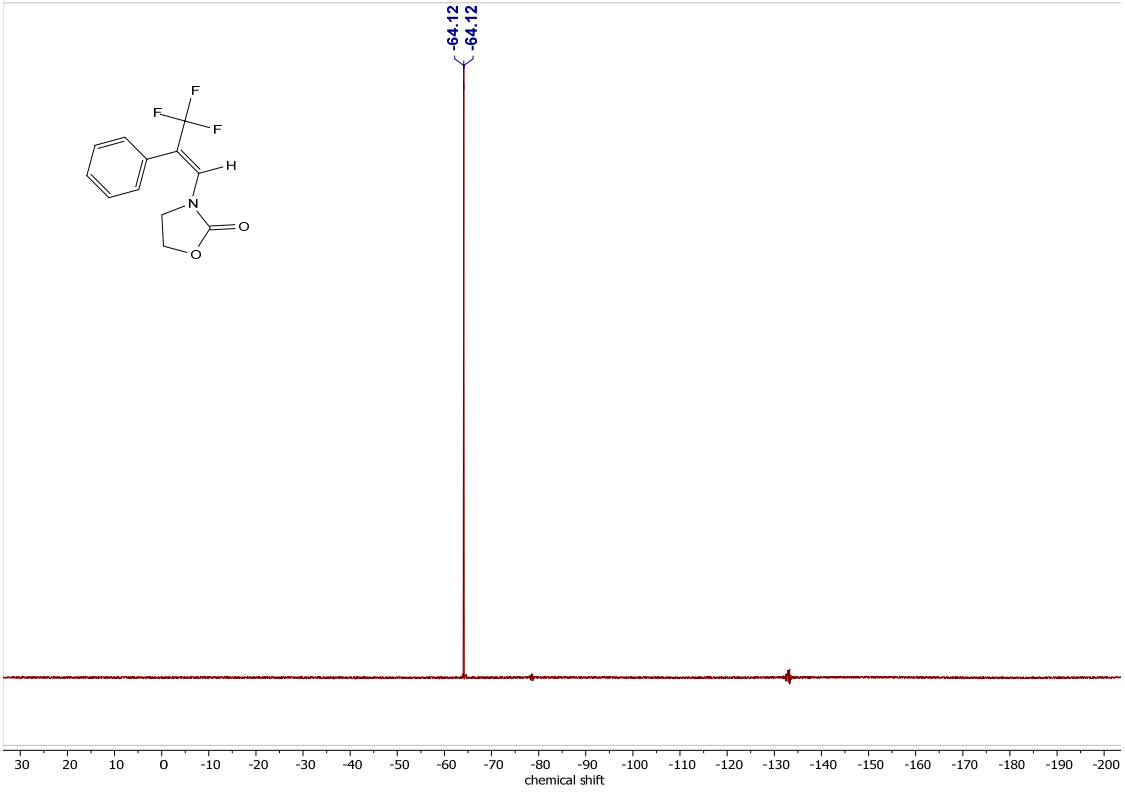
^{1}H-3c


7.50
7.49
7.43
7.41
7.41
7.41
7.39
7.37
7.37
7.34
7.32
7.32
4.22
4.20
4.18
3.11
3.09
3.07
0.00 TMS
1.00
5.19
2.34
2.25
chemical shift

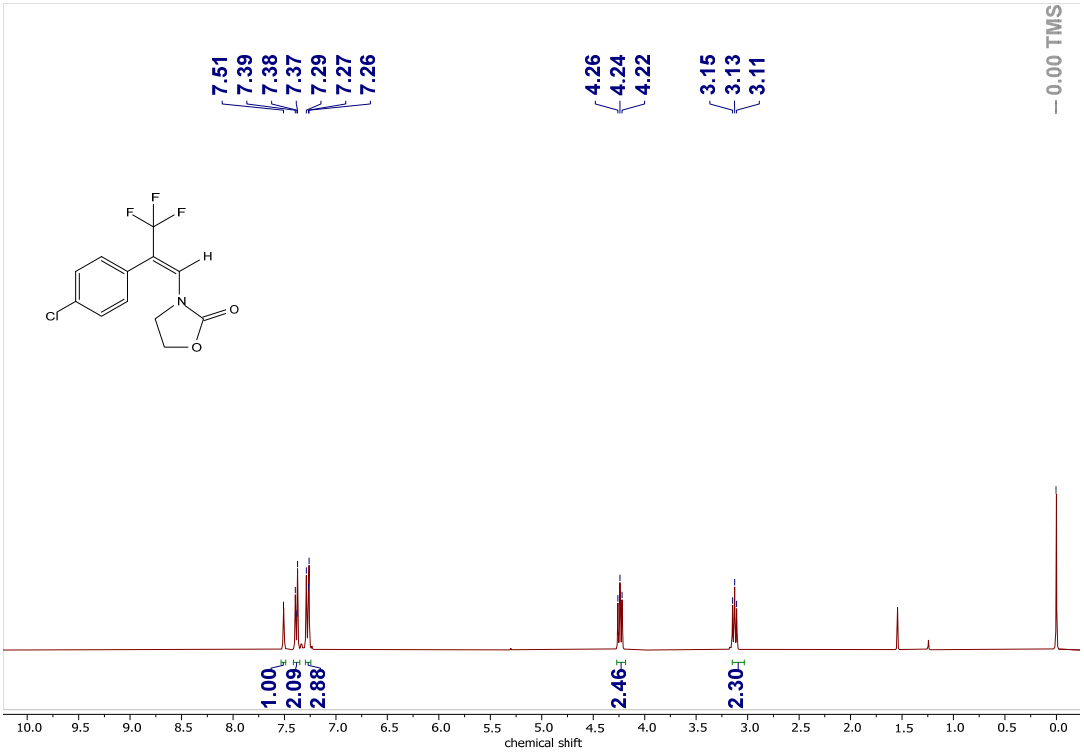
^{13}C-3c


156.15
131.50
130.15
129.25
128.22
128.12
127.80
127.75
127.69
127.64
127.12
125.28
123.12
120.96
112.20
111.95
111.70
111.46
62.70
44.00
0.00 TMS
F
F
F
H
N
O
O
chemical shift

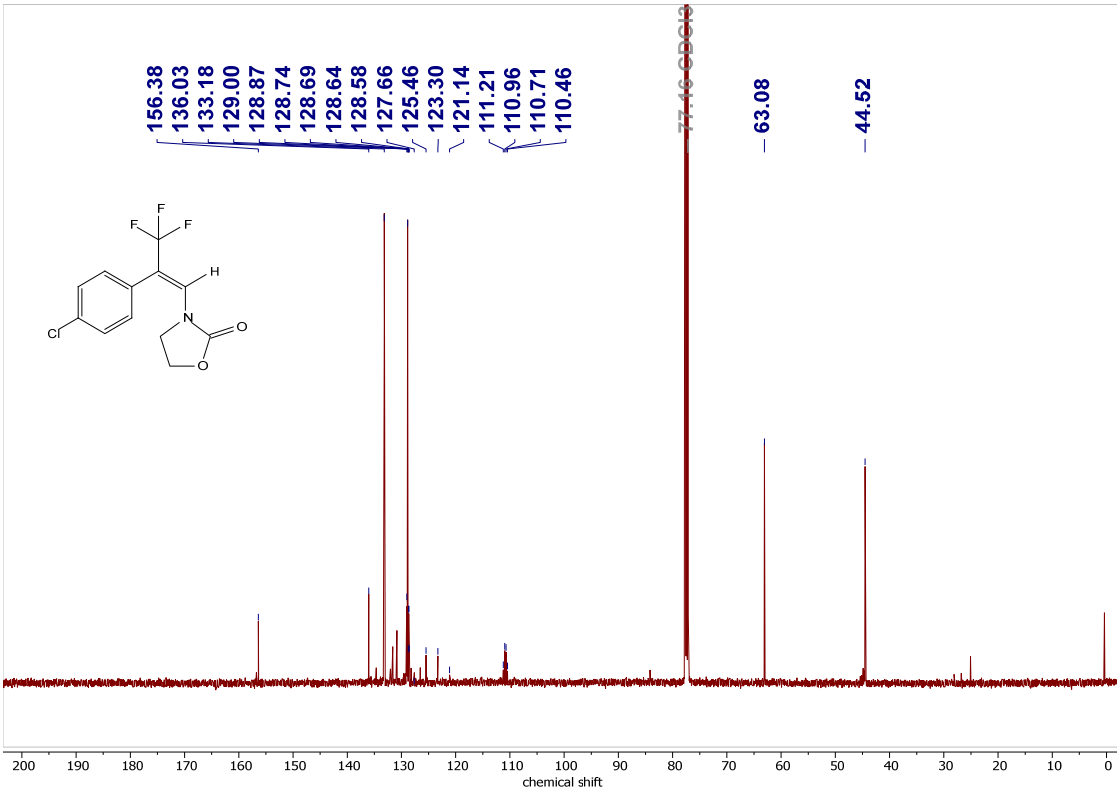
^{19}F-3c


-64.12
-64.12
F
F
F
H
N
O
O
chemical shift

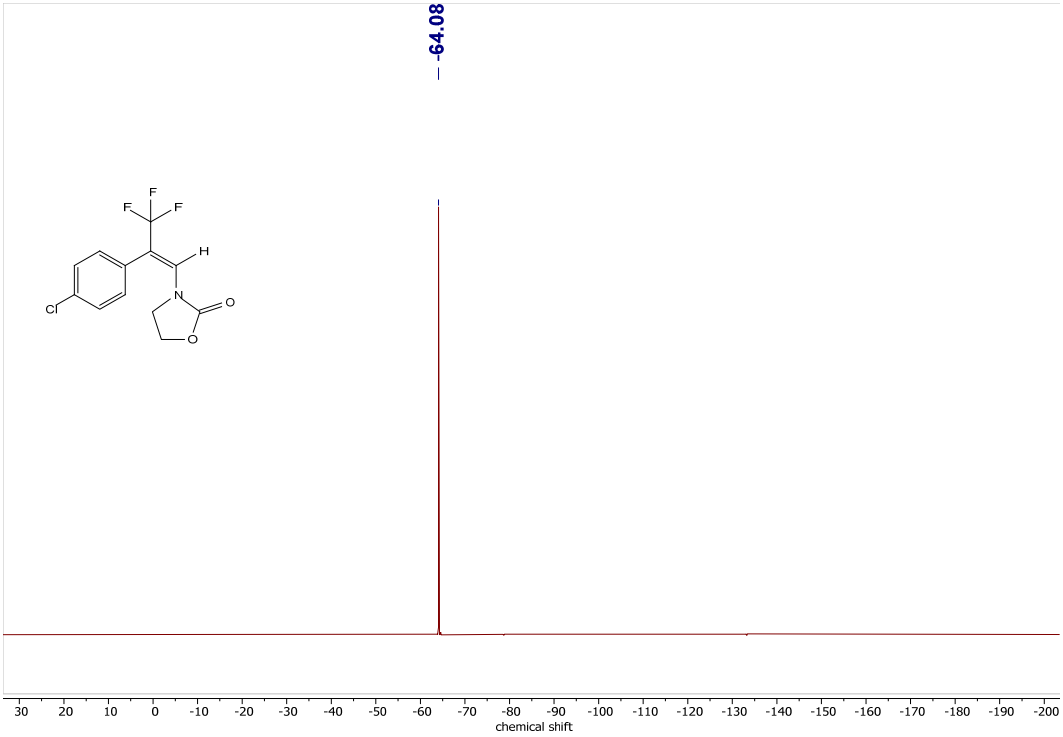
^{1}H- 3d


7.51
7.39
7.38
7.37
7.29
7.27
7.26
4.26
4.24
4.22
3.15
3.13
3.11
0.00 TMS
F
F
F
H
Cl
N
O
O
1.00
2.09
2.88
2.46
2.30
chemical shift

^{13}C-3d

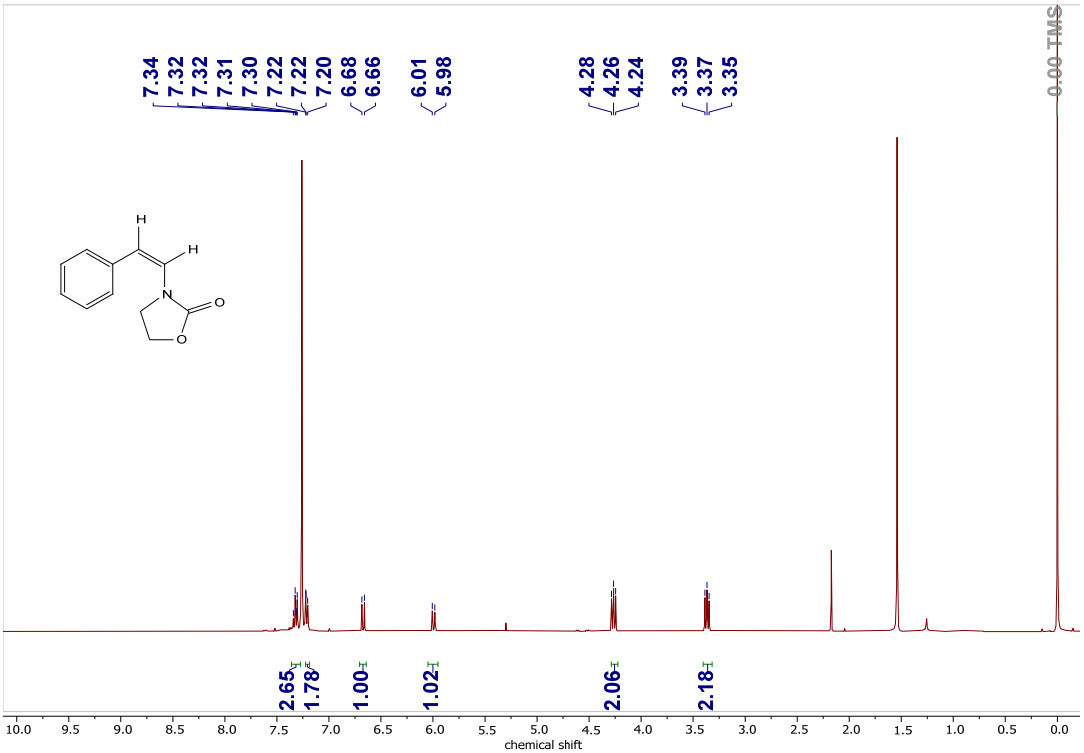

156.38
136.03
133.18
129.00
128.87
128.74
128.69
128.64
128.58
127.66
125.46
123.30
121.14
111.21
110.96
110.71
110.46
77.16 CDCl3
63.08
44.52
F
F
F
H
Cl
N
O
O
chemical shift

^{19}F- 3d

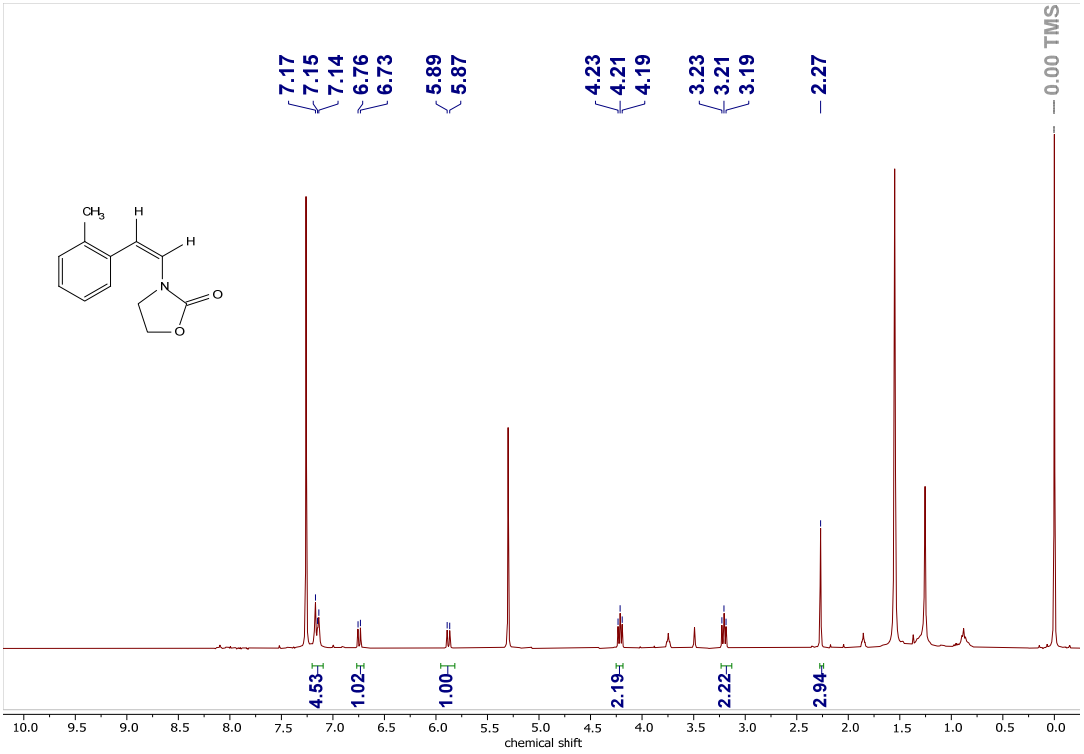


Crude NMR's for the protodeborylations (^{1}H NMR's).

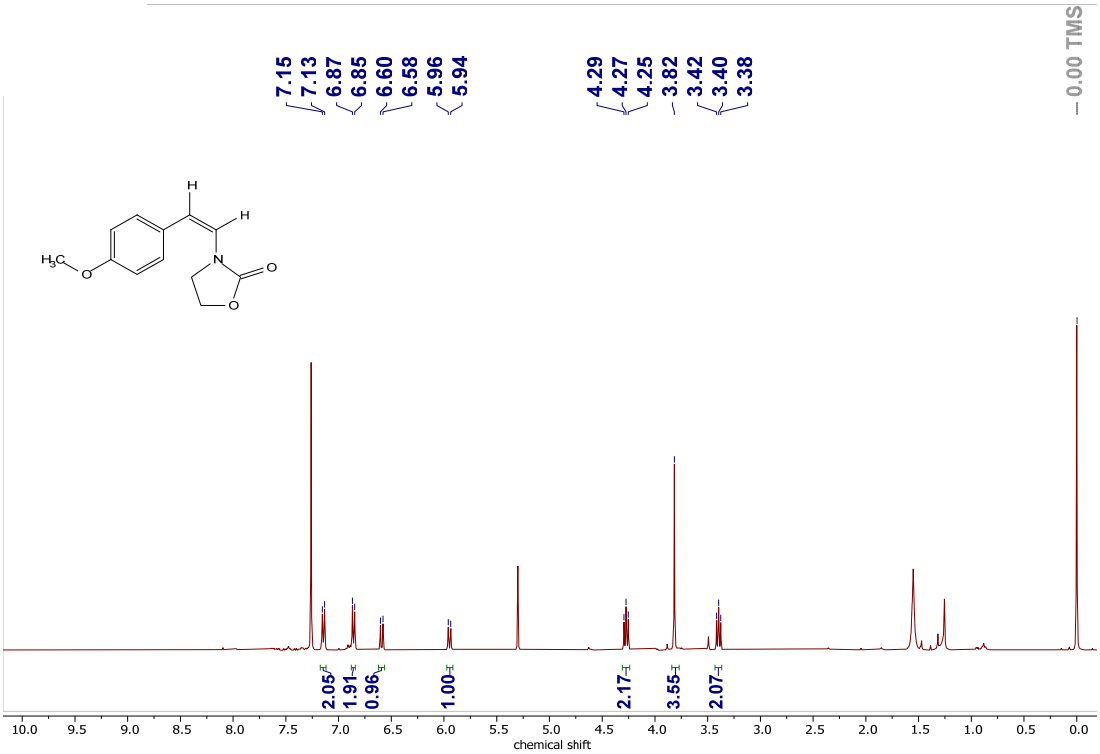
3aa - Crude NMR



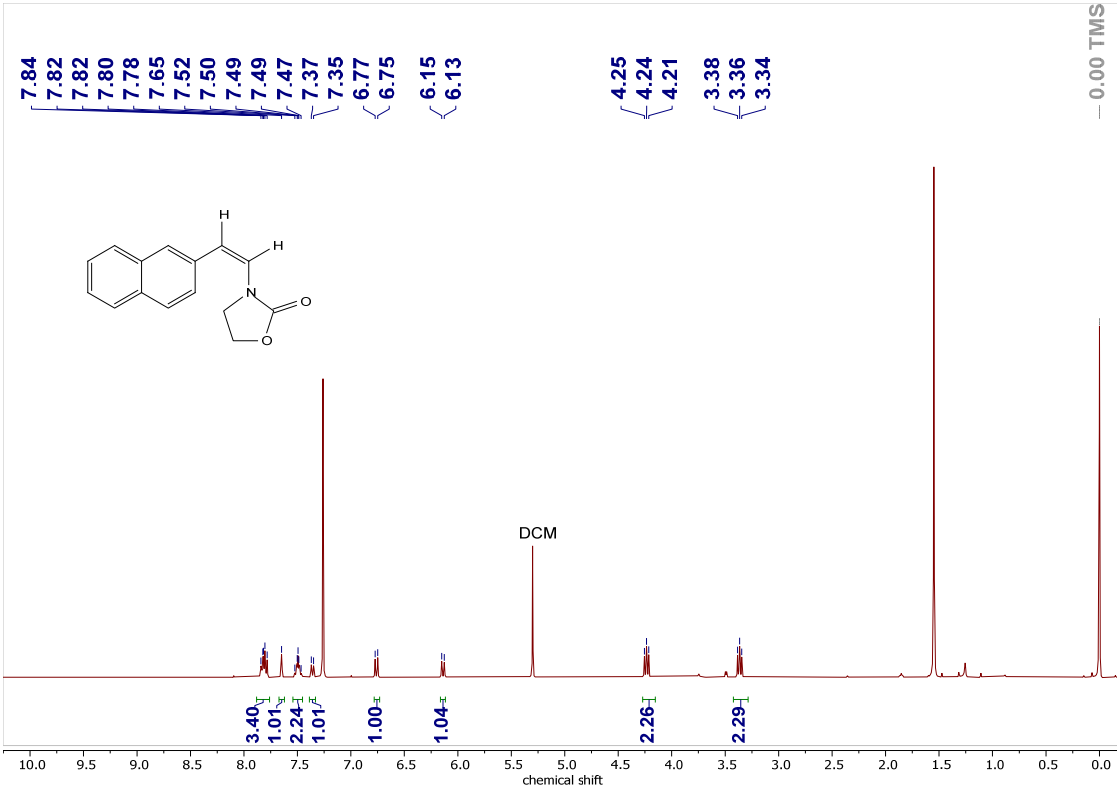
3b- Crude NMR



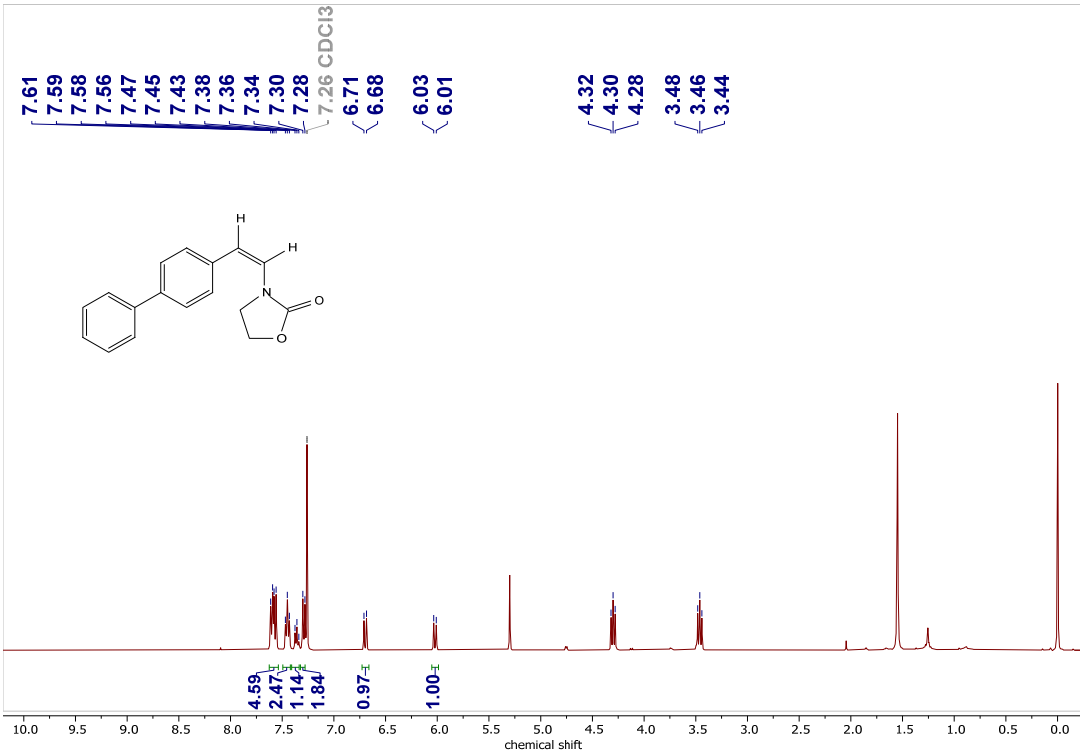
3i- Crude NMR



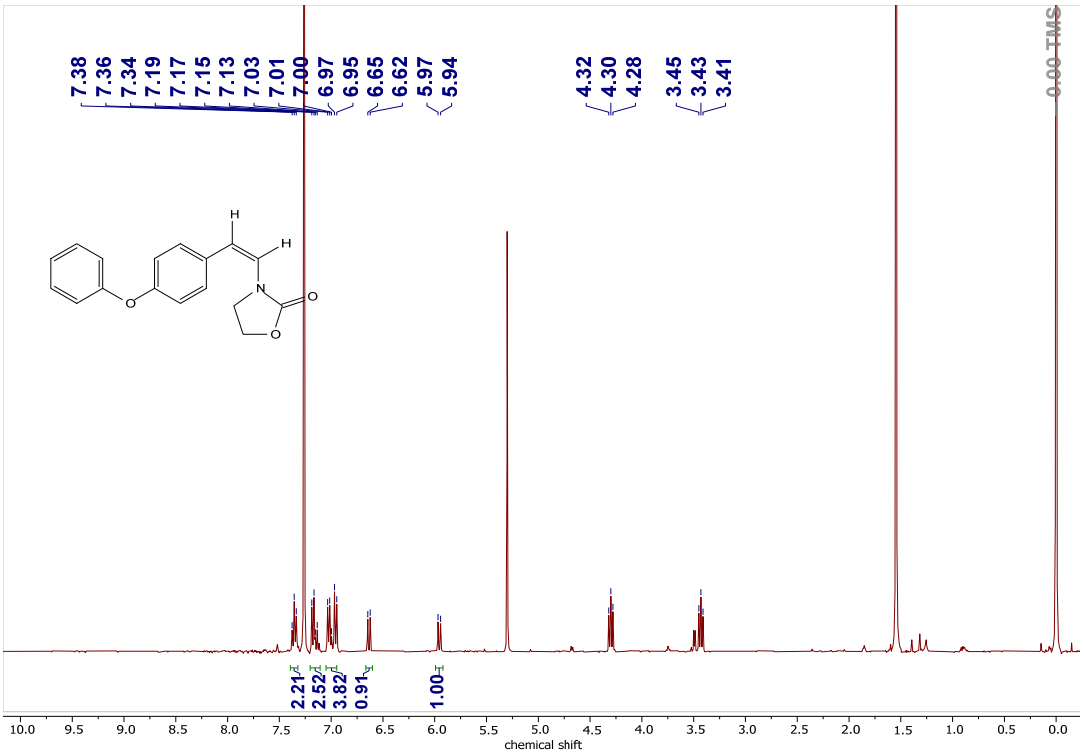
3k-Crude NMR



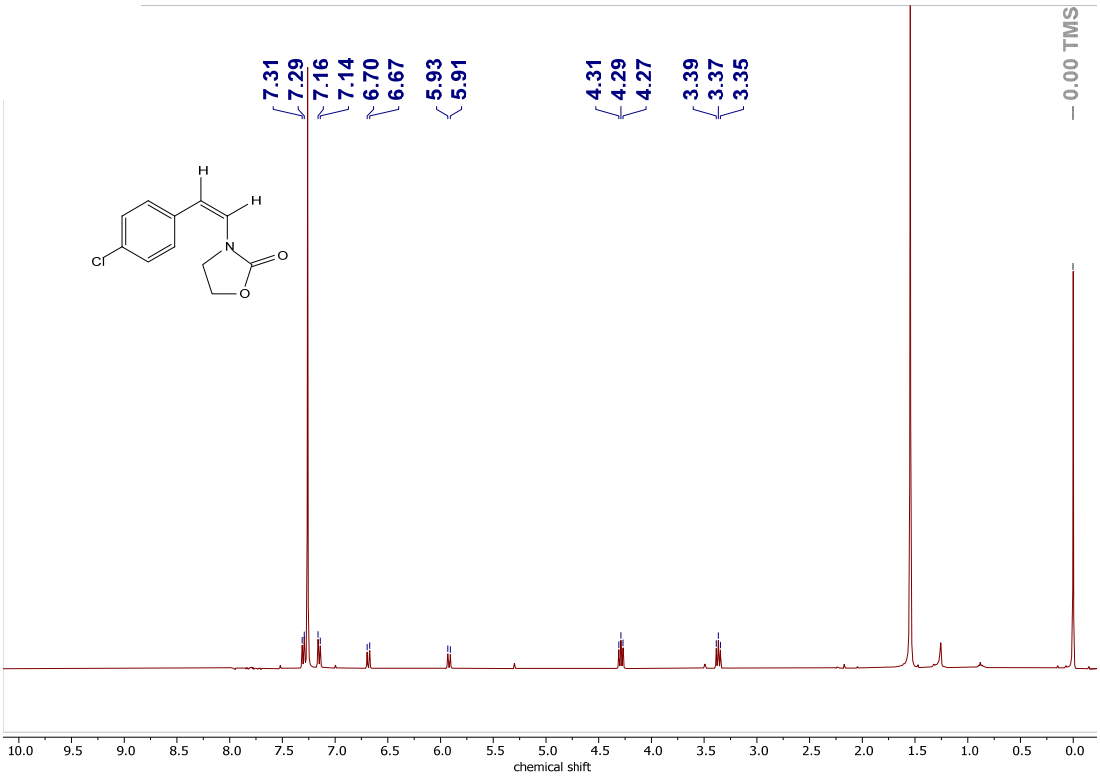
3l- Crude NMR



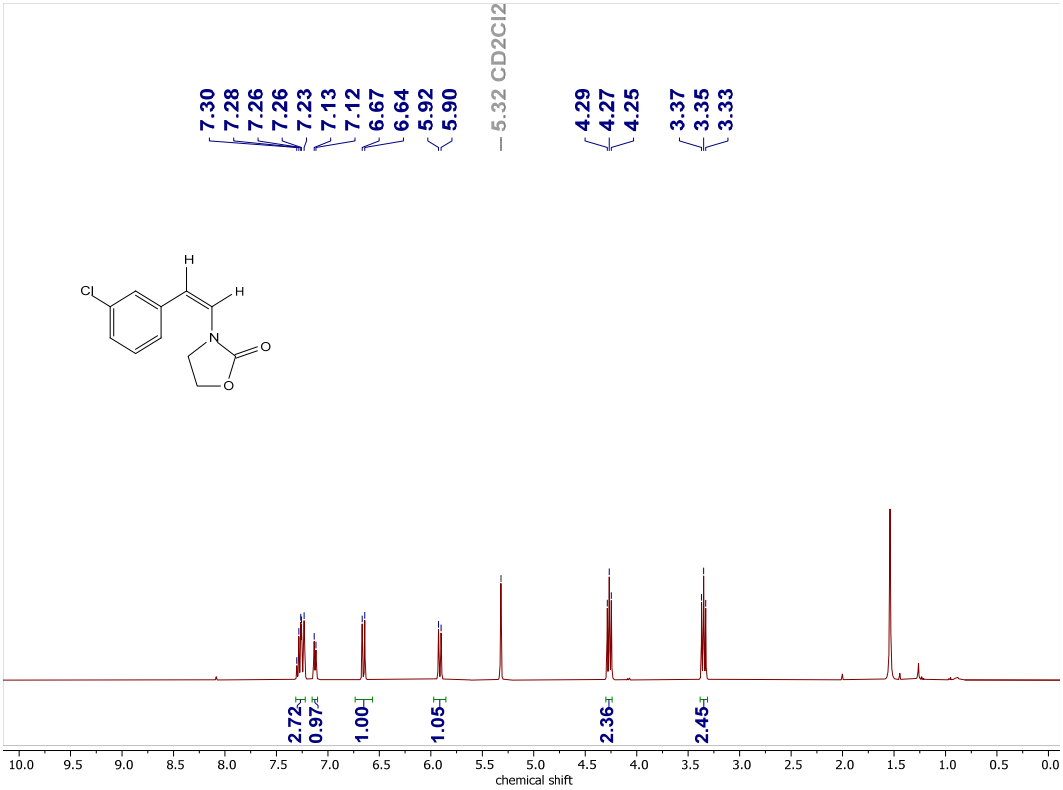
3m-Crude NMR



3o-Crude NMR



3p- Crude NMR


7.30
7.28
7.26
7.26
7.23
7.13
7.12
6.67
6.64
5.92
5.90
5.32 CD2Cl2
4.29
4.27
4.25
3.37
3.35
3.33
Cl
H
H
N
O
O
2.72
0.97
1.00
1.05
2.36
2.45
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
chemical shift