Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information for

Carboxylate Phosphabetaine as Bifunctional Organocatalyst for the Intramolecular Ring Opening of Oxetane

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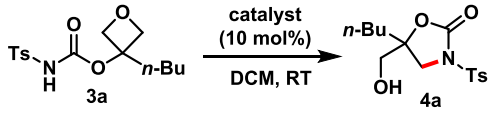
Table of Contents

1. General information

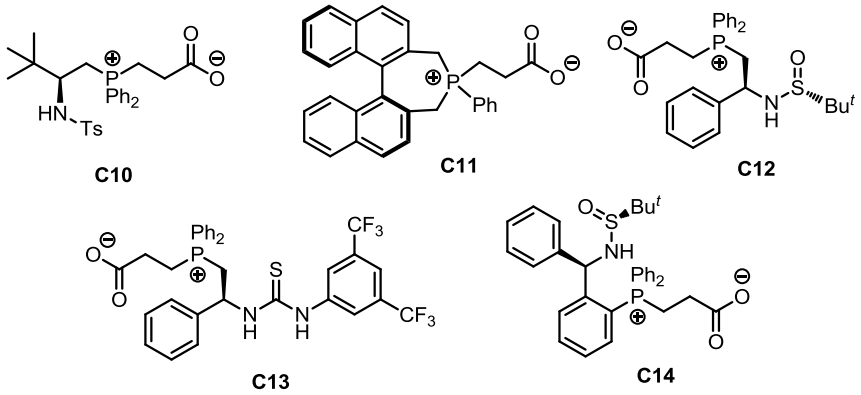
Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction were conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvent were treated as follow: tetrahydrofuran and diethyl ether were distilled from sodium under argon atmosphere, dichcloromethane and toluene was distilled distilled from calcium hydride under argon atmosphere. Anhydrous chloroform, acetonitrile and ethyl acetate were commercial available. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm, 200-400 mesh, Silicycle P60). NMR data including ^{1}H NMR, or ^{13}C NMR spectra were recorded on Agilent 500 and Agilent 400. ^{1}H NMR Chemical shifts were reported in ppm from the solvent resonanceas the internal standard ($CDCl_3$: 7.26 ppm; d_6-Acetone: 2.05 ppm; d_6-DMSO: 2.50 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$:77.16 ppm; d_6-Acetone: 29.8 ppm; d_6-DMSO: 39.52 ppm). Low mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (EI)

2. Screening of Other Catalysts for Ring Opening of Oxetane 3a[a]

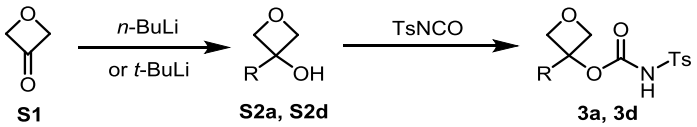


entry	catalyst	yield (%)[b]	ee (%)[c]
1	$Ph_4P^+ \bullet^-OAC$ (**C8**)	75	NA
2	$n\text{-}Bu_4N^+ \bullet^-OAC$ (**C9**)	76	NA
3	**C10**	70	4
4	**C11**	49	3
5	**C12**	57	6
6	**C13**	66	--
7	**C14**	62	6

[a] Reaction conditions: Reactions were performed with **3a** (0.05 mmol) and the catalyst (10 mol %) in solvent (0.5 mL)), wihich was stirred at RT. [b] Isolated yields. [c] Determined by HPLC analysis.



3. General procedure for the preparation of substrates

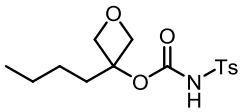


General procedure A[1]**:** To a solution of *Oxetan-3-one* (10 mmol, 1.0 equiv) in dry THF (10 mL) was added BuLi (12 mmol, 1.2 equiv) slowly at -78℃ and the reaction mixture was stirred at this temperature for 4 h. Saturated NH_4Cl (aq) (10 mL) was added. The organic layer was extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl

1. Ponzano S, Berteotti A, Petracca R, Vitale R, Mengatto L. *Journal of Medicinal Chemistry* **2014**, 57, (23), 10101-10111.

acetate/petroleum ether = 1/5, v/v) to afford the desired product **S2**.

To a solution of **S2** (1 mmol, 1.0 equiv) in dry DMF (4 mL) was added Tosyl isocyanate (1.1 mmol, 1.1 equiv) slowly. And the reaction mixture was stirred at room temperature for 30min, water (10 mL) was added. The organic layer was extracted with ethyl acetate (4×10 mL). The organic layers were combined and washed with brine (3×30 mL), filtered, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the desired product **3**.



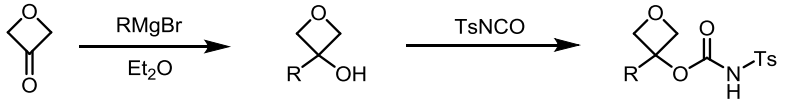
3a

This compound was prepared according to the general procedure A as a white soild (265 mg, 81% yield in 1 mmol scale)

R_f = 0.48, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.65 (d, *J* = 7.7 Hz, 2H), 4.47 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 2.10-1.93 (m, 2H), 1.33-1.18 (m, 2H), 1.19-1.05 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.95, 145.64, 135.80, 130.08, 128.63, 82.57, 80.43, 34.01, 25.36, 22.86, 22.08, 14.24.

HRMS (ESI) exact mass calcd for $C_{15}H_{22}NO_5S$ $[M+H]^+$: m/z 328.1214 $[M+H]^+$, found: m/z 328.1213.



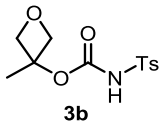
S1 **S2b-c, S2e-g, S2o-t** **S2b-c, S2e-g, S2o-t**

General procedure B[2]**:** To a solution of *Oxetan-3-one* (10 mmol, 1.0 equiv) in dry THF (10 mL) was added corresponding *Grignard reagent* 12 mL (1 M in Et_2O) slowly at 0℃ and the reaction mixture was warmed to room temperature. After stirred at this temperature for 2 h, saturated NH_4Cl (aq) (10 mL) was added. The organic

2. Yang W, Sun J. *Angew. Chem., Int. Ed.* **2016**, 55, 1868-1871.

layer was extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford the desired product **S2**.

To a solution of **S2** (1 mmol, 1.0 equiv) in dry DMF (4 mL) was added Tosyl isocyanate (1.1 mmol, 1.1 equiv) slowly. And the reaction mixture was stirred at room temperature for 30min, water (10 mL) was added. The organic layer was extracted with ethyl acetate (4×10 mL). The organic layers were combined and washed with brine (3×30 mL), filtered, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the desired product **3**.



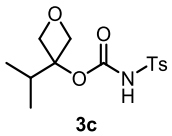
3b

This compound was prepared according to the general procedure B as a white soild (228 mg, 80% yield in 1 mmol scale)

R_f = 0.50, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.54 (d, *J* = 7.2 Hz, 2H), 4.35 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 1.58 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 150.22, 145.63, 137.68, 130.43, 128.81, 81.45, 79.42, 21.62, 21.52.

HRMS (ESI) exact mass calcd for $C_{12}H_{16}NO_5S$ $[M+H]^+$: m/z 286.0744 $[M+H]^+$, found: m/z 286.0744.



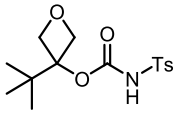
3c

This compound was prepared according to the general procedure B as a white soild (257 mg, 72% yield in 1 mmol scale)

R_f = 0.43, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 4.58-4.49 (m, 4H), 2.47 (s, 3H), 2.35-2.23 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, Acetone) δ 150.09, 145.60, 137.69, 130.43, 128.81, 85.41, 77.33, 31.26, 21.51, 16.39.

HRMS (ESI) exact mass calcd for $C_{14}H_{20}NO_5S$ $[M+H]^+$: m/z 314.1057 $[M+H]^+$, found: m/z 314.1057.



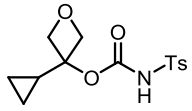
3d

This compound was prepared according to the general procedure A as a white soild (245 mg, 76% yield in 1 mmol scale)

R_f = 0.41, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.84-4.77 (m, 2H), 4.57-4.49 (m, 2H), 2.45 (s, 3H), 0.95 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.04, 145.32, 129.81, 128.35, 87.73, 76.34, 35.67, 24.24, 21.82.

HRMS (ESI) exact mass calcd for $C_{15}H_{22}NO_5S$ $[M+H]^+$: m/z 328.1213 $[M+H]^+$, found: m/z 328.1213.



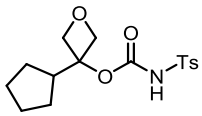
3e

This compound was prepared according to the general procedure B as a white soild (261 mg, 84% yield in 1 mmol scale)

R_f = 0.48, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 4.49 (d, *J* = 8.2 Hz, 2H), 4.25 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 1.46-1.34 (m, 1H), 0.57-0.52 (m, 2H), 0.51-0.46 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 150.34, 145.58, 137.77, 130.42, 128.82, 83.09, 78.28, 21.52, 14.10, 2.03.

HRMS (ESI) exact mass calcd for $C_{14}H_{18}NO_5S$ $[M+H]^+$: m/z 312.0904 $[M+H]^+$, found: m/z 312.0900.



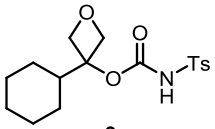
3f

This compound was prepared according to the general procedure B as a white soild (282 mg, 83% yield in 1 mmol scale)

R_f = 0.44, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.56 (d, *J* = 8.1 Hz, 2H), 4.46 (d, *J* = 8.3 Hz, 2H), 2.62-2.51 (m, 1H), 2.45 (s, 3H), 1.73-1.57 (m, 4H), 1.57-1.48 (m, 2H), 1.43-1.32 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 150.14, 145.58, 137.74, 130.42, 128.82, 84.77, 78.45, 42.68, 27.57, 26.38, 21.51.

HRMS (ESI) exact mass calcd for $C_{16}H_{22}NO_5S$ $[M+H]^+$: m/z 340.1211 $[M+H]^+$, found: m/z 340.1213.



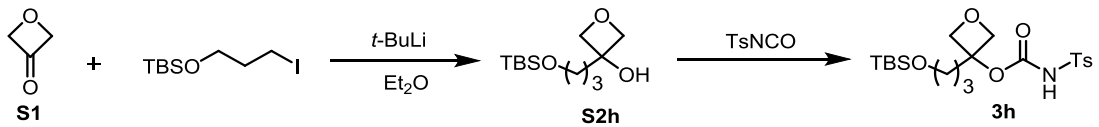
3g

This compound was prepared according to the general procedure B as a white soild (314 mg, 89% yield in 1 mmol scale)

R_f = 0.52, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.58-4.47 (m, 4H), 2.45 (s, 3H), 1.94-1.86 (m, 1H), 1.76-1.61 (m, 5H), 1.21-1.08 (m, 3H), 1.04-0.94 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 150.08, 145.58, 137.69, 130.43, 128.82, 84.96, 77.50, 41.47, 26.78, 26.72, 26.59, 21.52.

HRMS (ESI) exact mass calcd for $C_{17}H_{24}NO_5S$ $[M+H]^+$: m/z 354.1368 $[M+H]^+$, found: m/z 354.1370.



S1 **S2h** **3h**

General procedure to 3h[3]: To a solution of *tert*-butyl(3-iodopropoxy)dimethylsilane

3. Pan J, Chen T, Zhang Z, Li Y. *Chem. Commun.* **2016**, 52, 2382-2385.

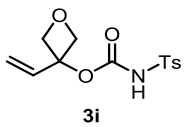
(4 mmol, 2.0 equiv) in dry Et_2O (8 mL) was added *t*-BuLi (3.0 mL, 1.3 M in pentane, 4 mmol, 2.0 equiv) slowly at -78℃, after stirring at this temperature for 30 min, *Oxetan-3-one* (2 mmol, 1.0 equiv) in dry Et_2O (5 mL) was added dropwise via syringe, and the reaction mixture was stirred at this temperature for 2 h. Saturated NH_4Cl (aq) (10 mL) was added. The organic layer was extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford the desired product **S2h**.

To a solution of **S2h** (1 mmol, 1.0 equiv) in dry DMF (4 mL) was added Tosyl isocyanate (1.1 mmol, 1.1 equiv) slowly. And the reaction mixture was stirred at room temperature for 30min, water (10 mL) was added. The organic layer was extracted with ethyl acetate (4×10 mL). The organic layers were combined and washed with brine (3×30 mL), filtered, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the desired product **3h**.

white soild (290 mg, 65%); R_f = 0.46, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.64 (d, *J* = 7.6 Hz, 2H), 4.55-4.38 (m, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 2.45 (s, 3H), 2.16-2.04 (m, 2H), 1.45-1.34 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.55, 145.42, 135.56, 129.86, 128.41, 82.33, 80.11, 62.35, 30.60, 26.46, 26.05, 21.85, 18.42, -5.20.

HRMS (ESI) exact mass calcd for $C_{20}H_{34}NO_6SSi$ $[M+H]^+$: m/z 444.1871 $[M+H]^+$, found: m/z 444.1871.



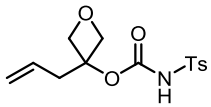
3i

This compound was prepared according to the general procedure B as a white soild (273 mg, 92% yield in 1 mmol scale)

R_f = 0.50, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.18-6.06 (m, 1H), 5.34-5.18 (m, 2H), 4.78-4.71 (m, 2H), 4.68-4.59 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.34, 145.27, 135.17, 134.22, 129.62, 128.17, 116.50, 80.51, 80.02, 21.60.

HRMS (ESI) exact mass calcd for $C_{13}H_{16}NO_5S$ $[M+H]^+$: m/z 298.0744 $[M+H]^+$, found: m/z 298.0744.



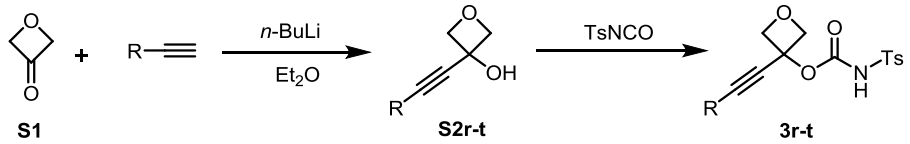
3j

This compound was prepared according to the general procedure B as a white soild (236 mg, 76% yield in 1 mmol scale)

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.71-5.57 (m, 1H), 5.06-4.94 (m, 2H), 4.54 (d, *J* = 7.8 Hz, 2H), 4.43 (d, *J* = 8.1 Hz, 2H), 2.76-2.70 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 150.02, 145.63, 137.59, 131.96, 130.42, 128.85, 119.63, 80.80, 79.68, 39.10, 21.51.

HRMS (ESI) exact mass calcd for $C_{14}H_{18}NO_5S$ $[M+H]^+$: m/z 312.0903 $[M+H]^+$, found: m/z 312.0900.



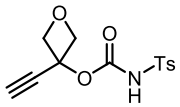
S1 **S2r-t** **3r-t**

General procedure C[4]**:** To a solution of corresponding *alkyne* (12 mmol, 1.2 equiv) in dry THF (10 mL) was added *n*-BuLi (12mmol, 1.2 equiv) slowly at -78℃, after stirring at this temperature for 1 h, *Oxetan-3-one* (10 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise via syringe, and the reaction mixture was stirred at this temperature for 2 h. Saturated NH_4Cl (aq) (10 mL) was added. The organic layer was

4. Wang Z, Chen Z, Sun J. *Angew. Chem., Int. Ed.* **2013**, 52, 6685-6688.

extracted with ethyl acetate (3×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford the desired product **S2**.

To a solution of **S2** (1 mmol, 1.0 equiv) in dry DMF (4 mL) was added Tosyl isocyanate (1.1 mmol, 1.1 equiv) slowly. And the reaction mixture was stirred at room temperature for 30min, water (10 mL) was added. The organic layer was extracted with ethyl acetate (4×10 mL). The organic layers were combined and washed with brine (3×30 mL), filtered, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the desired product **3**.



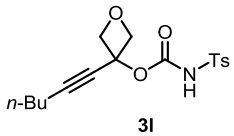
3k

This compound was prepared according to the general procedure C as a white soild (224 mg, 76% yield in 1 mmol scale)

R_f = 0.52, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.74-4.69 (m, 2H), 4.67-4.62 (m, 2H), 3.40 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 149.65, 145.82, 137.39, 130.50, 128.83, 81.31, 80.20, 78.02, 72.05, 21.53.

HRMS (ESI) exact mass calcd for $C_{13}H_{14}NO_5S$ $[M+H]^+$: m/z 296.0587 $[M+H]^+$, found: m/z 296.0587.



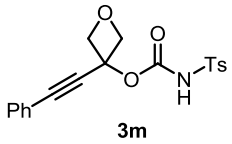
3l

This compound was prepared according to the general procedure C as a white soild (299 mg, 85% yield in 1 mmol scale)

R_f = 0.54, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.73-4.57 (m, 4H), 2.45 (s, 3H), 2.19 (t, *J* = 6.9 Hz, 2H), 1.40-1.31 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, Acetone) δ 148.85, 144.79, 136.65, 129.56, 127.97, 88.54, 81.00, 76.18, 71.92, 30.06, 21.46, 20.67, 17.69, 12.90.

HRMS (ESI) exact mass calcd for $C_{17}H_{22}NO_5S$ $[M+H]^+$: m/z 352.1214 $[M+H]^+$, found: m/z 352.1213.



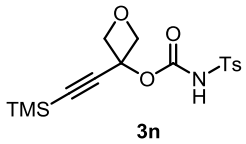
3m

This compound was prepared according to the general procedure C as a white soild (297 mg, 80% yield in 1 mmol scale)

R_f = 0.55, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.43-7.19 (m, 7H), 4.91 (d, *J* = 7.7 Hz, 2H), 4.80 (d, *J* = 7.6 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.68, 145.74, 135.73, 132.29, 130.11, 129.59, 128.74, 128.67, 121.66, 88.69, 83.95, 81.75, 73.30, 22.06.

HRMS (ESI) exact mass calcd for $C_{19}H_{18}NO_5S$ $[M+H]^+$: m/z 372.0903 $[M+H]^+$, found: m/z 372.0900.



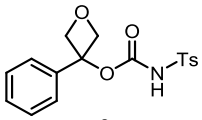
3n

This compound was prepared according to the general procedure C as a white soild (320 mg, 87% yield in 1 mmol scale)

R_f = 0.55, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.73-4.64 (m, 4H), 2.45 (s, 3H), 0.09 (s, 9H).

^{13}C NMR (126 MHz, Acetone) δ 149.63, 145.73, 137.48, 130.46, 128.87, 101.43, 93.29, 81.47, 72.46, 21.56, -0.44.

HRMS (ESI) exact mass calcd for $C_{16}H_{22}NO_5SSi$ $[M+H]^+$: m/z 368.0983 $[M+H]^+$, found: m/z 368.0982.



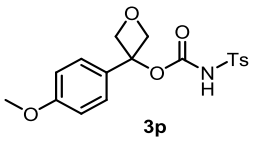
3o

This compound was prepared according to the general procedure B as a white soild (323 mg, 93% yield in 1 mmol scale)

R_f = 0.43, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.35-7.27 (m, 7H), δ 4.95 (d, *J* = 8.3 Hz, 2H), 4.87 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.67, 145.43, 138.21, 135.60, 129.86, 128.86, 128.57, 128.39, 124.68, 82.09, 81.62, 21.82.

HRMS (ESI) exact mass calcd for $C_{17}H_{18}NO_5S$ $[M+H]^+$: m/z 348.0901 $[M+H]^+$, found: m/z 348.0901.



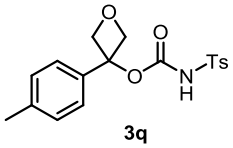
3p

This compound was prepared according to the general procedure B as a white soild (306 mg, 81% yield in 1 mmol scale)

R_f = 0.45, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.30-7.22 (m, 2H), 6.91-6.84 (m, 2H), 4.88-4.85 (m, 2H), 4.80-4.76 (m, 2H), 3.79 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 160.46, 149.94, 145.65, 137.61, 131.84, 130.46, 128.82, 127.23, 114.63, 81.98, 81.71, 55.58, 21.52.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_6S$ $[M+H]^+$: m/z 378.1009 $[M+H]^+$, found: m/z 378.1006.



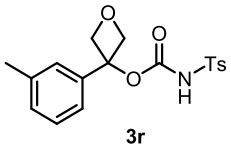
3q

This compound was prepared according to the general procedure B as a white soild (307 mg, 85% yield in 1 mmol scale)

R_f = 0.43, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.19-7.07 (m, 4H), 4.79 (d, *J* = 7.6 Hz, 2H), 4.74 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 149.26, 144.30, 137.42, 136.26, 135.84, 129.64, 129.02, 127.37, 124.35, 80.51, 80.46, 21.03, 20.55.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$: m/z 362.1059 $[M+H]^+$, found: m/z 362.1057.



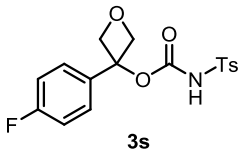
3r

This compound was prepared according to the general procedure B as a white soild (278 mg, 77% yield in 1 mmol scale)

R_f = 0.43, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.25-7.18 (m, 1H), 7.15-7.10 (m, 3H), 4.94-4.84 (m, 2H), 4.82-4.72 (m, 2H), 2.45 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 149.91, 145.68, 140.03, 138.99, 137.59, 130.48, 129.60, 129.34, 128.85, 125.84, 122.41, 81.97, 81.86, 21.53, 21.44.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$: m/z 362.1057 $[M+H]^+$, found: m/z 362.1057.



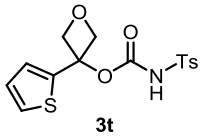
3s

This compound was prepared according to the general procedure B as a white soild (259 mg, 71% yield in 1 mmol scale)

R_f = 0.46, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.42-7.36 (m, 2H), 7.14-7.08 (m, 2H), 4.88 (d, *J* = 8.4 Hz, 2H), 4.79 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 163.23 (d, *J* = 245.6 Hz), 149.95, 145.77, 137.53, 136.22 (d, *J* = 3.2 Hz), 130.49, 128.84, 127.92 (d, *J* = 8.3 Hz), 116.12 (d, *J* = 21.8 Hz), 81.61, 81.57, 21.51.

HRMS (ESI) exact mass calcd for $C_{17}H_{17}FNO_5S$ $[M+H]^+$: m/z 366.0806 $[M+H]^+$, found: m/z 366.0806.



3t

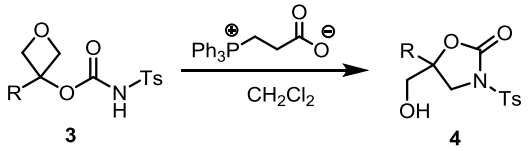
This compound was prepared according to the general procedure B as a white soild (307 mg, 87% yield in 1 mmol scale)

R_f = 0.51, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.46-7.40 (m, 3H), 7.15-7.12 (m, 1H), 7.00-6.96 (m, 1H), 4.91 (d, *J* = 8.3 Hz, 2H), 4.80 (d, *J* = 8.3 Hz, 2H), 2.44 (s, 3H).

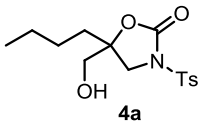
^{13}C NMR (126 MHz, Acetone) δ 149.92, 145.71, 143.28, 137.53, 130.46, 128.83, 127.78, 126.97, 126.29, 82.16, 79.72, 21.53.

HRMS (ESI) exact mass calcd for $C_{15}H_{16}NO_5S_2$ $[M+H]^+$: m/z 354.0465 $[M+H]^+$, found: m/z 354.0464.

4. General procedure for the ring opening of oxetane



General procedure D: To a solution of corresponding *oxetone* (0.1 mmol, 1.0 equiv) in dry CH_2Cl_2 (1 mL) was added catalyst **C1** (0.01 mmol, 0.1 equiv) at room temperture. The reaction mixture was stirred until all starting material was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the product.

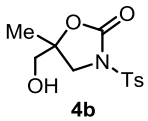


4a

This compound was prepared according to the general procedure D as a white solid (31.7 mg, 97% yield in 0.1 mmol scale).

Rf = 0.49, Petroleum ether/EtOAc = 1:1; 1H NMR (500 MHz, Acetone) δ 7.93 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 4.47 (t, J = 5.9 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.85 (d, J = 9.2 Hz, 1H), 3.65 (dd, J = 12.1, 5.4 Hz, 1H), 3.56 (dd, J = 12.1, 6.3 Hz, 1H), 2.46 (s, 3H), 1.74-1.61 (m, 2H), 1.36-1.17 (m, 4H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 152.14, 146.29, 135.92, 130.57, 128.91, 83.96, 65.77, 50.28, 35.62, 25.12, 23.44, 21.55, 14.11.

HRMS (ESI) exact mass calcd for $C_{15}H_{22}NO_5S$ $[M+H]^+$: m/z 328.1214 $[M+H]^+$, found: m/z 328.1213.



4b

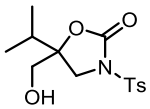
This compound was prepared according to the general procedure D as a white solid (26 mg, 91% yield in 0.1 mmol scale).

R_f = 0.50, Petroleum ether/EtOAc = 1:1; ^1H NMR (500 MHz, Acetone) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.47 (t, *J* = 5.9 Hz, 1H), 4.13 (d, *J* = 9.2 Hz,

1H), 3.85 (d, *J* = 9.2 Hz, 1H), 3.65 (dd, *J* = 12.1, 5.4 Hz, 1H), 3.56 (dd, *J* = 12.1, 6.3 Hz, 1H), 2.46 (s, 3H), 1.74-1.61 (m, 2H), 1.36-1.17 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Acetone) δ 206.31, 206.16, 206.00, 152.14, 146.29, 135.92, 130.57, 128.91, 83.96, 65.77, 50.28, 35.62, 25.12, 23.44, 21.55, 14.11.

HRMS (ESI) exact mass calcd for $C_{12}H_{16}NO_5S$ $[M+H]^+$: m/z 286.0744 $[M+H]^+$, found: m/z 286.0744.



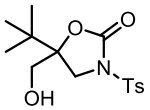
4c

This compound was prepared according to the general procedure D as a white solid (26 mg, 84% yield in 0.1 mmol scale).

R_f = 0.47, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 4.45-4.36 (m, 1H), 4.06 (d, *J* = 9.3 Hz, 1H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.77-3.69 (m, 1H), 3.67-3.58 (m, 1H), 2.45 (s, 3H), 2.09-1.98 (m, 1H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, Acetone) δ 152.19, 146.25, 136.03, 130.53, 128.92, 64.55, 48.27, 33.53, 21.55, 16.39, 16.11.

HRMS (ESI) exact mass calcd for $C_{14}H_{20}NO_5S$ $[M+H]^+$: m/z 314.1057 $[M+H]^+$, found: m/z 314.1057.



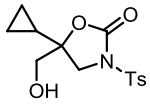
4d

This compound was prepared according to the general procedure D as a white solid (27 mg, 82% yield in 0.1 mmol scale).

R_f = 0.48, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.05 (d, *J* = 9.2 Hz, 1H), 3.94 (d, *J* = 9.3 Hz, 1H), 3.92-3.86 (m, 1H), 3.55-3.47 (m, 1H), 2.43 (s, 3H), 0.93 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.10, 145.62, 134.60, 129.87, 128.28, 87.41, 63.02, 46.79, 36.26, 24.44, 21.86.

HRMS (ESI) exact mass calcd for $C_{15}H_{22}NO_5S$ $[M+H]^+$: m/z 328.1216 $[M+H]^+$, found: m/z 328.1213.



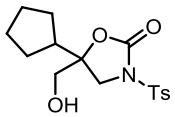
4e

This compound was prepared according to the general procedure D as a white solid (25 mg, 81% yield in 0.1 mmol scale).

R_f = 0.51, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 4.61-4.42 (m, 1H), 4.18 (d, *J* = 9.2 Hz, 1H), 3.75 (d, *J* = 9.2 Hz, 1H), 3.73-3.70 (m, 1H), 3.66-3.60 (m, 1H), 2.46 (s, 3H), 1.21-1.14 (m, 1H), 0.52-0.45 (m, 2H), 0.45-0.37 (m, 1H), 0.30-0.19 (m, 1H).

^{13}C NMR (126 MHz, Acetone) δ 152.17, 146.46, 135.96, 130.70, 129.00, 83.04, 66.28, 50.29, 21.67, 15.96, 0.69, -0.18.

HRMS (ESI) exact mass calcd for $C_{14}H_{18}NO_5S$ $[M+H]^+$: m/z 312.0900 $[M+H]^+$, found: m/z 312.0900.



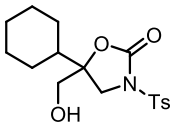
4f

This compound was prepared according to the general procedure D as a white solid (25 mg, 74% yield in 0.1 mmol scale).

R_f = 0.48, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.55-4.39 (m, 1H), 4.13 (d, *J* = 9.2 Hz, 1H), 3.83 (d, *J* = 9.2 Hz, 1H), 3.76-3.65 (m, 1H), 3.63-3.50 (m, 1H), 2.45 (s, 3H), 2.32-2.18 (m, 1H), 1.77-1.63 (m, 2H), 1.63-1.46 (m, 4H), 1.34-1.11 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 152.41, 146.43, 136.13, 130.69, 129.04, 85.82, 66.01, 49.15, 45.08, 27.00, 26.93, 26.22, 26.13, 21.69.

HRMS (ESI) exact mass calcd for $C_{16}H_{22}NO_5S$ $[M+H]^+$: m/z 340.1213 $[M+H]^+$, found: m/z 340.1213.



4g

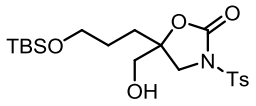
This compound was prepared according to the general procedure D as a white solid

(31 mg, 88% yield in 0.1 mmol scale).

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 4.44-4.28 (m, 1H), 4.04 (d, *J* = 9.3 Hz, 1H), 3.92 (d, *J* = 9.2 Hz, 1H), 3.75-3.67 (m, 1H), 3.66-3.59 (m, 1H), 2.45 (s, 3H), 1.76-1.70 (m, 3H), 1.68-1.61 (m, 3H), 1.27-1.12 (m, 3H), 1.09-0.95 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 152.34, 146.39, 136.19, 130.67, 129.09, 86.00, 64.58, 48.84, 43.88, 26.93, 26.84, 26.82, 26.78, 26.54, 21.70.

HRMS (ESI) exact mass calcd for $C_{17}H_{24}NO_5S$ $[M+H]^+$: m/z 354.1372 $[M+H]^+$, found: m/z 354.1370.



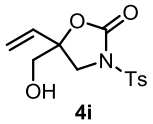
4h

This compound was prepared according to the general procedure D as a white solid (39 mg, 87% yield in 0.1 mmol scale).

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 4.54-4.46 (m, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.72-3.50 (m, 4H), 2.45 (s, 3H), 1.85-1.73 (m, 2H), 1.57-1.39 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (126 MHz, Acetone) δ 152.06, 146.25, 135.88, 130.55, 128.90, 83.87, 65.74, 63.19, 50.43, 32.42, 26.56, 26.26, 21.57, 18.76, -5.21.

HRMS (ESI) exact mass calcd for $C_{20}H_{34}NO_6SSi$ $[M+H]^+$: m/z 444.1875 $[M+H]^+$, found: m/z 444.1871.



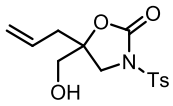
4i

This compound was prepared according to the general procedure D as a white solid (22 mg, 73% yield in 0.1 mmol scale).

R_f = 0.56, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.09-5.94 (m, 1H), 5.45-5.27 (m, 2H), 4.67-4.55 (m, 1H), 4.28 (d, *J* = 9.1 Hz, 1H), 3.95 (d, *J* = 9.1 Hz, 1H), 3.73-3.58 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.84, 146.43, 136.37, 135.77, 130.62, 129.01, 117.31, 83.35, 65.54, 50.99, 21.57.

HRMS (ESI) exact mass calcd for $C_{13}H_{16}NO_5S$ $[M+H]^+$: m/z 298.0744 $[M+H]^+$, found: m/z 298.0744.



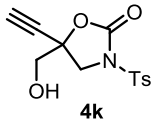
4j

This compound was prepared according to the general procedure D as a white solid (27 mg, 87% yield in 0.1 mmol scale).

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 5.74-5.61 (m, 1H), 5.24-5.17 (m, 1H), 5.12-5.05 (m, 1H), 4.55-4.48 (m, 1H), 4.10 (d, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 9.2 Hz, 1H), 3.67 (dd, *J* = 12.1, 5.5 Hz, 1H), 3.58 (dd, *J* = 12.1, 6.4 Hz, 1H), 2.53-2.39 (m, 5H).

^{13}C NMR (126 MHz, Acetone) δ 152.10, 146.41, 136.05, 131.32, 130.65, 129.06, 121.19, 83.20, 65.95, 49.81, 40.06, 21.66.

HRMS (ESI) exact mass calcd for $C_{14}H_{18}NO_5S$ $[M+H]^+$: m/z 312.0900 $[M+H]^+$, found: m/z 312.0900.



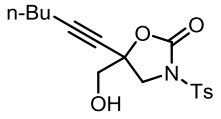
4k

This compound was prepared according to the general procedure D as a white solid (22 mg, 75% yield in 0.1 mmol scale).

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.97-4.84 (m, 1H), 4.39 (d, *J* = 9.2 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 3.91-3.83 (m, 1H), 3.79-3.70 (m, 1H), 3.48 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.21, 146.70, 135.47, 130.70, 129.08, 79.95, 79.05, 76.35, 66.18, 52.19, 21.58.

HRMS (ESI) exact mass calcd for $C_{13}H_{14}NO_5S$ $[M+H]^+$: m/z 296.0589 $[M+H]^+$, found: m/z 296.0587.



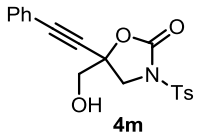
4l

This compound was prepared according to the general procedure D as a white solid (32 mg, 91% yield in 0.1 mmol scale).

R_f = 0.49, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.25 (d, *J* = 9.0 Hz, 1H), 4.05 (d, *J* = 9.1 Hz, 1H), 3.83 (d, *J* = 12.6 Hz, 1H), 3.57 (d, *J* = 12.6 Hz, 1H), 2.45 (s, 3H), 2.22 (t, *J* = 7.1 Hz, 2H), 1.52-1.44 (m, 2H), 1.42-1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.35, 145.12, 133.46, 129.23, 127.64, 90.78, 75.32, 74.26, 65.53, 51.20, 29.39, 21.26, 21.11, 17.69, 12.88.

HRMS (ESI) exact mass calcd for $C_{17}H_{22}NO_5S$ $[M+H]^+$: m/z 352.1213 $[M+H]^+$, found: m/z 352.1213.



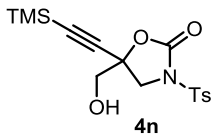
4m

This compound was prepared according to the general procedure D as a white solid (25 mg, 68% yield in 0.1 mmol scale).

R_f = 0.47, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.52-7.39 (m, 7H), 5.02-4.93 (m, 1H), 4.47 (d, *J* = 9.3 Hz, 1H), 4.29 (d, *J* = 9.3 Hz, 1H), 4.01-3.92 (m, 1H), 3.88-3.81 (m, 1H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.38, 146.66, 135.57, 132.77, 130.70, 130.51, 129.51, 129.08, 121.82, 88.94, 85.01, 77.18, 66.30, 52.44, 21.58.

HRMS (ESI) exact mass calcd for $C_{19}H_{18}NO_5S$ $[M+H]^+$: m/z 372.0901 $[M+H]^+$, found: m/z 372.0900.



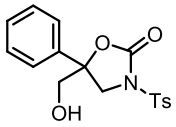
4n

This compound was prepared according to the general procedure D as a white solid (27 mg, 73% yield in 0.1 mmol scale).

R_f = 0.47, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 4.96-4.79 (m, 1H), 4.38 (d, *J* = 9.2 Hz, 1H), 4.13 (d, *J* = 9.2 Hz, 1H), 3.93-3.78 (m, 1H), 3.78-3.64 (m, 1H), 2.46 (s, 3H), 0.17 (s, 9H).

^{13}C NMR (126 MHz, Acetone) δ 151.27, 146.65, 135.56, 130.69, 129.05, 100.96, 94.76, 76.67, 66.23, 52.31, 21.58, -0.49.

HRMS (ESI) exact mass calcd for $C_{16}H_{22}NO_5SSi$ $[M+H]^+$: m/z 368.0982 $[M+H]^+$, found: m/z 368.0982.



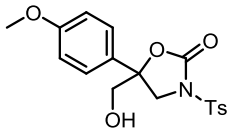
4o

This compound was prepared according to the general procedure D as a white solid (30 mg, 88% yield in 0.1 mmol scale).

R_f = 0.53, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.46-7.35 (m, 7H), 4.79-4.75 (m, 1H), 4.66 (d, *J* = 9.2 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 3.84-3.74 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.77, 146.41, 140.25, 135.66, 130.58, 129.57, 129.36, 128.95, 125.54, 84.71, 68.03, 52.87, 21.55.

HRMS (ESI) exact mass calcd for $C_{17}H_{18}NO_5S$ $[M+H]^+$: m/z 348.0900 $[M+H]^+$, found: m/z 348.0900.



4p

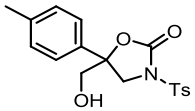
This compound was prepared according to the general procedure D as a white solid (32 mg, 84% yield in 0.1 mmol scale).

R_f = 0.54, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.31-7.26 (m, 2H), 6.99-6.92 (m, 1H),

5.73-5.55 (m, 1H), 4.51 (d, *J* = 9.3 Hz, 1H), 4.09 (d, *J* = 9.3 Hz, 1H), 3.76 (s, 3H), 3.60 (dd, *J* = 12.3, 6.0 Hz, 1H), 3.53 (dd, *J* = 12.3, 5.5 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, DMSO) δ 159.23, 150.81, 145.48, 133.86, 130.67, 129.89, 127.72, 126.05, 113.99, 84.02, 66.32, 55.17, 51.74, 21.10.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_6S$ $[M+H]^+$: m/z 378.1002 $[M+H]^+$, found: m/z 378.1006.



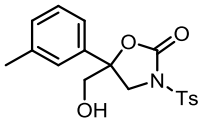
4q

This compound was prepared according to the general procedure D as a white solid (32 mg, 88% yield in 0.1 mmol scale).

R_f = 0.52, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21-7.14 (m, 4H), 4.54 (d, *J* = 8.9 Hz, 1H), 4.12 (d, *J* = 8.9 Hz, 1H), 3.78 (d, *J* = 12.7 Hz, 1H), 3.65 (d, *J* = 12.7 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.52, 145.76, 139.03, 135.26, 134.25, 129.94, 129.73, 128.31, 124.50, 83.89, 67.89, 52.17, 21.82, 21.20.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$: m/z 362.1057 $[M+H]^+$, found: m/z 362.1057.



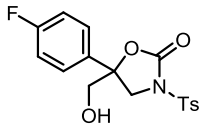
4r

This compound was prepared according to the general procedure D as a white solid (30 mg, 83% yield in 0.1 mmol scale).

R_f = 0.53, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.33-7.26 (m, 1H), 7.24-7.16 (m, 3H), 4.80-4.73 (m, 1H), 4.64 (d, *J* = 9.2 Hz, 1H), 4.17 (d, *J* = 9.2 Hz, 1H), 3.84-3.71 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.81, 146.40, 140.26, 139.29, 135.67, 130.58, 130.02, 129.49, 128.95, 126.09, 122.58, 84.75, 68.05, 52.90, 21.55, 21.44.

HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$: m/z 362.1057 $[M+H]^+$, found: m/z 362.1057.



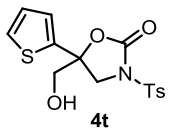
4s

This compound was prepared according to the general procedure D as a white solid (30 mg, 82% yield in 0.1 mmol scale).

R_f = 0.53, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.50-7.45 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.23-7.15 (m, 2H), 4.87-4.73 (m, 1H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.19 (d, *J* = 9.3 Hz, 1H), 3.88-3.72 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 163.49 (d, *J* = 245.7 Hz), 151.66, 146.47, 136.40 (d, *J* = 3.2 Hz), 135.64, 130.60, 128.97, 127.95 (d, *J* = 8.5 Hz), 116.32 (d, *J* = 21.9 Hz), 84.38, 67.94, 52.87, 21.55.

HRMS (ESI) exact mass calcd for $C_{17}H_{17}FNO_5S$ $[M+H]^+$: m/z 366.0807 $[M+H]^+$, found: m/z 366.0806.



4t

This compound was prepared according to the general procedure D as a white solid (24 mg, 69% yield in 0.1 mmol scale).

R_f = 0.51, Petroleum ether/EtOAc = 1:1; ^{1}H NMR (500 MHz, Acetone) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.55-7.51 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.25-7.21 (m, 1H), 7.10-7.06 (m, 1H), 4.96-4.86 (m, 1H), 4.60 (d, *J* = 9.4 Hz, 1H), 4.28 (d, *J* = 9.4 Hz, 1H), 4.00-3.92 (m, 1H), 3.92-3.83 (m, 1H), 2.45 (s, 3H).

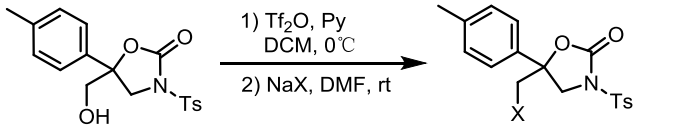
^{13}C NMR (126 MHz, Acetone) δ 151.43, 146.57, 142.70, 135.52, 130.65, 128.99, 128.24, 127.26, 125.90, 83.02, 67.21, 53.18, 21.57.

HRMS (ESI) exact mass calcd for $C_{15}H_{16}NO_5S_2$ $[M+H]^+$: m/z 354.0464 $[M+H]^+$, found: m/z 354.0464.

5. Derivatization of the oxazolidin-2-one poduct.

Gram scale synthesis of 4g, 4n, 4q

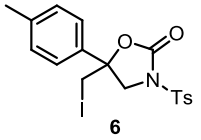
To a solution of corresponding *oxetone* (2.8 mmol, 1.0 equiv) in dry CH_2Cl_2 (28 mL) was added catalyst **C1** (0.28 mmol, 0.1 equiv) at room temperture. The reaction mixture was stirred until all starting material was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3 to 1/1, v/v) to afford the product **4**.



4q

6: X= I, 75% (2 steps)
7: X= N_3, 80% (2 steps)

General procedure E: To a solution of 4q (0.1 mmol, 1.0 equiv) in dry DCM (1 mL) was added pyridine (0.12 mmol, 1.2 equiv), and the mixture was cooled to 0℃. Then the Trifluoromethanesulfonic anhydride (0.12 mmol, 1.2 equiv) was added slowly. The mixture was stirred at the same temperature for 2 h to complete the reaction. The mixture was washed with HCl (1 N, 2×5 mL), water (3×5 mL), dried over Na_2SO_4, and concentrated in vacuo to afford the triflate which was used without further purification in the next step. The above triflate was taken in a 10 mL round bottomed flask which was charged with DMF (1 mL) and then cooled to 0 ℃. To this solution, NaX (0.15 mmol, 1.5 equiv) was added. The mixture was stirred at room temperature for 3 h. Water (3 mL) was added. The organic layer was extracted with ethyl acetate (4×5 mL). The organic layers were combined and washed with brine (3×5 mL), filtered, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the desired product.



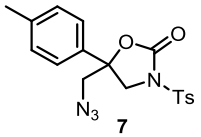
6

This compound was prepared according to the general procedure E as a Light yellow solid (19 mg, 75% two steps)

R_f = 0.49, Petroleum ether/EtOAc = 3:1; 1H NMR (500 MHz, Acetone) δ 7.93-7.87 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37-7.32 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.60-4.48 (m, 1H), 4.46-4.31 (m, 1H), 4.03-3.93 (m, 1H), 3.83-3.71 (m, 1H), 2.44 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.08, 146.90, 139.80, 137.53, 135.45, 130.85, 130.45, 129.21, 125.56, 81.68, 56.32, 21.71, 21.18, 14.68.

HRMS (ESI) exact mass calcd for $C_{18}H_{19}INO_4S$ $[M+H]^+$: m/z 472.0072 $[M+H]^+$, found: m/z 472.0074.



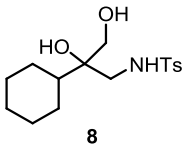
7

This compound was prepared according to the general procedure E as a white solid (31 mg, 80% two steps)

R_f = 0.57, Petroleum ether/EtOAc = 3:1; ^{1}H NMR (500 MHz, Acetone) δ 7.93-7.89 (m, 2H), 7.49-7.43 (m, 2H), 7.34-7.30 (m, 2H), 7.28-7.24 (m, 2H), 4.55 (d, *J* = 9.7 Hz, 1H), 4.22 (d, *J* = 9.7 Hz, 1H), 3.93-3.81 (m, 2H), 2.45 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, Acetone) δ 151.33, 146.82, 139.77, 136.96, 135.45, 130.77, 130.47, 129.10, 125.50, 83.33, 58.93, 54.08, 21.69, 21.16.

HRMS (ESI) exact mass calcd for $C_{18}H_{19}N_4O_4S$ $[M+H]^+$: m/z 387.1122 $[M+H]^+$, found: m/z 387.1122.



8

8 was synthesized according to literature with little modification[5]. To a solution of **4g** (0.2 mmol, 1.0 equiv) in THF (3 mL) and water (1 mL) was added lithium hydroxide (0.4 mmol, 2.0 equiv) at room temperature. The mixture was stirred for 4 h. After addition of saturated NH_4Cl solution (4 mL), the reaction mixture was extracted with ethyl acetate(3×4 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) to

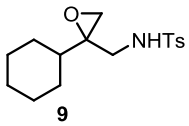
5. Shen Z, Lu X, Lei A. *Tetrahedron* **2006**, 62, 9237-9246.

give compound **8** as white solid (47 mg, 72%).

R_f = 0.55, Petroleum ether/EtOAc = 1:2; ^{1}H NMR (500 MHz, Acetone) δ 7.85-7.68 (m, 2H), 7.48-7.33 (m, 2H), 6.20-6.04 (m, 1H), 3.85-3.70 (m, 1H), 3.59-3.49 (m, 2H), 3.33 (s, 1H), 3.07-2.92 (m, 2H), 2.42 (s, 3H), 1.82-1.68 (m, 4H), 1.64-1.55 (m, 2H), 1.24-1.03 (m, 5H).

^{13}C NMR (126 MHz, Acetone) δ 143.89, 138.79, 130.49, 127.94, 75.09, 65.03, 47.71, 42.97, 27.62, 27.58, 27.41, 27.30, 27.21, 21.46.

HRMS (ESI) exact mass calcd for $C_{16}H_{26}NO_4S$ $[M+H]^+$: m/z 328.1577 $[M+H]^+$, found: m/z 328.1577.



9

9 was synthesized according to literature with little modification[6]. To a solution of Ph_3P (0.15 mmol, 1.5 equiv) in THF (2 mL) was added diethyl azodicarboxylate (0.15 mmol, 1.5 equiv) slowly at room temperature. After stirring at this temperature for 10 min, compound **8** (0.1 mmol, 1.0 equiv) in dry THF (0.5 mL) was added dropwise via syringe, and warm to 60℃. After the starting material was consumed as judged by TLC, the reaction mixture was rinsed through a pad of silica gel with Et_2O, evaporated and finally purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) the title compound **9** was obtained as yellow oil (24 mg, 78%).

R_f = 0.51, Petroleum ether/EtOAc = 3:1; ^{1}H NMR (500 MHz, Acetone) δ 7.77-7.73 (m, 2H), 7.42-7.37 (m, 2H), 6.40 (t, *J* = 6.6 Hz, 1H), 3.19-3.10 (m, 1H), 3.06-2.99 (m, 1H), 2.65-2.56 (m, 2H), 2.42 (s, 3H), 1.76-1.53 (m, 6H), 1.28-1.08 (m, 3H), 1.04-0.92 (m, 2H).

^{13}C NMR (126 MHz, Acetone) δ 143.91, 139.16, 130.50, 127.87, 61.10, 49.18, 45.96, 40.12, 29.31, 28.19, 26.98, 26.94, 26.91, 21.47.

HRMS (ESI) exact mass calcd for $C_{16}H_{24}NO_3S$ $[M+H]^+$: m/z 310.1473 $[M+H]^+$, found: m/z 310.1471.

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6. Enders D, Gries J. *Synthesis* **2005**, 2005, 3508-3516.

6. Mechanism study of intramolecular ring opening of oxetanes

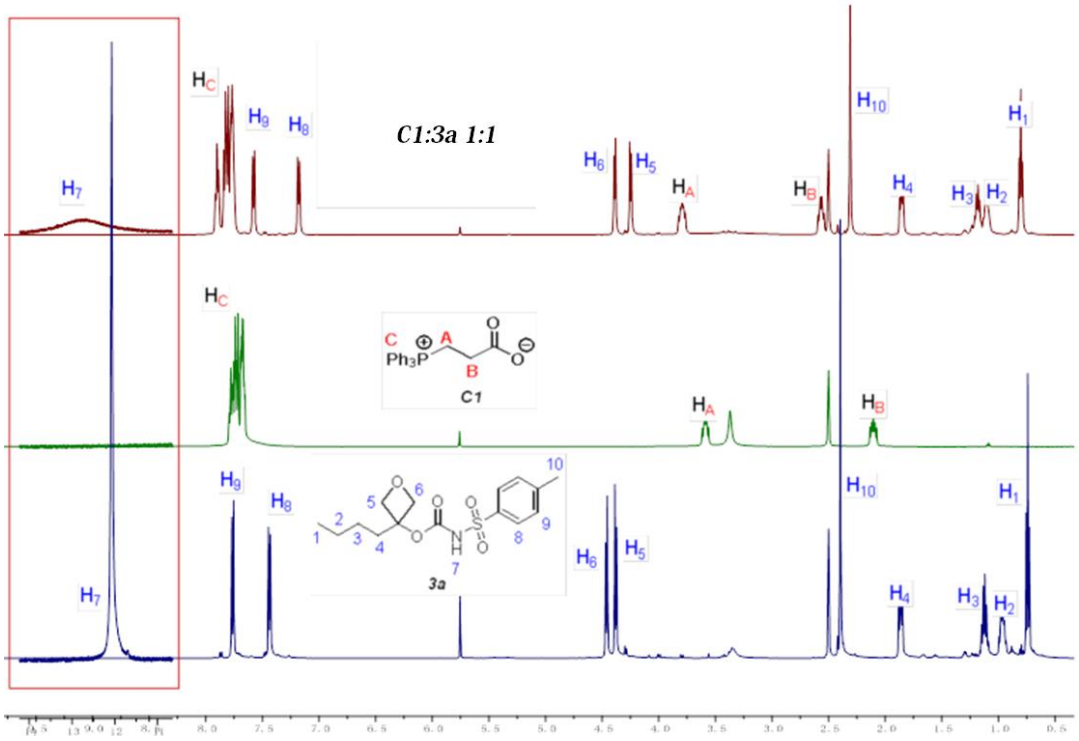


Figure S1. NMR spectrum of 1:1 mixture of oxetane 3a and carboxylate phosphabetaine C1, oxetane 3a and carboxylate phosphabetaine C1

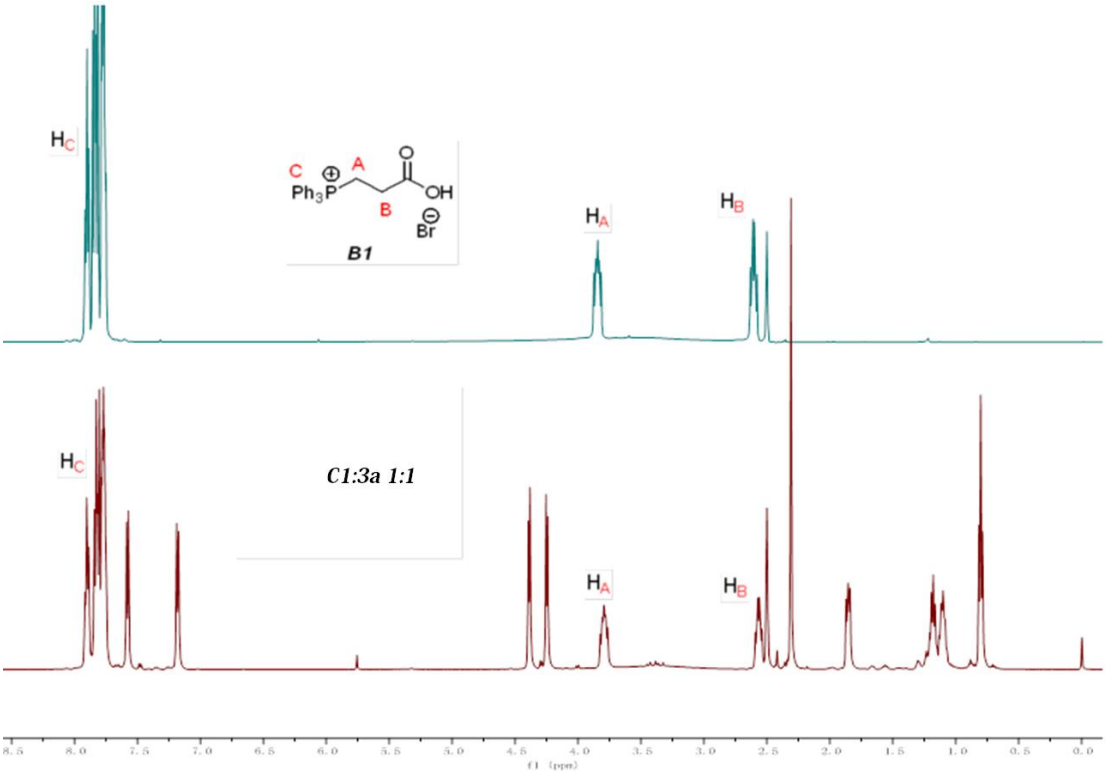
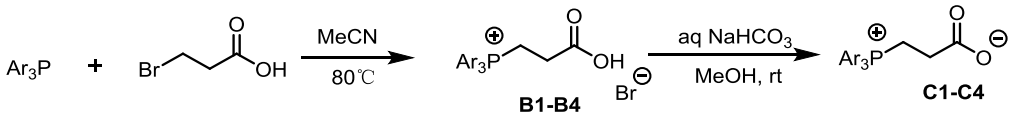


Figure S2. NMR spectrum of B1 and 1:1 mixture of oxetane 3a and carboxylate phosphabetaine C1

7. Preparation of catalyst

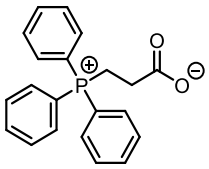
Catalysts C5[7] was prepared according to literature.

C6 was purchased from commercial source



General procedure for the synthesis of catalysts (C1-C4)[8-9]: To a solution of 3-bromopropionic acid (5.0 mmol, 1.0 equiv) in acetonitrile (50 mL) was added corresponding triphenylphosphine (5.0 mmol, 1.0 equiv). The resulting mixture was stirred at 80 ℃ for 24 h and then concentrated in vacuo. The residue was taken up with a minimal amount of chloroform and the product was precipitated from diethyl ether. The white precipitate was filtered and recrystallized from acetonitrile to give the title compound **B** as a colorless solid.

All of the **B** was dissolved in methanol (25 mL) was added a solution of $NaHCO_3$ (6 mmol, 1.2 equiv) in water (10 ml). The resulting mixture was stirred at room temperature for 30 min and then concentrated in vacuo. The residue was taken up with a minimal amount of chloroform, dried over Na_2SO_4, filtered, and concentrated. and the residue was dissolved with chloroform again and the product **3** precipitated from diethyl ether.



C1

Catalyst **C1** was prepared according to the General procedure, **C1** was synthesized from commercial available triphenylphosphine as a white solid (1.34 g, 80%).

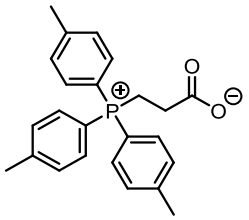
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.72 (m, 3H), 7.70-7.58 (m, 12H), 3.61-3.51 (m, 2H), 2.64-2.51 (m, 2H).

---

7. Yu C, Liu B, Hu L. *Journal of Organic Chemistry* **2001**, 66, (16), 5413-5418.
8. Ahmed R, Altieri A, D Souza D M, Leigh D A. *Journal of the American Chemical Society* **2011**, 133, (31), 12304-12310.
9. Aly A A M, Schmidbaur H. *Z. Naturforsch*, 1991, 46, 775.

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.35, 134.98 (d, *J* = 3.0 Hz), 133.40 (d, *J* = 9.8 Hz), 130.47 (d, *J* = 12.4 Hz), 119.49 (d, *J* = 86.7 Hz), 29.99 (d, *J* = 5.0 Hz), 20.92 (d, *J* = 51.7 Hz).

^{31}P NMR (202 MHz, $CDCl_3$) δ 24.02.



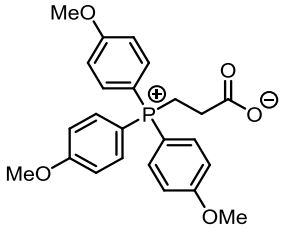
C2

Catalyst **C2** was prepared according to the General procedure, **C2** was synthesized from commercial available *tri*-p-tolylphosphine as a white solid (1.6 g, 83%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.67-7.60 (m, 6H), 7.56-7.50 (m, 6H), 3.58-3.49 (m, 2H), 2.42 (s, 9H), 2.15-2.03 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 172.52, 145.67 (d, *J* = 3.1 Hz), 133.79 (d, *J* = 10.2 Hz), 131.12 (d, *J* = 12.7 Hz), 116.74 (d, *J* = 88.2 Hz), 30.20 (d, *J* = 4.8 Hz), 19.21 (d, *J* = 51.7 Hz).

^{31}P NMR (202 MHz, DMSO) δ 23.40.



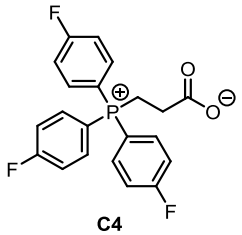
C3

Catalyst **C3** was prepared according to the General procedure, **C3** was synthesized from commercial available tris (4-methoxyphenyl) phosphine as a white solid (1.5 g, 70%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73-7.55 (m, 6H), 7.31-7.17 (m, 6H), 3.86 (s, 9H), 3.50-3.44 (m, 2H), 2.32-2.10 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 175.15, 164.35 (d, *J* = 2.9 Hz), 135.85 (d, *J* = 11.5 Hz), 116.35 (d, *J* = 13.5 Hz), 110.01 (d, *J* = 93.6 Hz), 56.45, 29.66, 19.25 (d, *J* = 52.7 Hz).

^{31}P NMR (202 MHz, DMSO) δ 22.21.



C4

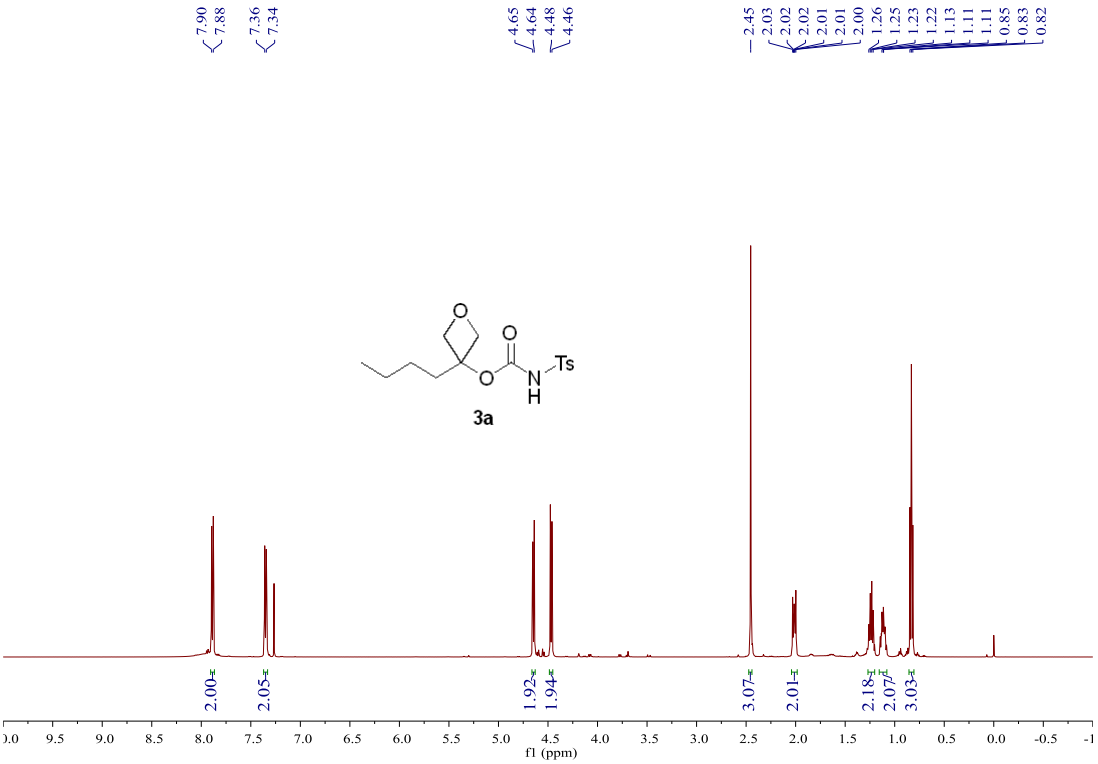
Catalyst **C4** was prepared according to the General procedure, **C4** was synthesized from commercial available Tris (4-fluorophenyl) phosphine as a white solid (1.4 g, 71%).

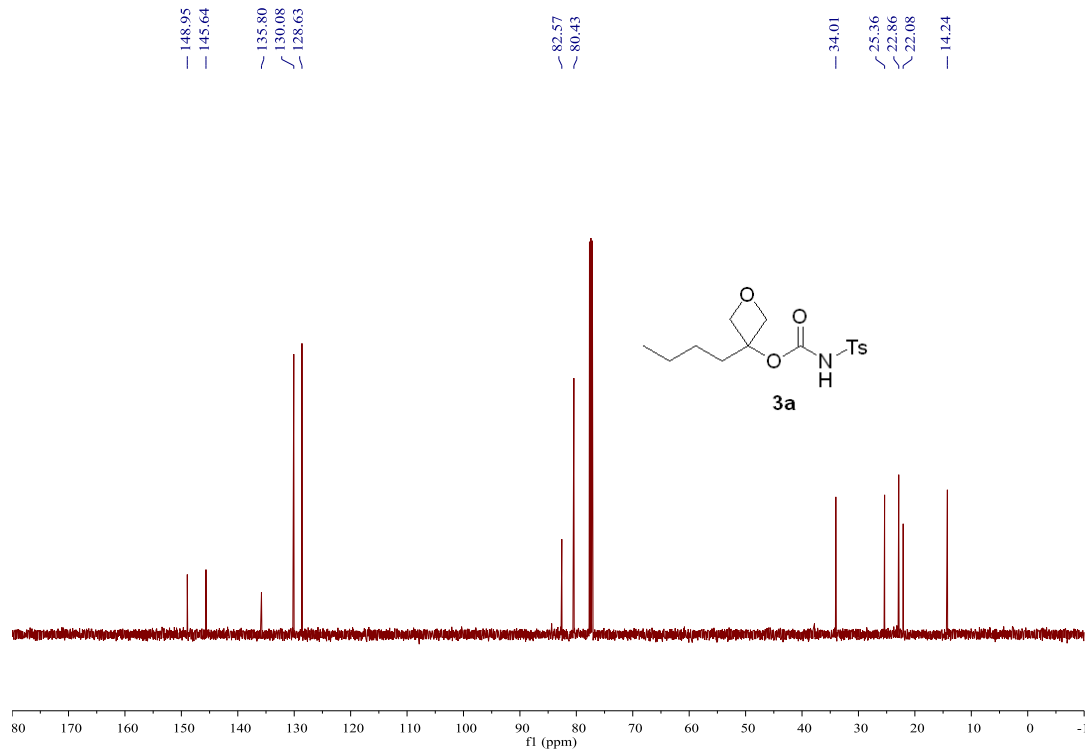
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.95-7.81 (m, 6H), 7.70-7.51 (m, 6H), 3.80-3.64 (m, 2H), 2.33-2.13 (m, 2H).

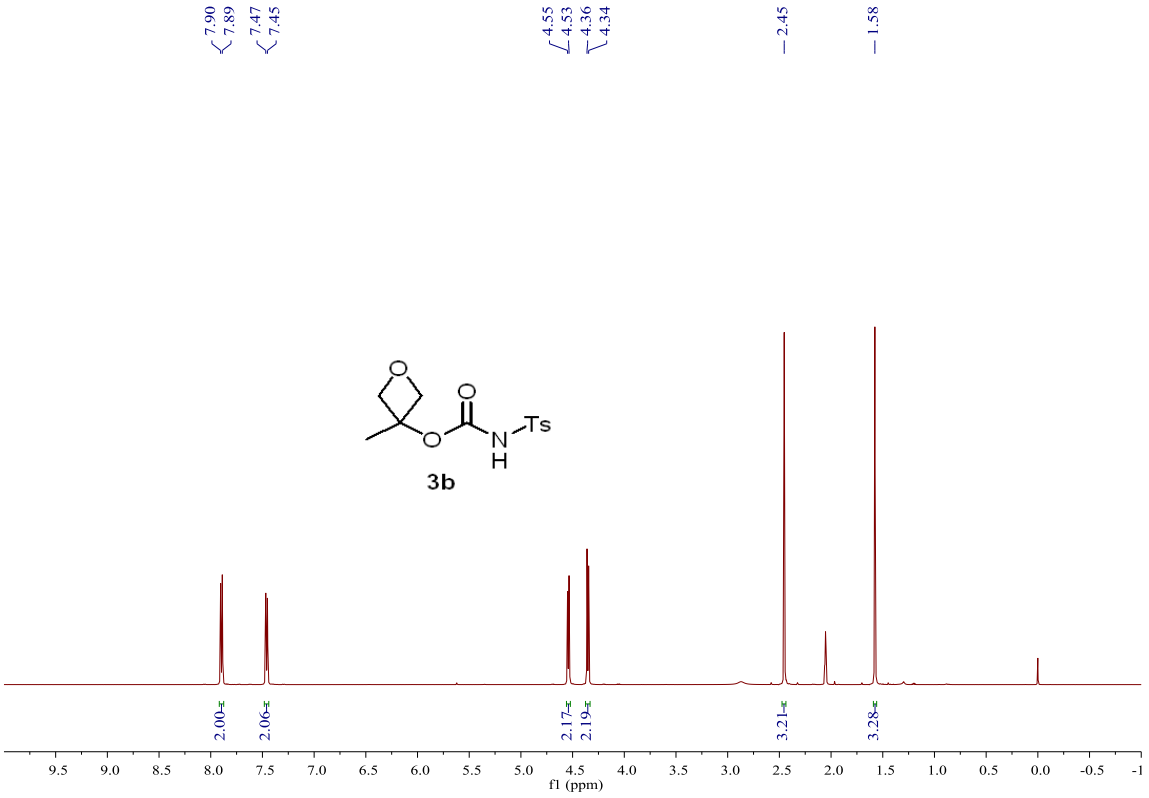
^{13}C NMR (126 MHz, DMSO-d_6) δ 174.35, 165.22 (d, J = 3.6 Hz), 137.39 (t, J = 10.8 Hz), 118.18 (dd, J = 22.2, 14.0 Hz), 115.89 (d, J = 87.6 Hz), 29.68, 19.14 (d, J = 53.0 Hz).

^{31}P NMR (202 MHz, DMSO) δ 23.64.

8. Copies of spectrums



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Ts
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H
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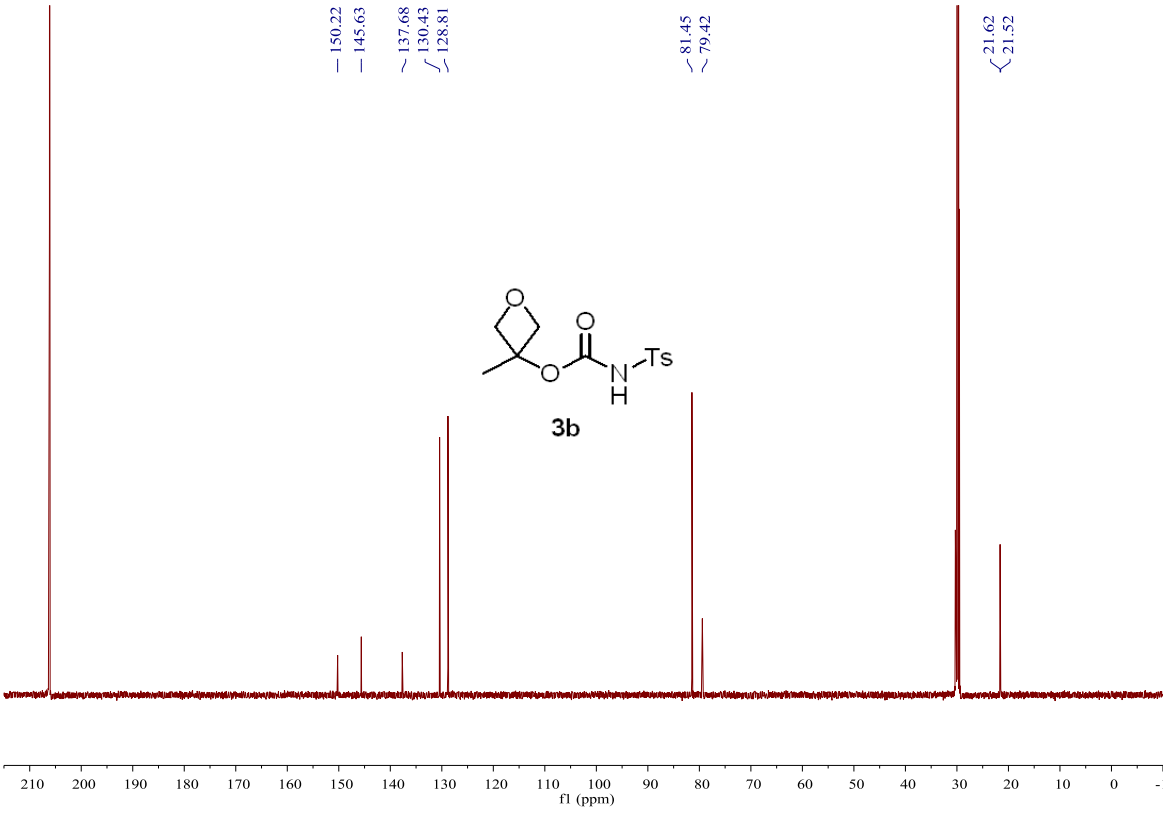
3.21
3.28
f1 (ppm)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Ts
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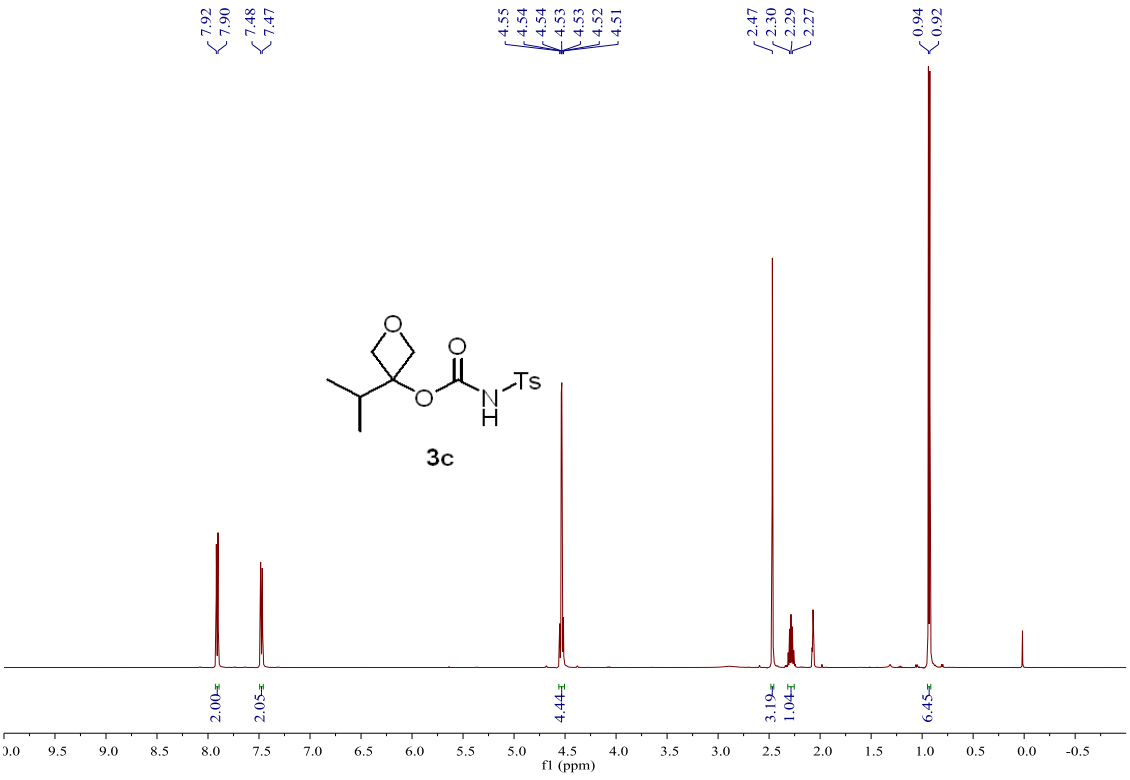
H
3b
f1 (ppm)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4.51
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2.30
2.29
2.27
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Ts
N
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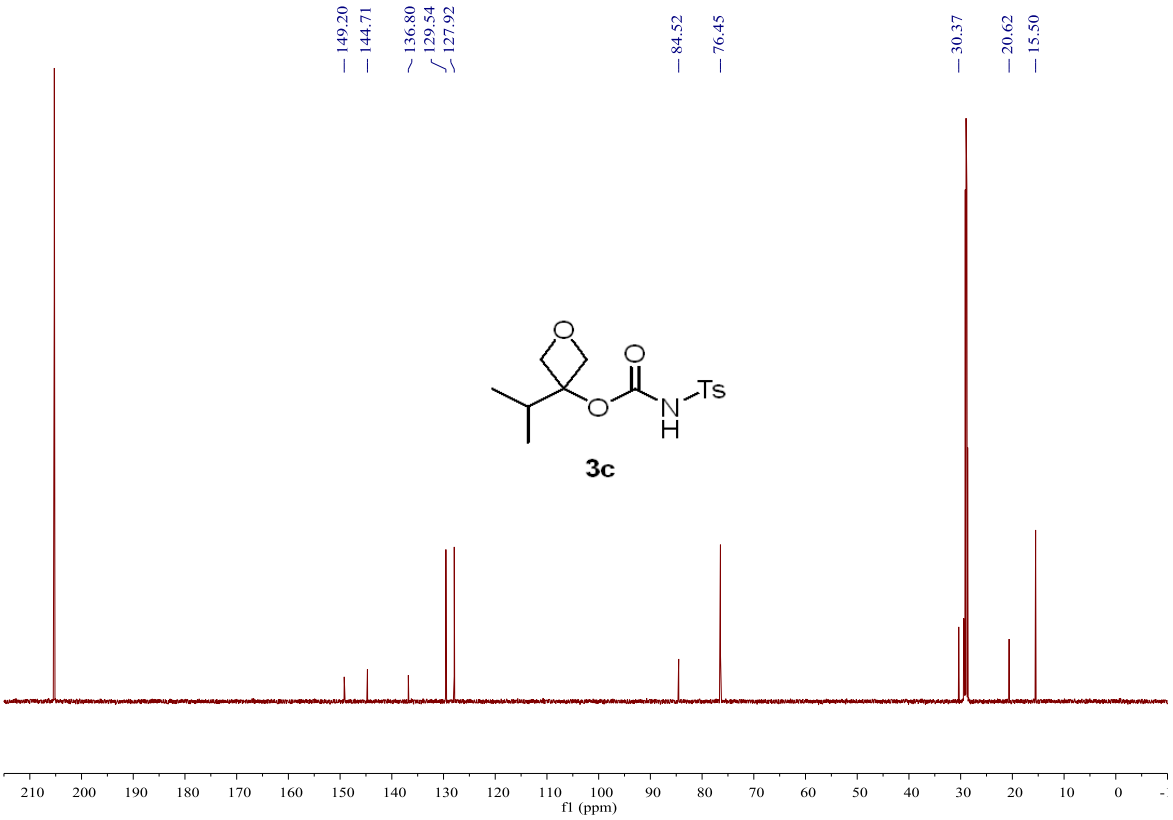
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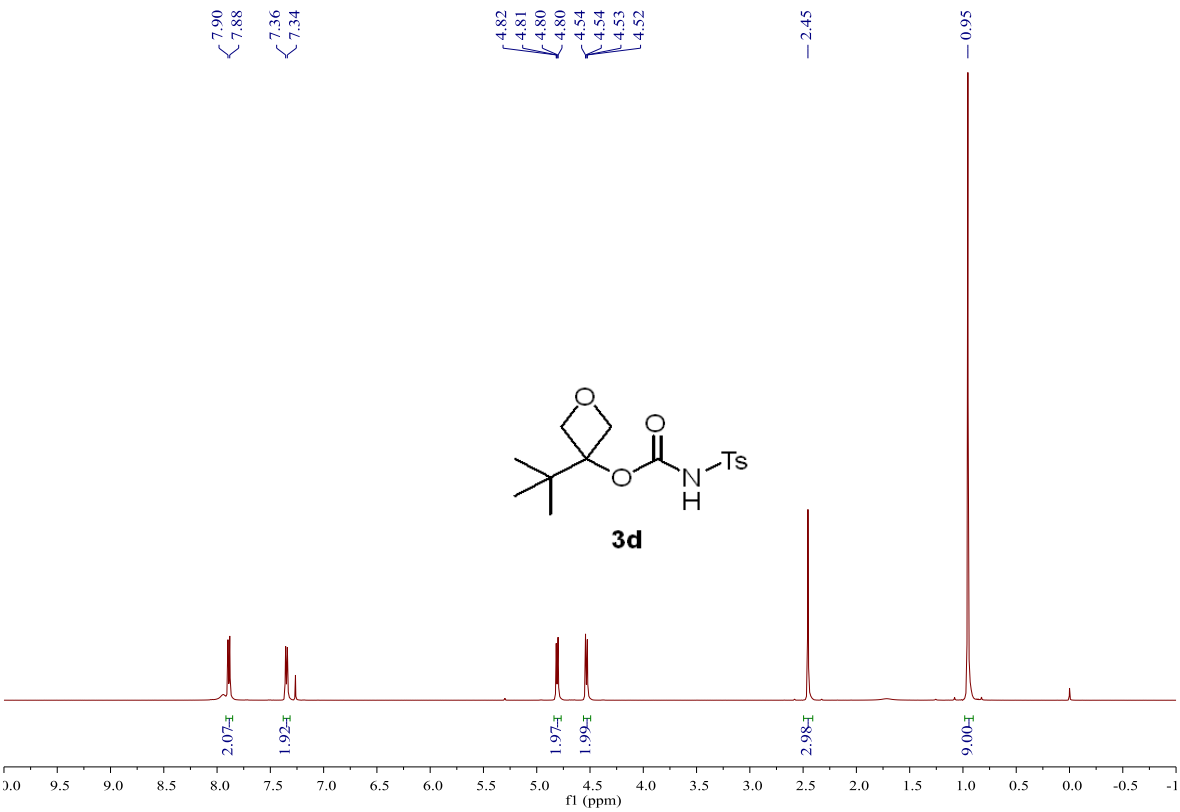
15.50
Ts
N
H
3c
f1 (ppm)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Ts
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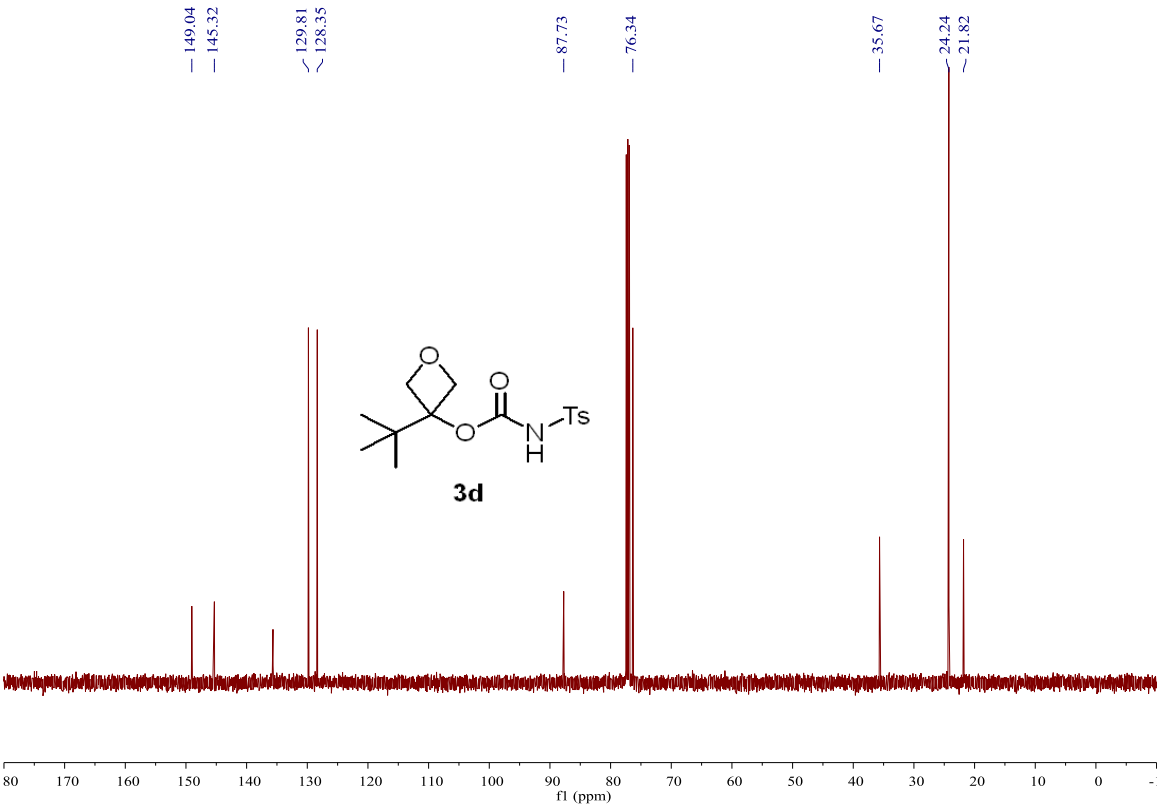
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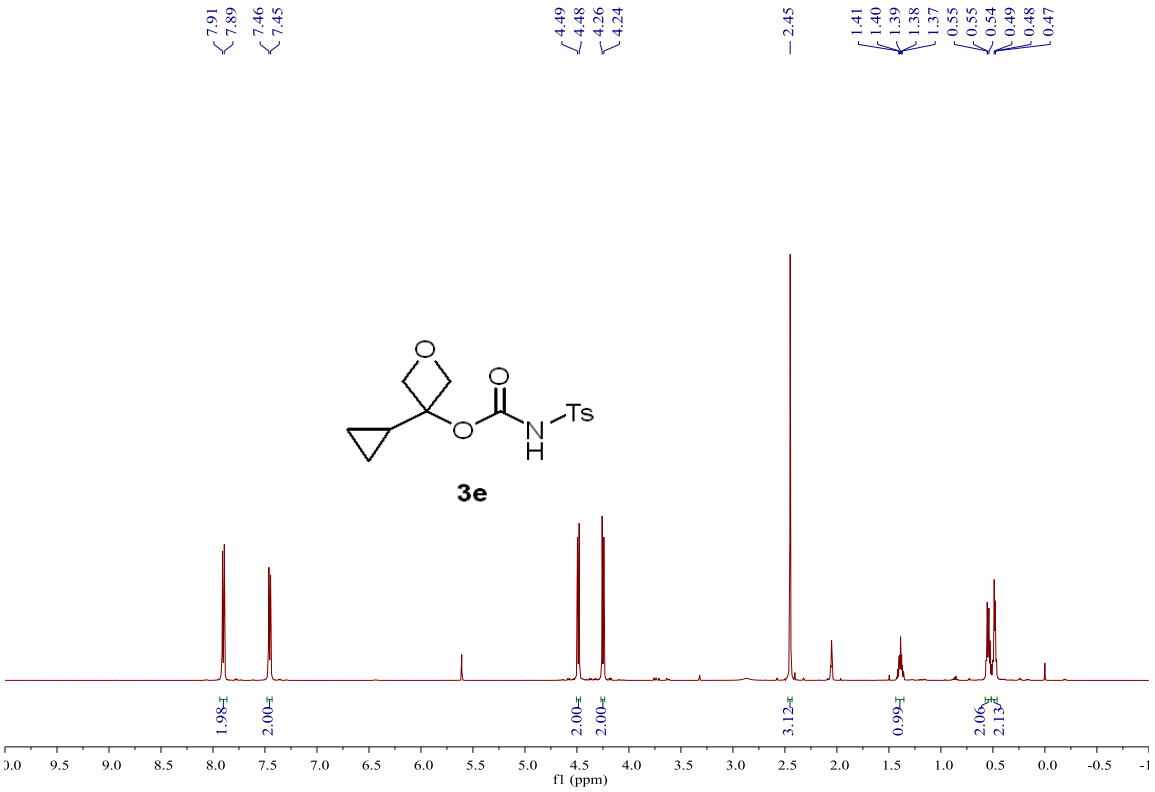
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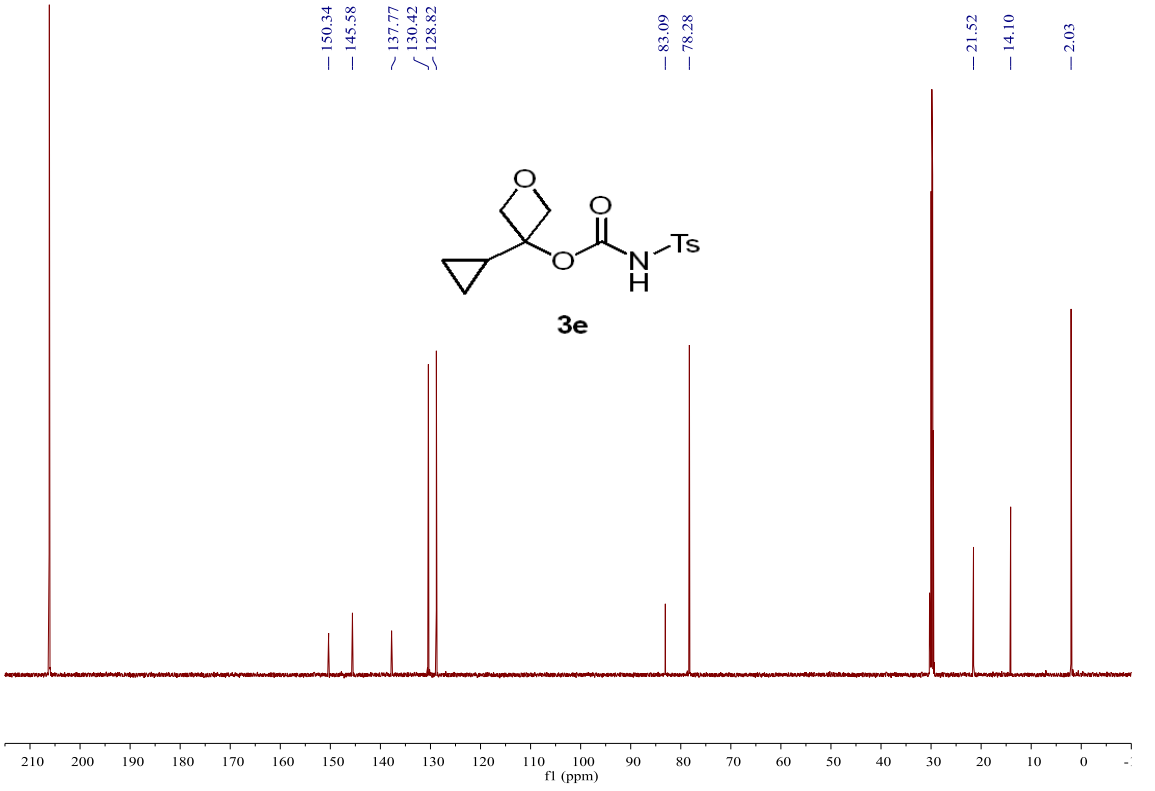
fl (ppm)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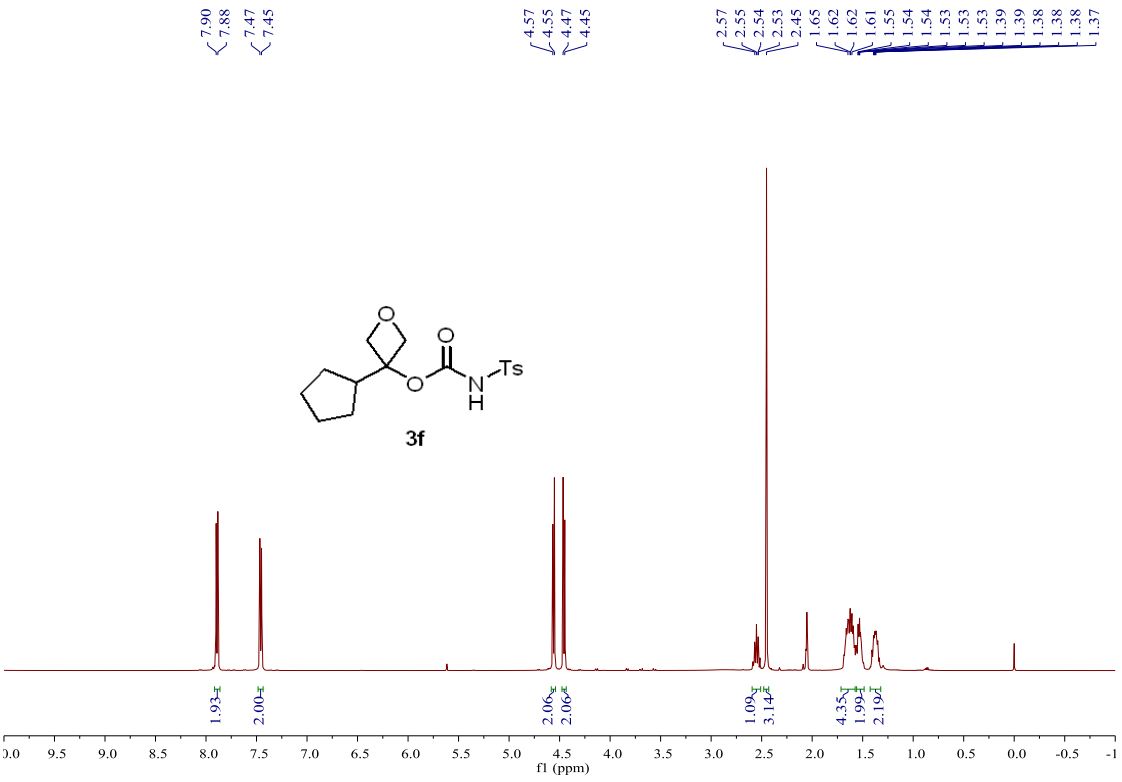
O
3e
fl (ppm)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1.61
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1.54
1.54
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1.39
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1.38
1.37
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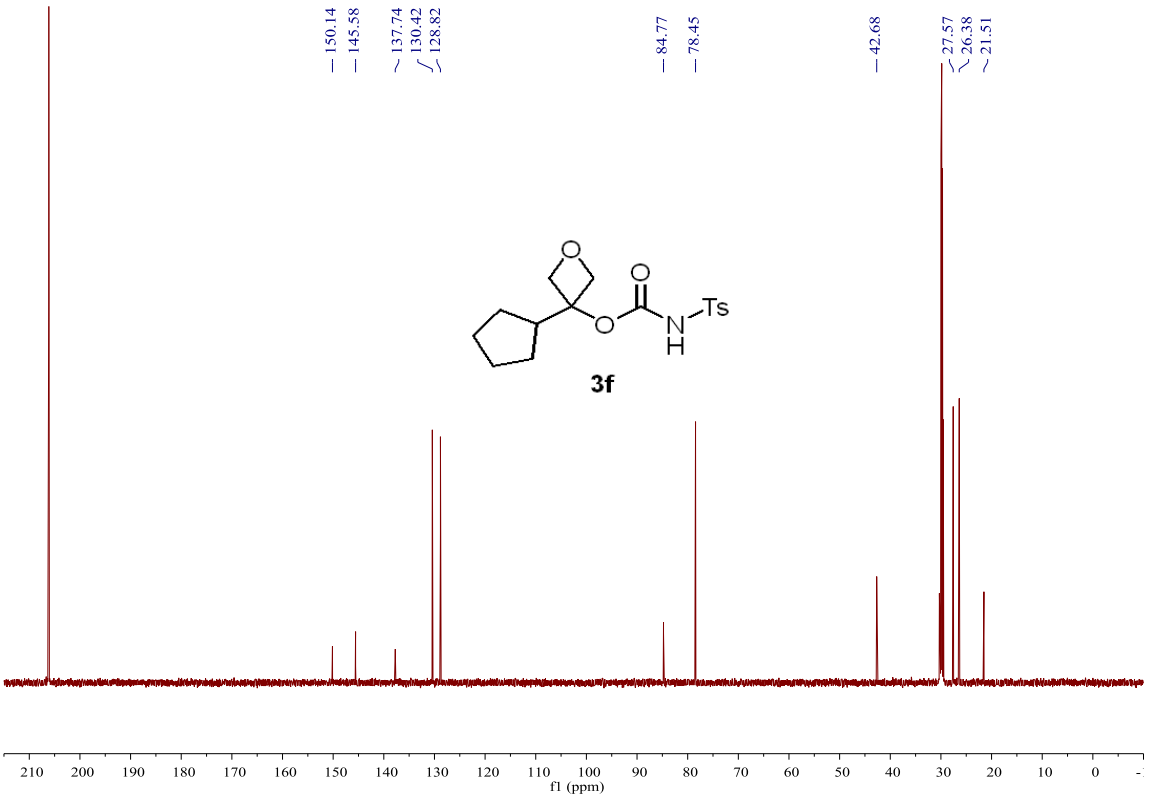
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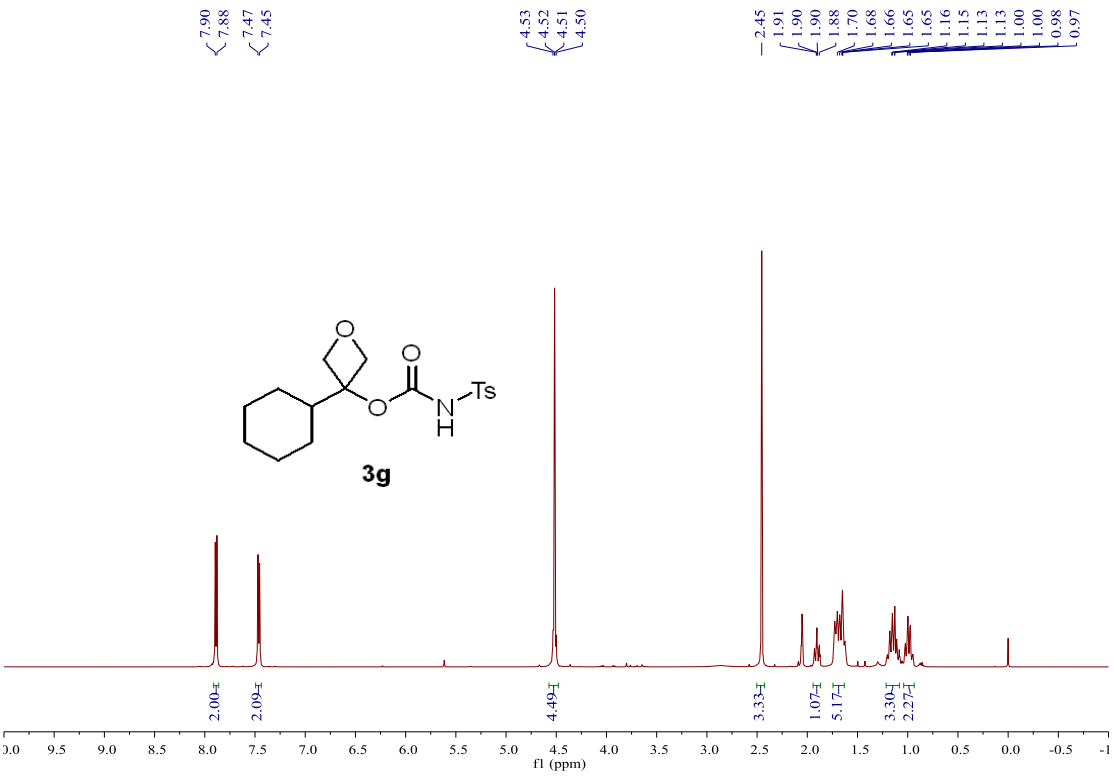
f1 (ppm)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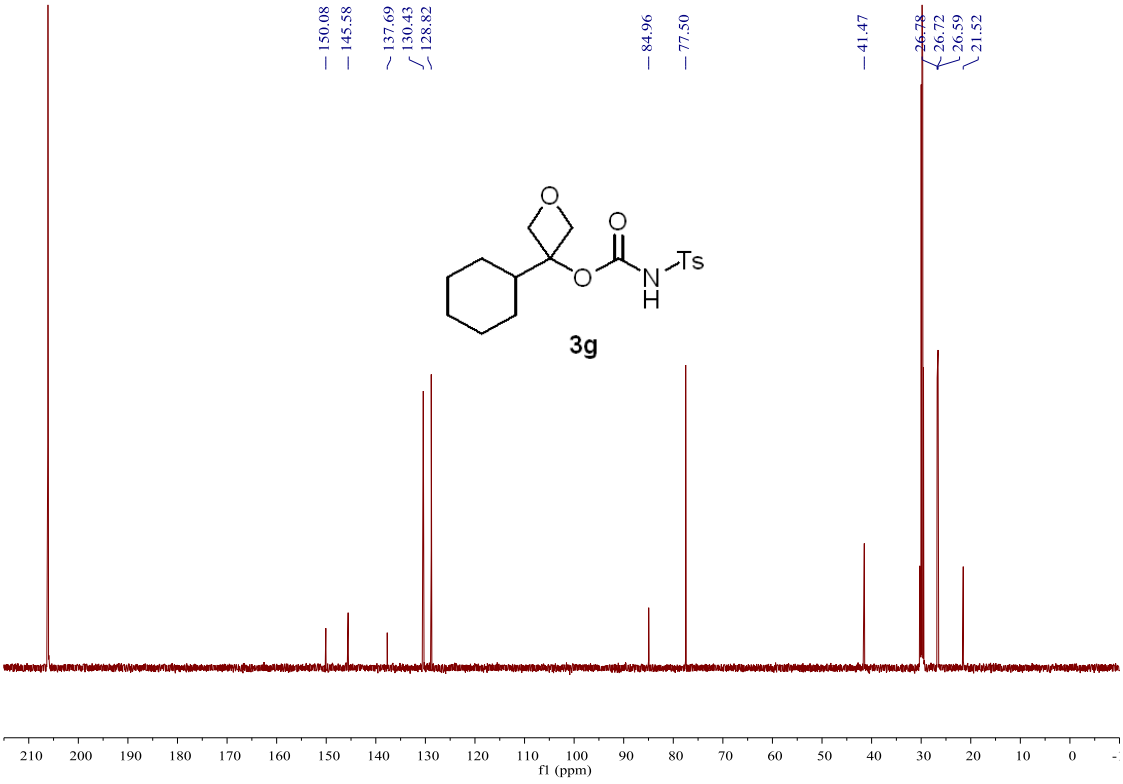
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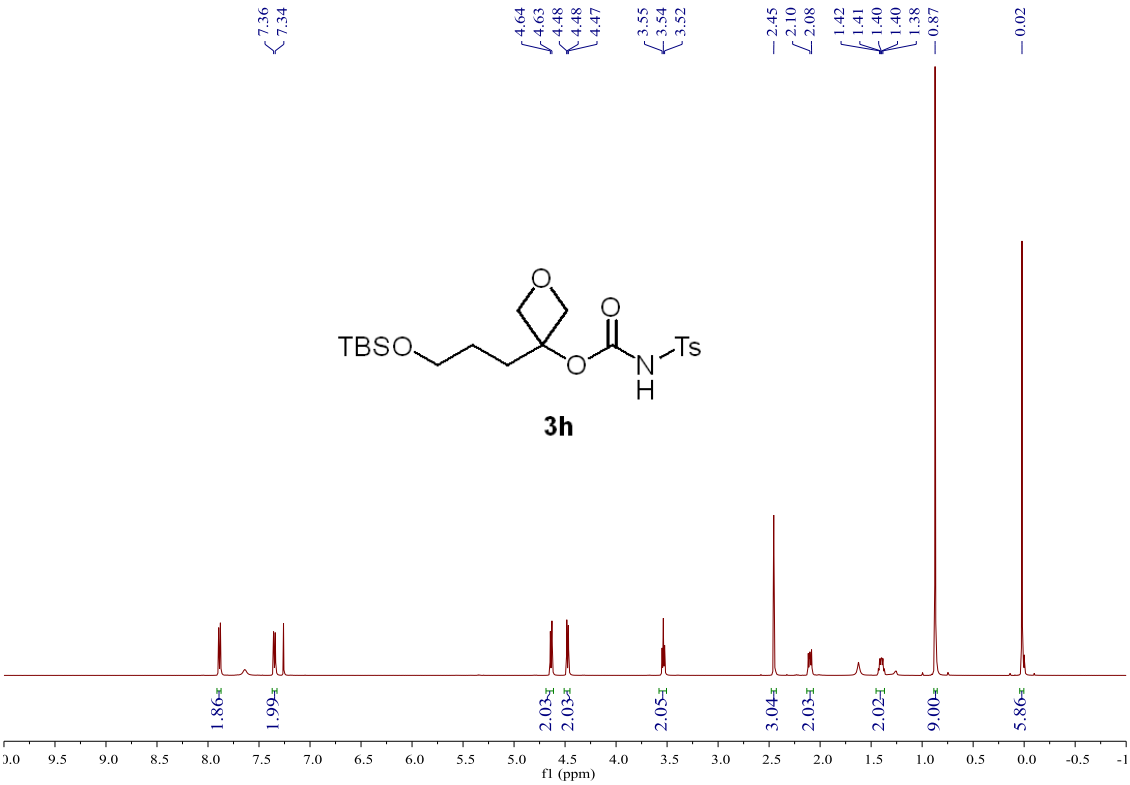
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O
O
O
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H
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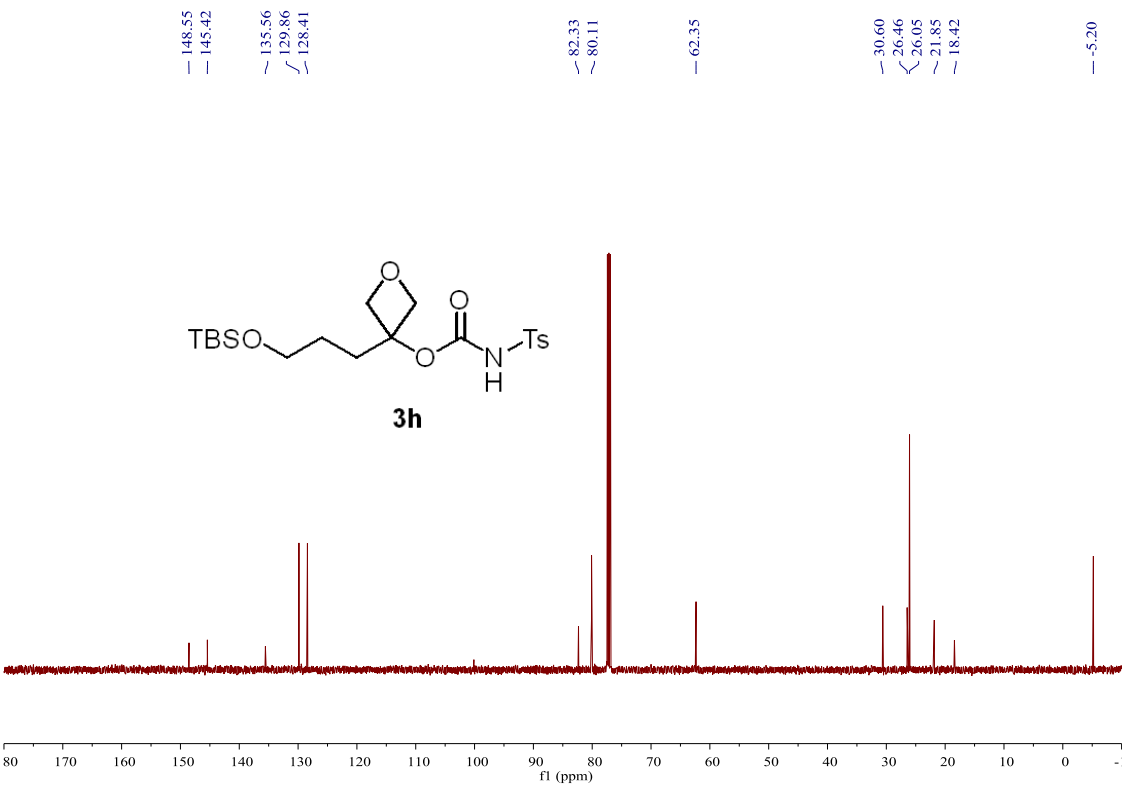
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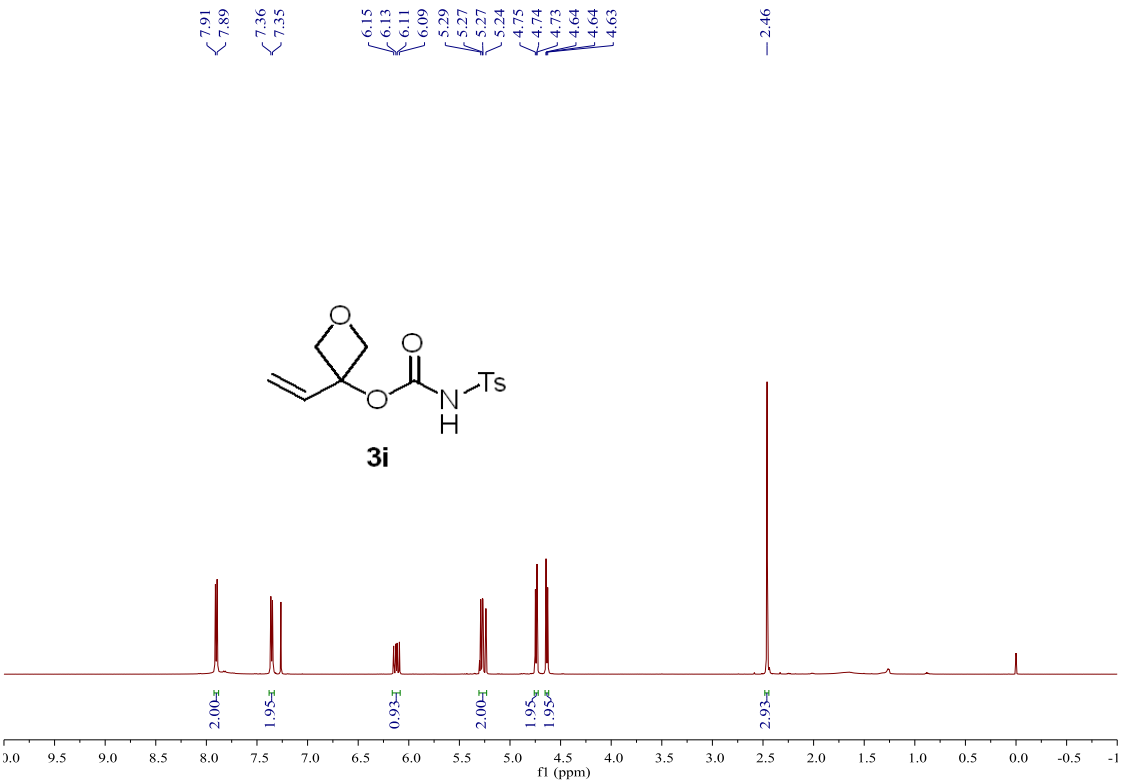
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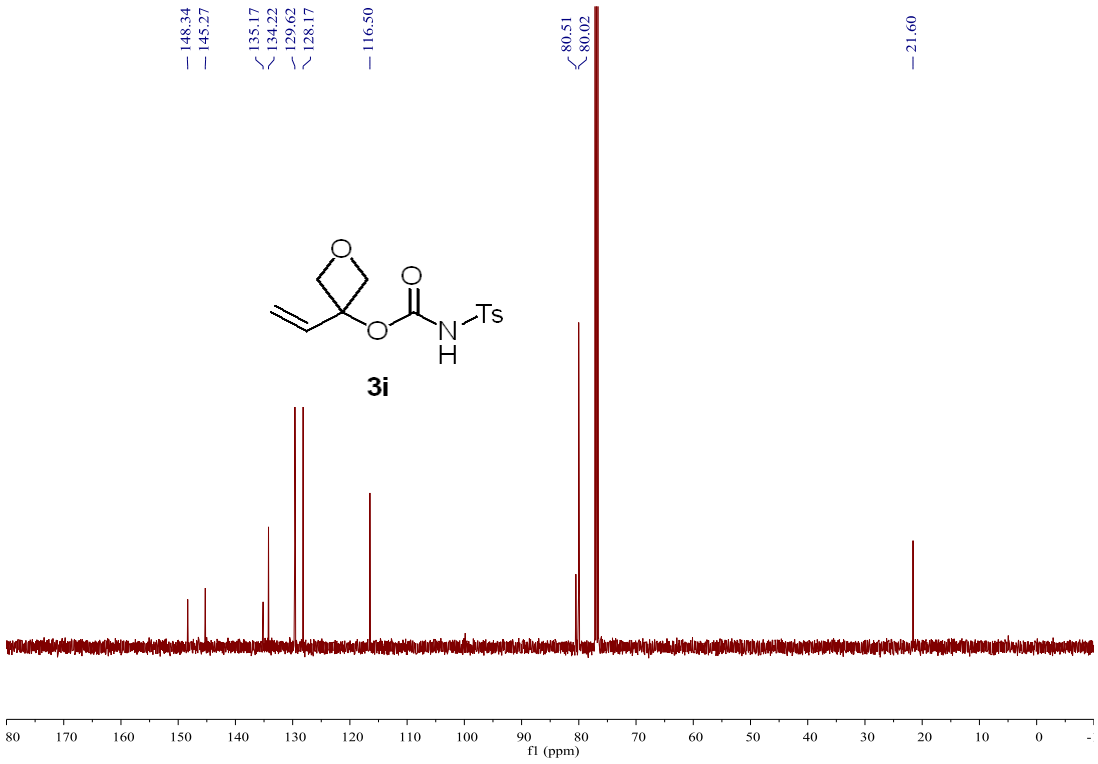
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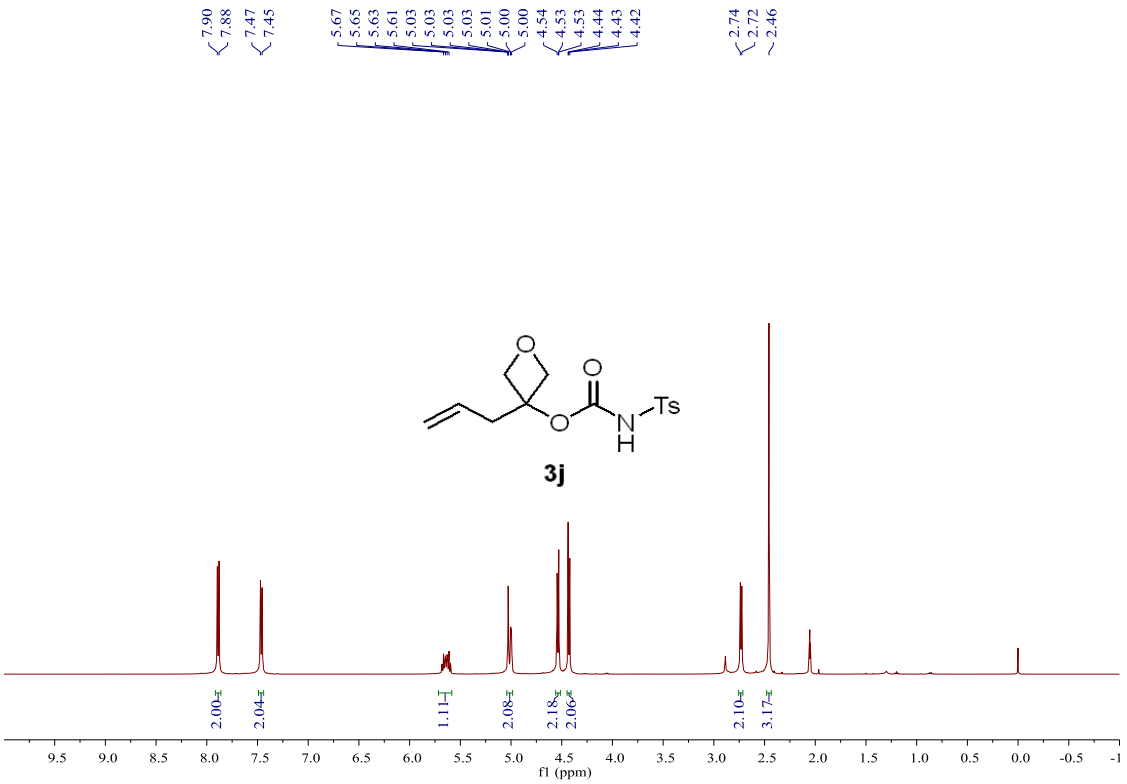
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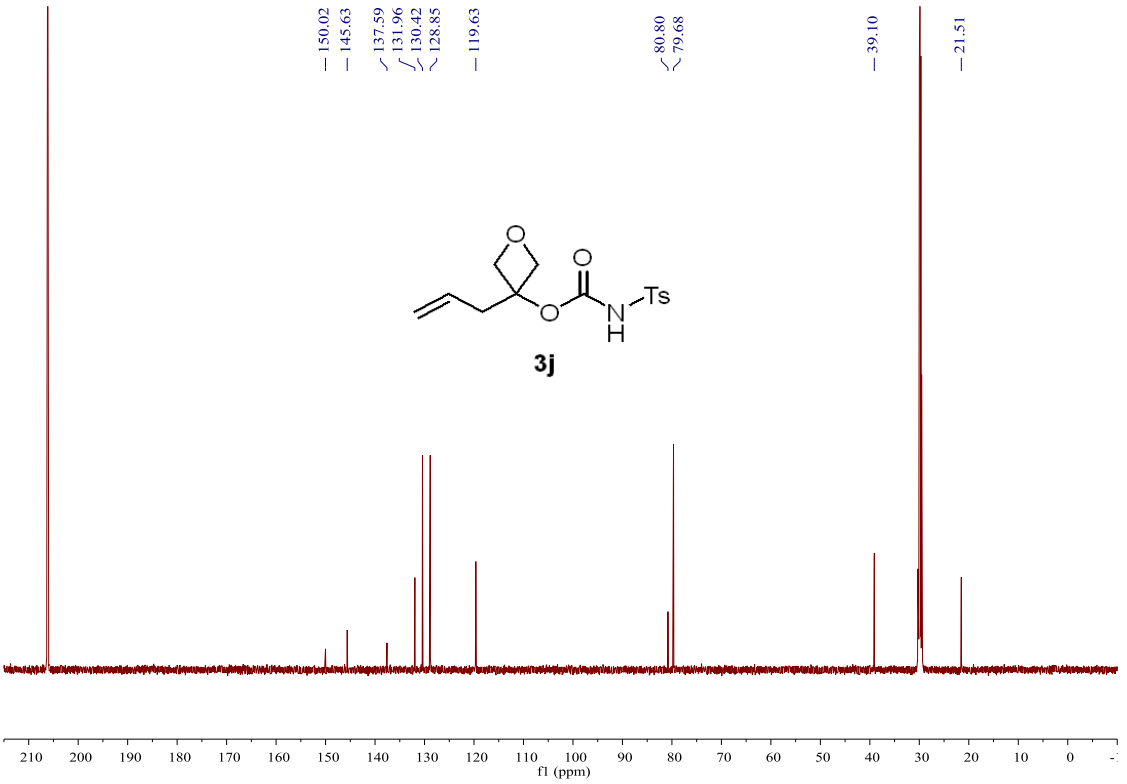
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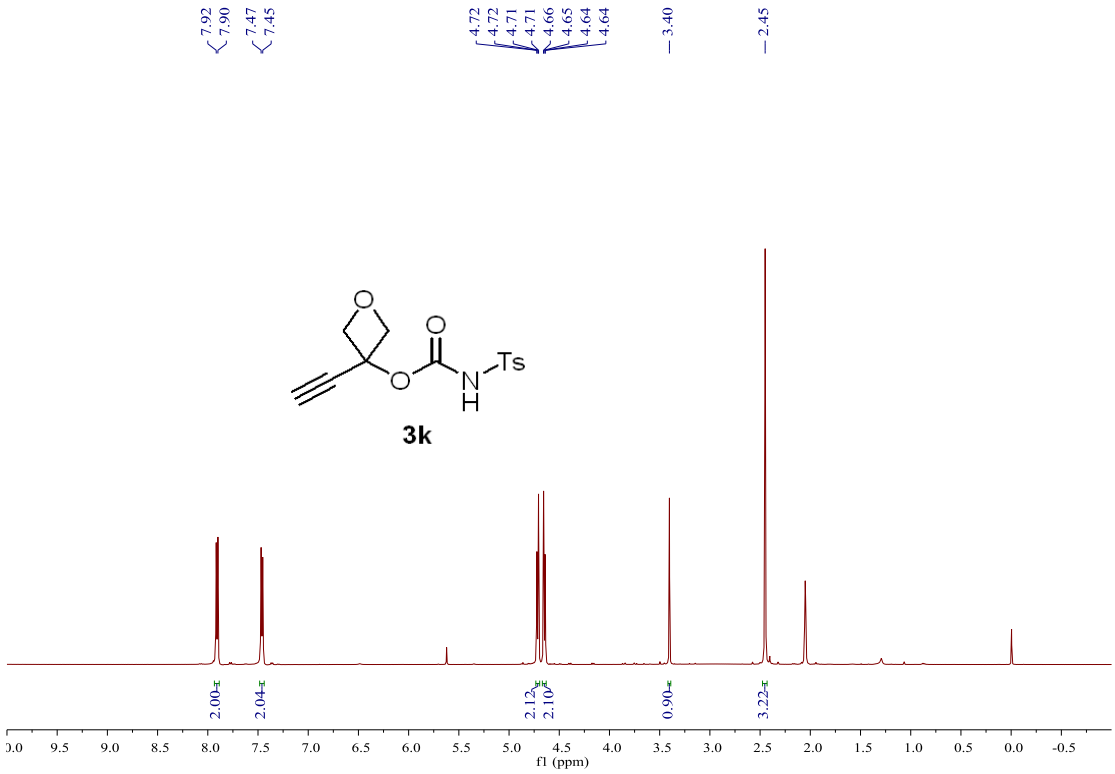
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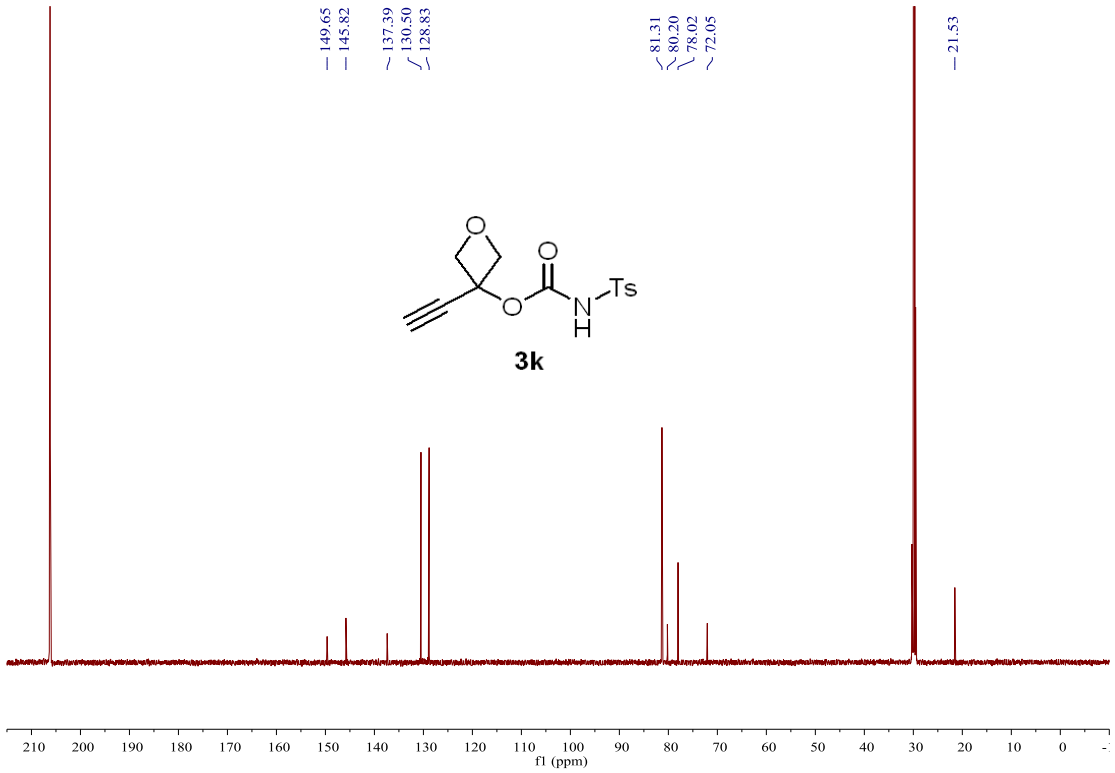
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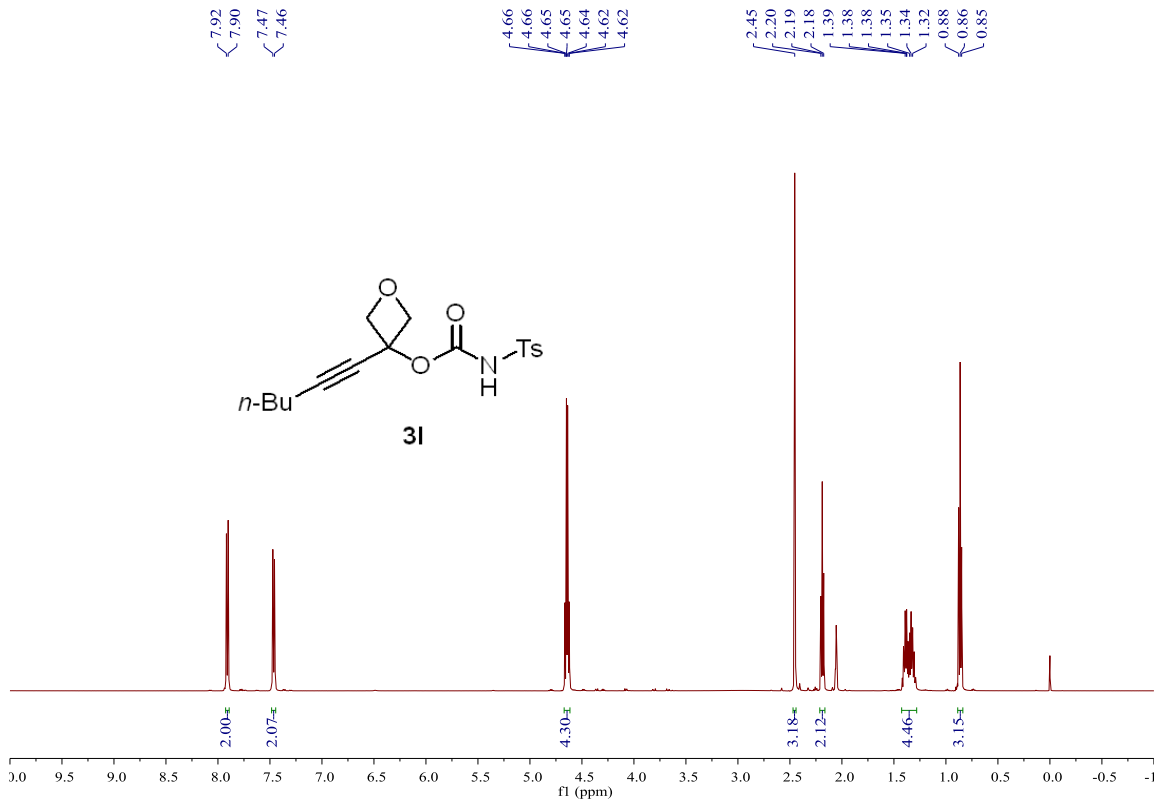
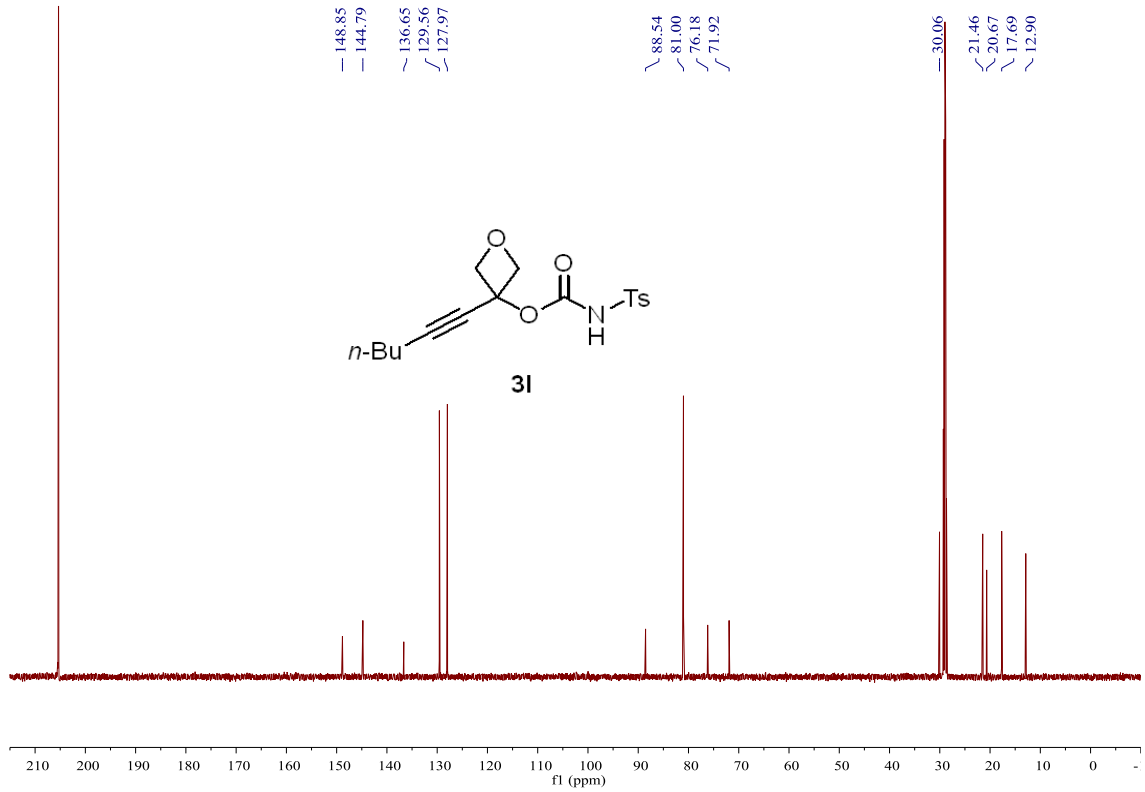
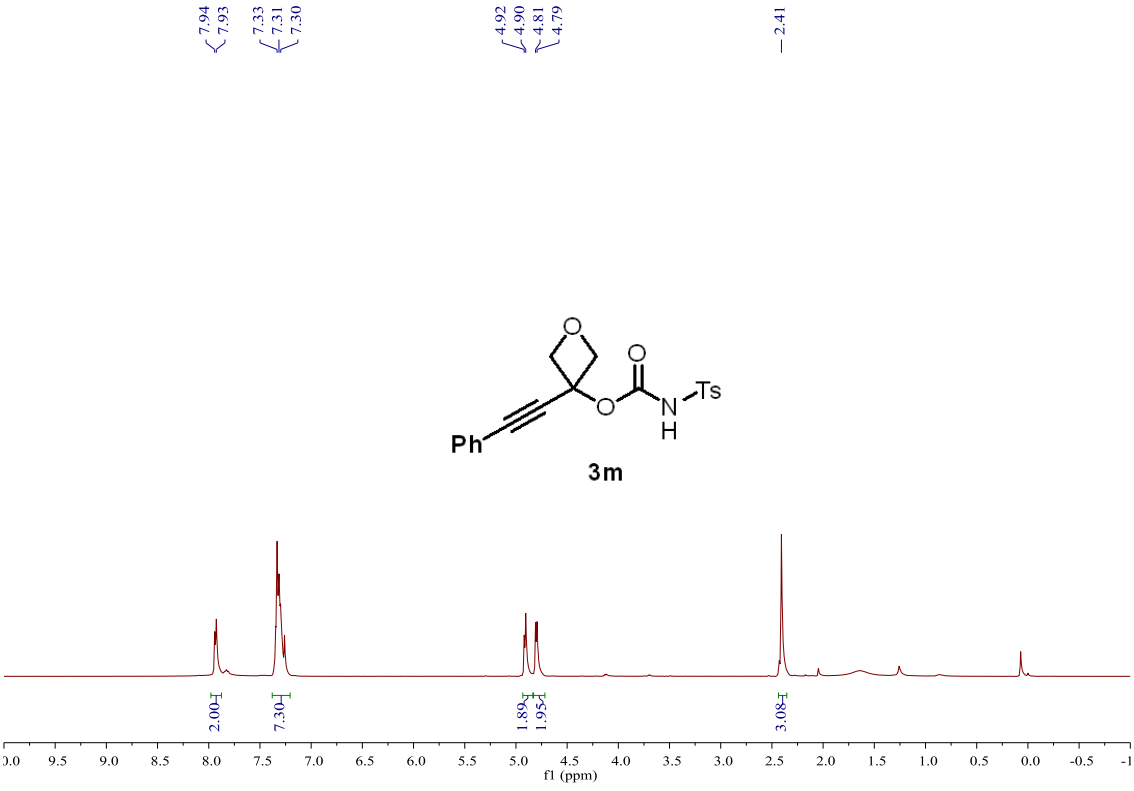
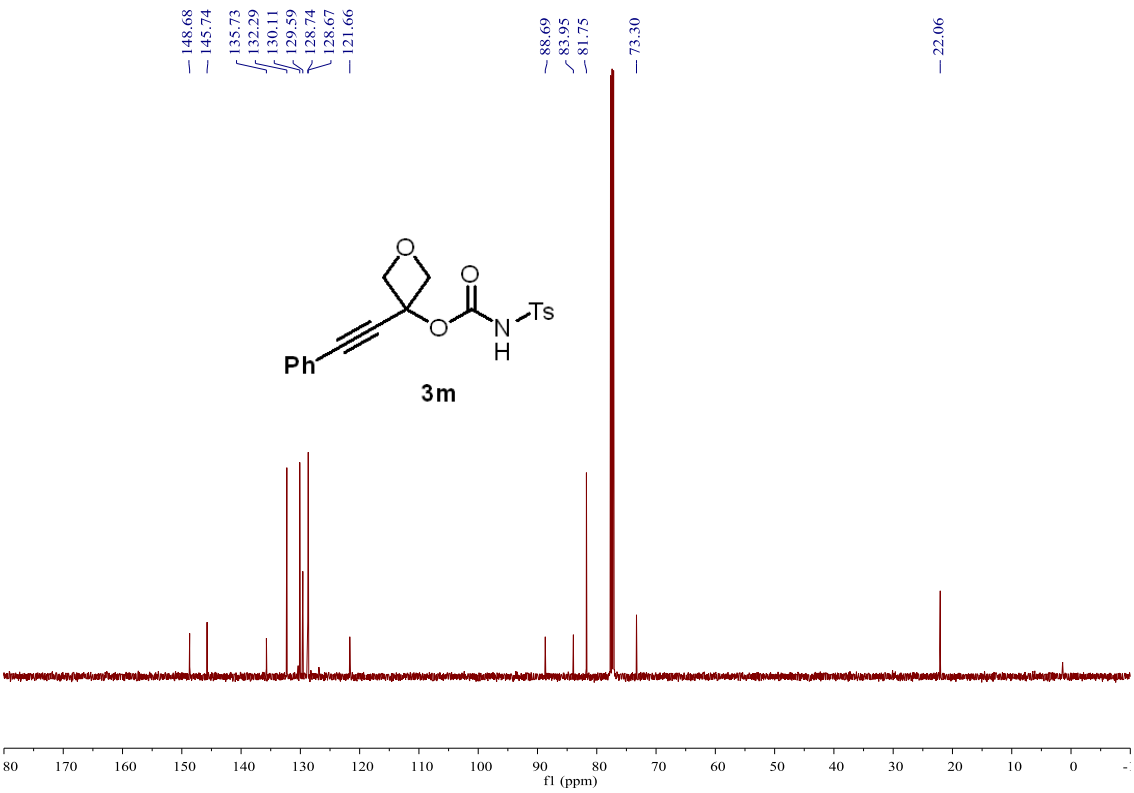
3k
f1 (ppm)


7.92
7.90
7.47
7.46
4.66
4.66
4.65
4.65
4.64
4.62
4.62
2.45
2.20
2.19
2.18
1.39
1.38
1.38
1.35
1.34
1.32
0.88
0.86
0.85
O
O
O
N
H
Ts
n-Bu
3l
2.00
2.07
4.30
3.18
2.12
4.46
3.15
f1 (ppm)


148.85
144.79
136.65
129.56
127.97
88.54
81.00
76.18
71.92
30.06
21.46
20.67
17.69
12.90
O
O
O
N
H
Ts
n-Bu
3l
f1 (ppm)


7.94
7.93
7.33
7.31
7.30
4.92
4.90
4.81
4.79
2.41
Ph
O
O
N
H
Ts
3m
2.00
7.30
1.89
1.95
3.08
fl (ppm)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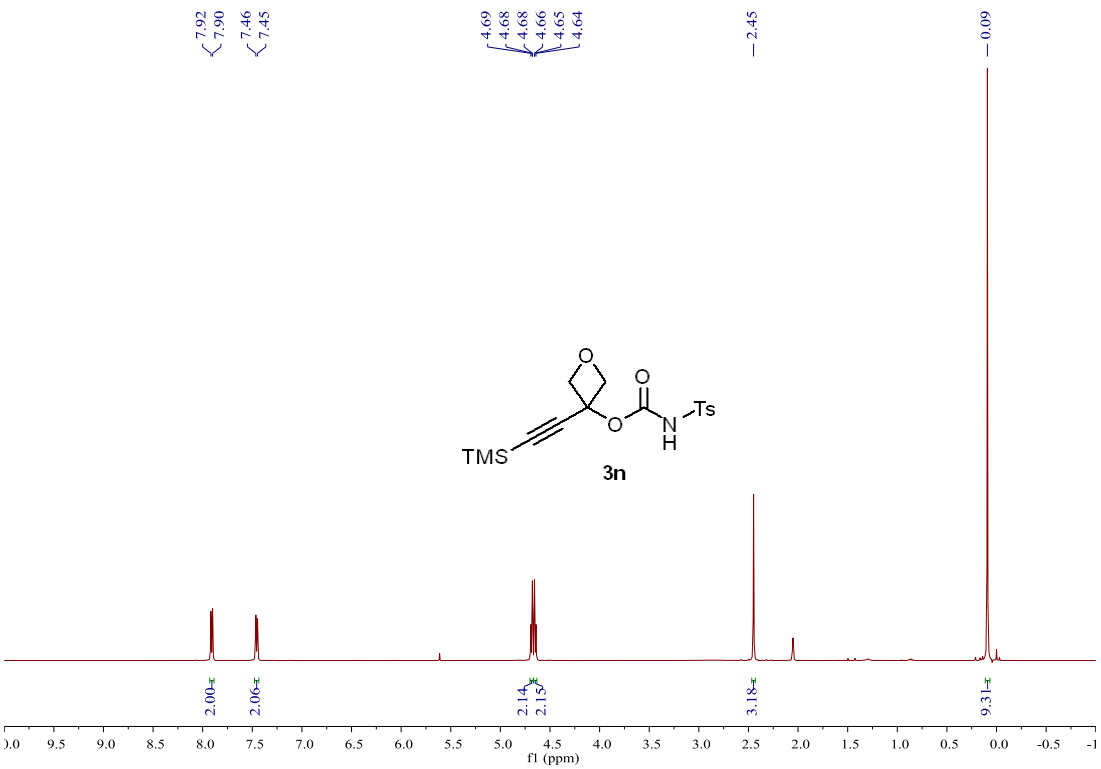
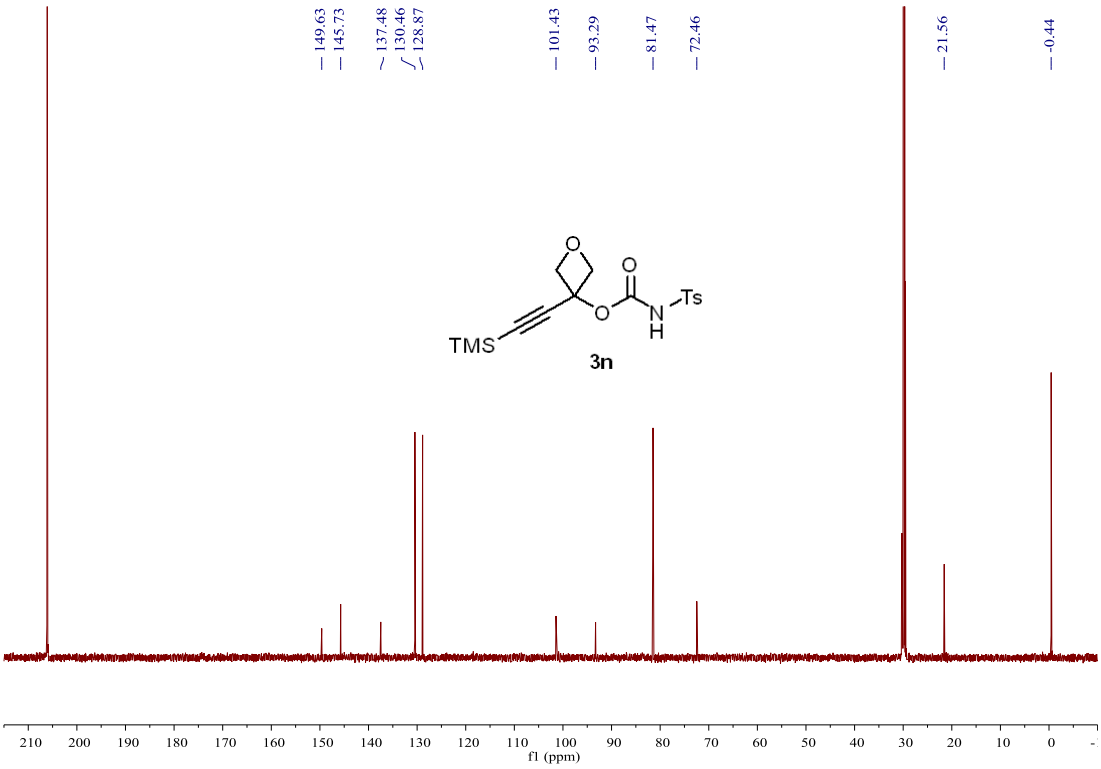
145.74
135.73
132.29
130.11
129.59
128.74
128.67
121.66
88.69
83.95
81.75
73.30
22.06
Ph
O
O
N
H
Ts
3m
fl (ppm)


7.92
7.90
7.46
7.45
4.69
4.68
4.68
4.66
4.65
4.64
2.45
0.09
TMS
Ts
3n
2.00
2.06
2.14
2.15
3.18
9.31
f1 (ppm)


149.63
145.73
137.48
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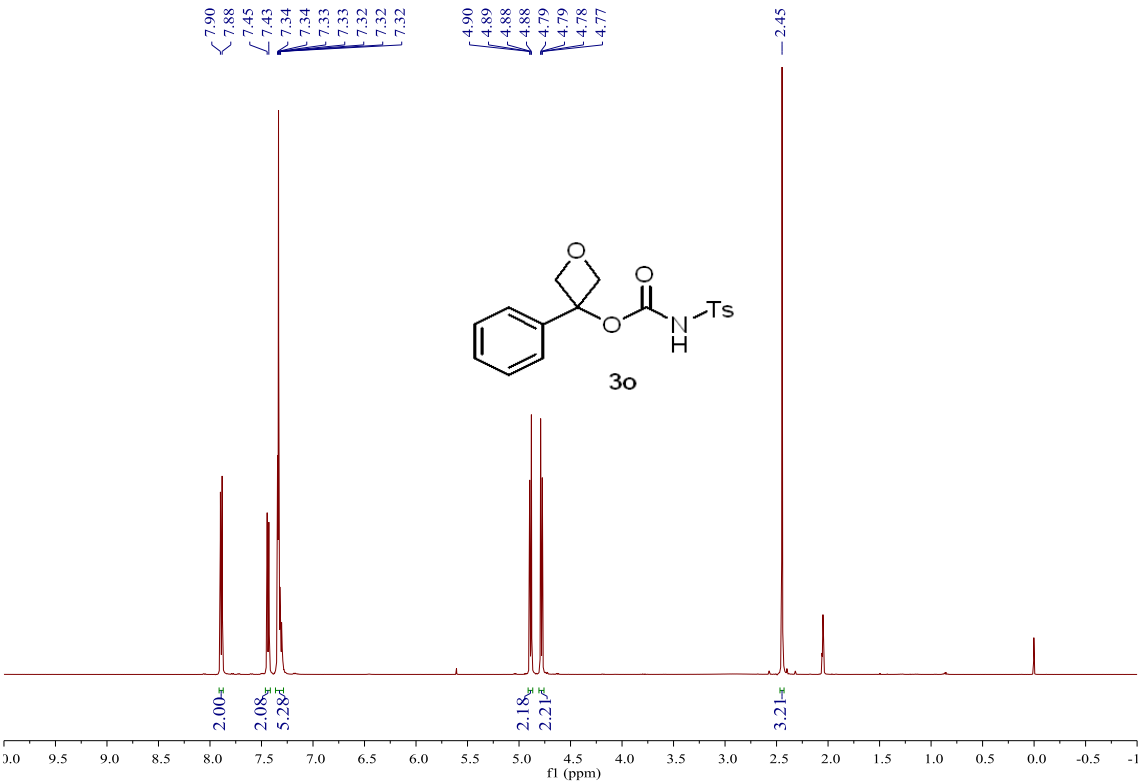
128.87
101.43
93.29
81.47
72.46
21.56
-0.44
TMS
Ts
3n
f1 (ppm)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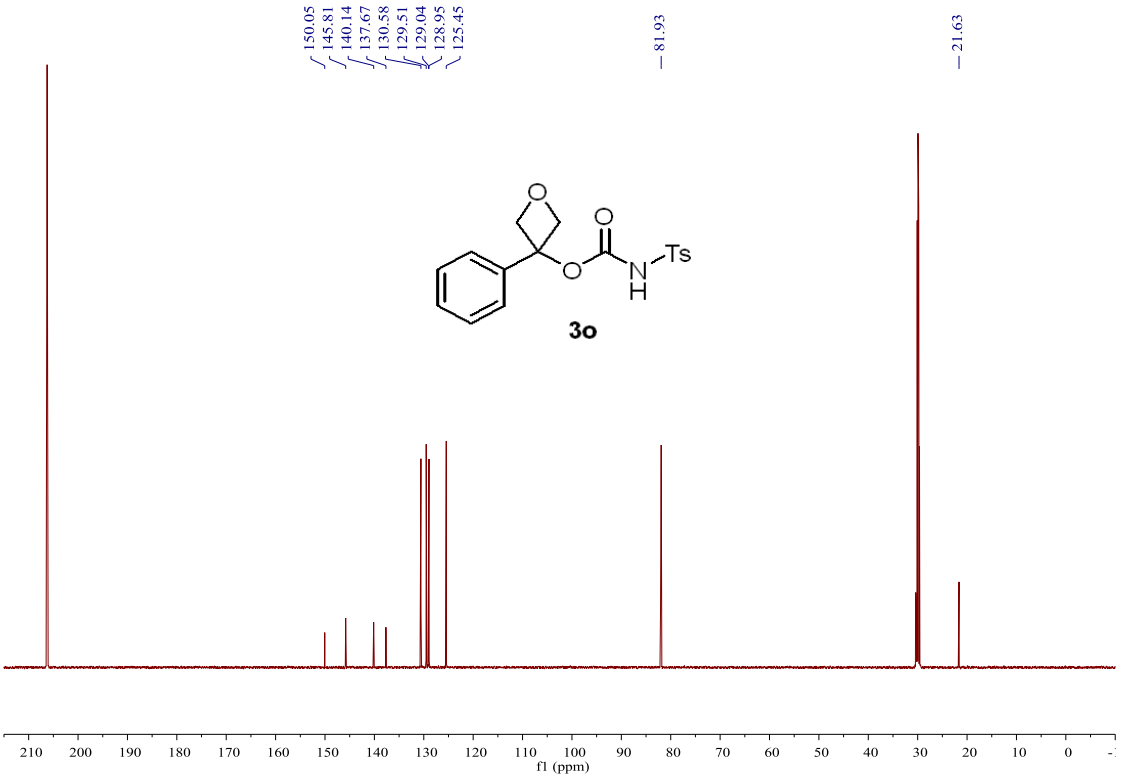
7.88
7.45
7.43
7.34
7.34
7.33
7.33
7.32
7.32
7.32
4.90
4.89
4.88
4.88
4.79
4.79
4.78
4.77
2.45
O
O
O
N
H
Ts
3o
2.00
2.08
5.28
2.18
2.21
3.21
fl (ppm)


150.05
145.81
140.14
137.67
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129.51
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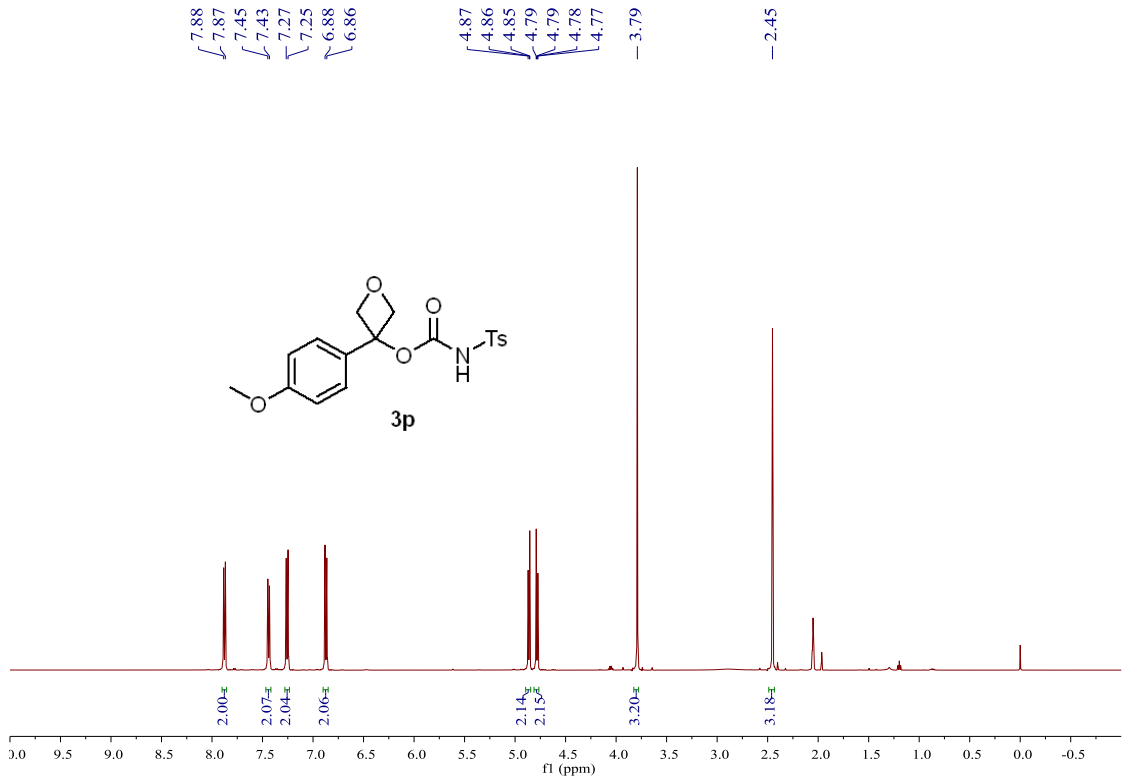
128.95
125.45
81.93
21.63
O
O
O
N
H
Ts
3o
fl (ppm)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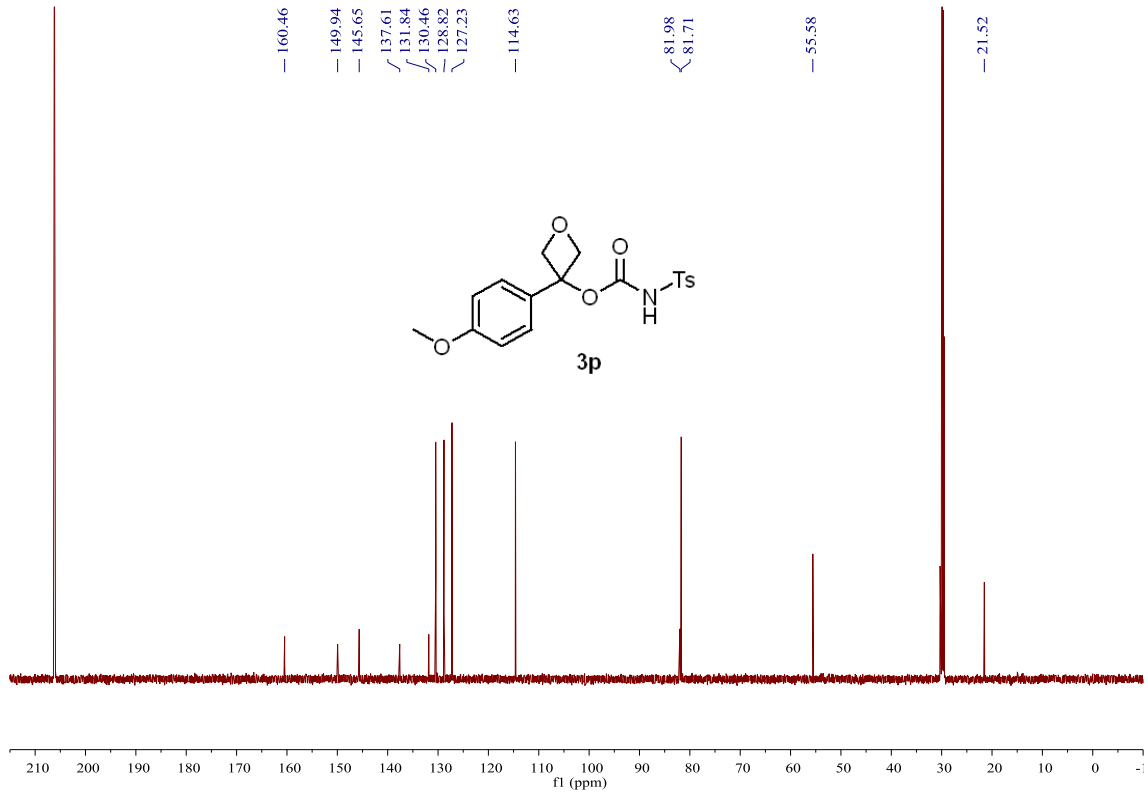
7.87
7.45
7.43
7.27
7.25
6.88
6.86
4.87
4.86
4.85
4.79
4.79
4.78
4.77
3.79
2.45
Ts
3p
2.00
2.07
2.04
2.06
2.14
2.15
3.20
3.18
f1 (ppm)


160.46
149.94
145.65
137.61
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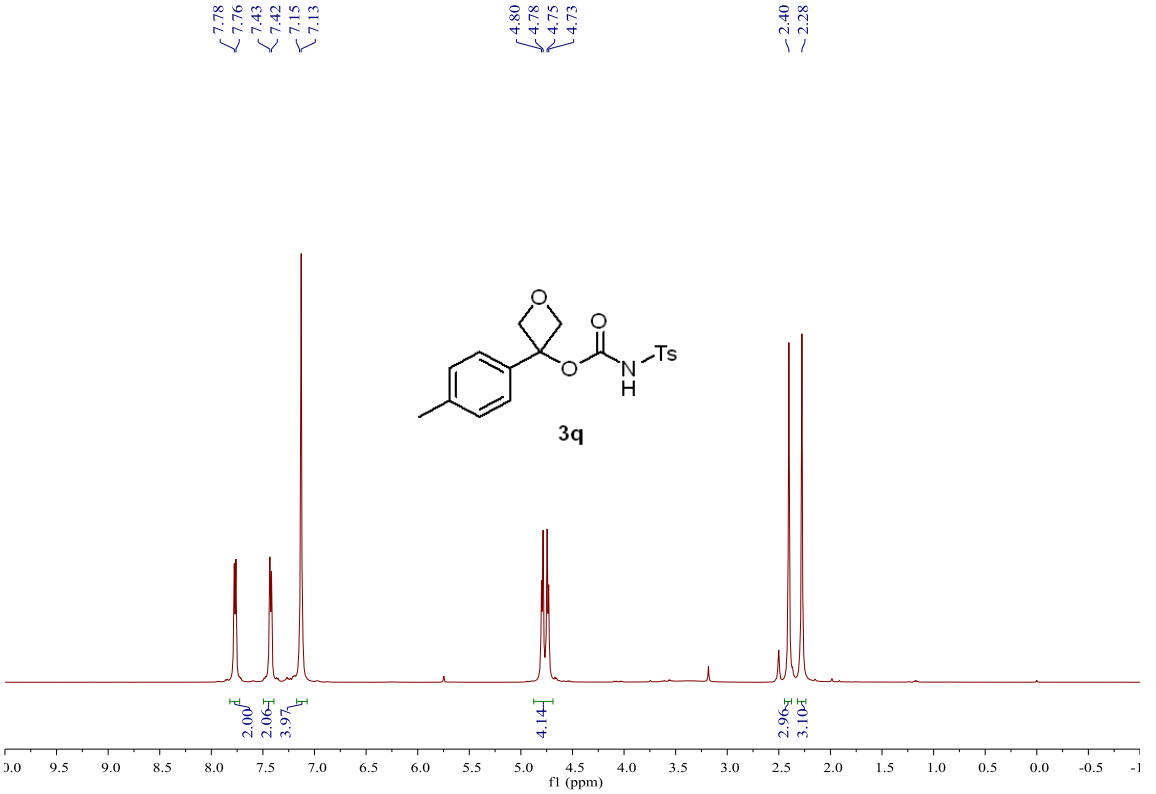
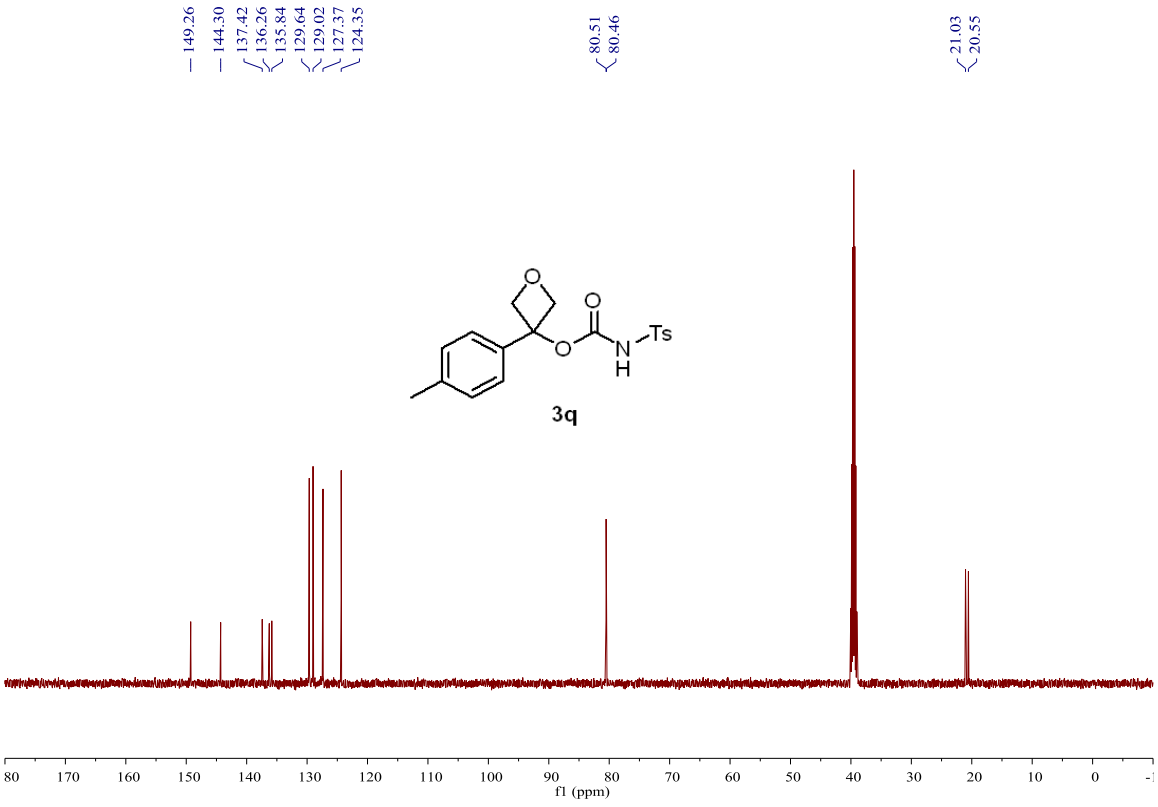
130.46
128.82
127.23
114.63
81.98
81.71
55.58
21.52
Ts
3p
f1 (ppm)


7.78
7.76
7.43
7.42
7.15
7.13
4.80
4.78
4.75
4.73
2.40
2.28
3q
2.00
2.06
3.97
4.14
2.96
3.10
f1 (ppm)


149.26
144.30
137.42
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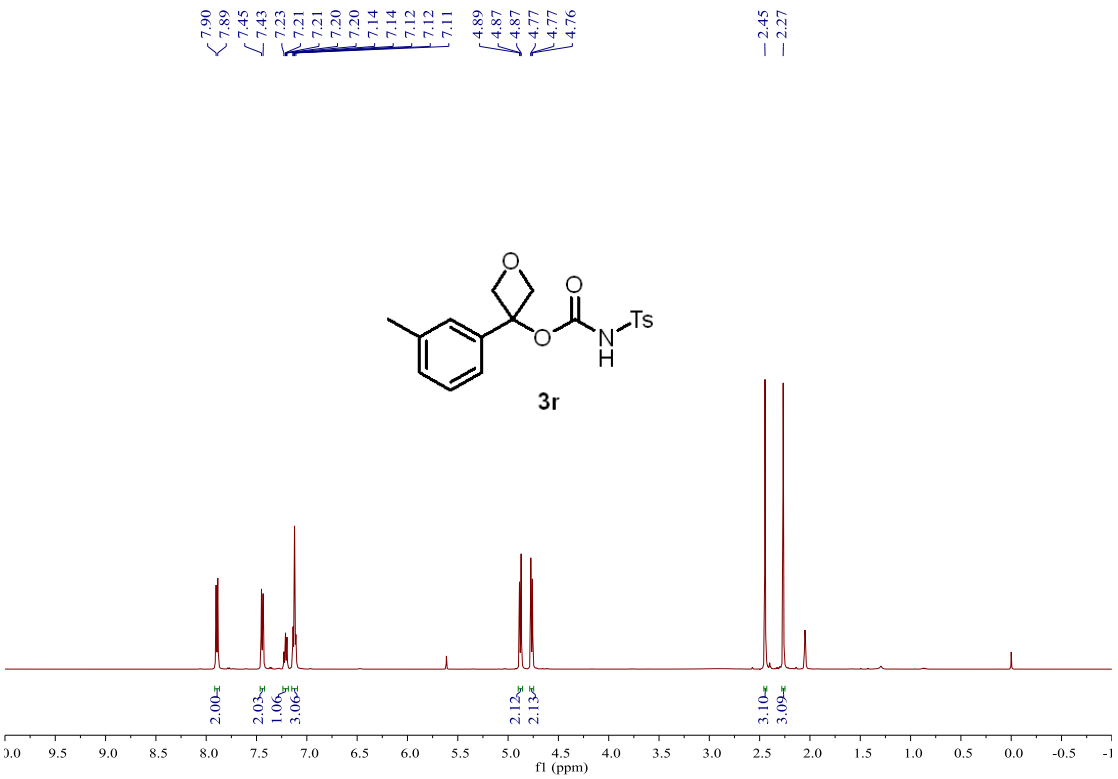
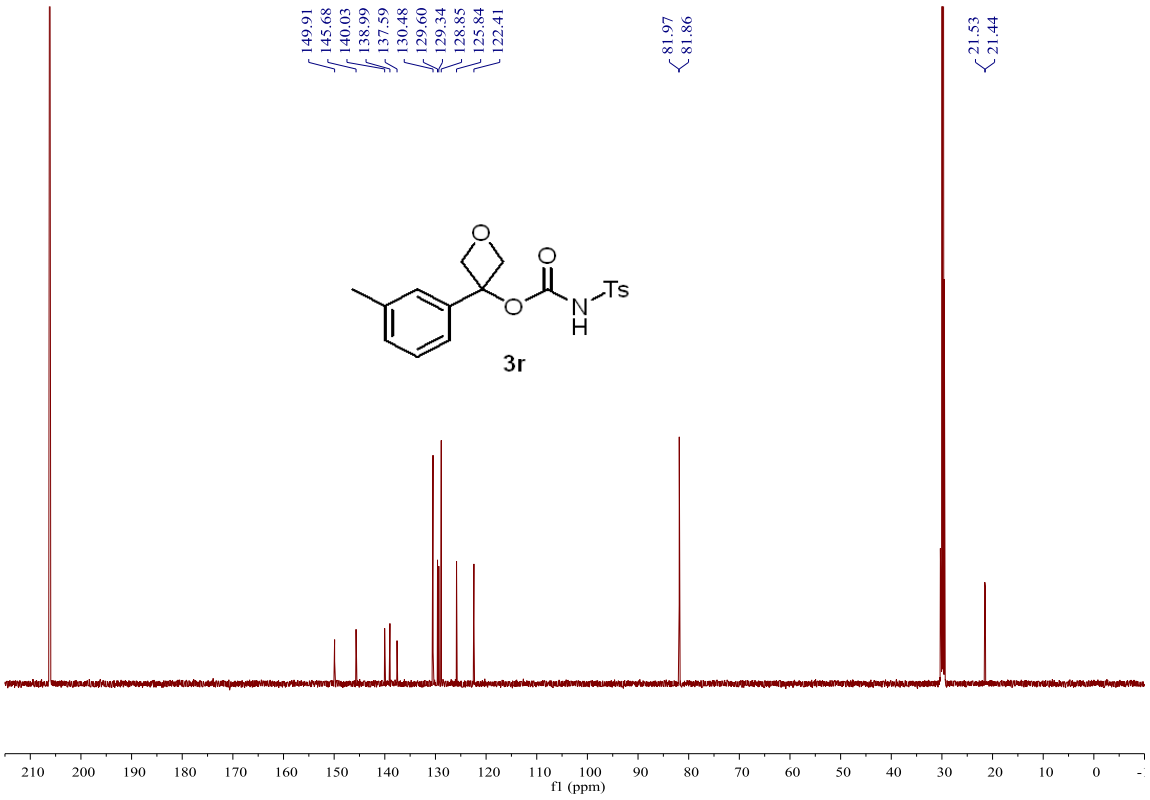
129.64
129.02
127.37
124.35
80.51
80.46
21.03
20.55
3q
f1 (ppm)


7.90
7.89
7.45
7.43
7.23
7.21
7.21
7.20
7.20
7.14
7.14
7.12
7.12
7.11
4.89
4.87
4.87
4.77
4.77
4.76
2.45
2.27
O
O
O
N
H
Ts
3r
2.00
2.03
1.06
3.06
2.12
2.13
3.10
3.09
f1 (ppm)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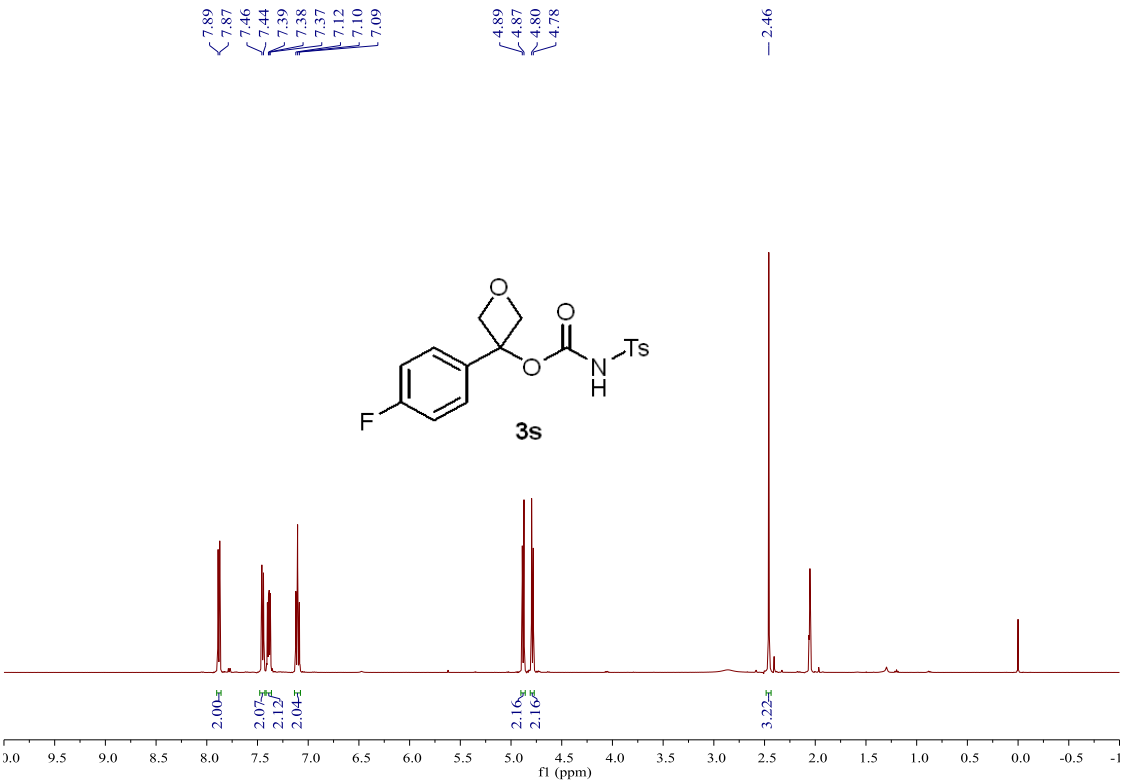
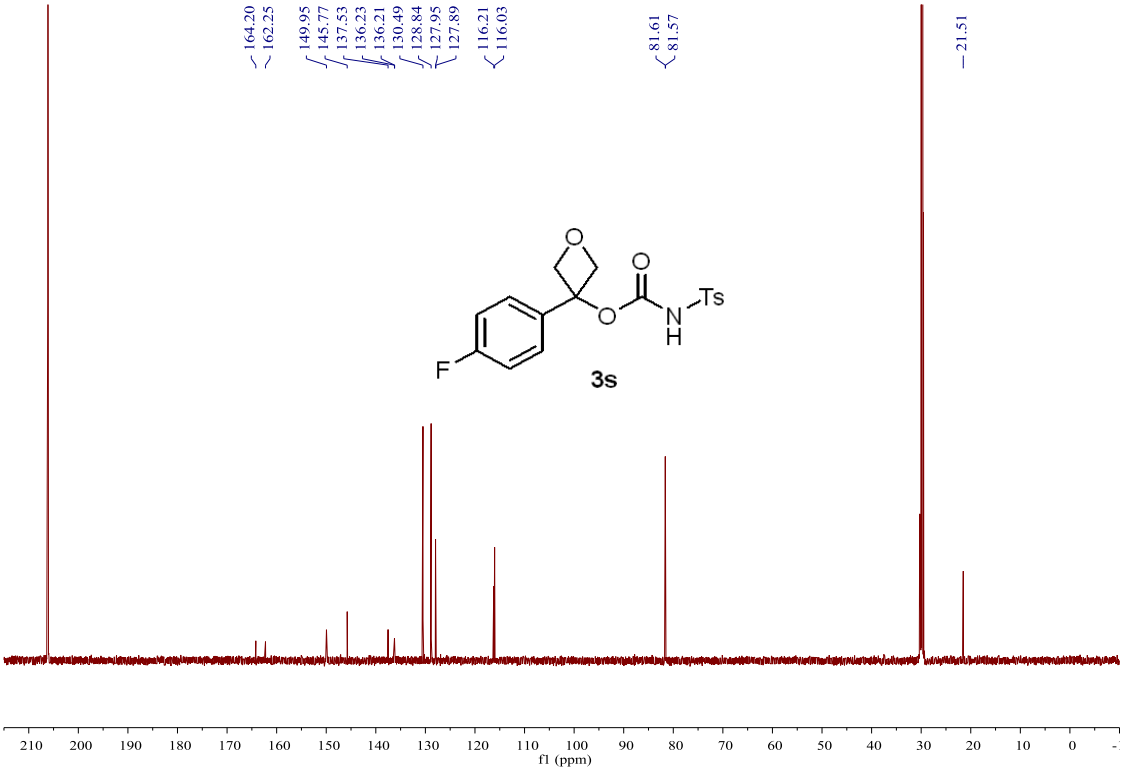
137.59
130.48
129.60
129.34
128.85
125.84
122.41
81.97
81.86
21.53
21.44
O
O
O
N
H
Ts
3r
f1 (ppm)


7.89
7.87
7.46
7.44
7.39
7.38
7.37
7.12
7.10
7.09
4.89
4.87
4.80
4.78
2.46
O
O
O
N
H
Ts
F
3s
2.00
2.07
2.12
2.04
2.16
2.16
3.22
f1 (ppm)


164.20
162.25
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145.77
137.53
136.23
136.21
130.49
128.84
127.95
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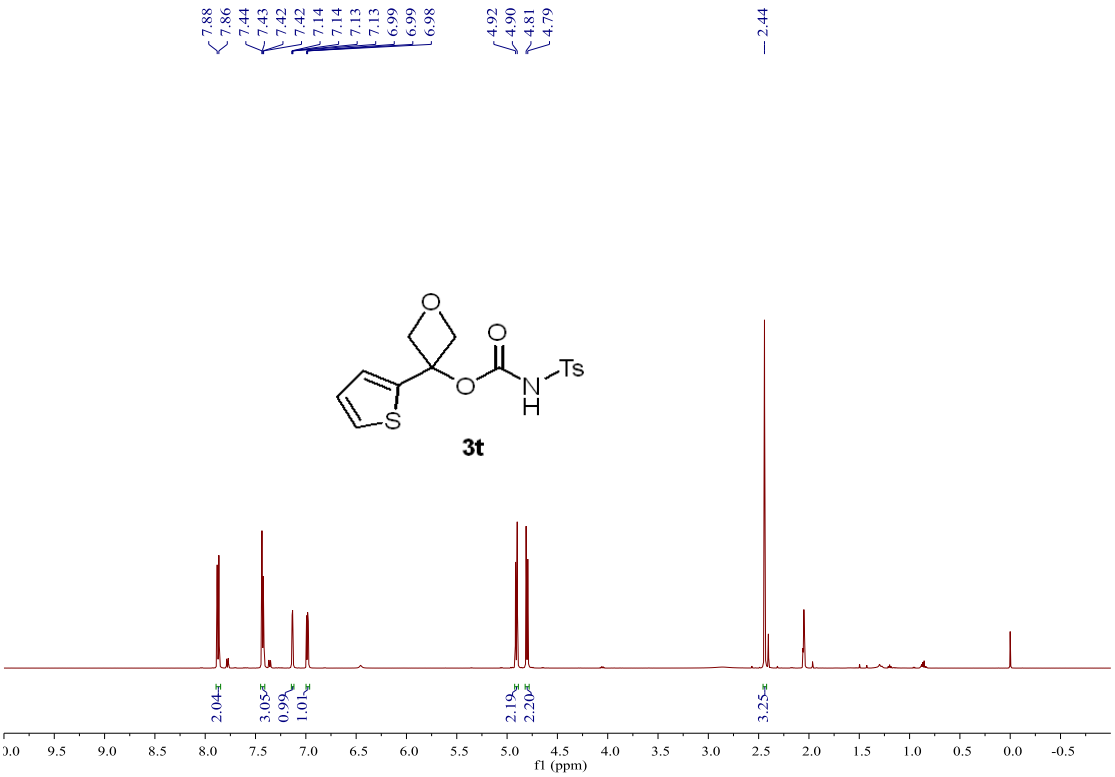
116.21
116.03
81.61
81.57
21.51
O
O
O
N
H
Ts
F
3s
f1 (ppm)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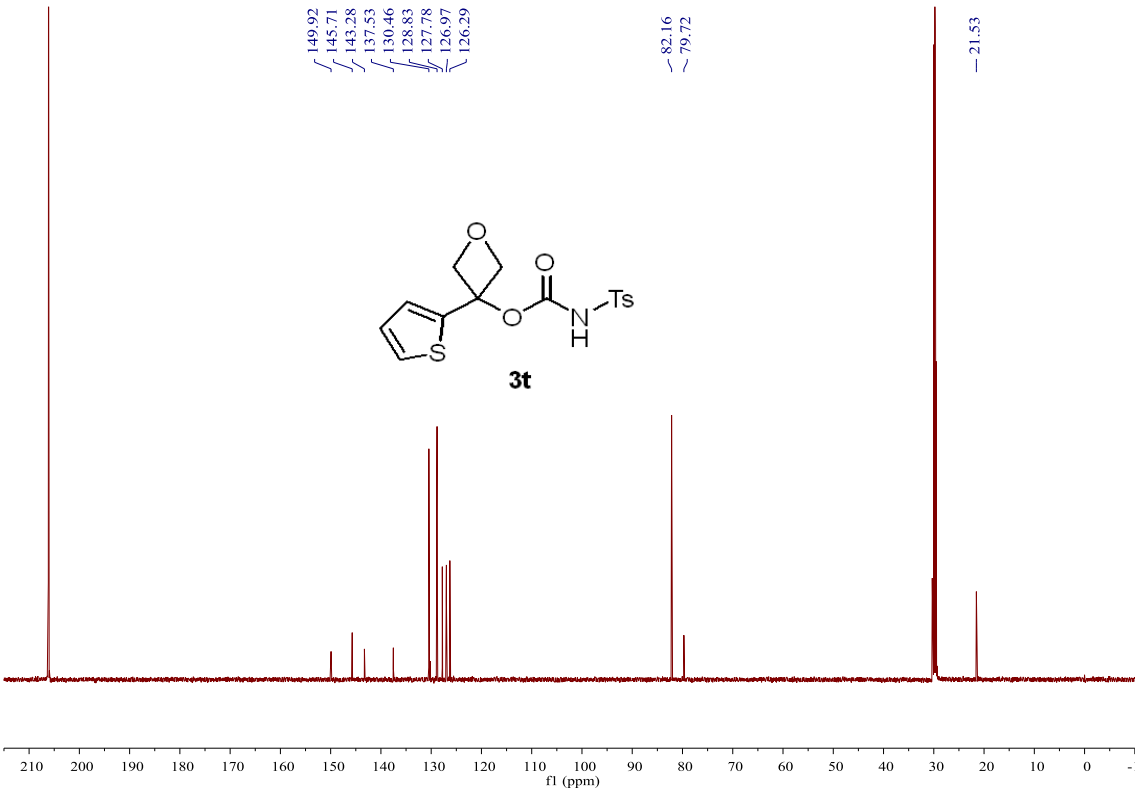
7.86
7.44
7.43
7.42
7.42
7.14
7.14
7.13
7.13
6.99
6.99
6.98
4.92
4.90
4.81
4.79
2.44
O
O
N
H
Ts
S
3t
2.04
3.05
0.90
1.01
2.19
2.20
3.25
f1 (ppm)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143.28
137.53
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128.83
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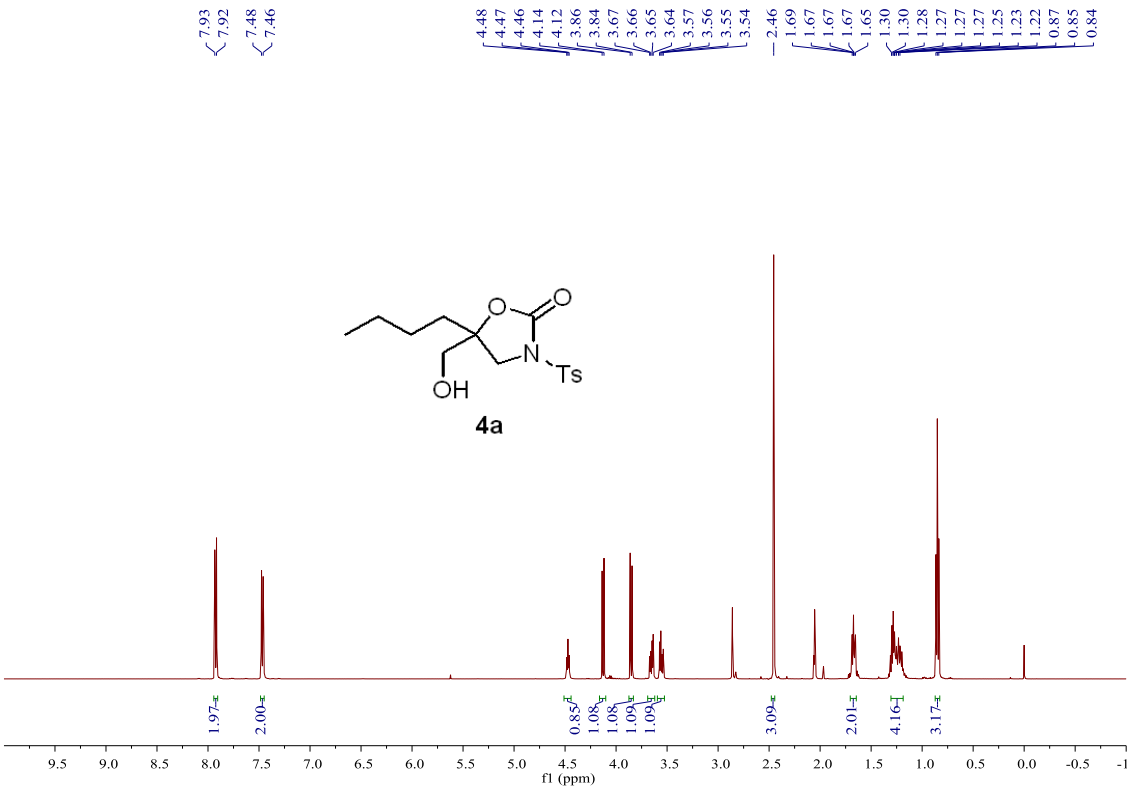
126.29
82.16
79.72
21.53
O
O
N
H
Ts
S
3t
f1 (ppm)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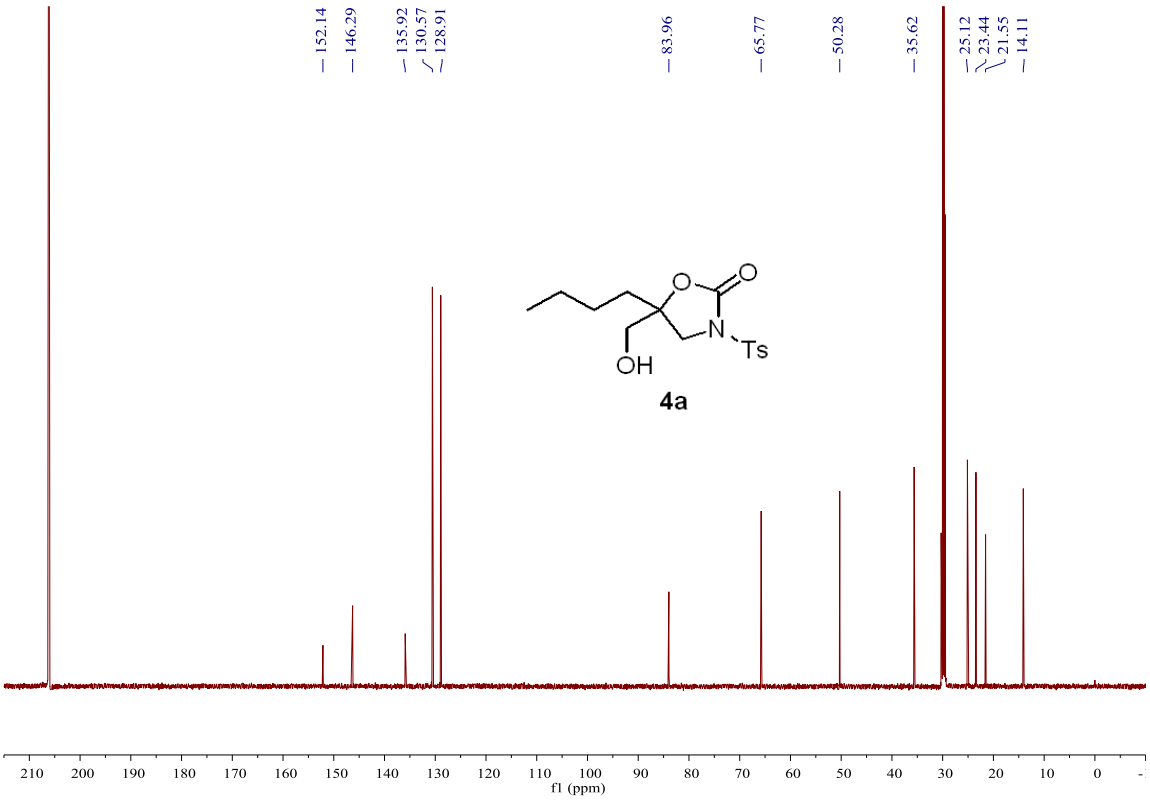
7.92
7.48
7.46
4.48
4.47
4.46
4.14
4.12
3.86
3.84
3.67
3.66
3.65
3.64
3.57
3.56
3.55
3.54
2.46
1.69
1.67
1.67
1.67
1.65
1.30
1.30
1.28
1.27
1.27
1.27
1.25
1.23
1.22
0.87
0.85
0.84
O
O
N
Ts
OH
4a
1.97
2.00
0.85
1.08
1.08
1.09
1.09
3.09
2.01
4.16
3.17
f1 (ppm)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146.29
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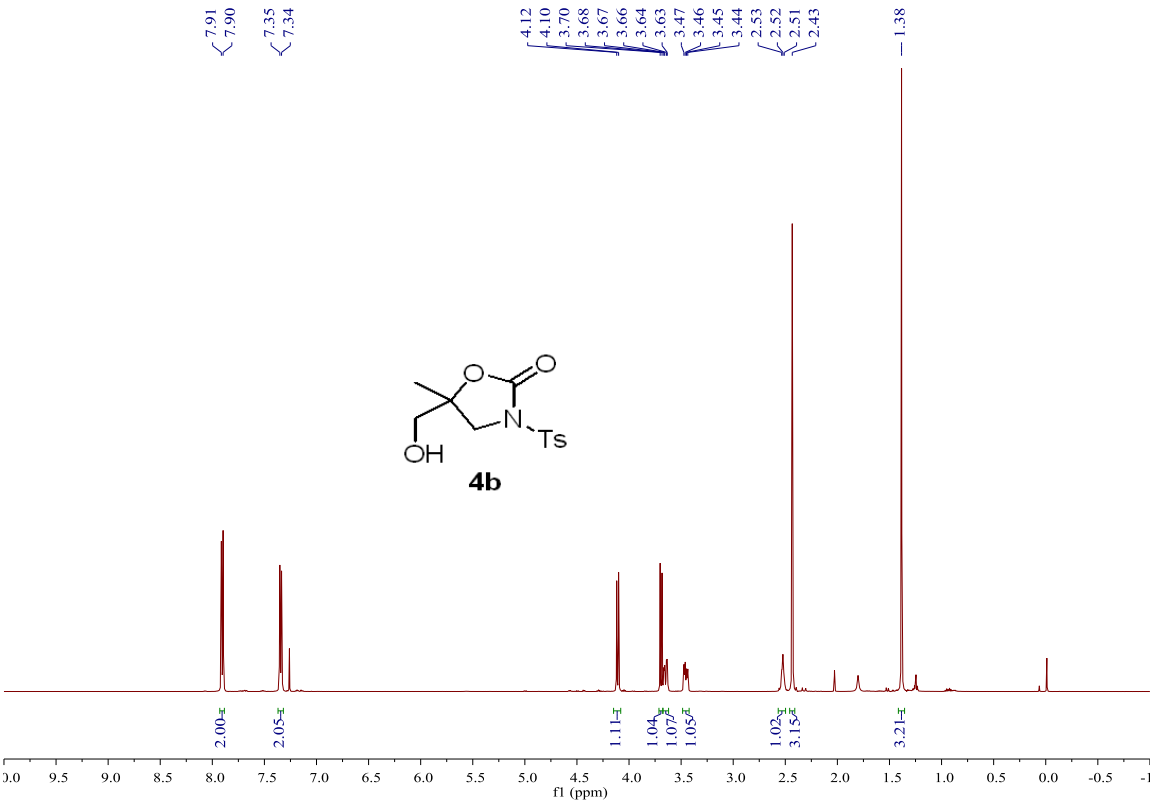
130.57
128.91
83.96
65.77
50.28
35.62
25.12
23.44
21.55
14.11
O
O
N
Ts
OH
4a
f1 (ppm)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7.90
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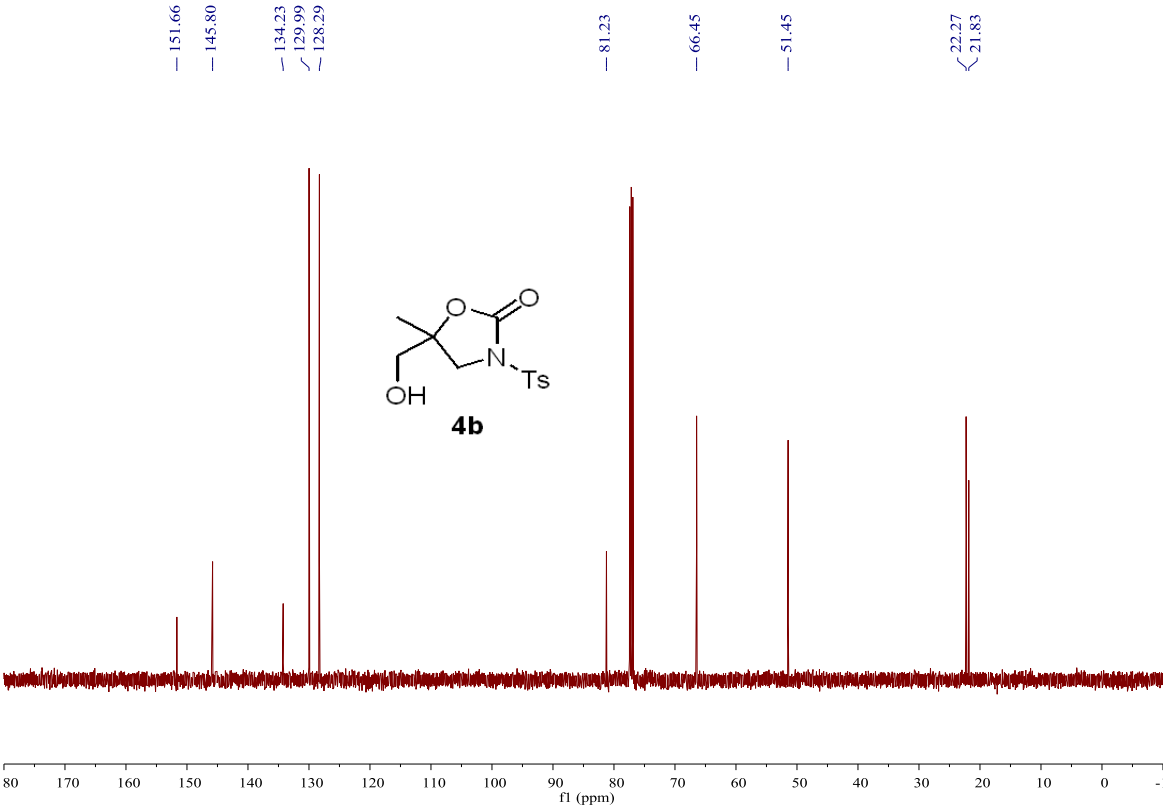
7.34
4.12
4.10
3.70
3.68
3.67
3.66
3.64
3.63
3.47
3.46
3.45
3.44
2.53
2.52
2.51
2.43
1.38
O
O
O
N
Ts
OH
4b
2.00
2.05
1.11
1.04
1.07
1.05
1.02
3.15
3.21
f1 (ppm)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129.99
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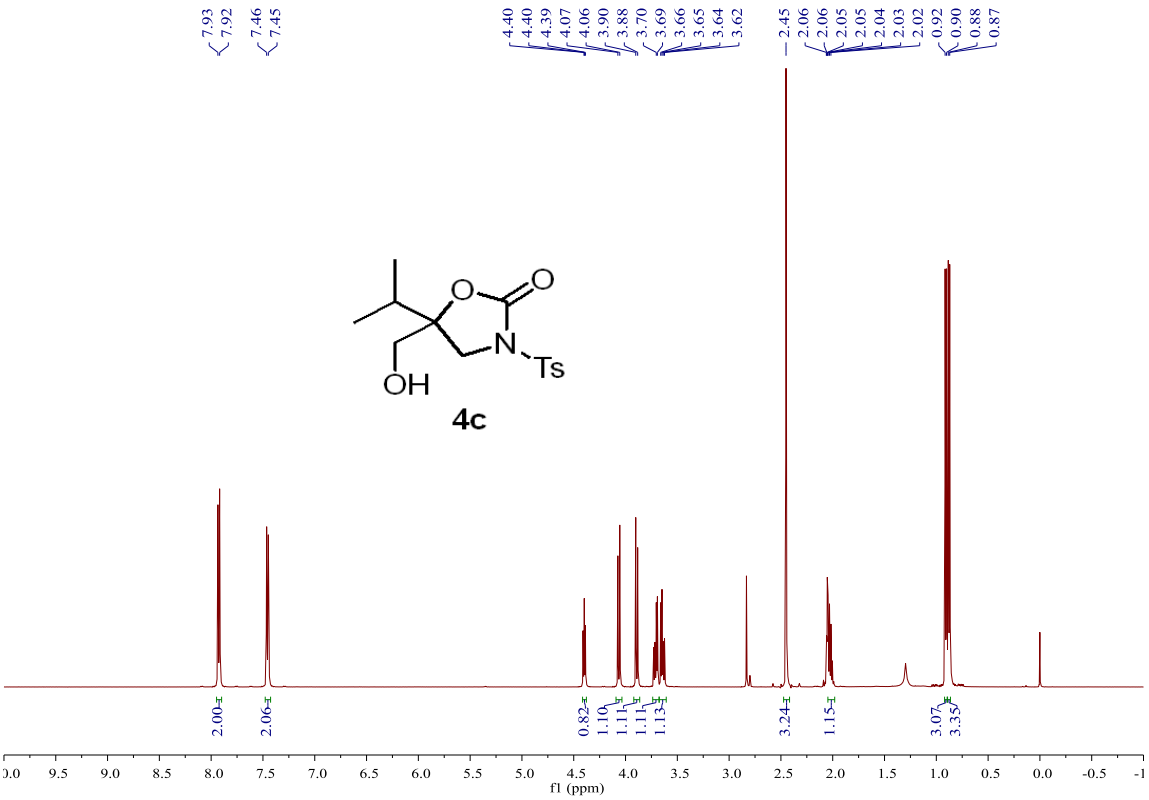
66.45
51.45
22.27
21.83
O
O
O
N
Ts
OH
4b
f1 (ppm)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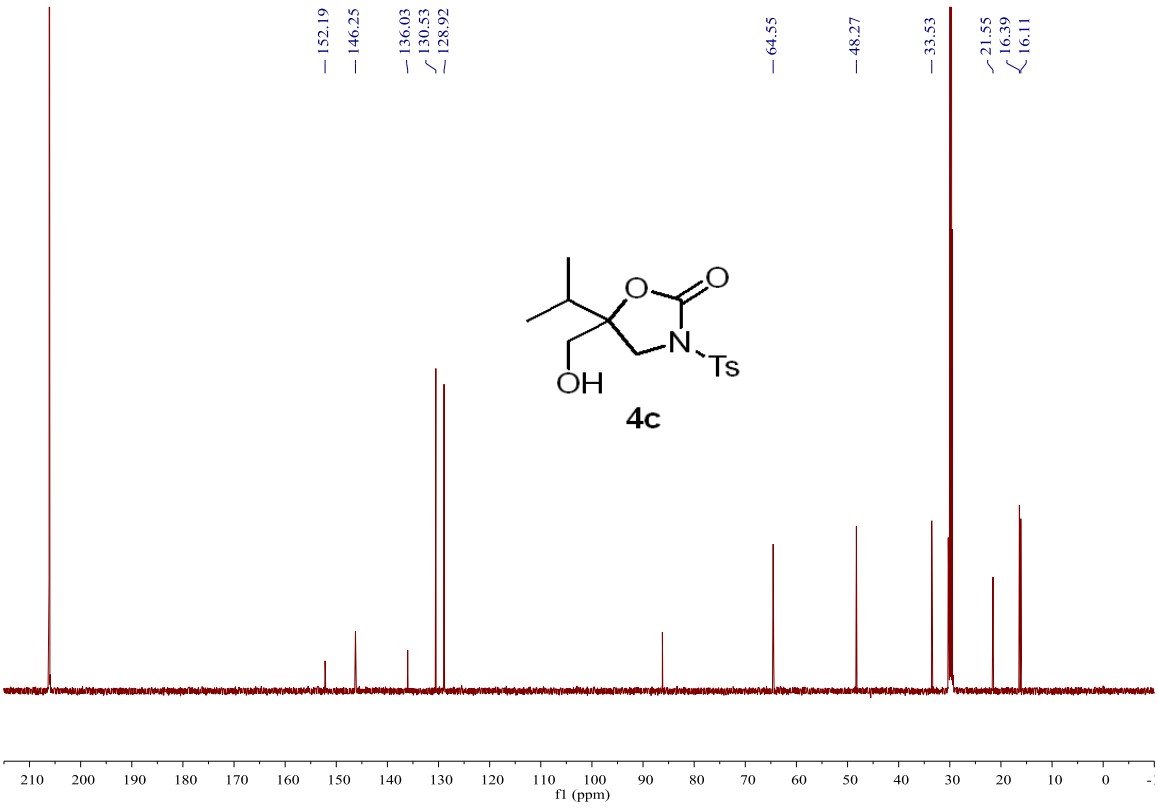
7.92
7.46
7.45
4.40
4.40
4.39
4.07
4.06
3.90
3.88
3.70
3.69
3.66
3.65
3.64
3.62
2.45
2.06
2.06
2.05
2.05
2.04
2.03
2.02
0.92
0.90
0.88
0.87
O
O
N
Ts
OH
4c
2.00
2.06
0.82
1.10
1.11
1.11
1.13
3.24
1.15
3.07
3.35
f1 (ppm)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130.53
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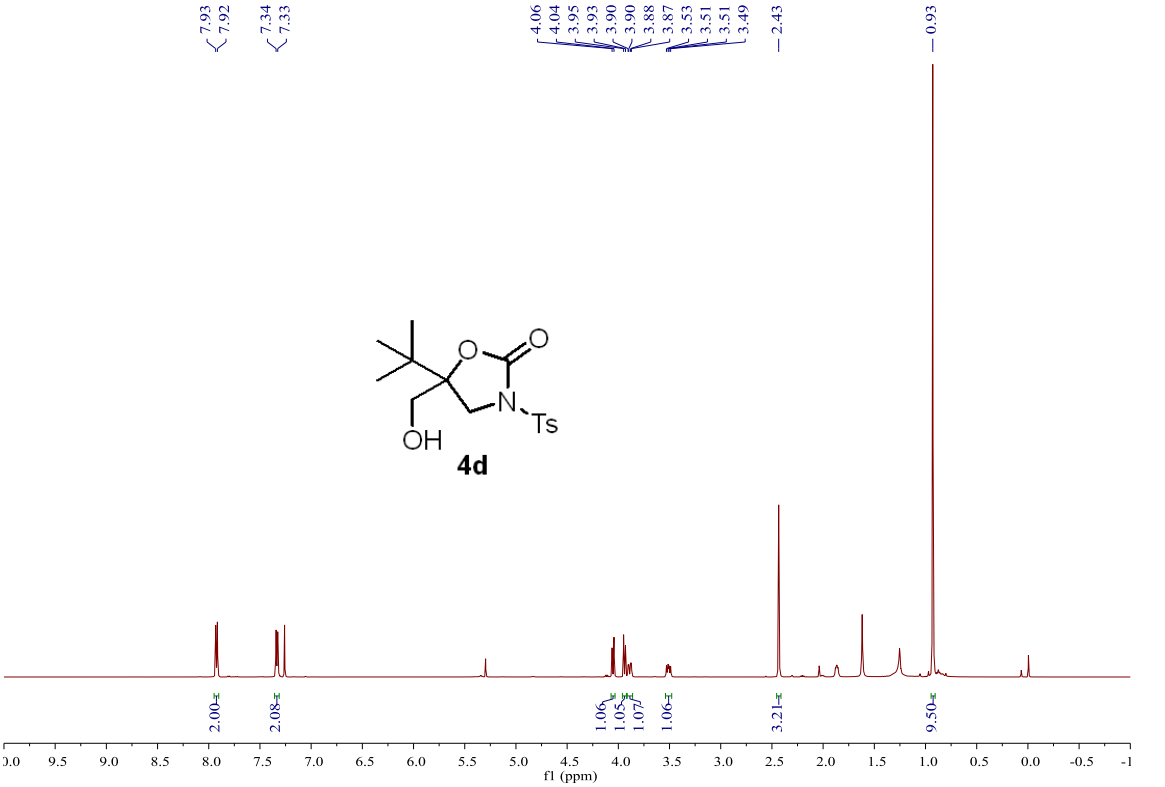
33.53
21.55
16.39
16.11
O
O
N
Ts
OH
4c
f1 (ppm)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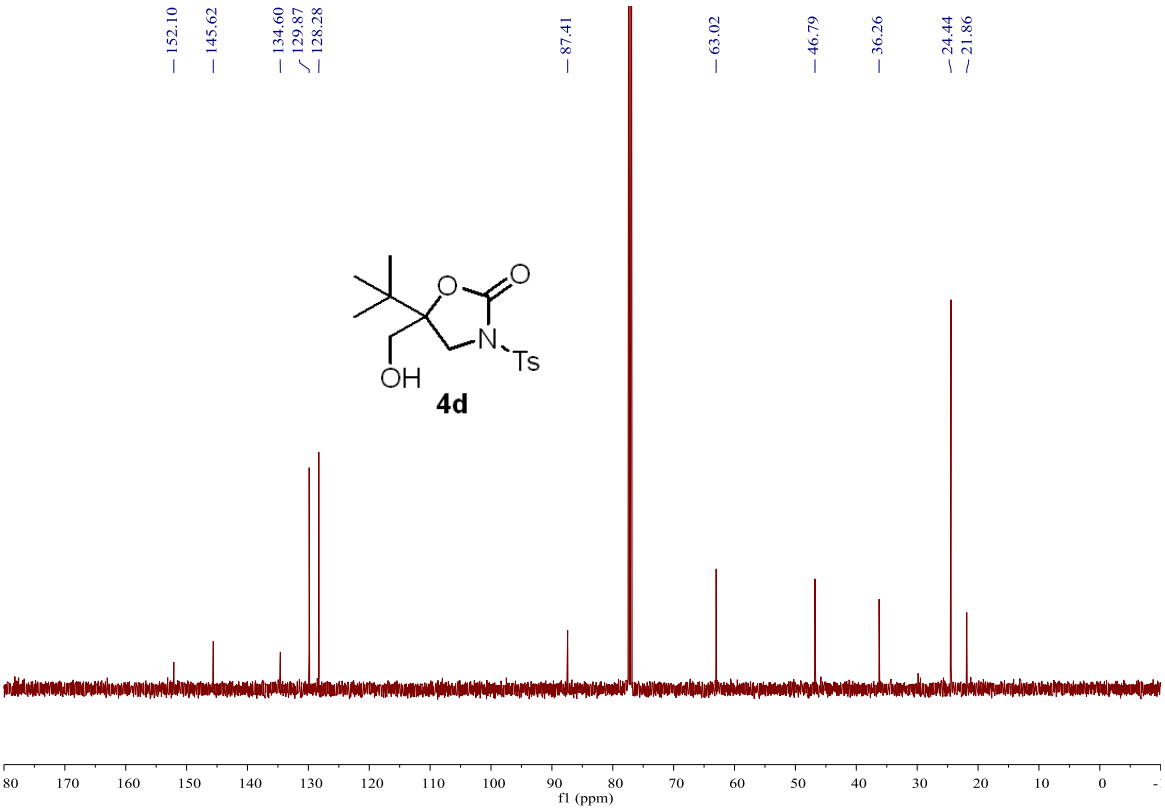
7.92
7.34
7.33
4.06
4.04
3.95
3.93
3.90
3.90
3.88
3.87
3.53
3.51
3.51
3.49
2.43
0.93
O
O
N
Ts
OH
4d
2.00
2.08
1.06
1.05
1.07
1.06
3.21
9.50
fl (ppm)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46.79
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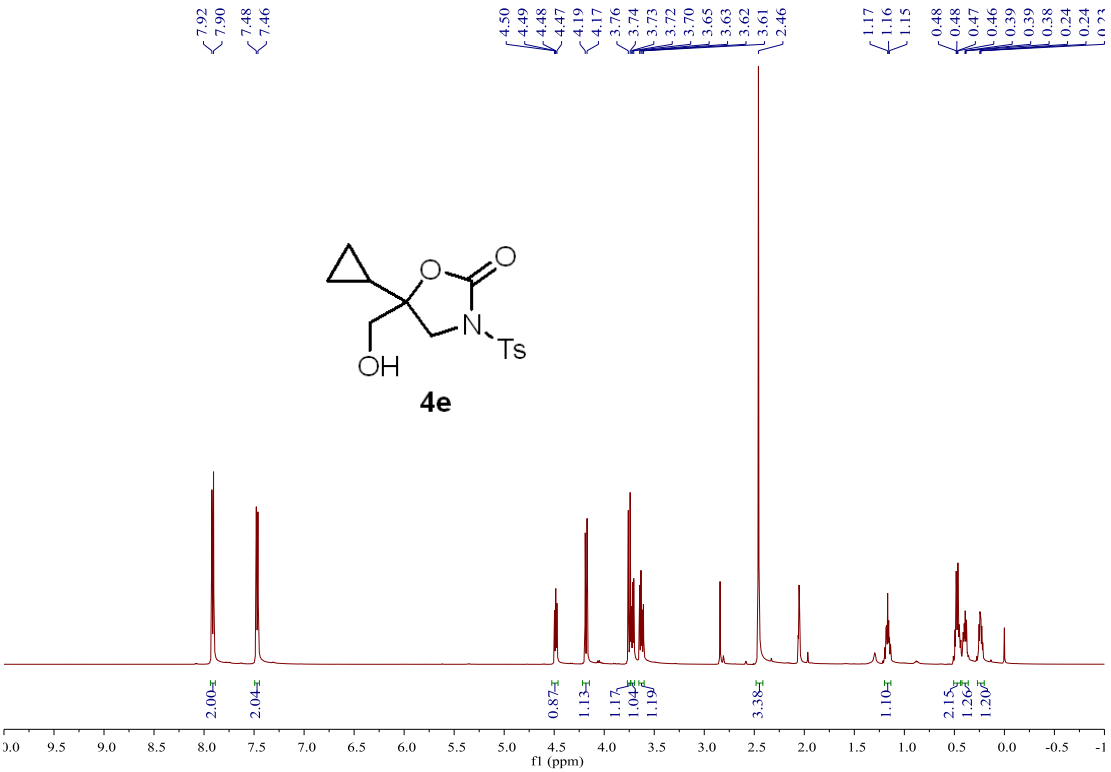
24.44
21.86
O
O
N
Ts
OH
4d
fl (ppm)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4.50
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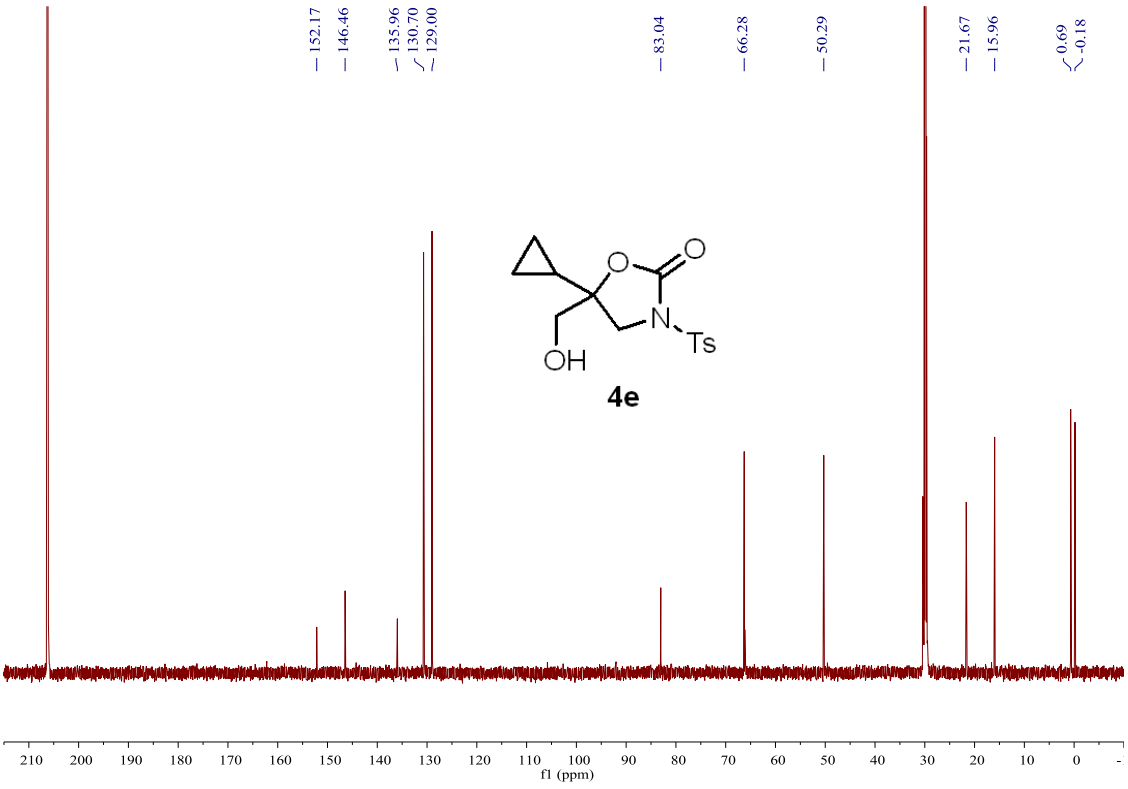
4.48
4.47
4.19
4.17
3.76
3.74
3.73
3.72
3.70
3.65
3.63
3.62
3.61
2.46
1.17
1.16
1.15
0.48
0.48
0.47
0.46
0.39
0.39
0.38
0.24
0.24
O
O
N
Ts
OH
4e
2.00
2.04
0.87
1.13
1.17
1.04
1.19
3.38
1.10
2.15
1.26
1.20
f1 (ppm)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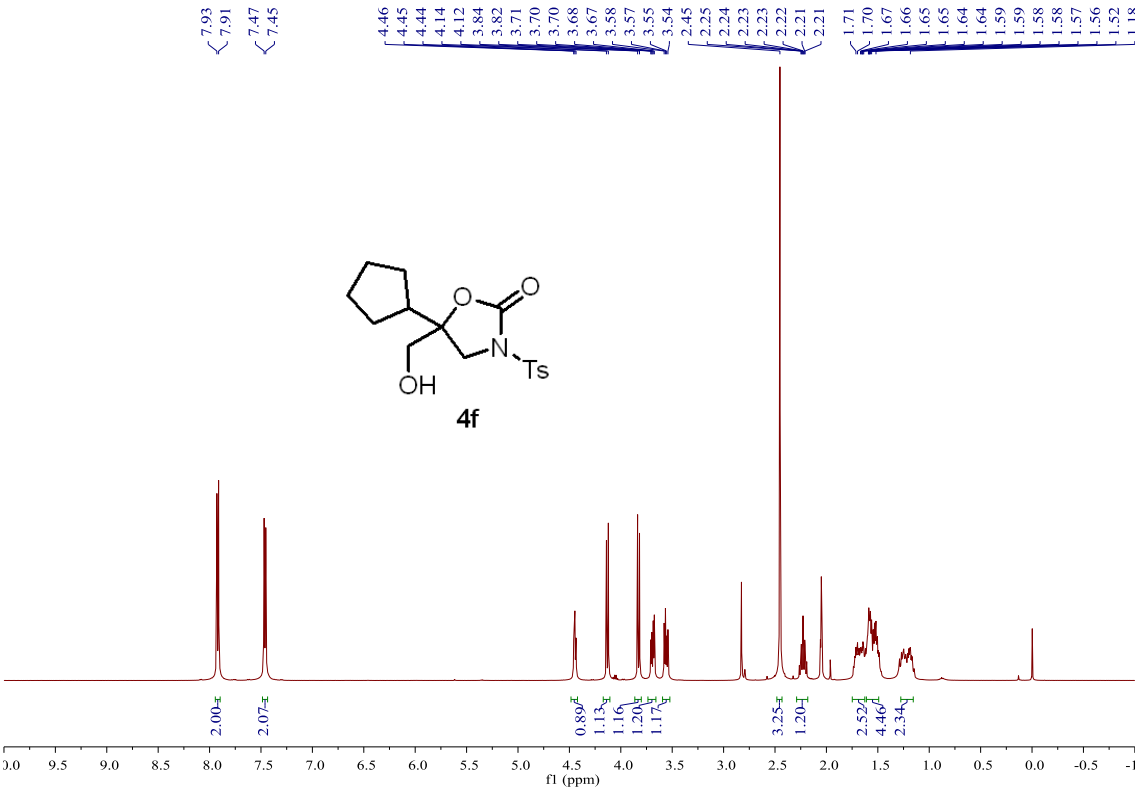
15.96
0.69
-0.18
O
O
N
Ts
OH
4e
f1 (ppm)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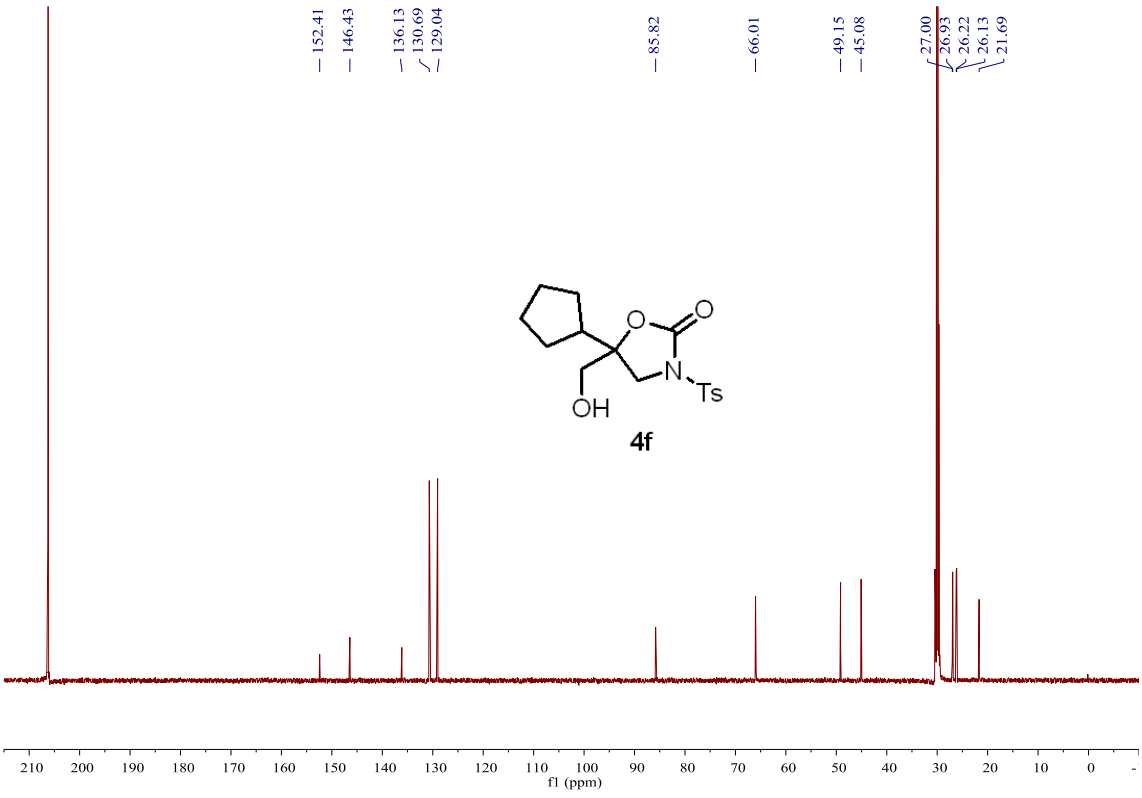
4.45
4.44
4.14
4.12
3.84
3.82
3.71
3.70
3.70
3.68
3.67
3.58
3.57
3.55
3.54
2.45
2.25
2.24
2.23
2.23
2.22
2.21
2.21
1.71
1.70
1.67
1.66
1.65
1.65
1.64
1.64
1.59
1.59
1.58
1.58
1.57
1.56
1.52
O
O
N
Ts
OH
2.00
2.07
0.89
1.13
1.16
1.20
1.17
3.25
1.20
2.52
4.46
2.34
f1 (ppm)

4f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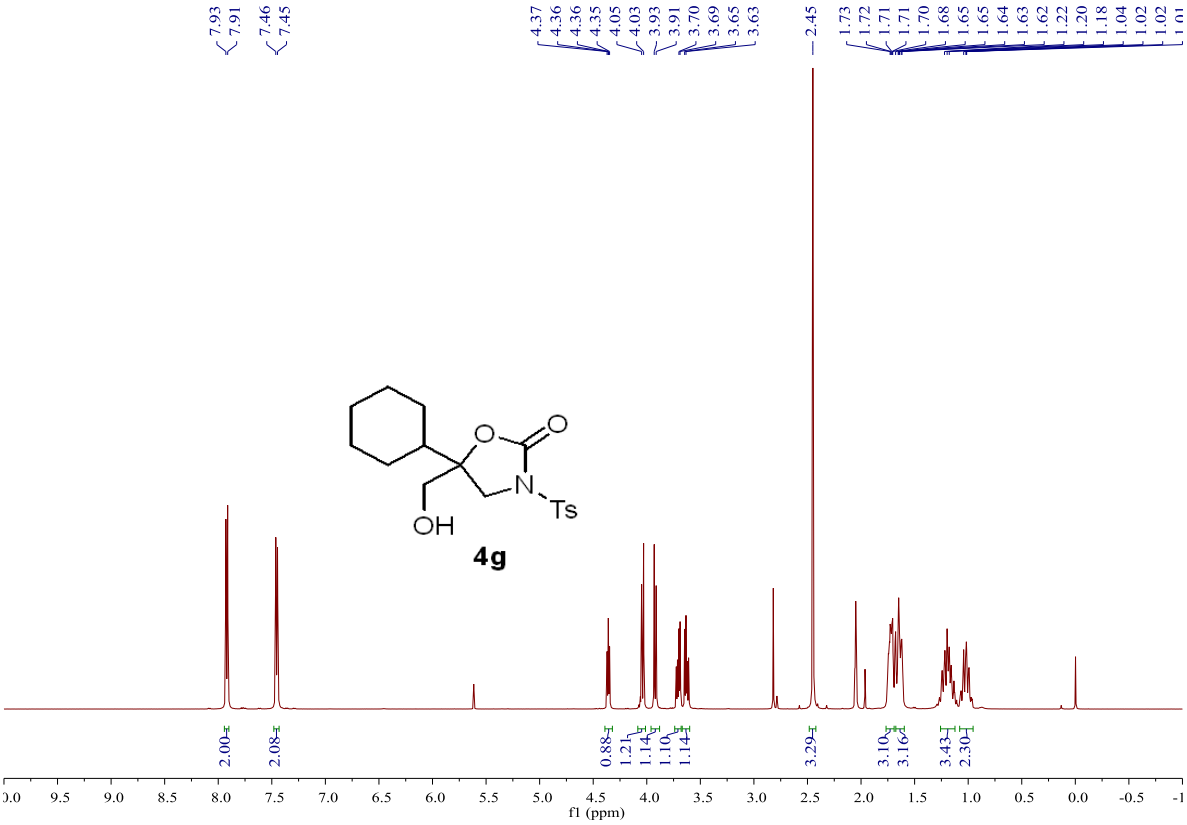
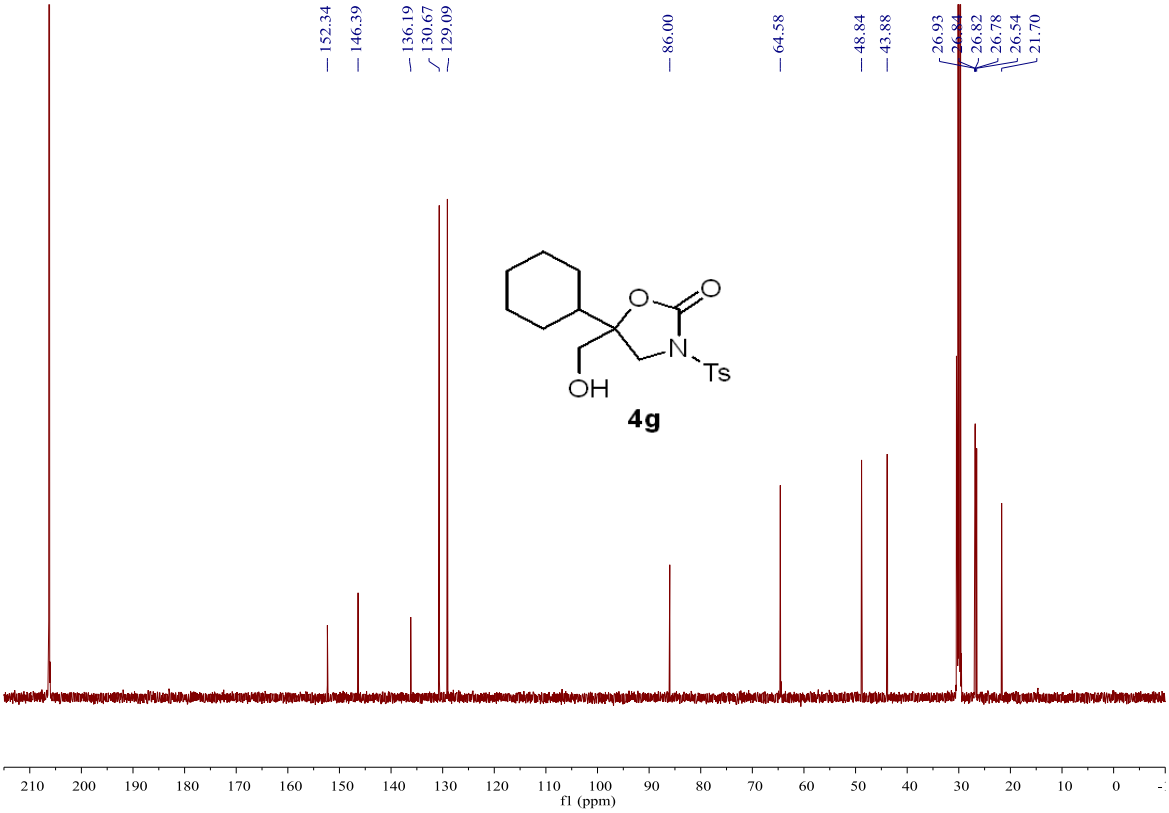
130.69
129.04
85.82
66.01
49.15
45.08
27.00
26.93
26.22
26.13
21.69
O
O
N
Ts
OH
f1 (ppm)

4f


7.93
7.91
7.46
7.45
4.37
4.36
4.36
4.35
4.05
4.03
3.93
3.91
3.70
3.69
3.65
3.63
2.45
1.73
1.72
1.71
1.71
1.70
1.68
1.65
1.65
1.64
1.63
1.62
1.22
1.20
1.18
1.04
1.02
1.02
2.00
2.08
0.88
1.21
1.14
1.10
1.14
3.29
3.10
3.16
3.43
2.30
f1 (ppm)
OH
Ts
4g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129.09
86.00
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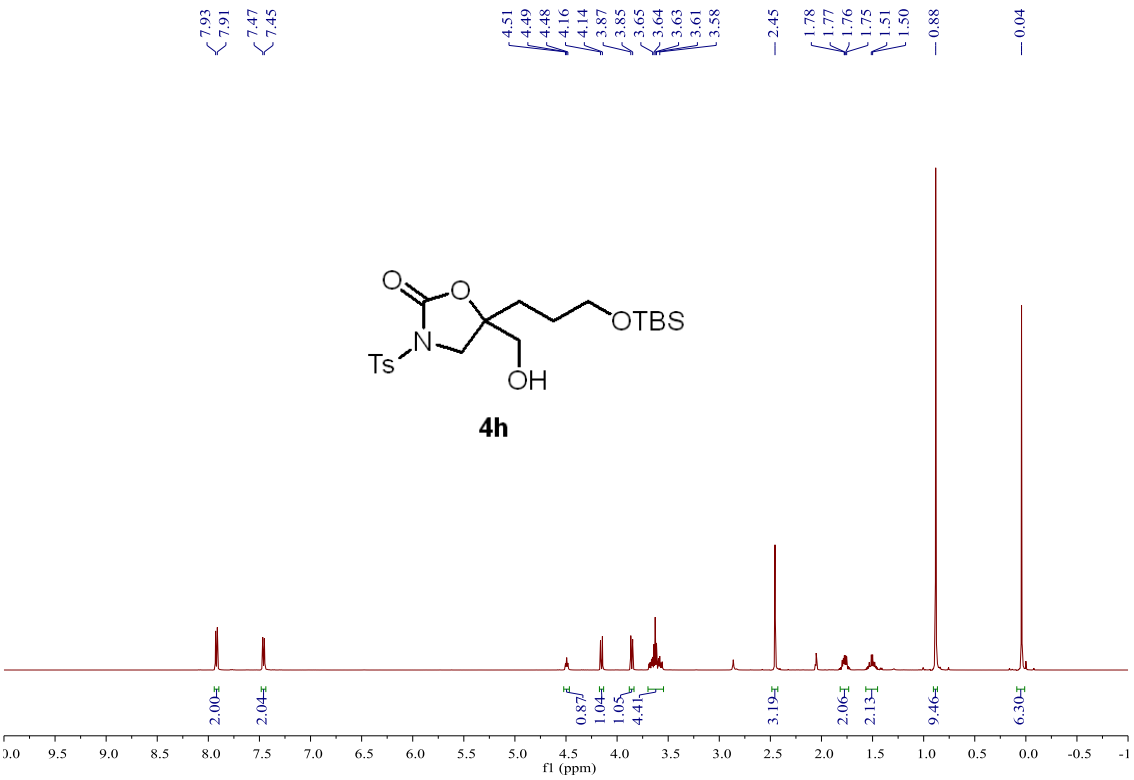
26.93
26.84
26.82
26.78
26.54
21.70
f1 (ppm)
OH
Ts
4g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7.91
7.47
7.45
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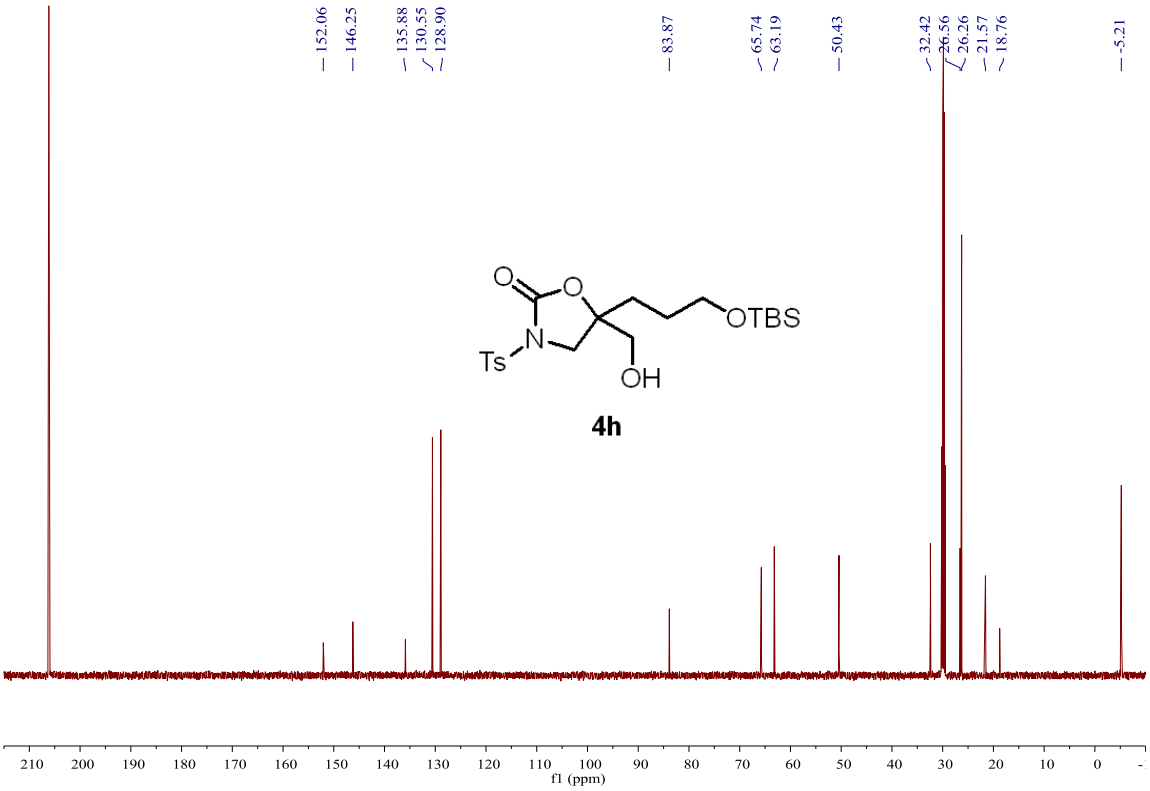
4.49
4.48
4.16
4.14
3.87
3.85
3.65
3.64
3.63
3.61
3.58
2.45
1.78
1.77
1.76
1.75
1.51
1.50
0.88
0.04
OTBS
Ts
N
O
OH
4h
2.00
2.04
0.87
1.04
1.05
4.41
3.19
2.06
2.13
9.46
6.30
f1 (ppm)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83.87
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63.19
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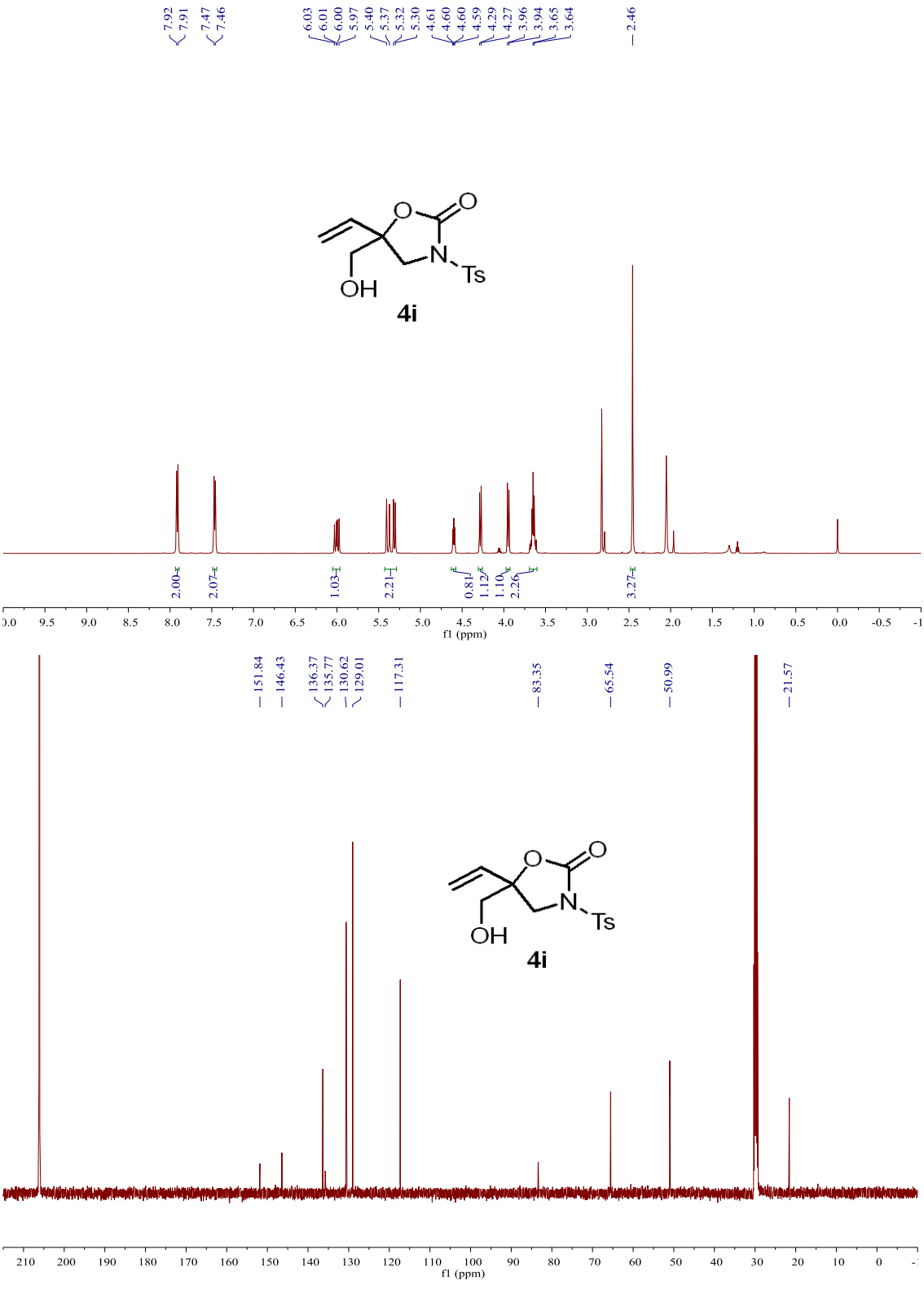
26.26
21.57
18.76
-5.21
OTBS
Ts
N
O
OH
4h
f1 (ppm)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6.00
5.97
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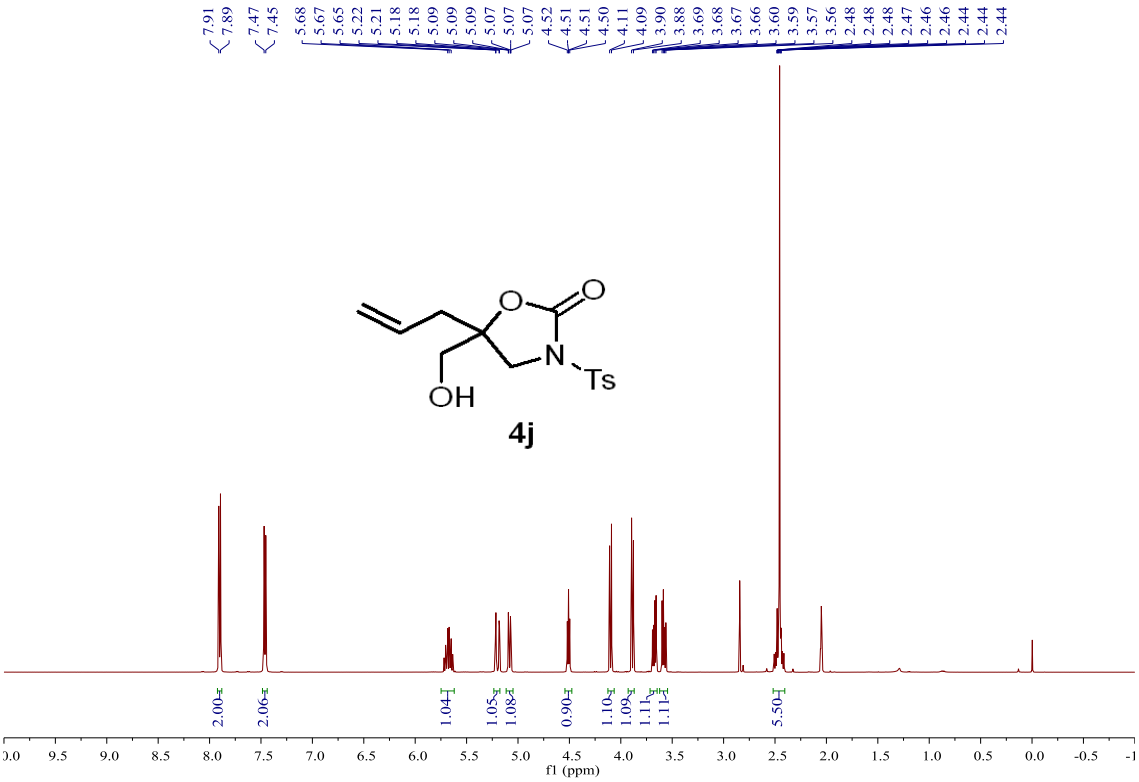
5.37
5.32
5.30
4.61
4.60
4.60
4.59
4.29
4.27
3.96
3.94
3.65
3.64
2.46
O
O
N
Ts
OH
4i
2.00
2.07
1.03
2.21
0.81
1.12
1.10
2.26
3.27
f1 (ppm)
151.84
146.43
136.37
135.77
130.62
129.01
117.31
83.35
65.54
50.99
21.57
f1 (ppm)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7.45
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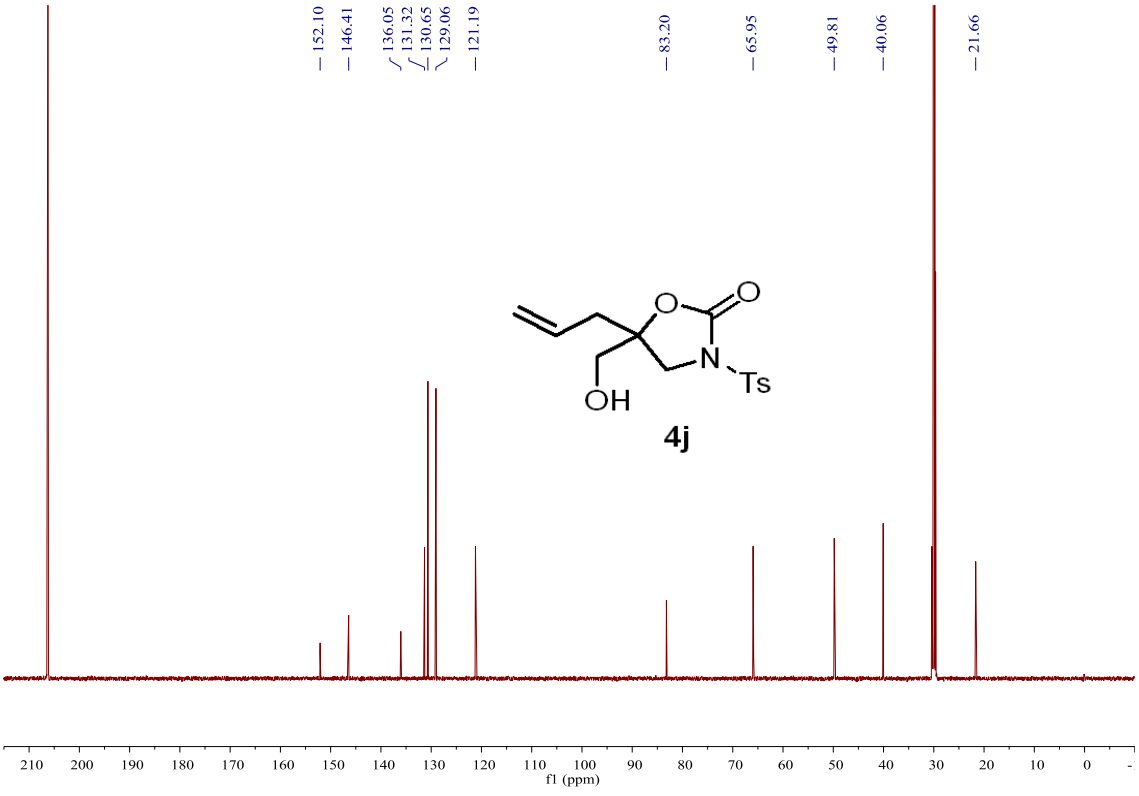
5.67
5.65
5.22
5.21
5.18
5.18
5.09
5.09
5.09
5.07
5.07
5.07
4.52
4.51
4.51
4.50
4.11
4.09
3.90
3.88
3.69
3.68
3.67
3.66
3.60
3.59
3.57
3.56
2.48
2.48
2.48
2.47
2.46
2.46
2.44
2.44
2.44
O
O
N
Ts
OH
4j
2.00
2.06
1.04
1.05
1.08
0.90
1.10
1.09
1.11
1.11
5.50
f1 (ppm)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146.41
136.05
131.32
130.65
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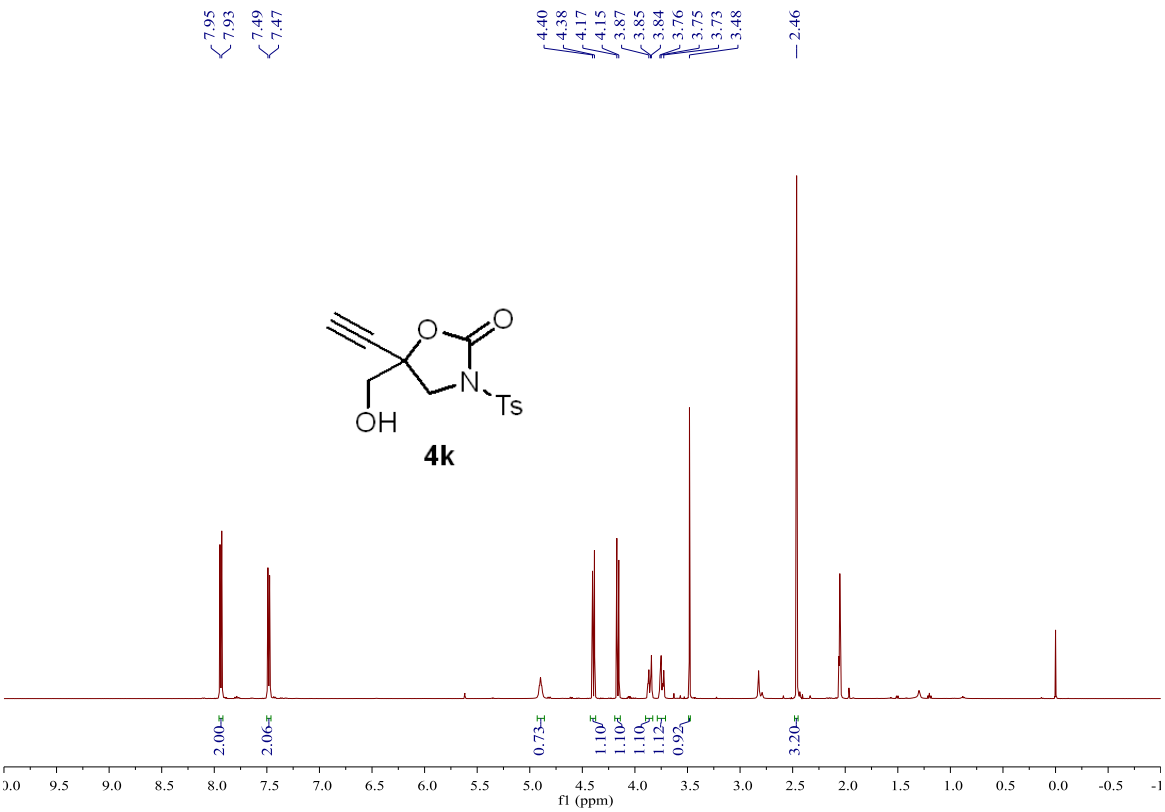
121.19
83.20
65.95
49.81
40.06
21.66
O
O
N
Ts
OH
4j
f1 (ppm)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7.93
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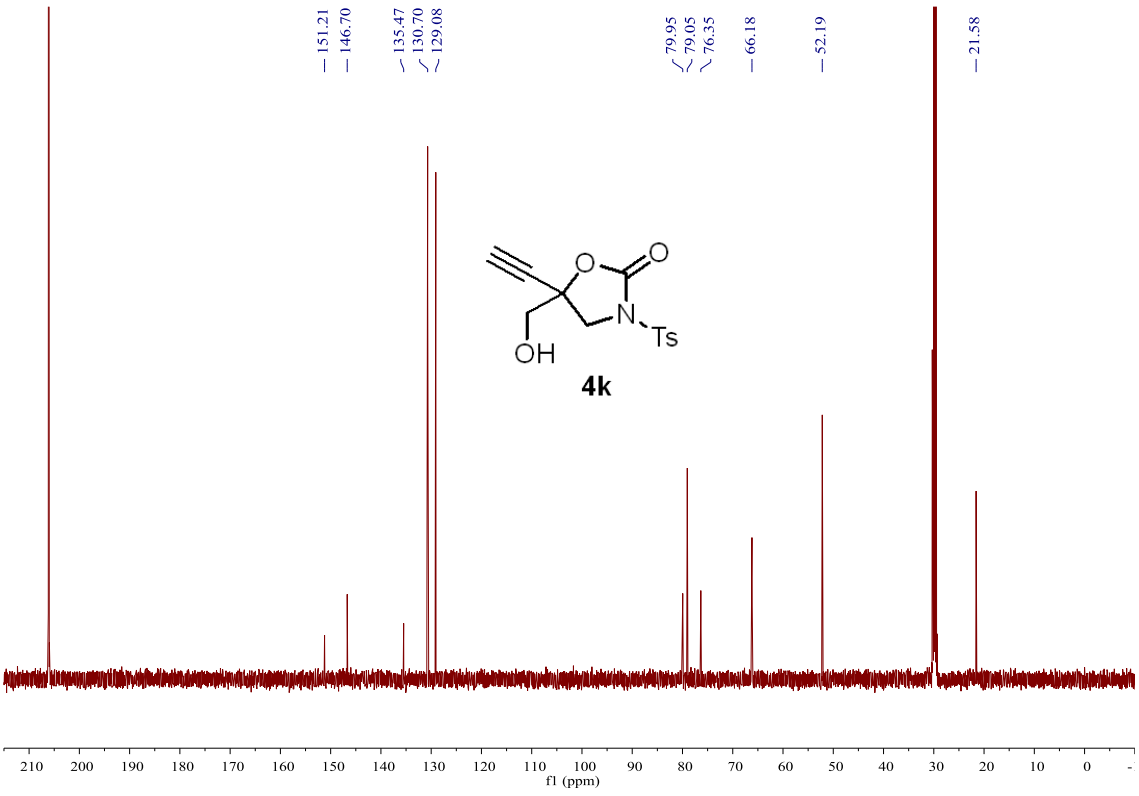
7.47
4.40
4.38
4.17
4.15
3.87
3.85
3.84
3.76
3.75
3.73
3.48
2.46
O
O
N
Ts
OH
4k
2.00
2.06
0.73
1.10
1.10
1.10
1.12
0.92
3.20
f1 (ppm)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146.70
135.47
130.70
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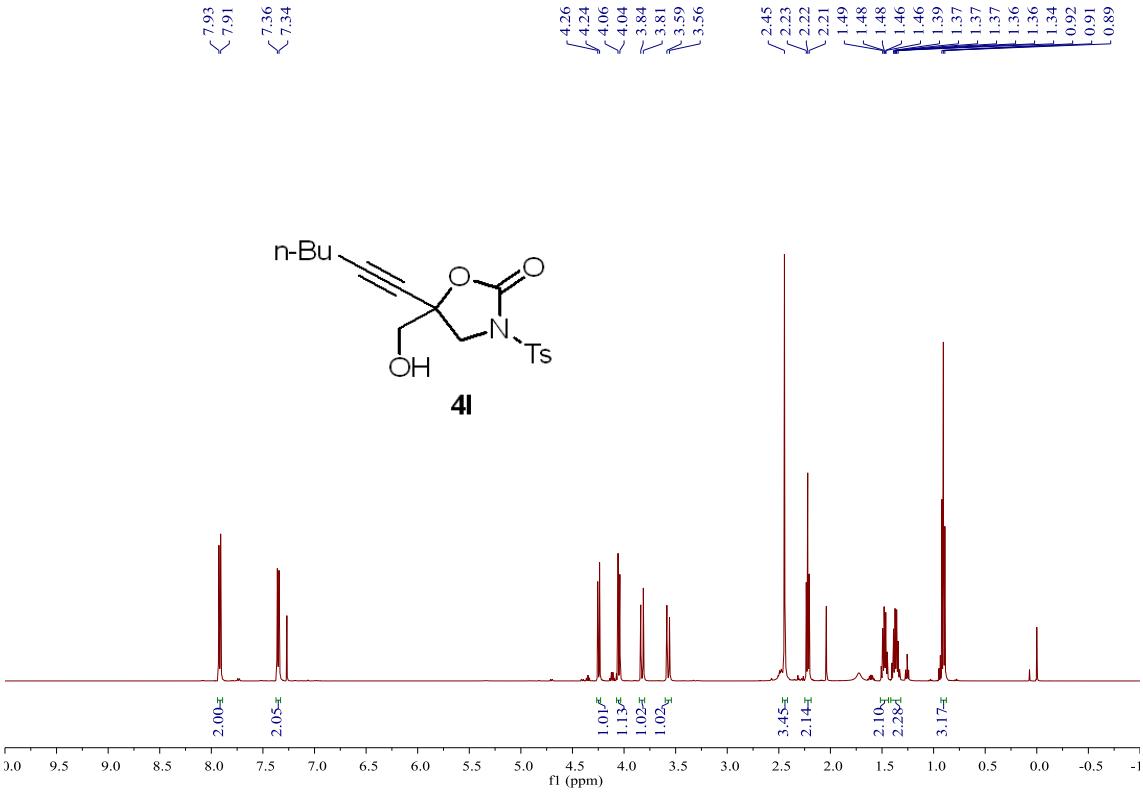
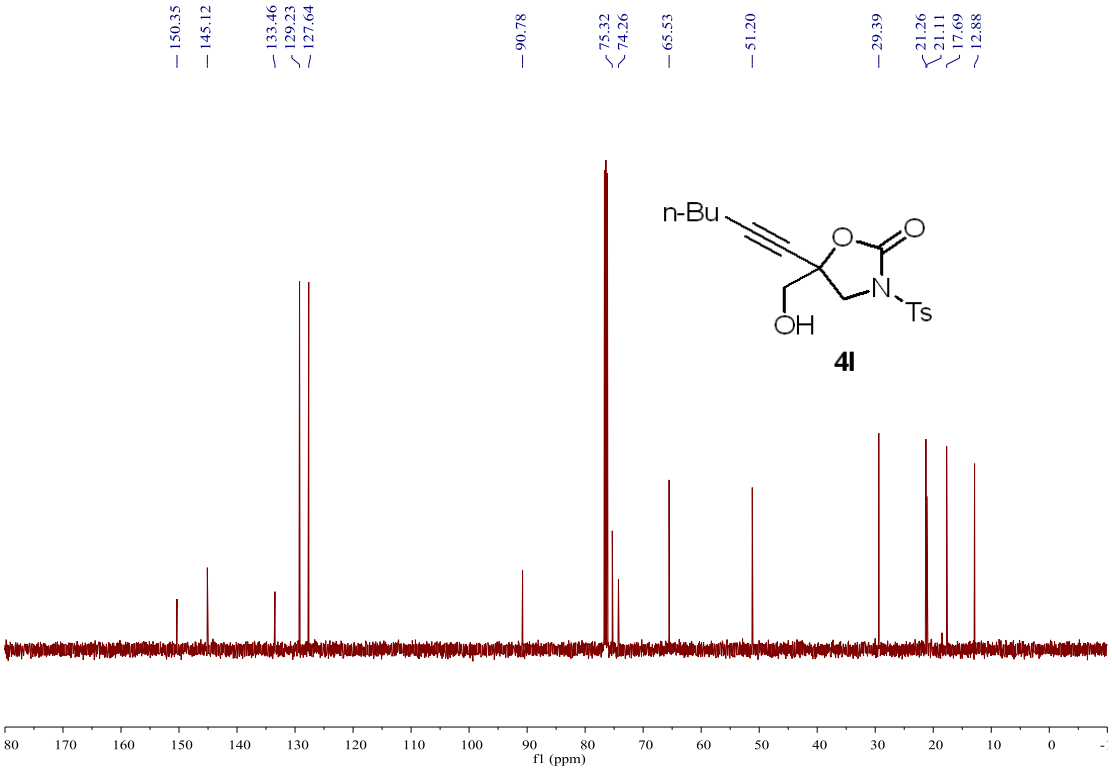
79.05
76.35
66.18
52.19
21.58
O
O
N
Ts
OH
4k
f1 (ppm)


7.93
7.91
7.36
7.34
4.26
4.24
4.06
4.04
3.84
3.81
3.59
3.56
2.45
2.23
2.22
2.21
1.49
1.48
1.48
1.46
1.46
1.39
1.37
1.37
1.37
1.36
1.36
1.34
0.92
0.91
0.89
n-Bu
O
O
N
Ts
OH
4l
2.00
2.05
1.01
1.13
1.02
1.02
3.45
2.14
2.10
2.28
3.17
f1 (ppm)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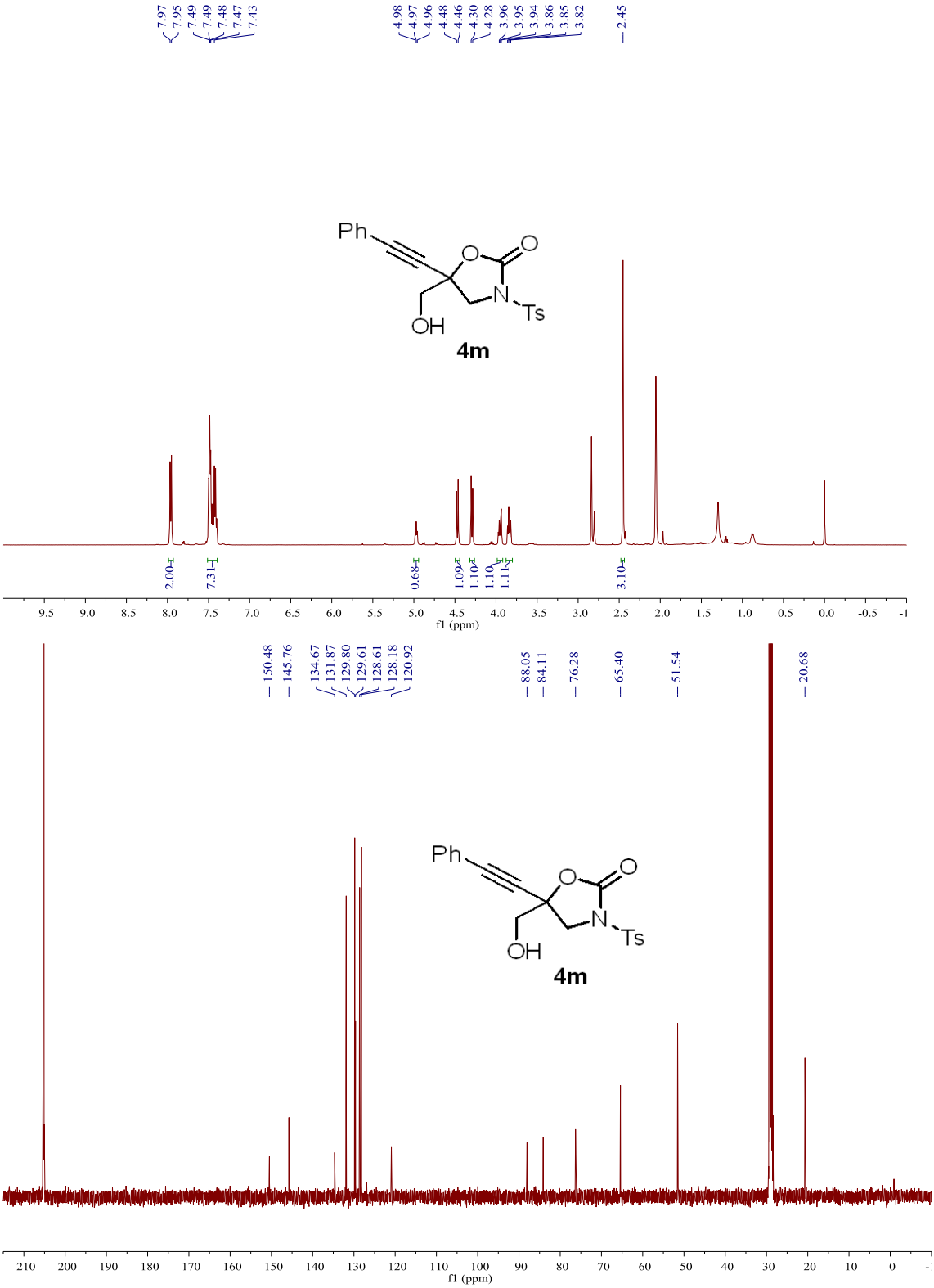
145.12
133.46
129.23
127.64
90.78
75.32
74.26
65.53
51.20
29.39
21.26
21.11
17.69
12.88
n-Bu
O
O
N
Ts
OH
4l
f1 (ppm)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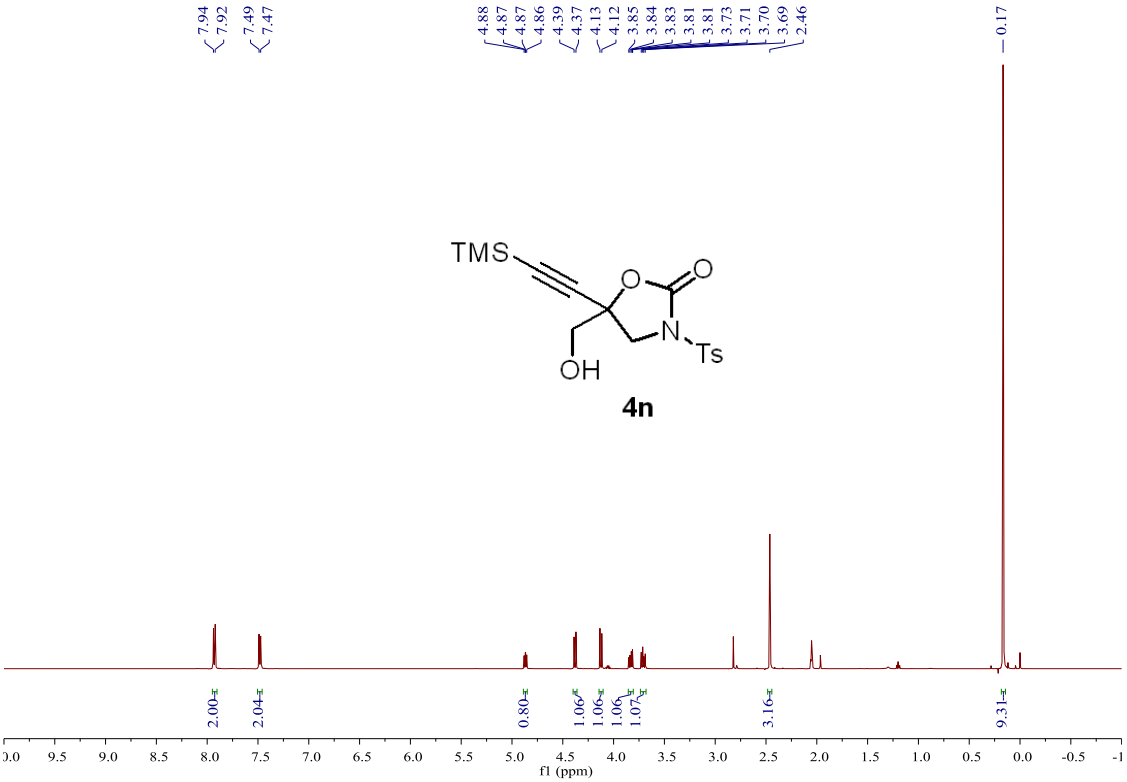
7.95
7.49
7.49
7.48
7.47
7.43
4.98
4.97
4.96
4.48
4.46
4.30
4.28
3.96
3.95
3.94
3.86
3.85
3.82
2.45
Ph
O
O
N
Ts
OH
4m
2.00
7.31
0.68
1.09
1.10
1.10
1.11
3.10
f1 (ppm)
150.48
145.76
134.67
131.87
129.80
129.61
128.61
128.18
120.92
88.05
84.11
76.28
65.40
51.54
20.68
Ph
O
O
N
Ts
OH
4m
f1 (ppm)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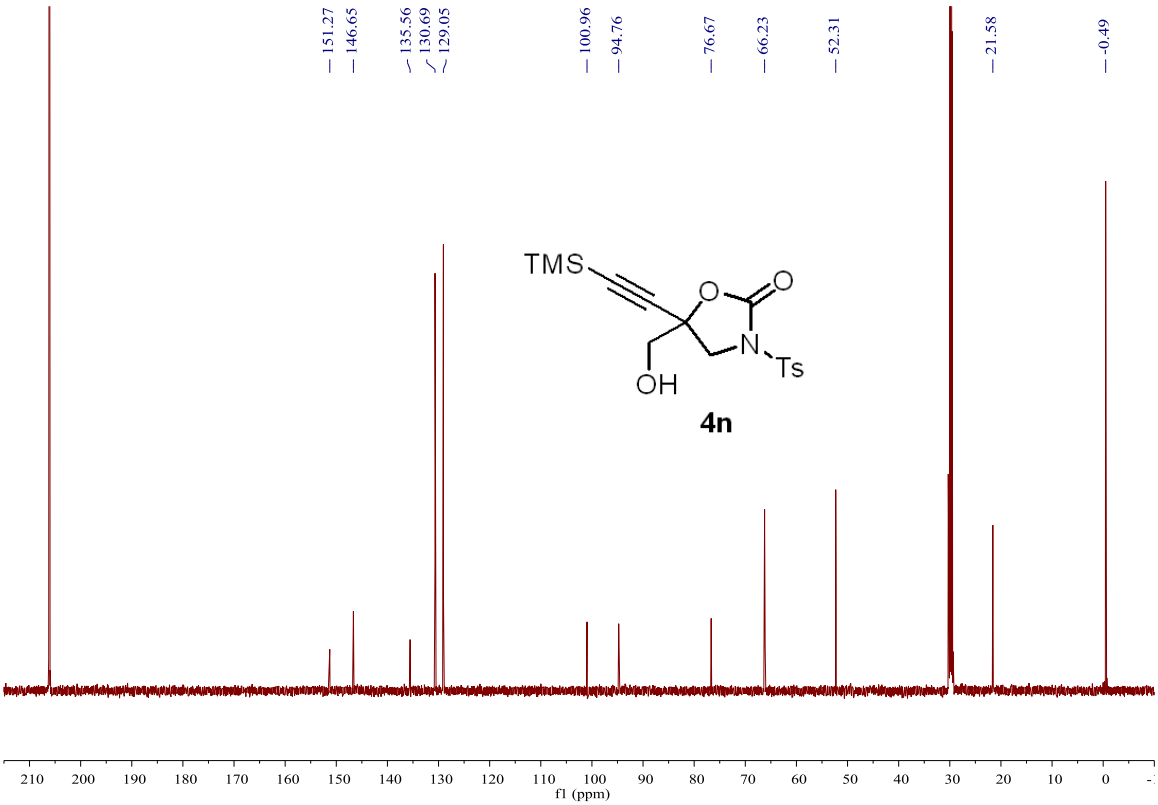
7.92
7.49
7.47
4.88
4.87
4.87
4.86
4.39
4.37
4.13
4.12
3.85
3.84
3.83
3.81
3.81
3.73
3.71
3.70
3.69
2.46
0.17
TMS
O
O
N
Ts
OH
4n
2.00
2.04
0.80
1.06
1.06
1.06
1.07
3.16
9.31
f1 (ppm)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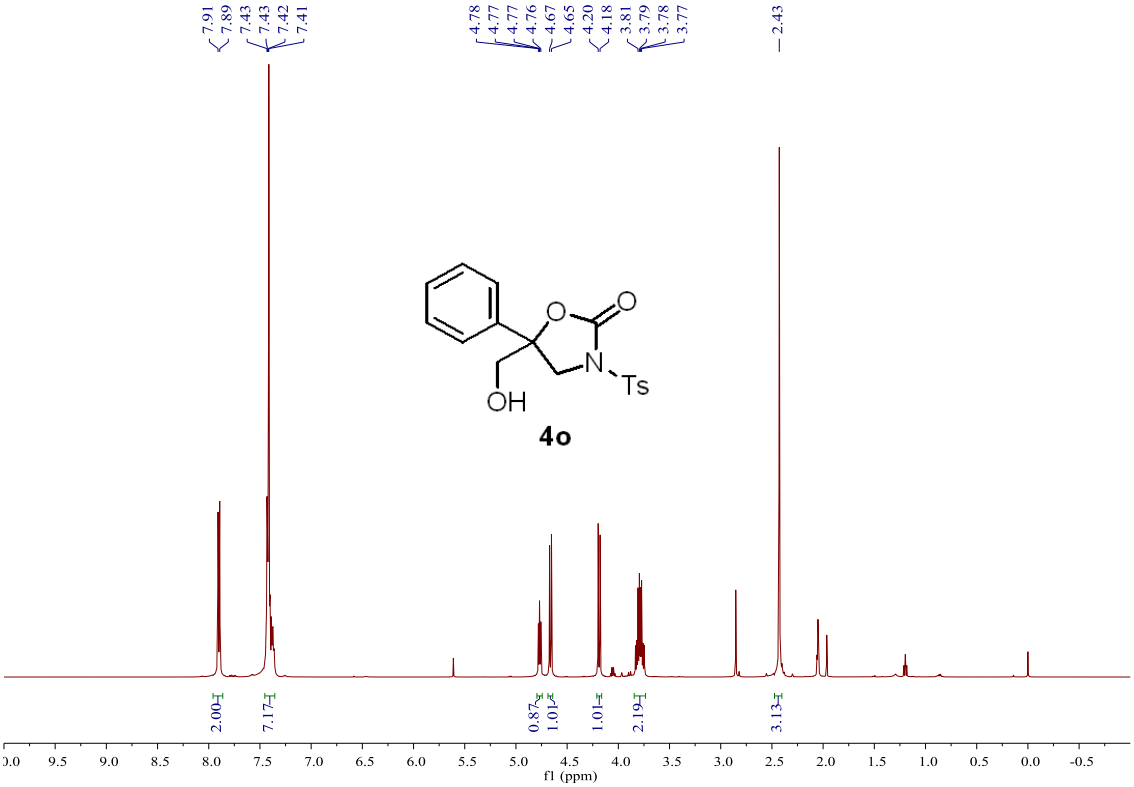
146.65
135.56
130.69
129.05
100.96
94.76
76.67
66.23
52.31
21.58
-0.49
TMS
O
O
N
Ts
OH
4n
f1 (ppm)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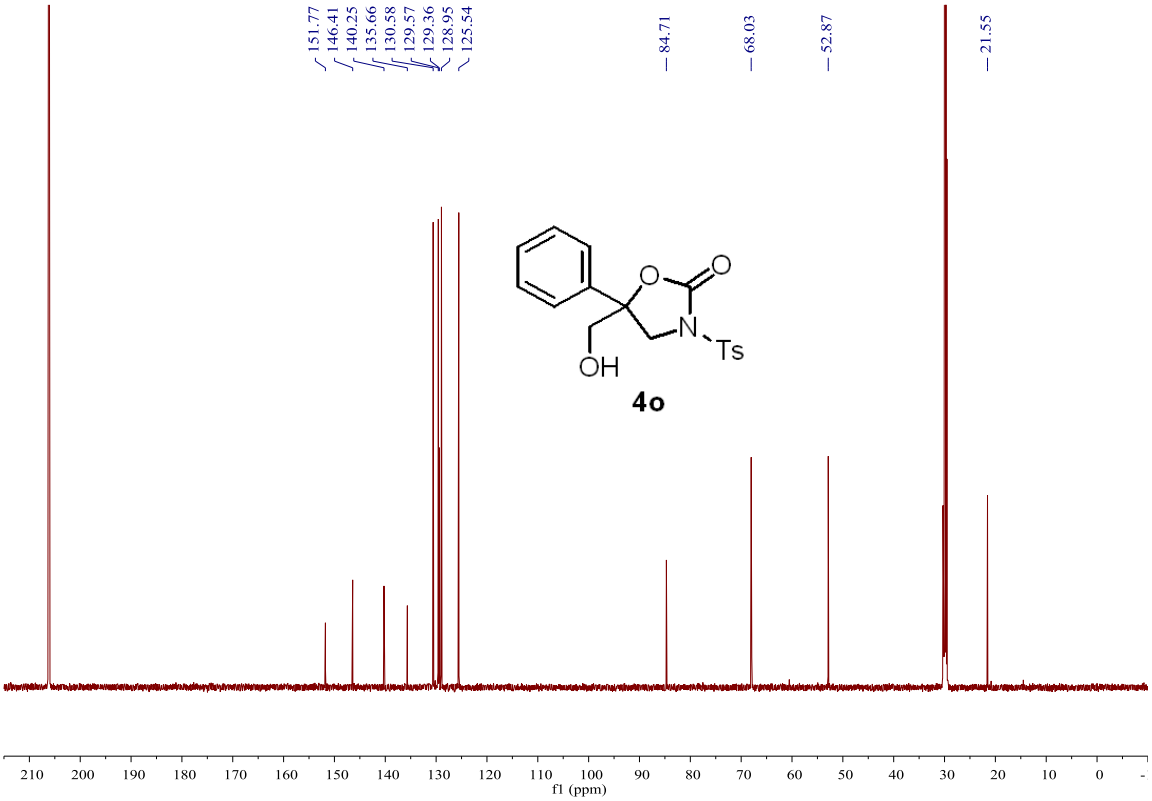
7.89
7.43
7.43
7.42
7.41
4.78
4.77
4.77
4.76
4.67
4.65
4.20
4.18
3.81
3.79
3.78
3.77
2.43
O
O
N
Ts
OH
4o
2.00
7.17
0.87
1.01
1.01
2.19
3.13
fl (ppm)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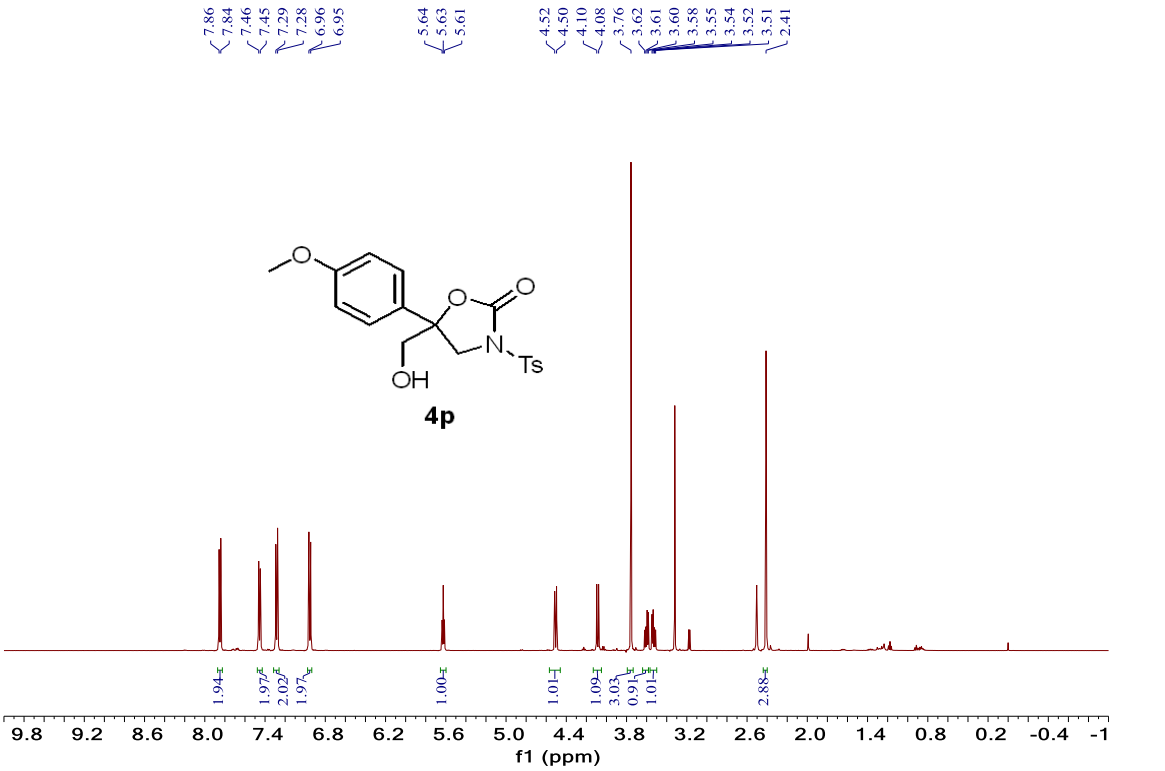
146.41
140.25
135.66
130.58
129.57
129.36
128.95
125.54
84.71
68.03
52.87
21.55
O
O
N
Ts
OH
4o
fl (ppm)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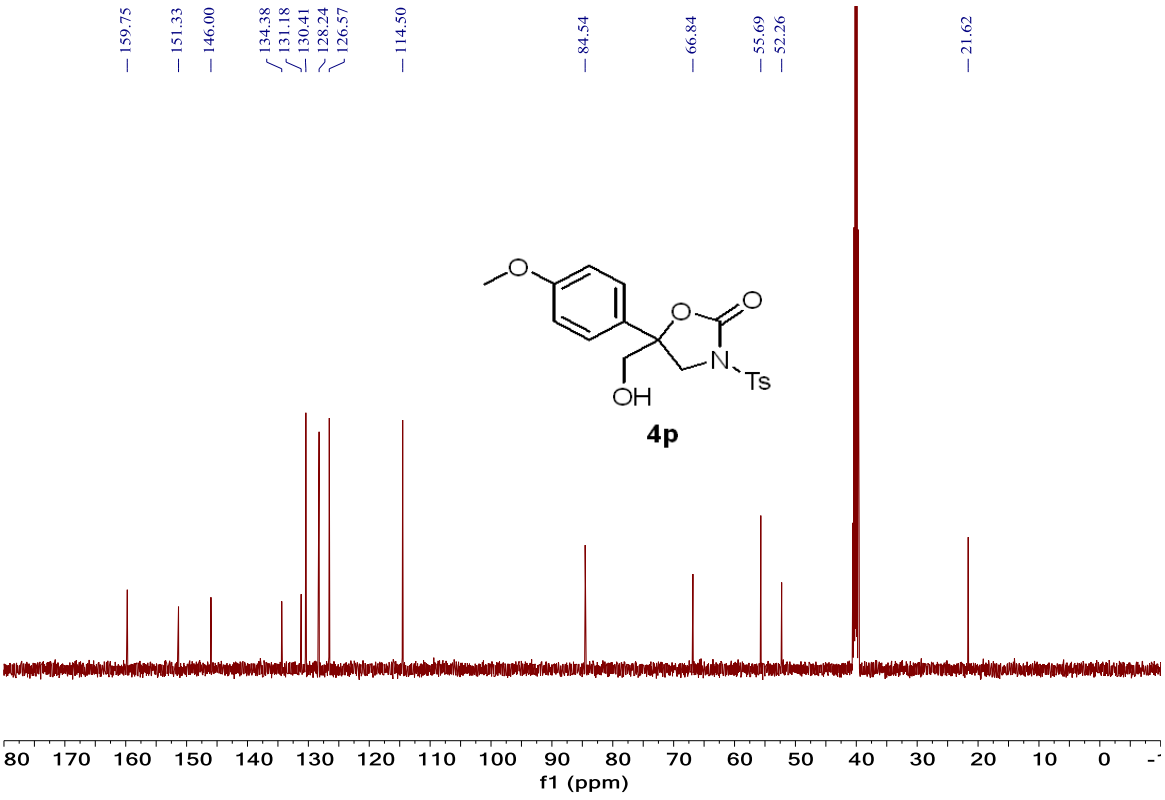
7.84
7.46
7.45
7.29
7.28
6.96
6.95
5.64
5.63
5.61
4.52
4.50
4.10
4.08
3.76
3.62
3.61
3.60
3.58
3.55
3.54
3.52
3.51
2.41
O
O
O
N
Ts
OH
4p
1.94
1.97
2.02
1.97
1.00
1.01
1.09
3.03
0.91
1.01
2.88
9.8 9.2 8.6 8.0 7.4 6.8 6.2 5.6 5.0 4.4 3.8 3.2 2.6 2.0 1.4 0.8 0.2 -0.4 -1
f1 (ppm)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151.33
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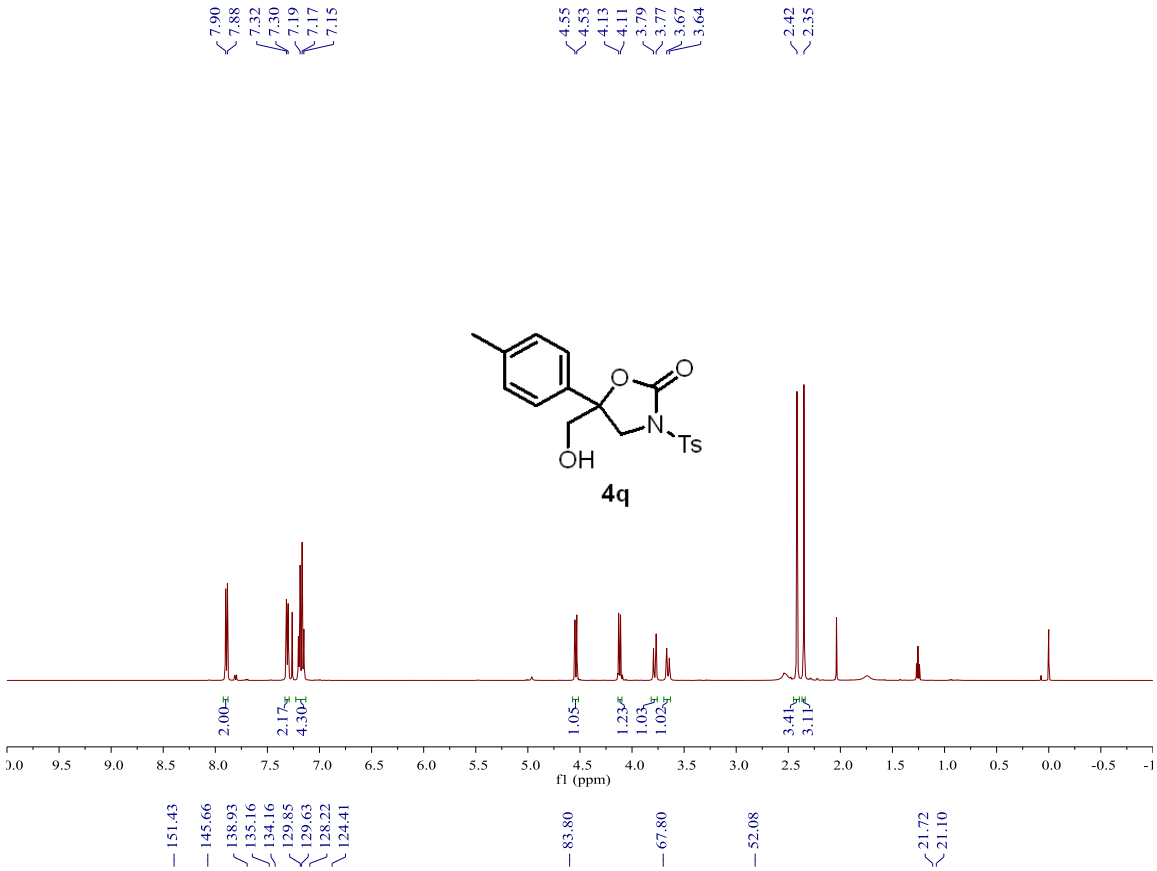
134.38
131.18
130.41
128.24
126.57
114.50
84.54
66.84
55.69
52.26
21.62
O
O
O
N
Ts
OH
4p
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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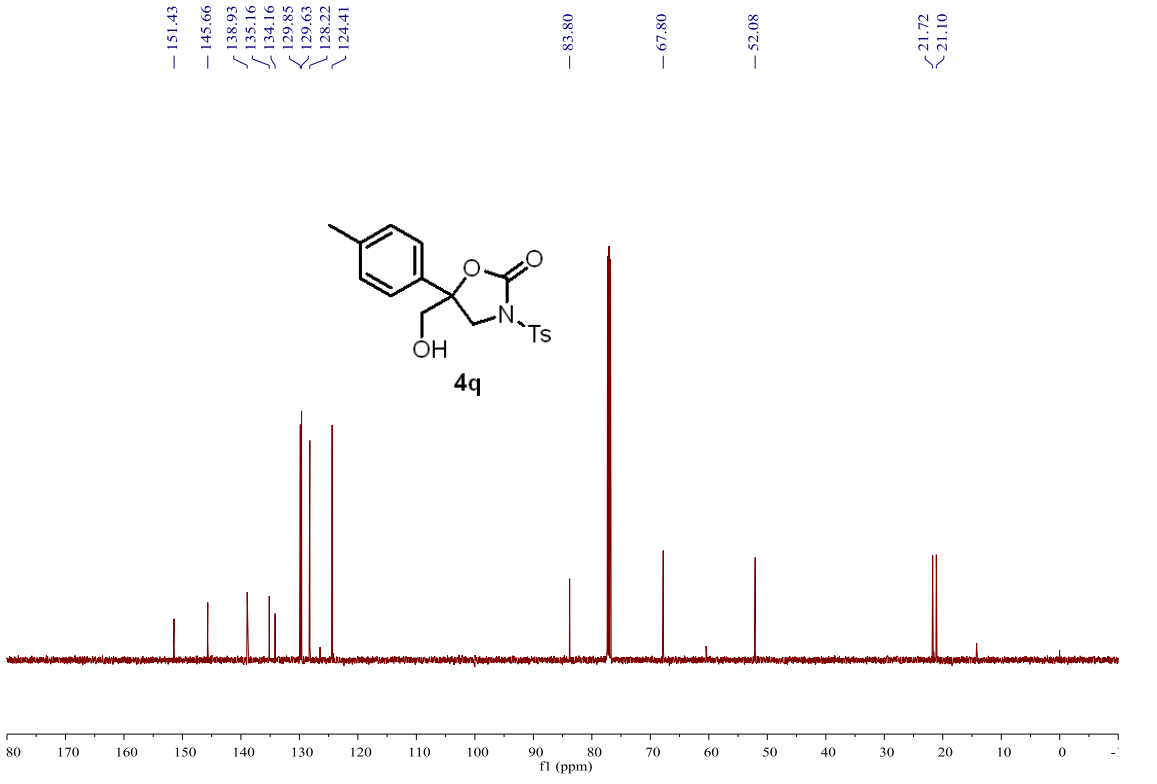
7.19
7.17
7.15
4.55
4.53
4.13
4.11
3.79
3.77
3.67
3.64
2.42
2.35
O
O
N
Ts
OH
4q
2.00
2.17
4.30
1.05
1.23
1.03
1.02
3.41
3.11
f1 (ppm)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134.16
129.85
129.63
128.22
124.41
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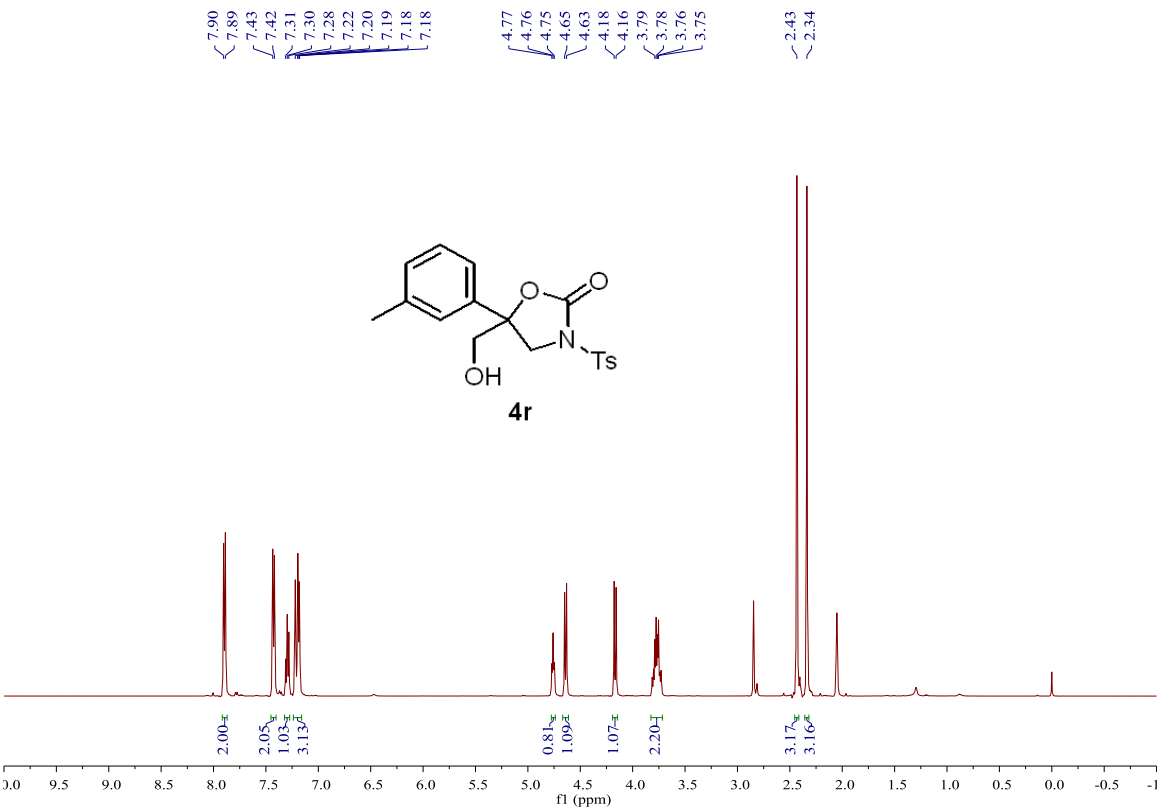
67.80
52.08
21.72
21.10
O
O
N
Ts
OH
4q
f1 (ppm)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7.89
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7.31
7.30
7.28
7.22
7.20
7.19
7.18
7.18
4.77
4.76
4.75
4.65
4.63
4.18
4.16
3.79
3.78
3.76
3.75
2.43
2.34
O
O
N
Ts
OH
4r
2.00
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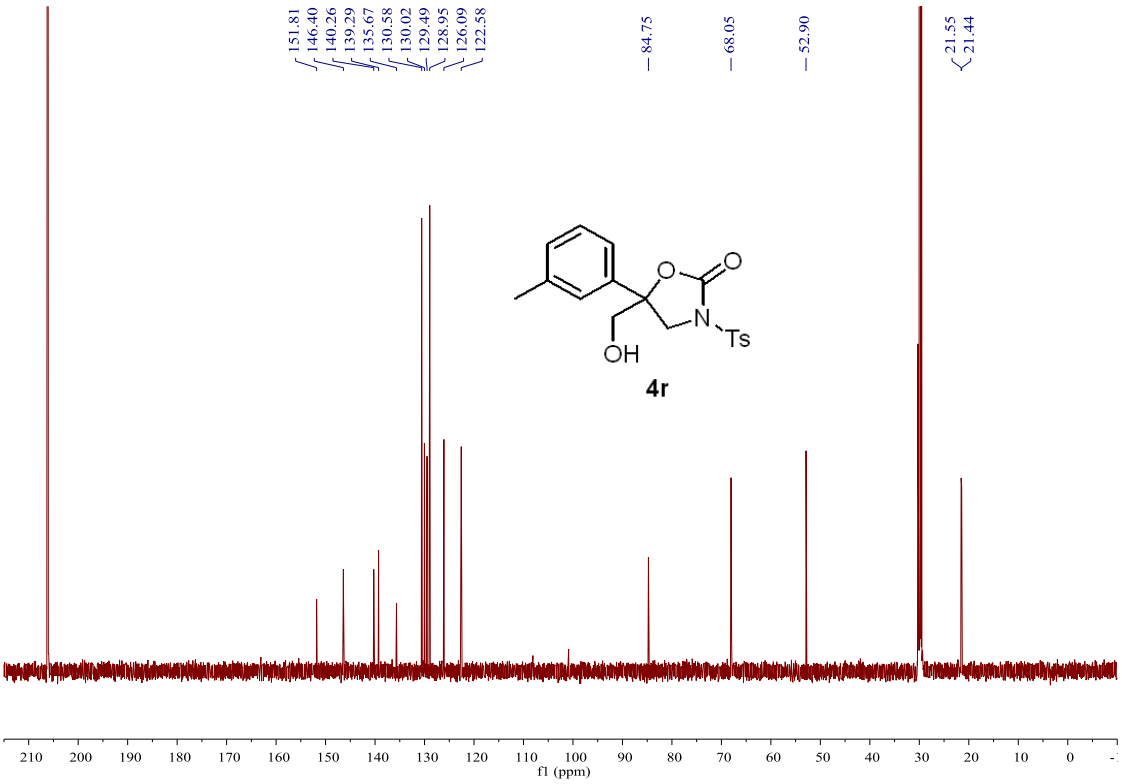
1.03
3.13
0.81
1.09
1.07
2.20
3.17
3.16
f1 (ppm)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130.02
129.49
128.95
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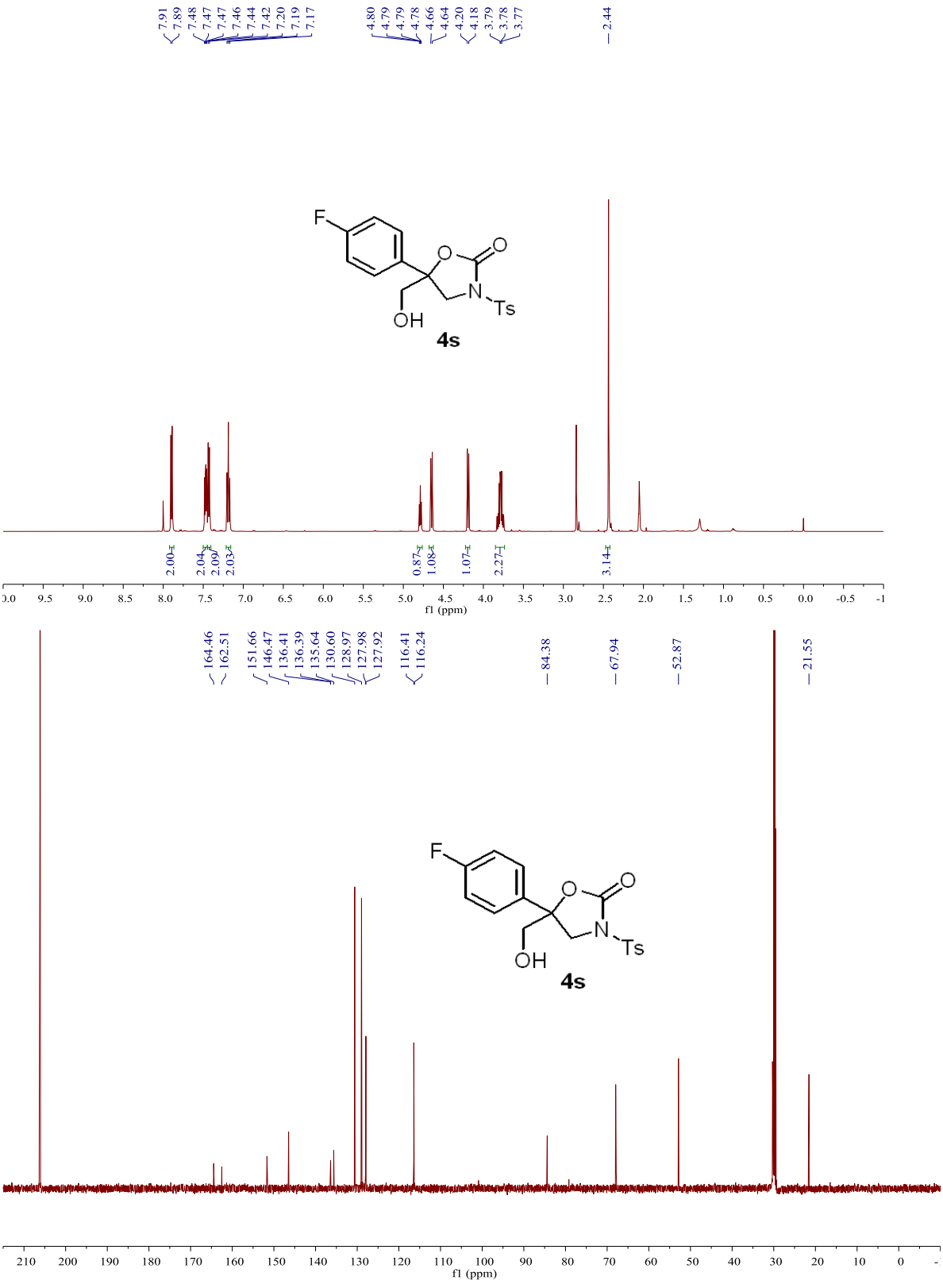
68.05
52.90
21.55
21.44
O
O
N
Ts
OH
4r
f1 (ppm)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7.47
7.46
7.44
7.42
7.20
7.19
7.17
4.80
4.79
4.79
4.78
4.66
4.64
4.20
4.18
3.79
3.78
3.77
2.44
F
O
O
N
Ts
OH
4s
2.00
2.04
2.09
2.03
0.87
1.08
1.07
2.27
3.14
f1 (ppm)
164.46
162.51
151.66
146.47
136.41
136.39
135.64
130.60
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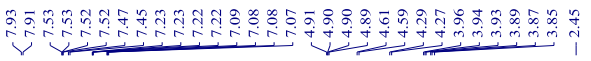
127.98
127.92
116.41
116.24
84.38
67.94
52.87
21.55
f1 (ppm)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7.52
7.47
7.45
7.23
7.23
7.22
7.22
7.09
7.08
7.08
7.07
4.91
4.90
4.90
4.89
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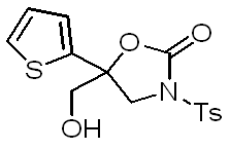
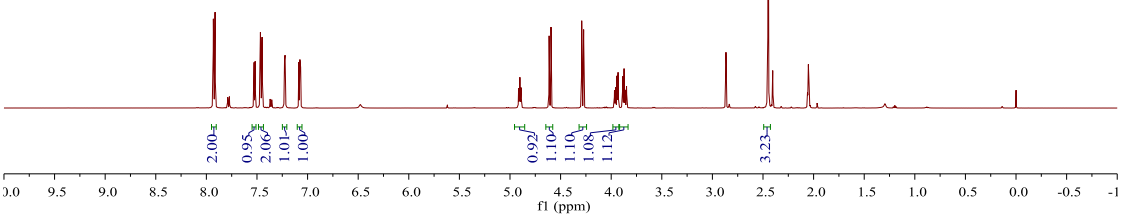
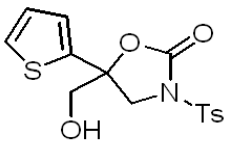
4.59
4.29
4.27
3.96
3.94
3.93
3.89
3.87
3.85
2.45


S
O
O
N
Ts
OH

4t

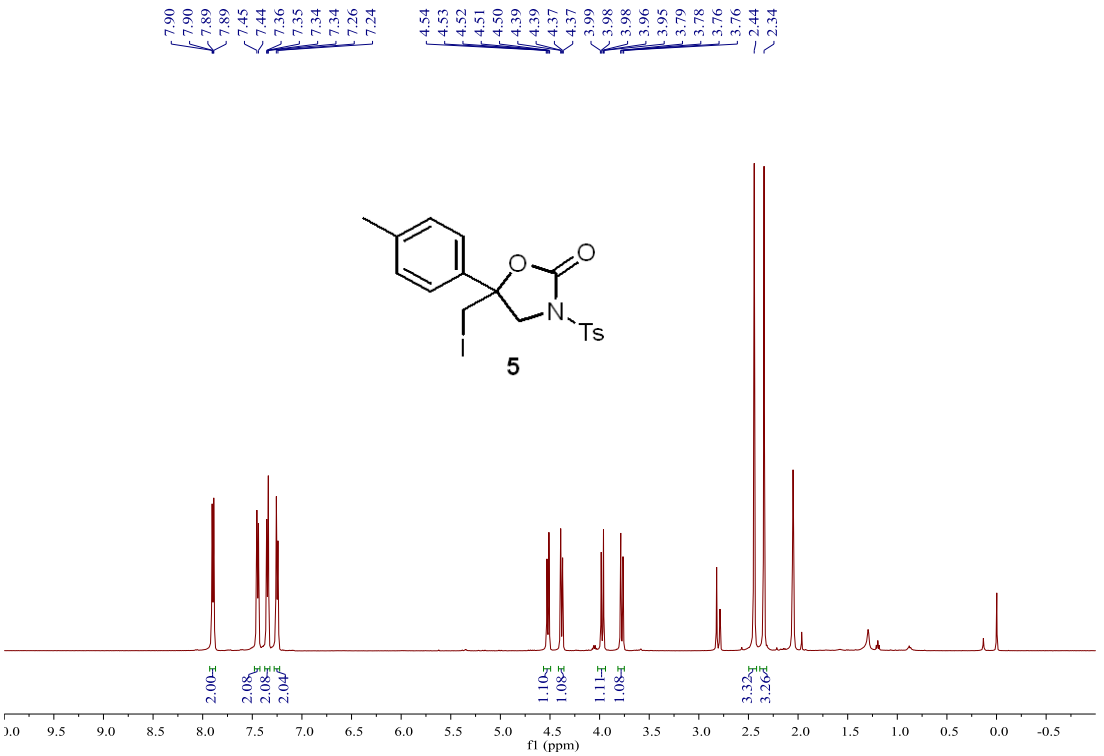

2.00
0.95
2.06
1.01
1.00
0.92
1.10
1.10
1.08
1.12
3.23
f1 (ppm)


151.43
146.57
142.70
135.52
130.65
128.99
128.24
127.26
125.90
83.02
67.21
53.18
21.57


S
O
O
N
Ts
OH

4t

f1 (ppm)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7.89
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7.44
7.36
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7.26
7.24
4.54
4.53
4.52
4.51
4.50
4.39
4.39
4.37
4.37
3.99
3.98
3.98
3.96
3.95
3.79
3.78
3.76
3.76
2.44
2.34
O
O
N
Ts
I
5
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2.08
2.04
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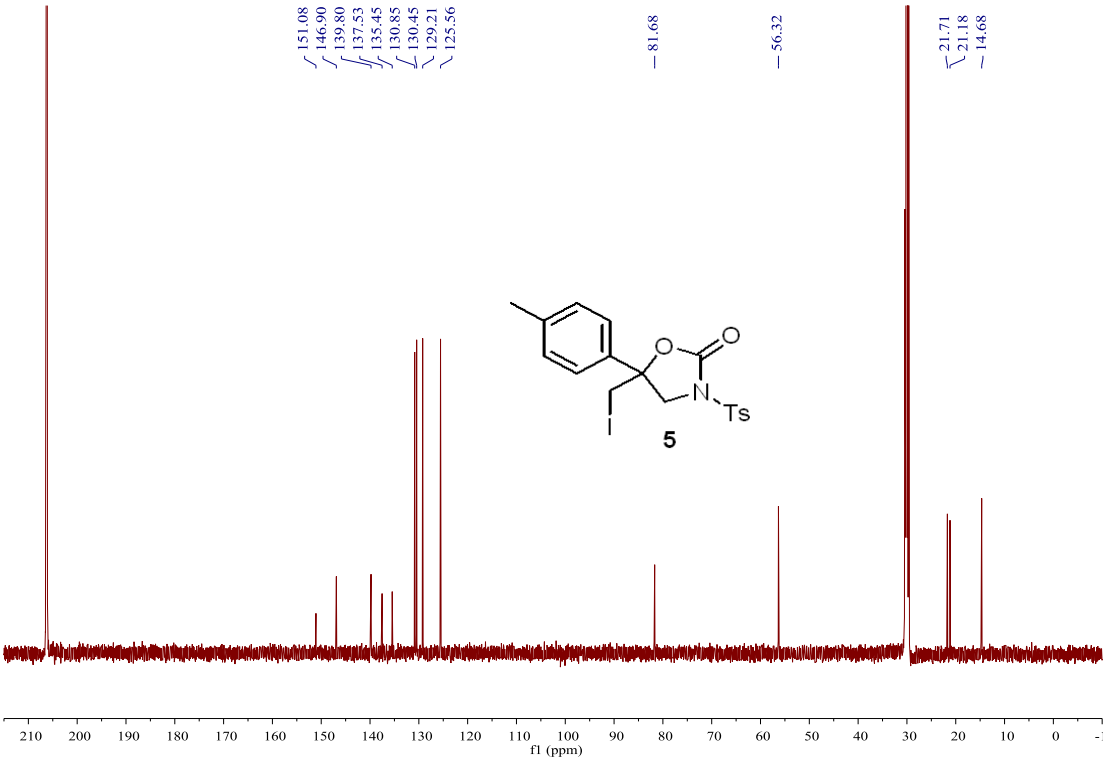
1.08
1.11
1.08
3.32
3.26
f1 (ppm)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137.53
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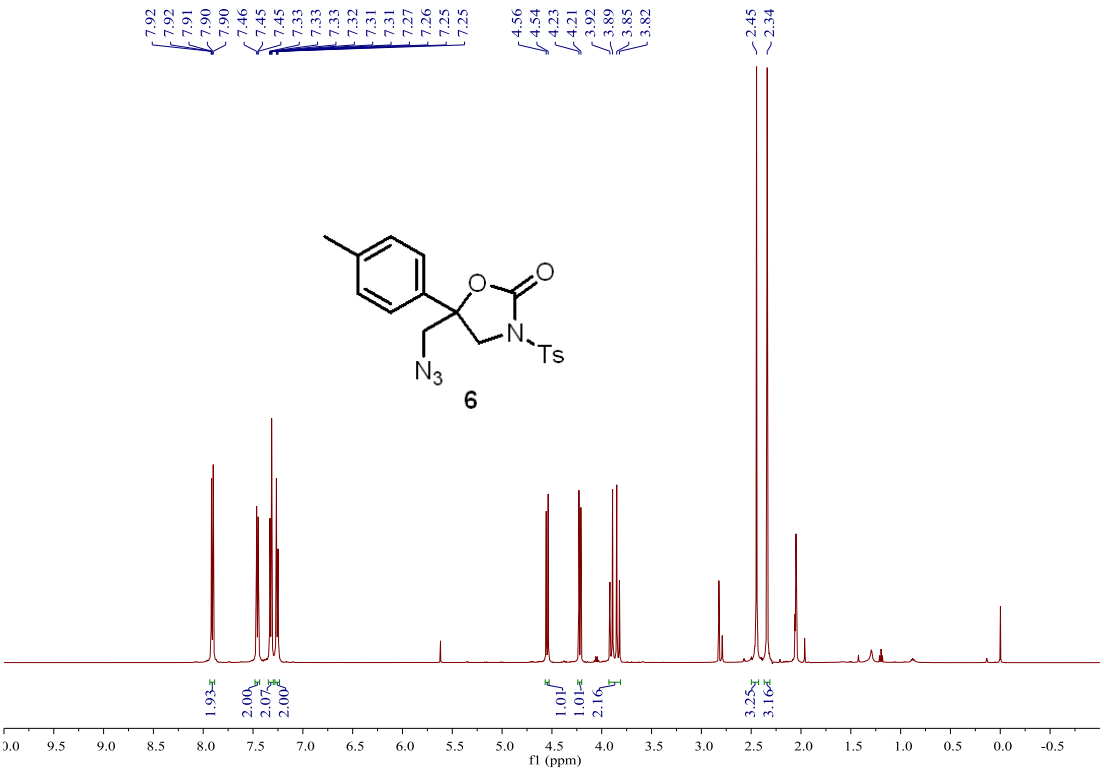
130.85
130.45
129.21
125.56
81.68
56.32
21.71
21.18
14.68
O
O
N
Ts
I
5
f1 (ppm)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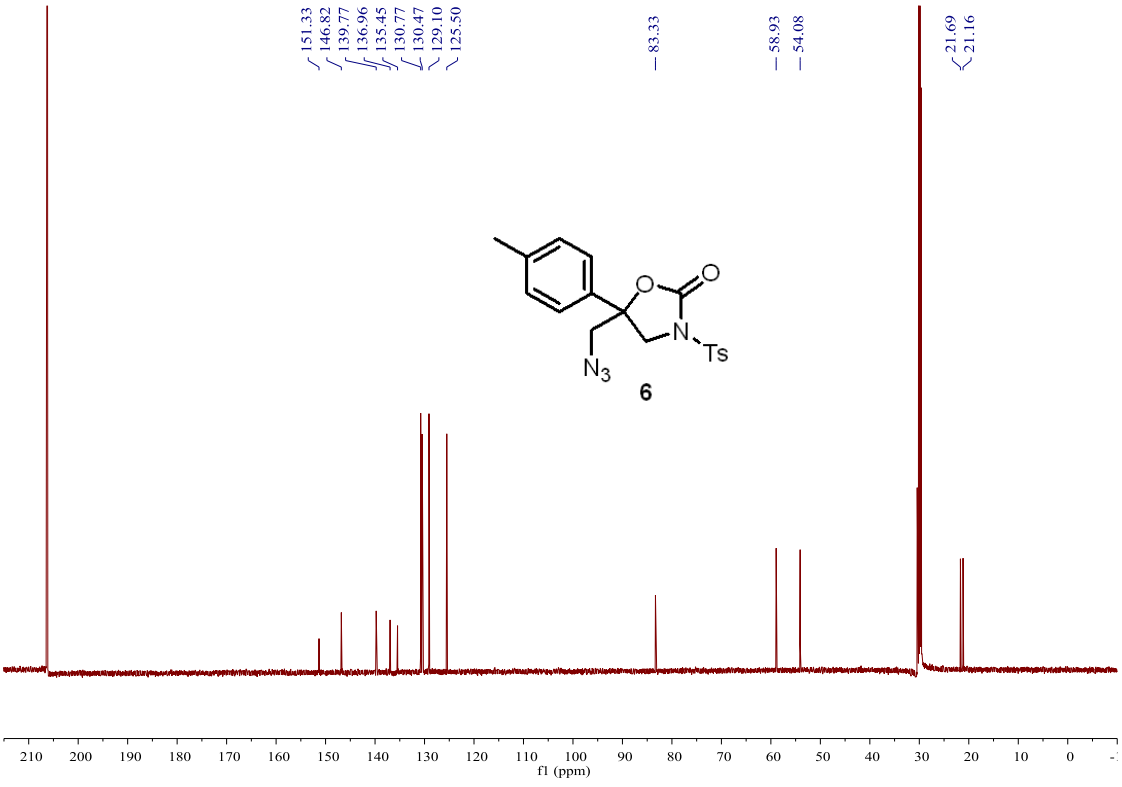
7.92
7.91
7.90
7.90
7.46
7.45
7.45
7.33
7.33
7.33
7.32
7.31
7.31
7.27
7.26
7.25
7.25
4.56
4.54
4.23
4.21
3.92
3.89
3.85
3.82
2.45
2.34
O
O
N
Ts
N3
6
1.93
2.00
2.07
2.00
1.01
1.01
2.16
3.25
3.16
f1 (ppm)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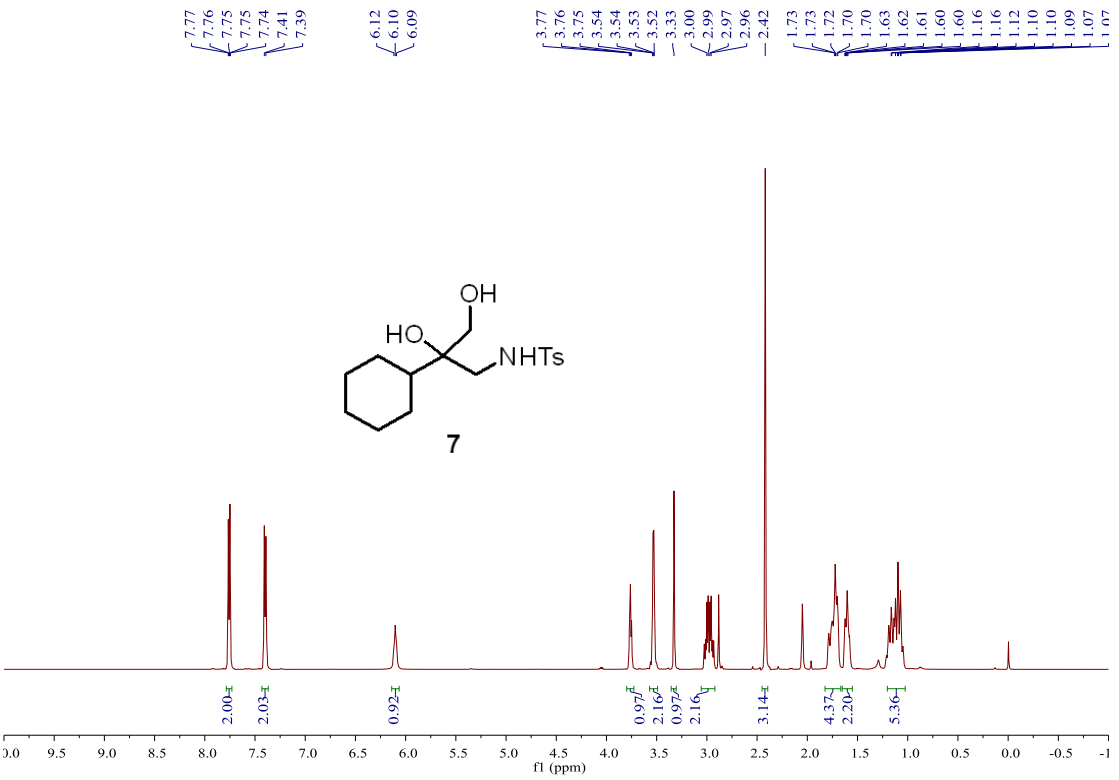
146.82
139.77
136.96
135.45
130.77
130.47
129.10
125.50
83.33
58.93
54.08
21.69
21.16
O
O
N
Ts
N3
6
f1 (ppm)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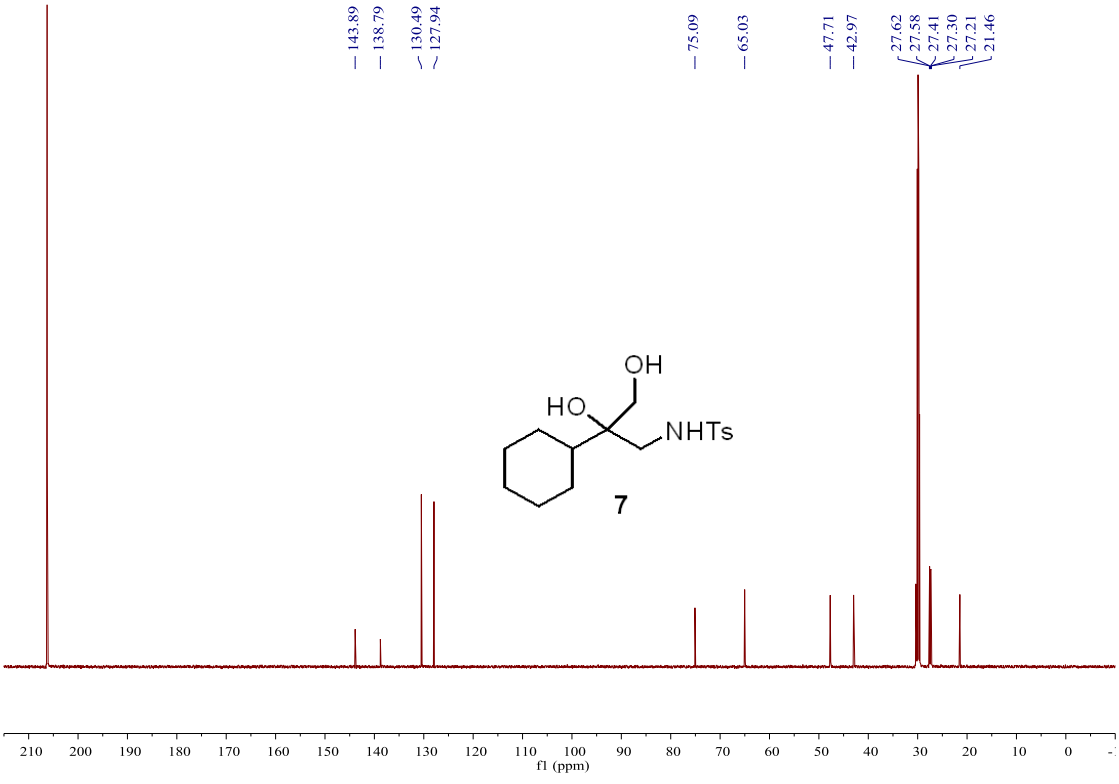
7.75
7.75
7.74
7.41
7.39
6.12
6.10
6.09
3.77
3.76
3.75
3.54
3.54
3.53
3.52
3.33
3.00
2.99
2.97
2.96
2.42
1.73
1.73
1.72
1.70
1.70
1.63
1.62
1.61
1.60
1.60
1.16
1.16
1.12
1.10
1.10
1.09
1.07
OH
HO
NHTs
7
2.00
2.03
0.92
0.97
2.16
0.97
2.16
3.14
4.37
2.20
5.36
f1 (ppm)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75.09
65.03
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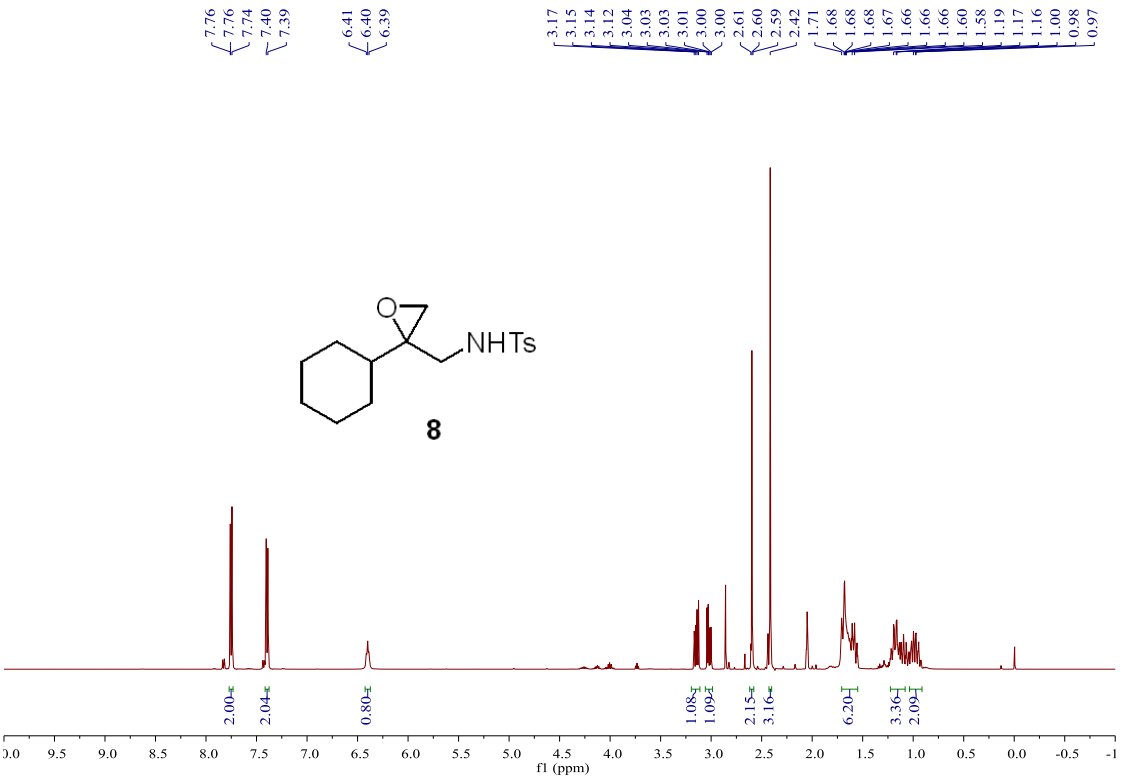
42.97
27.62
27.58
27.41
27.30
27.21
21.46
OH
HO
NHTs
7
f1 (ppm)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7.76
7.74
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6.41
6.40
6.39
3.17
3.15
3.14
3.12
3.04
3.03
3.03
3.01
3.00
3.00
2.61
2.60
2.59
2.42
1.71
1.68
1.68
1.68
1.67
1.66
1.66
1.66
1.60
1.58
1.19
1.17
1.16
1.00
0.98
0.97
NHTs
8
2.00
2.04
0.80
1.08
1.09
2.15
3.16
6.20
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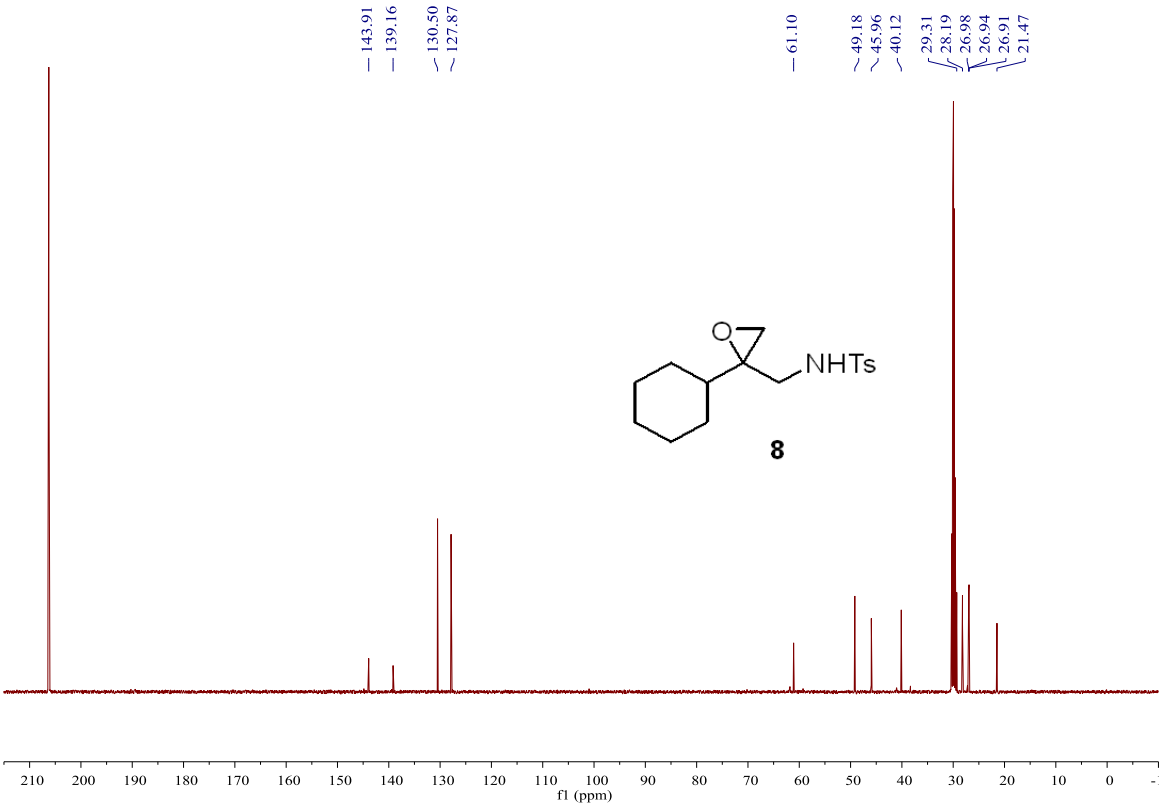
2.09
f1 (ppm)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139.16
130.50
127.87
61.10
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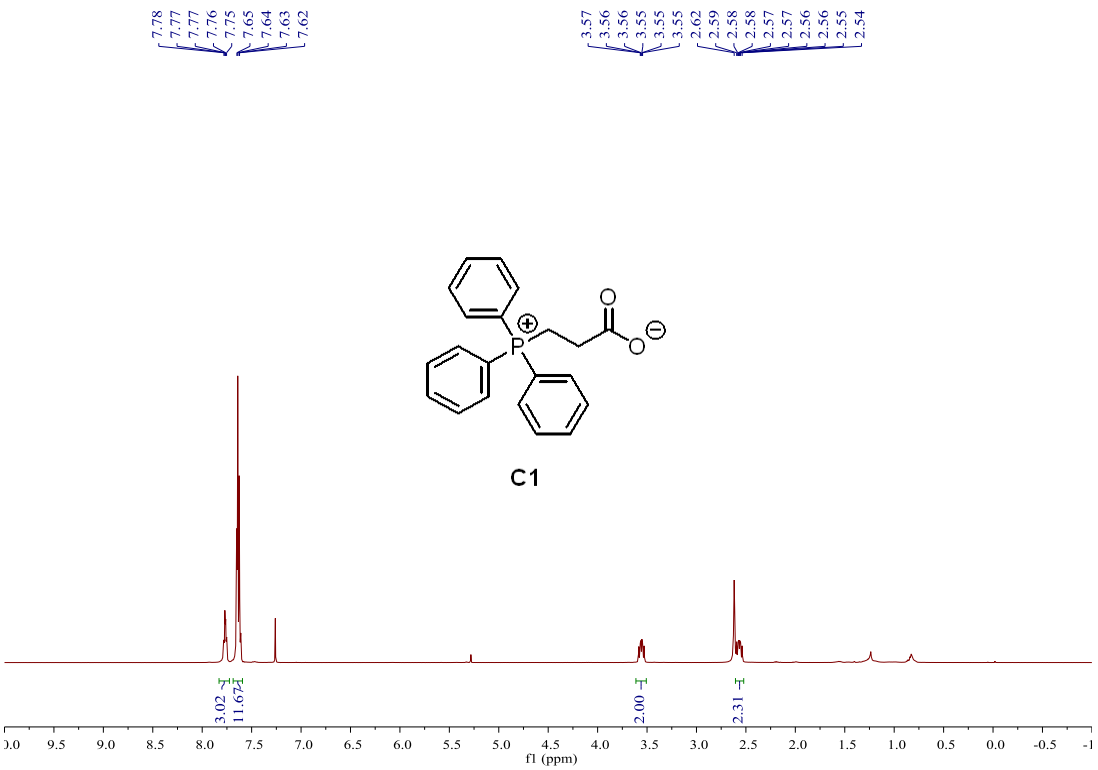
45.96
40.12
29.31
28.19
26.98
26.94
26.91
21.47
NHTs
8
f1 (ppm)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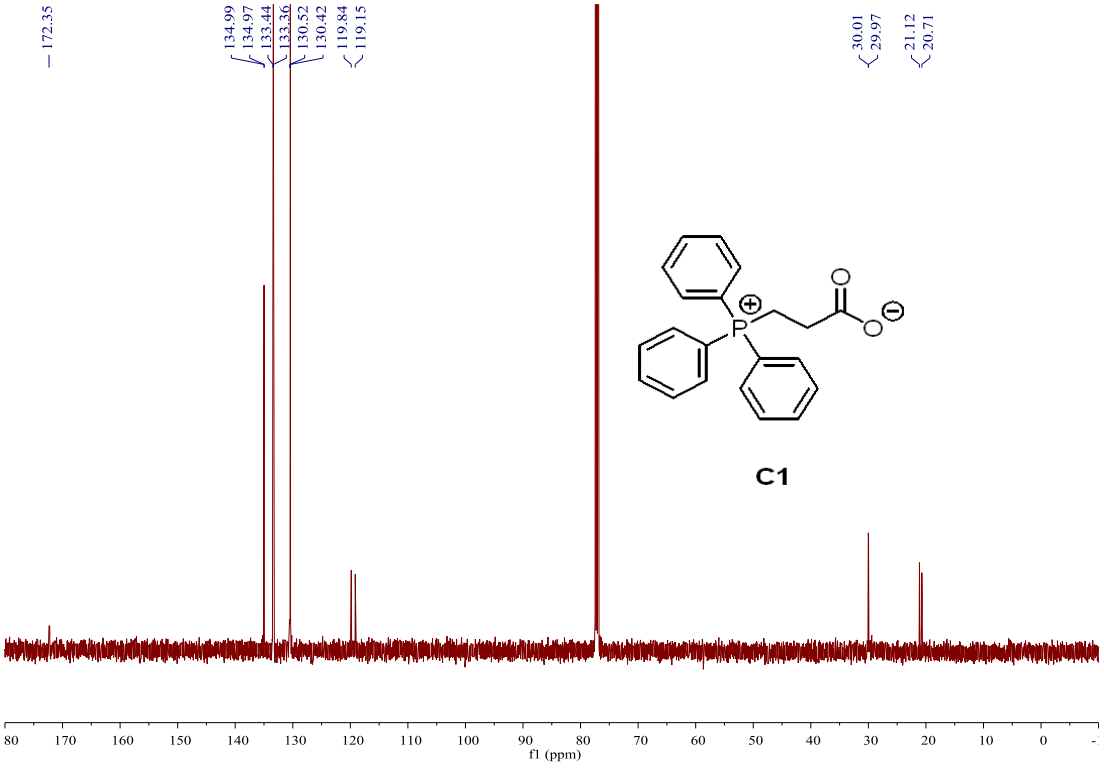
7.77
7.76
7.75
7.65
7.64
7.63
7.62
3.57
3.56
3.56
3.55
3.55
3.55
2.62
2.59
2.58
2.58
2.57
2.57
2.56
2.56
2.55
2.54
C1
3.02
11.67
2.00
2.31
f1 (ppm)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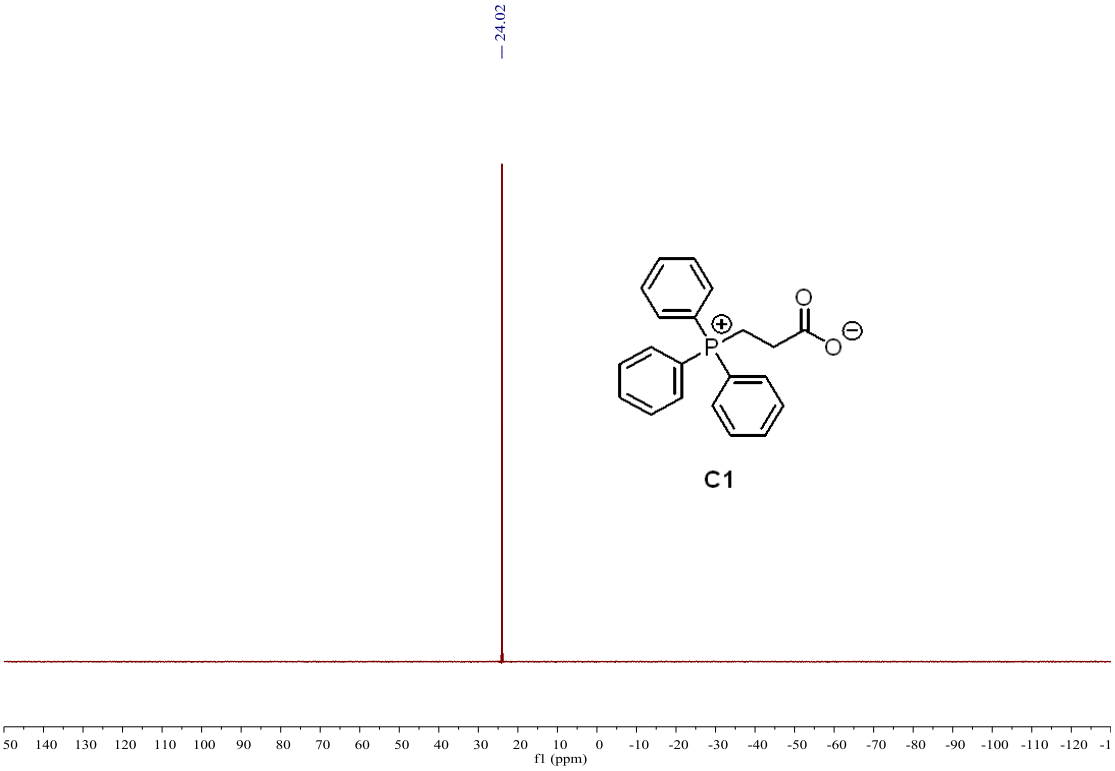
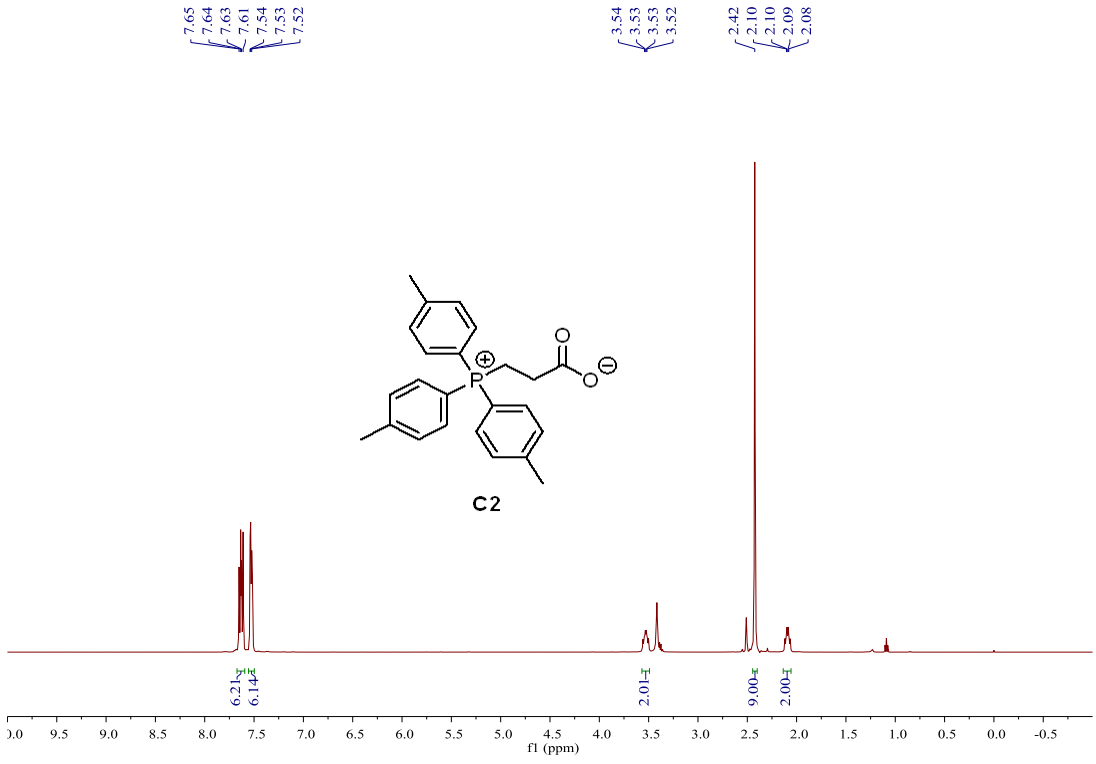
134.99
134.97
133.44
133.36
130.52
130.42
119.84
119.15
30.01
29.97
21.12
20.71
C1
f1 (ppm)


24.02
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -1
f1 (ppm)

C1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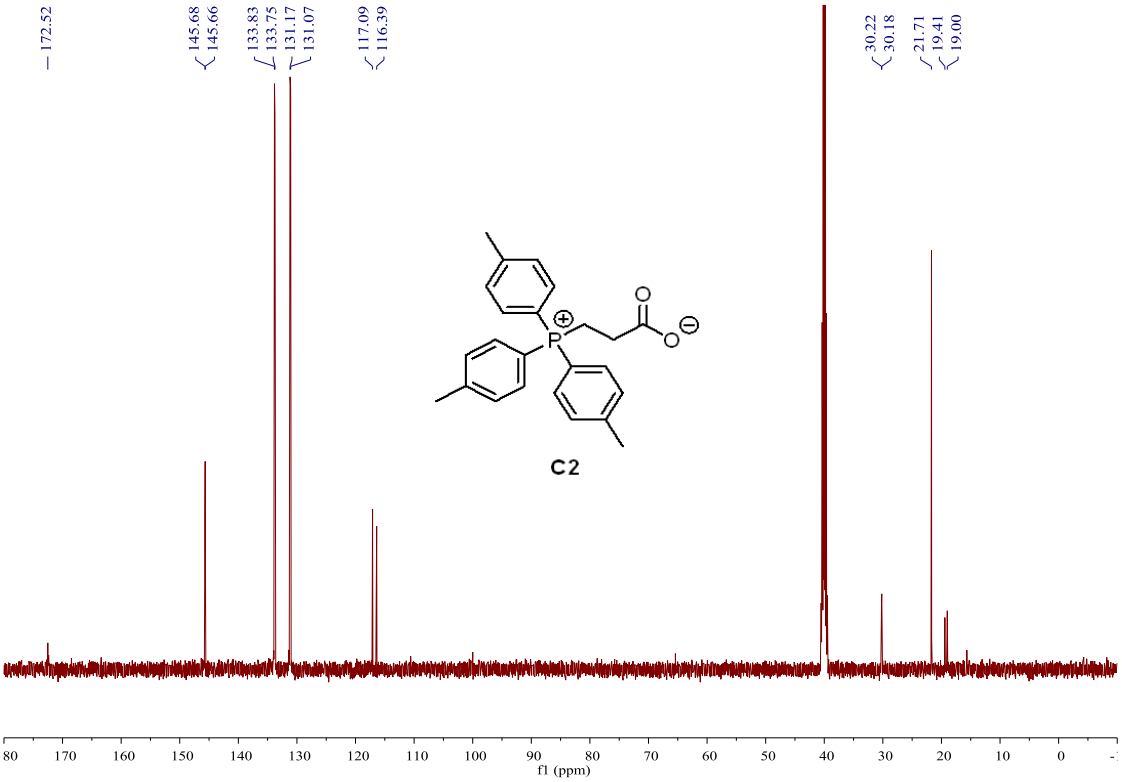
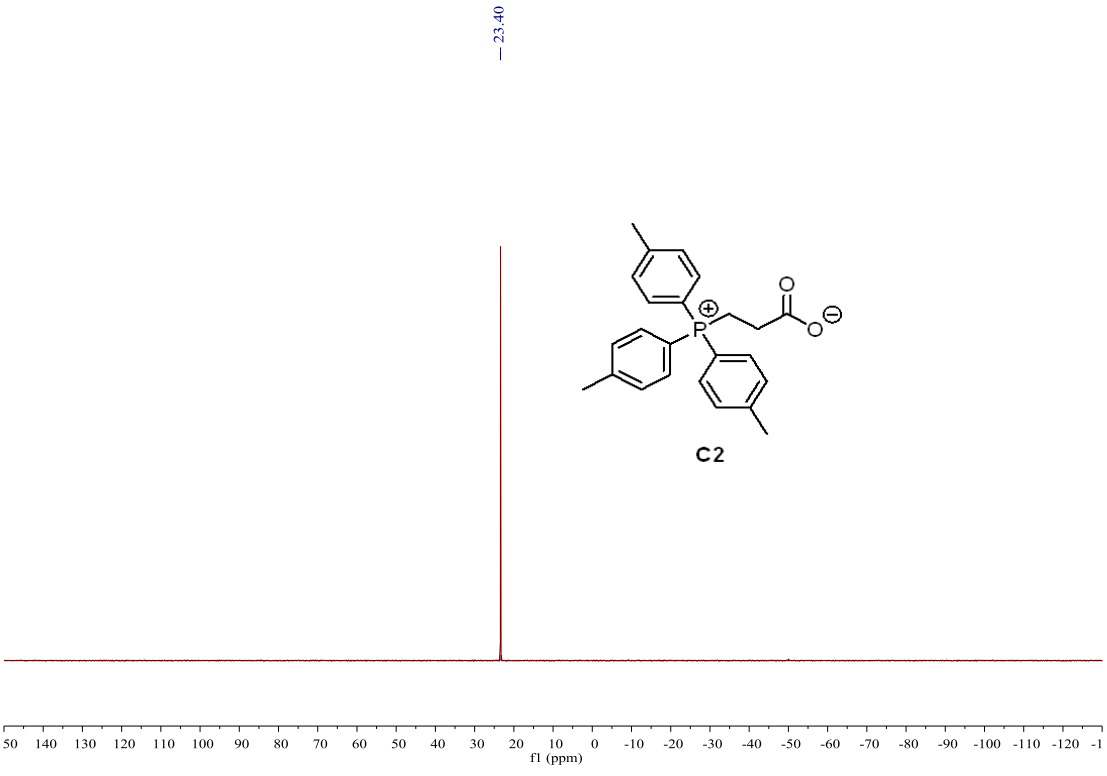
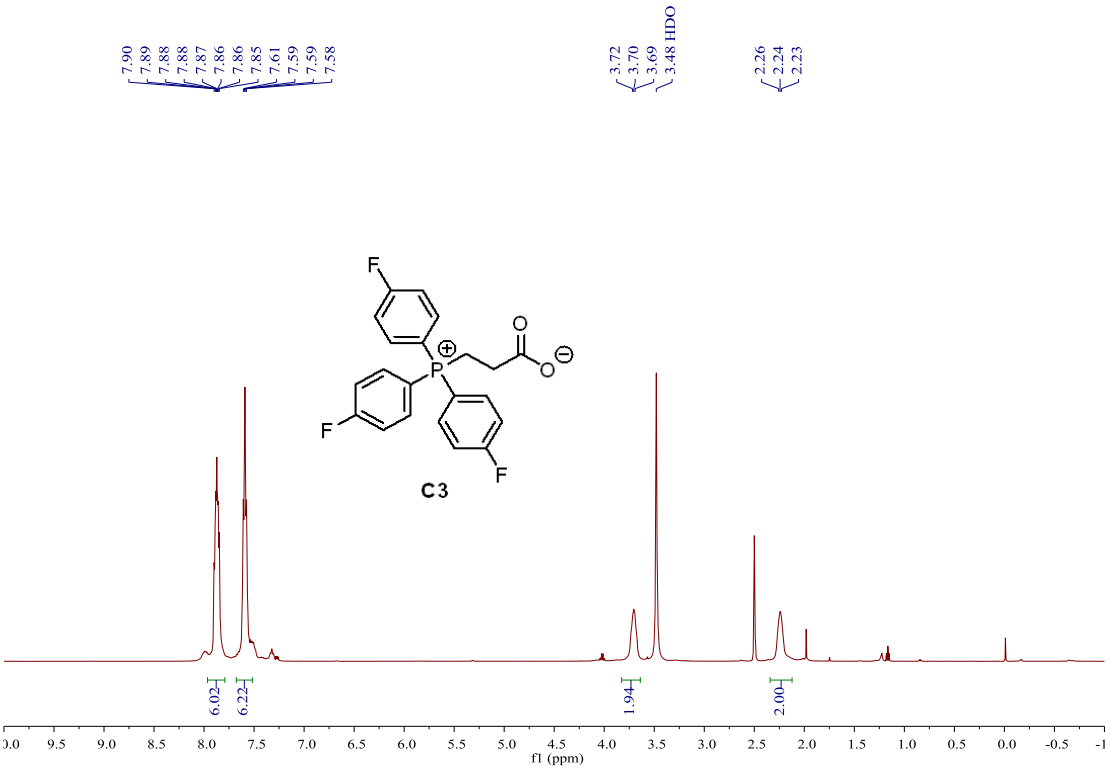
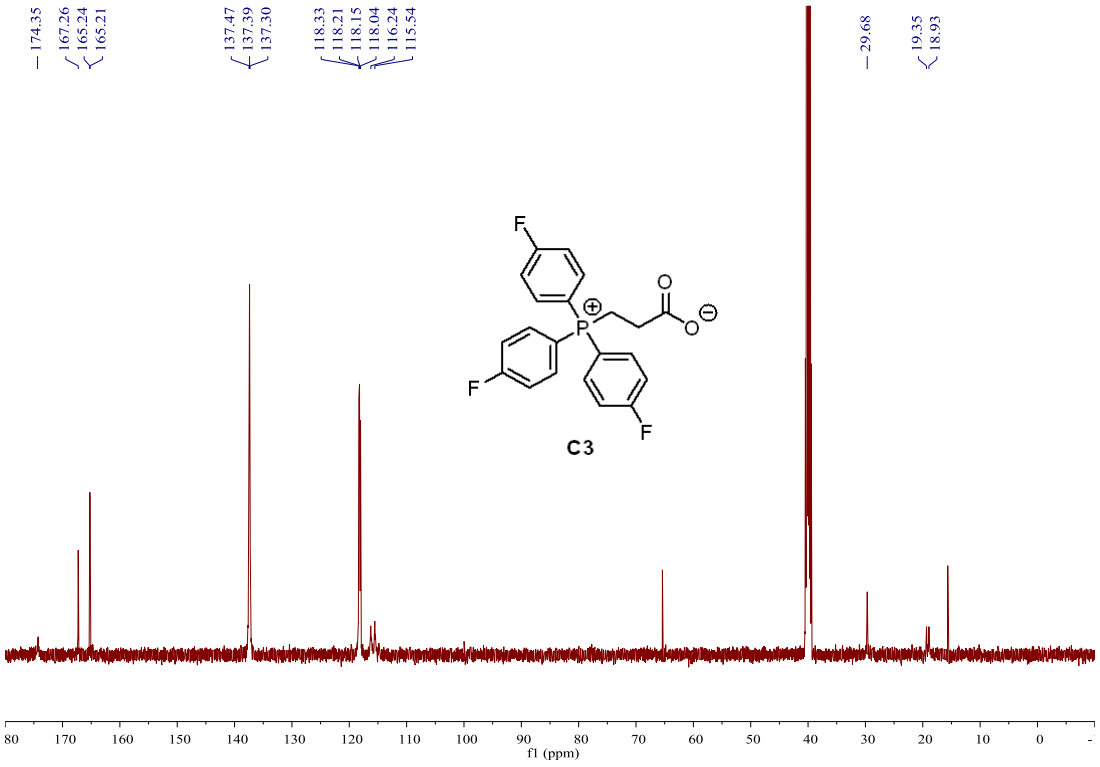
7.63
7.61
7.54
7.53
7.52
3.54
3.53
3.53
3.52
2.42
2.10
2.10
2.09
2.08
6.21
6.14
2.01
9.00
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

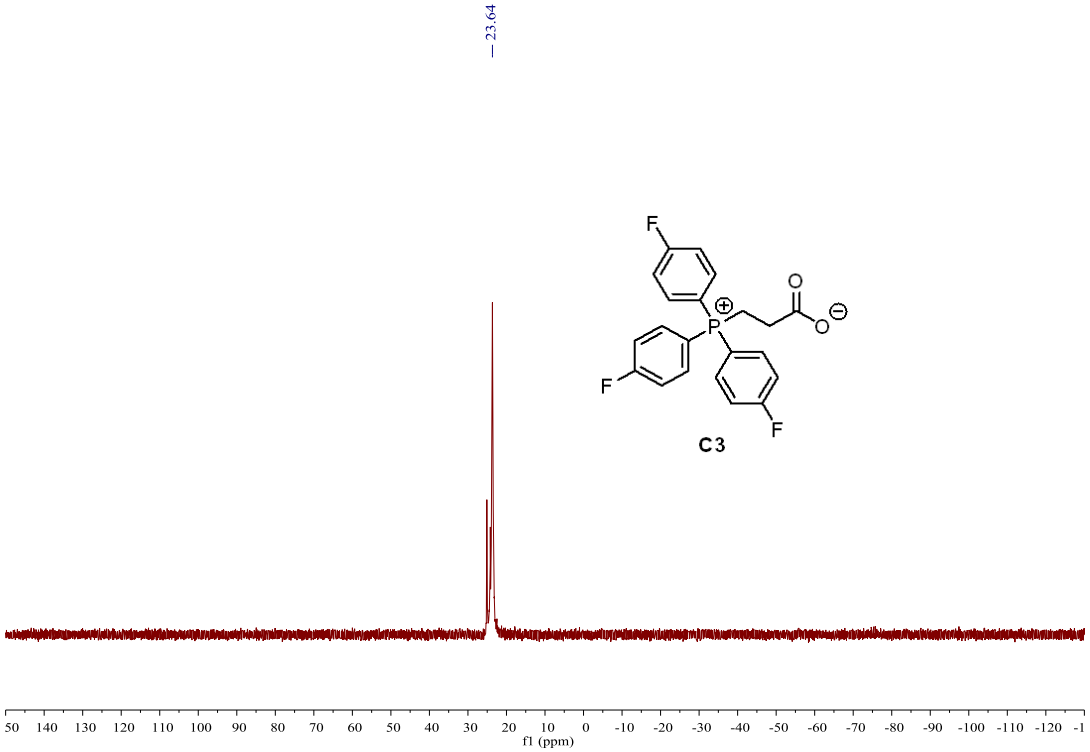
C2

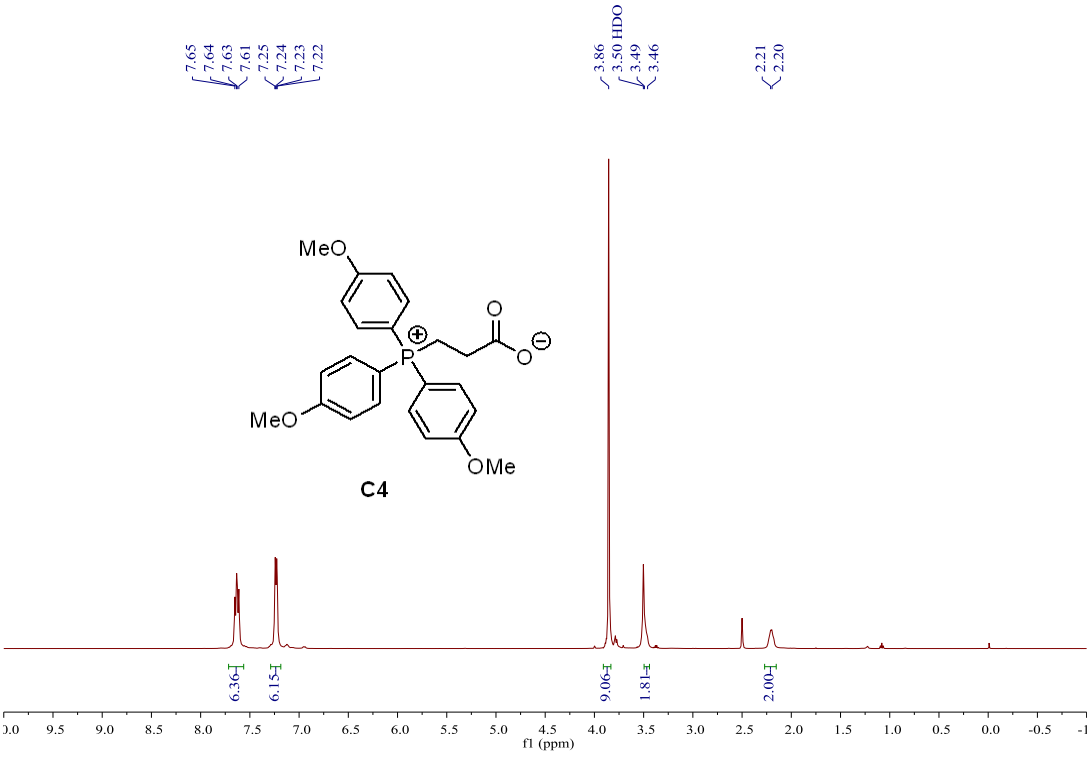

172.52
145.68
145.66
133.83
133.75
131.17
131.07
117.09
116.39
30.22
30.18
21.71
19.41
19.00
C2
f1 (ppm)

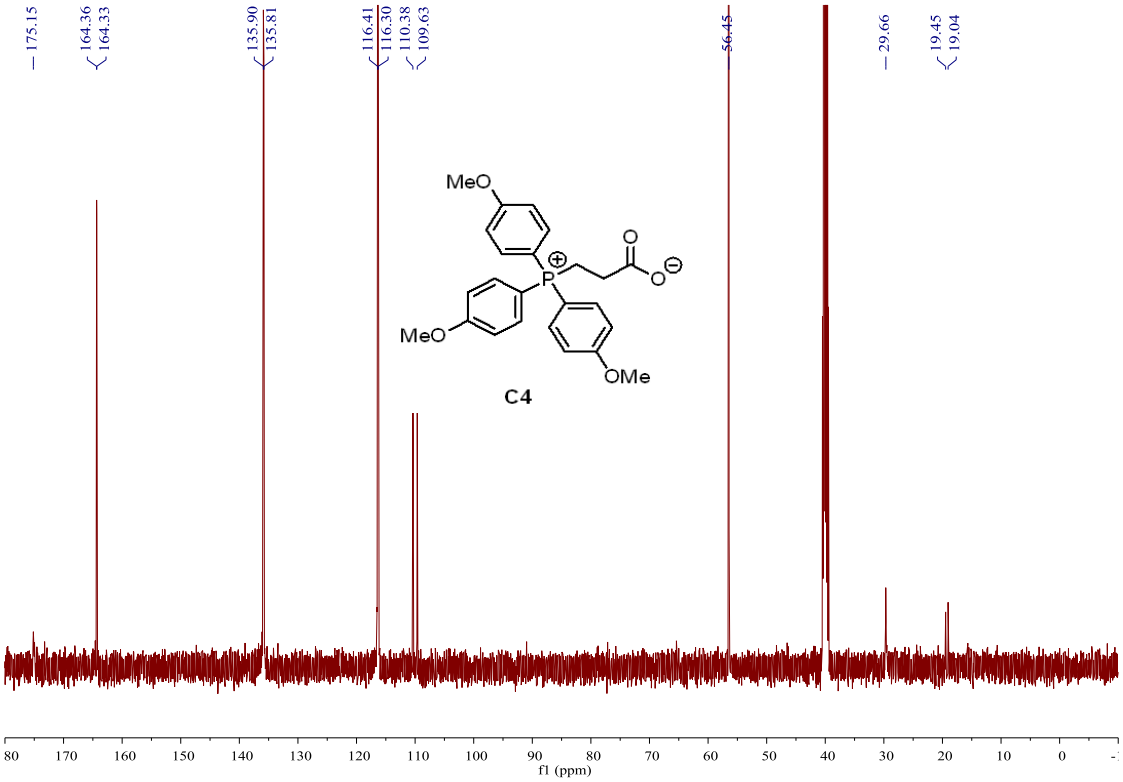

23.40
C2
f1 (ppm)

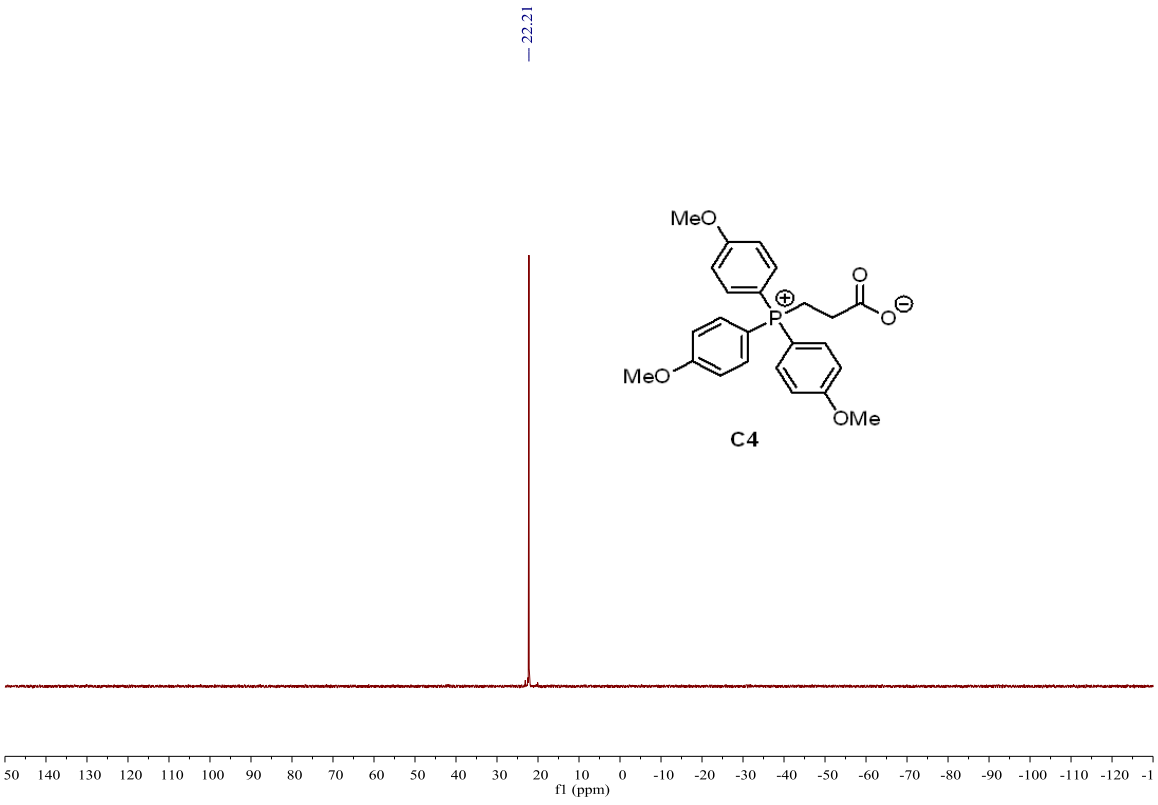

7.90
7.89
7.88
7.88
7.87
7.86
7.86
7.85
7.61
7.59
7.59
7.58
3.72
3.70
3.69
3.48 HDO
2.26
2.24
2.23
F
O
P
O
F
F
C3
6.02
6.22
1.94
2.00
f1 (ppm)


174.35
167.26
165.24
165.21
137.47
137.39
137.30
118.33
118.21
118.15
118.04
116.24
115.54
29.68
19.35
18.93
F
O
P
O
F
F
C3
f1 (ppm)


23.64
F
F
F
O
O
P
C3
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -1
f1 (ppm)


7.65
7.64
7.63
7.61
7.25
7.24
7.23
7.22
3.86
3.50 HDO
3.49
3.46
2.21
2.20
MeO
MeO
OMe
O
O
P
C4
6.36
6.15
9.06
1.81
2.00
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 0.0 -0.5 -1
f1 (ppm)


175.15
164.36
164.33
135.90
135.81
116.41
116.30
110.38
109.63
56.45
29.66
19.45
19.04
MeO
MeO
OMe
C4
f1 (ppm)


22.21
MeO
MeO
OMe
C4
f1 (ppm)

9. Theoretical Computation Section

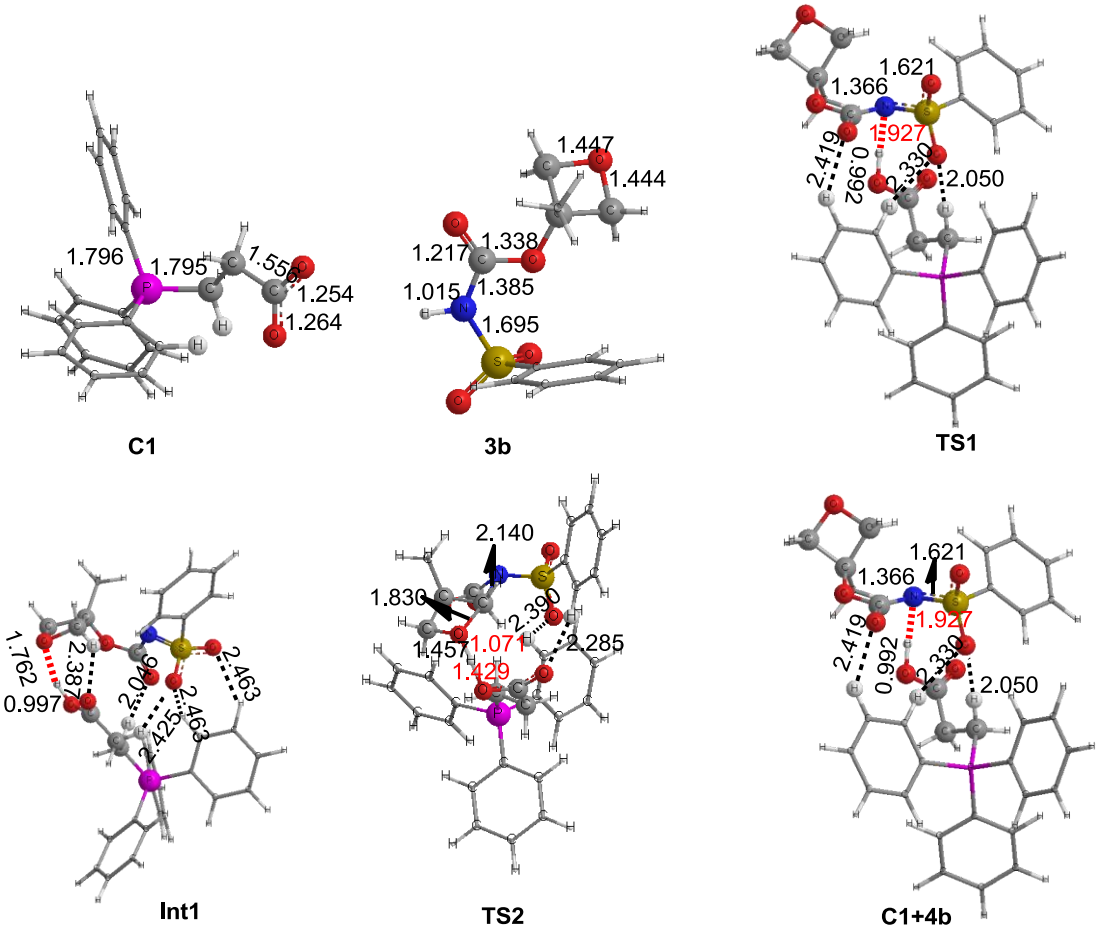


Figure S3. Structure of Intermediates and Transition States.

Table S1. Standard orientation of **C1** structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.589865	-0.144925	-1.667112
2	8	0	-3.537353	1.112843	-1.784412

3	8	0	-4.584327	-0.898697	-1.793287
4	6	0	-2.266544	-0.855592	-1.260758
5	1	0	-2.352051	-1.042422	-0.179284
6	1	0	-2.210355	-1.845178	-1.721570
7	6	0	-1.025684	-0.022270	-1.590656
8	1	0	-1.365258	1.005820	-1.790514
9	1	0	-0.506762	-0.383637	-2.484795
10	6	0	1.681489	0.844245	-0.801505
11	6	0	1.608845	1.829187	-1.797762
12	6	0	2.910792	0.549847	-0.192027
13	6	0	2.763385	2.506771	-2.185965
14	1	0	0.658749	2.067575	-2.271071
15	6	0	4.059428	1.233524	-0.584274
16	1	0	2.974084	-0.219171	0.576628
17	6	0	3.986558	2.210531	-1.580386
18	1	0	2.706698	3.264975	-2.961488
19	1	0	5.010377	1.000579	-0.114403
20	1	0	4.884614	2.739753	-1.886957
21	6	0	0.601457	-1.652345	0.237085
22	6	0	-0.013001	-2.250150	1.345918
23	6	0	1.475950	-2.397567	-0.570472
24	6	0	0.260155	-3.583117	1.652265

25	1	0	-0.698703	-1.677922	1.968664
26	6	0	1.743312	-3.727770	-0.257360
27	1	0	1.947774	-1.939657	-1.438421
28	6	0	1.137289	-4.320029	0.854103
29	1	0	-0.214072	-4.044432	2.513293
30	1	0	2.423524	-4.301302	-0.880152
31	1	0	1.348841	-5.357591	1.097121
32	6	0	-0.535893	0.897712	1.132546
33	6	0	-1.793482	1.508664	1.014619
34	6	0	0.200673	1.007741	2.323615
35	6	0	-2.310872	2.215813	2.100986
36	1	0	-2.371582	1.440653	0.088691
37	6	0	-0.325212	1.720385	3.397488
38	1	0	1.180866	0.540821	2.414582
39	6	0	-1.582763	2.322789	3.286456
40	1	0	-3.286372	2.685706	2.015622
41	1	0	0.244499	1.806979	4.318163
42	1	0	-1.992171	2.877237	4.126383
43	15	0	0.178309	0.020492	-0.260649

Sum of electronic and zero-point Energies= -1303.138669

Sum of electronic and thermal Energies= -1303.118060

Sum of electronic and thermal Enthalpies= -1303.117115

Sum of electronic and thermal Free Energies= -1303.189837

Table S2. Standard orientation of 3b structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.475878	1.491209	-0.524573
2	8	0	-2.611566	2.316773	-0.156715
3	8	0	-0.873096	1.595369	-1.836901
4	6	0	-1.831206	-0.210036	-0.200471
5	6	0	-2.556837	-0.536468	0.947791
6	6	0	-1.402405	-1.181210	-1.106264
7	6	0	-2.847553	-1.876528	1.196883
8	1	0	-2.888971	0.242834	1.629534
9	6	0	-1.708740	-2.517096	-0.848412
10	1	0	-0.838447	-0.886243	-1.987036
11	6	0	-2.425304	-2.862718	0.300445
12	1	0	-3.409793	-2.149715	2.084654
13	1	0	-1.385319	-3.286560	-1.543419
14	1	0	-2.659081	-3.905254	0.497319
15	7	0	-0.326826	1.900115	0.652098
16	1	0	-0.621739	2.597337	1.327974

17	6	0	0.897782	1.291133	0.873097
18	8	0	1.641113	1.589191	1.788801
19	8	0	1.113485	0.352253	-0.056148
20	6	0	2.265772	-0.501424	0.150138
21	6	0	2.711224	-1.115235	-1.172223
22	6	0	3.624225	0.196353	0.124241
23	1	0	2.250519	-0.632718	-2.045898
24	1	0	2.643260	-2.205495	-1.265035
25	1	0	3.574021	1.248641	-0.185244
26	1	0	4.247282	0.100330	1.020226
27	8	0	4.065882	-0.665237	-0.951274
28	6	0	2.012672	-1.463386	1.283954
29	1	0	1.910878	-0.930179	2.232479
30	1	0	1.101984	-2.042174	1.098668
31	1	0	2.852916	-2.158054	1.367091

Sum of electronic and zero-point Energies= -1255.799762

Sum of electronic and thermal Energies= -1255.782887

Sum of electronic and thermal Enthalpies= -1255.781943

Sum of electronic and thermal Free Energies= -1255.845086

Table S3. Standard orientation of **Int1** structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.298713	1.055835	-1.065220
2	8	0	2.876038	1.432637	-2.359083
3	8	0	0.826852	0.924999	-1.041257
4	6	0	2.700393	2.335868	0.104142
5	6	0	4.037270	2.586087	0.424684
6	6	0	1.676589	3.129687	0.617351
7	6	0	4.345633	3.635390	1.288718
8	1	0	4.820605	1.959227	0.000000
9	6	0	1.993828	4.183344	1.476937
10	1	0	0.644107	2.914936	0.349040
11	6	0	3.325036	4.435120	1.813509
12	1	0	5.381744	3.832346	1.549932
13	1	0	1.200862	4.804348	1.885077
14	1	0	3.569689	5.253447	2.485489
15	6	0	2.996887	-1.367534	-1.065838
16	8	0	2.260890	-1.679606	-2.000655

17	8	0	3.838643	-2.340577	-0.590921
18	6	0	4.891243	-2.000408	0.325338
19	6	0	6.113168	-2.890428	0.090537
20	6	0	5.825032	-0.864012	-0.092194
21	1	0	6.070530	-3.428205	-0.866711
22	1	0	6.402532	-3.576899	0.895509
23	1	0	5.669627	-0.518174	-1.124152
24	1	0	5.888234	0.000000	0.583982
25	8	0	6.976812	-1.734245	0.023308
26	6	0	4.420501	-1.948888	1.761931
27	1	0	3.819028	-1.054837	1.953593
28	1	0	3.835493	-2.839021	2.011240
29	1	0	5.287942	-1.909693	2.428138
30	7	0	3.081200	-0.188372	-0.381388
31	1	0	1.953924	-0.810579	1.051621
32	6	0	0.477218	-0.335486	2.166569
33	8	0	1.054961	-1.160642	1.284599
34	8	0	1.076036	0.487043	2.836101
35	6	0	-1.025045	-0.486743	2.113659
36	1	0	-1.267264	-1.524787	1.859519
37	1	0	-1.476467	-0.245499	3.076707
38	6	0	-1.509009	0.488949	1.022666

39	1	0	-0.707846	0.684422	0.296160
40	1	0	-1.789531	1.456552	1.451785
41	6	0	-3.414116	1.174983	-1.068268
42	6	0	-2.419728	1.979050	-1.649039
43	6	0	-4.752676	1.301847	-1.469873
44	6	0	-2.778535	2.925546	-2.607007
45	1	0	-1.370089	1.862079	-1.376999
46	6	0	-5.098403	2.251487	-2.428197
47	1	0	-5.521901	0.665253	-1.035800
48	6	0	-4.113388	3.065138	-2.993454
49	1	0	-2.011235	3.549121	-3.056040
50	1	0	-6.135212	2.352850	-2.735103
51	1	0	-4.385785	3.804503	-3.741609
52	6	0	-4.263645	-0.453633	1.236127
53	6	0	-4.422791	-1.738302	1.777534
54	6	0	-5.052595	0.609587	1.704036
55	6	0	-5.386058	-1.959987	2.760514
56	1	0	-3.799174	-2.561403	1.433428
57	6	0	-6.013422	0.378267	2.685569
58	1	0	-4.916599	1.613353	1.305520
59	6	0	-6.182956	-0.905492	3.210684
60	1	0	-5.511390	-2.956215	3.173604

61	1	0	-6.626798	1.200612	3.041016
62	1	0	-6.934579	-1.082974	3.974558
63	6	0	-2.459608	-1.593248	-0.801811
64	6	0	-1.119132	-1.787055	-1.173357
65	6	0	-3.455110	-2.481068	-1.243131
66	6	0	-0.778953	-2.888325	-1.959154
67	1	0	-0.334075	-1.089128	-0.878556
68	6	0	-3.102167	-3.576819	-2.026101
69	1	0	-4.499365	-2.319011	-0.980219
70	6	0	-1.764868	-3.782750	-2.379269
71	1	0	0.263011	-3.022010	-2.239315
72	1	0	-3.870609	-4.266599	-2.363181
73	1	0	-1.494773	-4.638251	-2.992633
74	15	0	-2.928524	-0.109348	0.088997

Sum of electronic and zero-point Energies= -2558.953971

Sum of electronic and thermal Energies= -2558.915928

Sum of electronic and thermal Enthalpies= -2558.914984

Sum of electronic and thermal Free Energies= -2559.027523

Table S4. Standard orientation of **Int2** structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.723845	1.153614	-0.600469
2	8	0	-1.775255	1.479893	0.477847
3	8	0	-2.500410	1.842184	-1.879889
4	6	0	-4.337516	1.639994	-0.024781
5	6	0	-4.733979	1.288944	1.268848
6	6	0	-5.163381	2.397568	-0.852688
7	6	0	-5.983085	1.698632	1.731671
8	1	0	-4.063691	0.709881	1.901916
9	6	0	-6.412284	2.807673	-0.379752
10	1	0	-4.821930	2.661156	-1.850484
11	6	0	-6.822339	2.457433	0.907886
12	1	0	-6.301691	1.431053	2.735713
13	1	0	-7.063455	3.399752	-1.017042
14	1	0	-7.794436	2.778262	1.273884
15	7	0	-2.966824	-0.436664	-0.726661
16	1	0	-1.160447	-3.013311	1.870988

17	6	0	-1.901400	-1.172503	-1.097300
18	8	0	-0.797651	-0.814582	-1.540778
19	8	0	-2.064814	-2.529637	-0.958519
20	6	0	-3.237932	-3.063102	-0.311204
21	6	0	-2.801717	-4.368156	0.359409
22	6	0	-3.430440	-2.560105	1.122926
23	1	0	-1.824760	-4.758030	0.054403
24	1	0	-3.555664	-5.163917	0.337082
25	1	0	-2.925730	-1.635898	1.413949
26	1	0	-4.480024	-2.529034	1.439500
27	8	0	-2.754603	-3.735761	1.669874
28	6	0	-4.421049	-3.090781	-1.244585
29	1	0	-4.708599	-2.072485	-1.515548
30	1	0	-4.172619	-3.641978	-2.156302
31	1	0	-5.273857	-3.581571	-0.766201
32	6	0	-0.392972	-1.284402	2.175569
33	8	0	-0.337137	-2.503964	1.631327
34	8	0	-1.254206	-0.929244	2.964270
35	6	0	0.726225	-0.379589	1.712184
36	1	0	0.249606	0.575474	1.458850
37	1	0	1.373818	-0.192908	2.578248
38	6	0	1.503960	-0.939188	0.527452

39	1	0	0.819792	-1.092316	-0.319550
40	1	0	1.951929	-1.910683	0.766169
41	6	0	3.644848	-0.700109	-1.429959
42	6	0	2.849159	-1.450388	-2.309963
43	6	0	4.996694	-0.465834	-1.724300
44	6	0	3.417738	-1.983057	-3.465795
45	1	0	1.790387	-1.609021	-2.109267
46	6	0	5.554832	-1.004026	-2.881810
47	1	0	5.611531	0.133424	-1.054297
48	6	0	4.767180	-1.763562	-3.750474
49	1	0	2.803171	-2.565289	-4.146067
50	1	0	6.602345	-0.826457	-3.106677
51	1	0	5.204460	-2.179869	-4.653825
52	6	0	4.050387	0.260815	1.328213
53	6	0	3.921619	1.328391	2.230066
54	6	0	5.006840	-0.740545	1.557090
55	6	0	4.761501	1.403845	3.339532
56	1	0	3.168989	2.097342	2.065775
57	6	0	5.845276	-0.655046	2.666811
58	1	0	5.097085	-1.582378	0.872772
59	6	0	5.725389	0.416890	3.555295
60	1	0	4.660524	2.232025	4.034305

61	1	0	6.589839	-1.426526	2.838242
62	1	0	6.381241	0.479467	4.418987
63	6	0	2.297056	1.722184	-0.505488
64	6	0	0.966331	1.891399	-0.909449
65	6	0	3.213495	2.783826	-0.599335
66	6	0	0.547166	3.136903	-1.378751
67	1	0	0.248593	1.071106	-0.865747
68	6	0	2.785100	4.019180	-1.074713
69	1	0	4.252688	2.647668	-0.301575
70	6	0	1.451344	4.195814	-1.461325
71	1	0	-0.492717	3.254982	-1.675686
72	1	0	3.489208	4.843608	-1.143397
73	1	0	1.121276	5.164231	-1.828744
74	15	0	2.872050	0.097025	-0.017133

Sum of electronic and zero-point Energies= -2558.963519

Sum of electronic and thermal Energies= -2558.924495

Sum of electronic and thermal Enthalpies= -2558.923551

Sum of electronic and thermal Free Energies= -2559.037997

Table S5. Standard orientation of **TS** structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.750514	-0.972034	-1.119227
2	8	0	1.621732	-1.434833	-0.303100
3	8	0	2.892986	-1.528546	-2.463315
4	6	0	4.232557	-1.318356	-0.206446
5	6	0	4.142573	-1.466263	1.179639
6	6	0	5.444521	-1.454708	-0.884997
7	6	0	5.303020	-1.756390	1.898222
8	1	0	3.180779	-1.348216	1.681406
9	6	0	6.597007	-1.743353	-0.152979
10	1	0	5.476006	-1.348397	-1.966617
11	6	0	6.525398	-1.894080	1.234975
12	1	0	5.250545	-1.875829	2.976944
13	1	0	7.548522	-1.855249	-0.665581
14	1	0	7.425002	-2.123746	1.800103
15	7	0	2.801971	0.672464	-1.118911
16	1	0	1.783408	2.273307	2.605290

17	6	0	1.642597	1.274404	-1.513408
18	8	0	0.724152	0.845055	-2.207933
19	8	0	1.520694	2.538781	-0.990254
20	6	0	2.556445	2.880605	-0.052244
21	6	0	2.002653	3.642490	1.141988
22	6	0	2.953608	1.666786	0.769680
23	1	0	0.910724	3.591128	1.199173
24	1	0	2.348136	4.672571	1.252724
25	1	0	2.223547	0.929651	1.080855
26	1	0	3.996710	1.419211	0.937931
27	8	0	2.605977	2.798898	2.165246
28	6	0	3.712519	3.552077	-0.758921
29	1	0	4.157698	2.873027	-1.489449
30	1	0	3.362590	4.451208	-1.271722
31	1	0	4.479382	3.843548	-0.035227
32	6	0	0.621506	0.312615	2.665907
33	8	0	0.533222	1.595367	2.742596
34	8	0	1.598539	-0.375101	3.012552
35	6	0	-0.608916	-0.366424	2.048847
36	1	0	-0.375093	-1.411161	1.823902
37	1	0	-1.413682	-0.350930	2.795502
38	6	0	-1.043410	0.396058	0.799953

39	1	0	-0.270435	0.344555	0.018393
40	1	0	-1.184463	1.454057	1.055818
41	6	0	-3.124008	1.045659	-1.156820
42	6	0	-2.281726	2.090350	-1.560021
43	6	0	-4.389371	0.886837	-1.746089
44	6	0	-2.719438	2.984100	-2.538020
45	1	0	-1.283114	2.198271	-1.140690
46	6	0	-4.817608	1.785196	-2.718277
47	1	0	-5.038934	0.065232	-1.445309
48	6	0	-3.982787	2.835969	-3.112274
49	1	0	-2.067103	3.793300	-2.853254
50	1	0	-5.797948	1.665292	-3.169540
51	1	0	-4.317713	3.536334	-3.872572
52	6	0	-3.840066	-0.351998	1.319949
53	6	0	-3.802826	-1.473260	2.166363
54	6	0	-4.791445	0.655427	1.532907
55	6	0	-4.721084	-1.586552	3.207082
56	1	0	-3.063512	-2.257101	2.009705
57	6	0	-5.709594	0.532270	2.575053
58	1	0	-4.815658	1.530853	0.887356
59	6	0	-5.675906	-0.586536	3.409643
60	1	0	-4.691514	-2.455825	3.856992

61	1	0	-6.448962	1.311286	2.734593
62	1	0	-6.393559	-0.679859	4.220036
63	6	0	-2.334752	-1.741955	-0.779351
64	6	0	-1.156330	-1.910551	-1.522305
65	6	0	-3.322656	-2.738972	-0.779637
66	6	0	-0.955034	-3.093573	-2.229684
67	1	0	-0.392004	-1.134374	-1.554143
68	6	0	-3.113162	-3.914724	-1.497522
69	1	0	-4.246944	-2.601753	-0.221155
70	6	0	-1.928348	-4.095130	-2.216443
71	1	0	-0.033655	-3.225995	-2.790787
72	1	0	-3.874476	-4.689601	-1.493553
73	1	0	-1.766546	-5.016701	-2.769476
74	15	0	-2.584251	-0.169191	0.049828

Sum of electronic and zero-point Energies= -2558.928504

Sum of electronic and thermal Energies= -2558.890336

Sum of electronic and thermal Enthalpies= -2558.889392

Sum of electronic and thermal Free Energies= -2558.999571

Table S6. Standard orientation of **C1+4b** structure.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.498639	-0.815871	-1.079764
2	8	0	1.314344	-1.210325	-0.337884
3	8	0	2.499556	-0.918421	-2.528697
4	6	0	3.902135	-1.639798	-0.405123
5	6	0	3.877474	-1.983898	0.949579
6	6	0	4.982075	-1.934898	-1.239291
7	6	0	4.984203	-2.648543	1.476092
8	1	0	3.018347	-1.712284	1.567720
9	6	0	6.076979	-2.604166	-0.693628
10	1	0	4.954426	-1.653161	-2.288542
11	6	0	6.076005	-2.957184	0.658934
12	1	0	4.993575	-2.926297	2.525906
13	1	0	6.927545	-2.850565	-1.322131
14	1	0	6.932153	-3.478736	1.078751
15	7	0	2.883831	0.808887	-0.702600
16	1	0	2.270896	2.316925	2.440893

17	6	0	1.899759	1.778514	-0.893154
18	8	0	0.865656	1.649352	-1.524169
19	8	0	2.290651	2.911904	-0.298165
20	6	0	3.636681	2.740968	0.289662
21	6	0	3.657472	3.468745	1.634032
22	6	0	3.769112	1.218752	0.393755
23	1	0	3.165504	4.443824	1.458429
24	1	0	4.707950	3.688364	1.869315
25	1	0	3.405686	0.844492	1.361525
26	1	0	4.797306	0.890782	0.218450
27	8	0	3.119100	2.775137	2.717857
28	6	0	4.618938	3.357102	-0.687691
29	1	0	4.540337	2.882309	-1.670143
30	1	0	4.420498	4.426317	-0.803379
31	1	0	5.642755	3.232931	-0.324302
32	6	0	0.792439	0.267321	2.198337
33	8	0	0.930936	1.508702	1.953446
34	8	0	1.623409	-0.495002	2.743719
35	6	0	-0.567766	-0.330467	1.780980
36	1	0	-0.395736	-1.325156	1.355795
37	1	0	-1.175015	-0.464611	2.685999
38	6	0	-1.268064	0.591608	0.792109

39	1	0	-0.594428	0.826109	-0.043313
40	1	0	-1.509330	1.548692	1.268359
41	6	0	-3.549685	1.261643	-0.904144
42	6	0	-2.828690	2.424441	-1.209575
43	6	0	-4.827328	1.060541	-1.451667
44	6	0	-3.392741	3.385846	-2.048362
45	1	0	-1.830575	2.583566	-0.808271
46	6	0	-5.383543	2.027192	-2.285164
47	1	0	-5.386935	0.152663	-1.229272
48	6	0	-4.666194	3.189694	-2.584052
49	1	0	-2.831995	4.285209	-2.284803
50	1	0	-6.373150	1.872057	-2.704636
51	1	0	-5.100477	3.940188	-3.238733
52	6	0	-3.919827	-0.554180	1.388526
53	6	0	-3.641187	-1.745160	2.080167
54	6	0	-4.991324	0.255734	1.788557
55	6	0	-4.437094	-2.122360	3.158554
56	1	0	-2.805665	-2.374683	1.776946
57	6	0	-5.786466	-0.132033	2.866742
58	1	0	-5.201724	1.185178	1.262973
59	6	0	-5.510300	-1.317632	3.550668
60	1	0	-4.218526	-3.042597	3.692156

61	1	0	-6.619009	0.494293	3.173209
62	1	0	-6.130191	-1.614341	4.392069
63	6	0	-2.453279	-1.433415	-0.990327
64	6	0	-1.325706	-1.364034	-1.822361
65	6	0	-3.339543	-2.516141	-1.089411
66	6	0	-1.075745	-2.390822	-2.730475
67	1	0	-0.636993	-0.521351	-1.760735
68	6	0	-3.084926	-3.534526	-2.005863
69	1	0	-4.222281	-2.565493	-0.454405
70	6	0	-1.953495	-3.473715	-2.823568
71	1	0	-0.191870	-2.340856	-3.360399
72	1	0	-3.768784	-4.375228	-2.079734
73	1	0	-1.756422	-4.272171	-3.534005
74	15	0	-2.797625	-0.036413	0.087124

Sum of electronic and zero-point Energies= -2558.995437

Sum of electronic and thermal Energies= -2558.956669

Sum of electronic and thermal Enthalpies= -2558.955724

Sum of electronic and thermal Free Energies= -2559.068438