Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Incorporation of Carbon Dioxide into Phthalides via Ligand-Free Copper-Catalyzed Direct Carboxylation of Benzoxasiloles

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General Information

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-400, JEOL ECX-500 and a JEOL ECX-600 in $CDCl_3$, DMSO-d_6, Acetone-d_6 or CD_3OD. Chemical shifts of ^{1}H and ^{13}C were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard (For ^{1}H NMR: $CDCl_3$: 7.27, DMSO-d_6: 2.50, Acetone-d_6: 2.05 and CD_3OD: 3.31; For ^{13}C NMR: $CDCl_3$: 77.0, DMSO-d_6: 39.5, Acetone-d_6: 29.8 and CD_3OD: 49.0). IR spectra were measured on a JASCO FT/IR-610 spectrometer. High-resolution mass spectrometry was carried out using a JEOL JMS-T100TD (ESI and DART). HPLC analysis was performed on Shimadzu LC-20AB with chiral HPLC column. Column chromatography was carried out using silica gel obtained from Merck & Co.

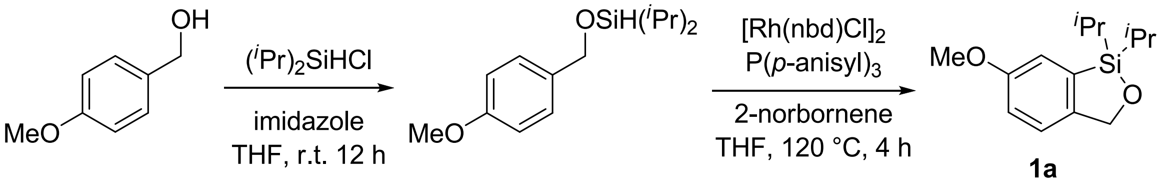
Reagents: Unless stated otherwise, commercial organic chemicals were purchased from Tokyo Chemical Industry Co. Ltd and used as received. $[Ir(cod)(OMe)]_2$ and $[Rh(nbd)Cl]_2$ were purchased from Strem Chemical Inc and stored in glovebox. CuI was purchased from Wako Pure Chemical Industries, Ltd. and stored in glovebox. CsF was obtained from Tokyo Chemical Industry Co. Ltd, dried at 200 °C for 18 h under strong vacuum (0.1 mmHg) and stored in glovebox. Alcohols used for the preparation of starting materials were either purchased from Tokyo Chemical Industry Co. Ltd or synthesized by reduction of the corresponding aldehydes or ketones with $NaBH_4$.

Organic solvents for reactions were purified by distillation under dry argon atmosphere or purchased as anhydrous solvent from Wako Pure Chemical Industries, Ltd.

Part I: Preparation of Starting Materials

*Synthesis of benzoxasiloles **1a-l**[1]*

1,1-Diisopropyl-6-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole **1a**:



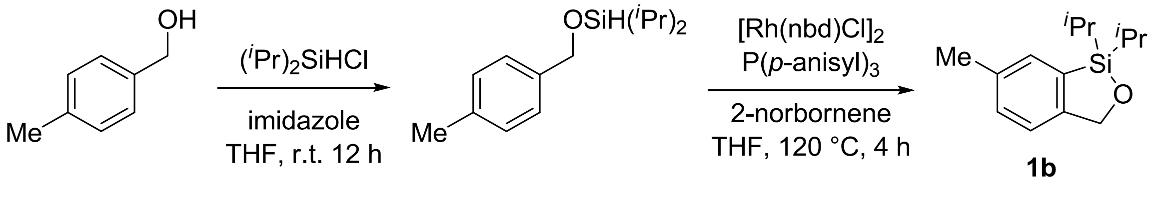
Step 1: To a 100 mL 2 neck round bottom flask was charged 4-methoxybenzyl alcohol (2.76 g, 20 mmol), imidazole (2.7 g, 20 mmol) and THF (40 mL). An argon balloon was attached and $({}^{i}Pr)_2SiHCl$ (3.64 g, 4.0 mL, 24 mmol) was added dropwise. The reaction was stirred overnight at room temperature and the solvent was removed under reduced pressure. Hexane (60 mL) was then added and the mixture was filtered through a Celite plug, affording a clear solution. Solvent was removed under reduced pressure to afford crude silyl ether which was directly used for the next step.

Step 2: Under air, to a 100 mL Schlenck tube was charged a solution of the silyl ether and 2-norbornene (3.8 g, 40 mmol) in THF (6 mL), a freshly prepared solution of $[Rh(nbd)Cl]_2$ (56 mg, 0.12 mmol) in THF (2 mL) and a freshly prepared solution of $P(p\text{-anisyl})_3$ (250 mg, 0.72 mmol) in THF (2 mL). The tube was flushed with argon, sealed and heated at 120 °C for 4-5 h, when ^1H NMR analysis indicated the full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified by Kugelrohr distillation (135-140 °C, 0.1 mmHg) to afford **1a** (3.8 g, 76 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.15 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 2.7 Hz, 1H), 6.97 (dd, *J* = 2.4, 8.6 Hz, 1H), 5.10 (s, 2H), 3.84 (s, 3H), 1.26-1.21 (m, 2H), 1.04-1.00 (m, 12H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 158.4, 142.8, 133.4, 122.3, 116.1, 116.0, 72.1, 55.4, 17.0, 16.9, 13.0.

1,1-Diisopropyl-6-methyl-1,3-dihydrobenzo[c][1,2]oxasilole **1b**:



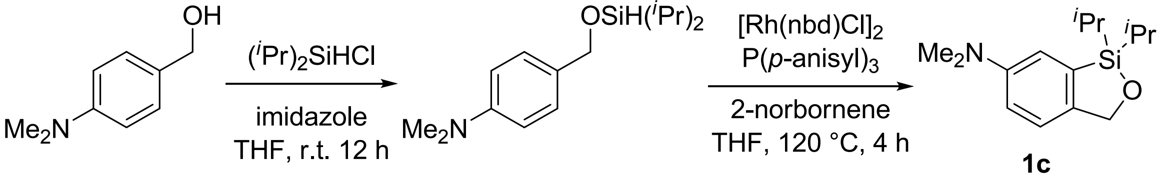
The synthesis of **1b** followed the synthesis of **1a** in smaller scale. Step 1: 4-methylbenzyl alcohol (1.22 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and $({}^{i}Pr)_2SiHCl$ (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), $[Rh(nbd)Cl]_2$ (28 mg, 0.06 mmol) in THF (1 mL) and $P(p\text{-anisyl})_3$ (126 mg, 0.36 mmol) in

THF (1 mL). The crude mixture was purified by Kugelrohr distillation (120 °C, 0.1 mmHg) to afford **1b** (1.8 g, 77 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.38 (s, 1H), 7.22 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.14-7.12 (m, 1H), 5.12 (s, 2H), 2.39 (s, 1H), 1.29-1.17 (m, 2H), 1.05-1.01 (m, 12H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 147.9, 135.8, 132.4, 131.8, 130.5, 121.2, 72.3, 21.2, 17.0, 13.1.

1,1-Diisopropyl-*N,N*-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilol-6-amine **1c**:



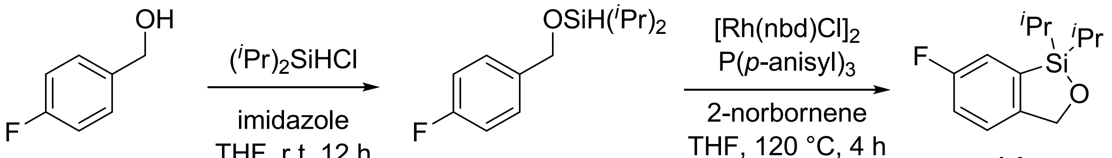
1c

The synthesis of **1c** followed the synthesis of **1a** in smaller scale. Step 1: 4-dimethylaminobenzyl alcohol (1.5 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (147 °C, 0.1 mmHg) followed by column chromatography to afford **1c** (1.7 g, 65 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 2.7 Hz, 1H), 6.86 (dd, *J* = 2.7, 8.2 Hz, 1H), 5.08 (s, 2H), 2.97 (s, 6H), 1.25-1.21 (m, 2H), 1.06-1.02 (m, 12H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 149.5, 139.0, 132.6, 121.8, 115.3, 115.2, 72.1, 41.1, 17.1, 17.0, 13.1.

6-Fluoro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole **1d**:



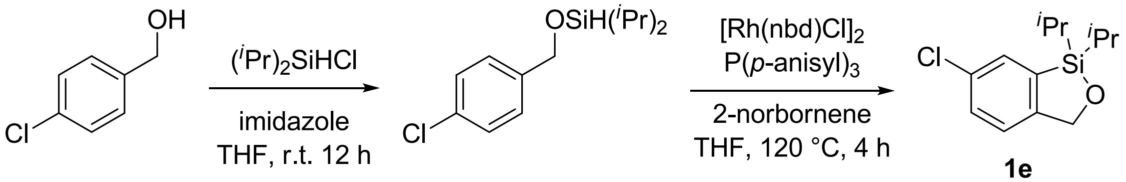
1d

The synthesis of **1d** followed the synthesis of **1a** in smaller scale. Step 1: 4-fluorobenzyl alcohol (1.1, 8.8 mmol), imidazole (1.23 g, 18 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.6 g, 1.8 mL, 10.6 mmol). Step 2: 2-norbornene (1.7 g, 17.6 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (25 mg, 0.05 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (110 mg, 0.32 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (110 °C, 0.1 mmHg) to afford **1d** (1.3 g, 60 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR (CDCl$_3$, 400MHz) δ 7.22-7.17 (m, 2H), 7.09-7.06 (m, 1H), 5.11 (s, 2H), 1.28-1.19 (m, 2H), 1.07-0.97 (m, 12H).

^{13}C NMR (CDCl$_3$, 101MHz) δ 162.0 (d, J = 246.4 Hz), 146.0 (d, J = 3.0 Hz), 134.5 (d, J = 5.8 Hz), 122.9 (d, J = 7.7 Hz), 117.8 (d, J = 19.2 Hz), 116.9 (d, J = 23 Hz), 72.0, 16.9, 16.8, 13.0.

<u>6-Chloro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole **1e**:</u>



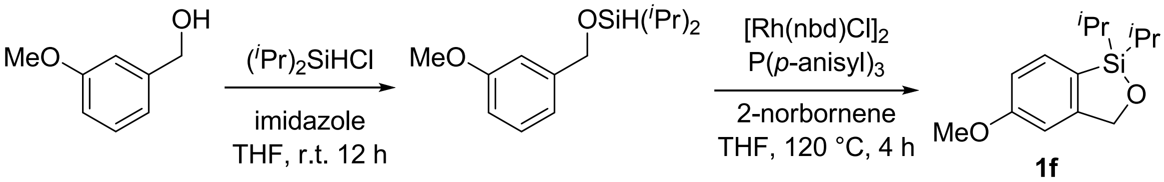
1e

The synthesis of **1e** followed the synthesis of **1a** in smaller scale. Step 1: 4-chlorobenzyl alcohol (1.43 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (125 °C, 0.1 mmHg) followed by column chromatography (EtOAc:*n*-Hexane = 5:95) to afford **1e** (1.3 g, 51 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 2.1, 8.0 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 5.10 (s, 2H), 1.28-1.21 (m, 2H), 1.07-1.00 (m, 12 H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 148.9, 134.6, 132.8, 131.5, 129.6, 122.9, 72.1, 16.9, 13.0.

1,1-Diisopropyl-5-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole **1f**:



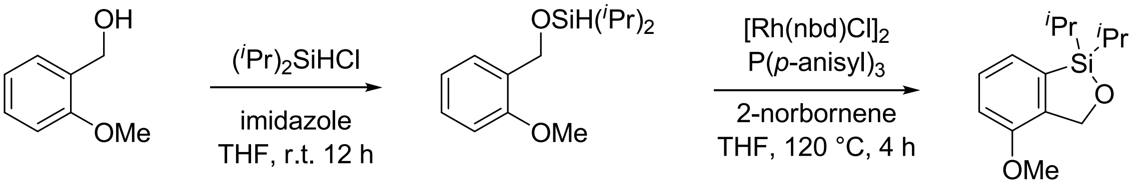
1f

The synthesis of **1f** followed the synthesis of **1a** in smaller scale. Step 1: 3-methoxybenzyl alcohol (1.38 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) to afford **1e** (1.7 g, 68 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.47 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 5.11 (s, 2H), 3.83 (s, 3H), 1.24-1.12 (m, 2H), 1.03-0.99 (m, 12H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 161.3, 153.0, 133.1, 122.5, 113.8, 106.2, 72.3, 55.1, 16.99, 16.97, 13.1.

1,1-Diisopropyl-4-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole **1g**:



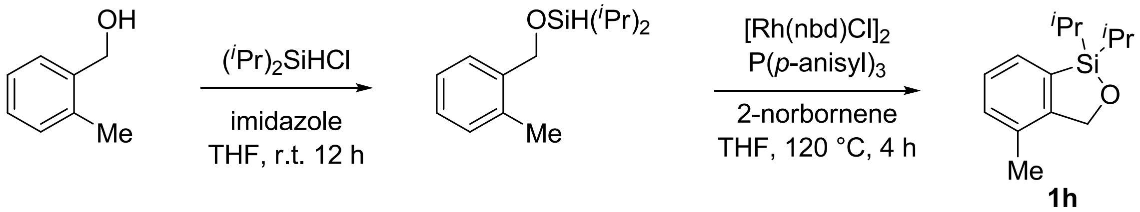
1g

The synthesis of **1g** followed the synthesis of **1a** in smaller scale. Step 1: 2-methoxybenzyl alcohol (1.38 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (125 °C, 0.1 mmHg) to afford **1e** (1.5 g, 60 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.30 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 6.9 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.11 (s, 2H), 3.84 (s, 3H), 1.24-1.20 (m, 2H), 1.04-1.00 (m, 12H).

^{13}C NMR (CDCl$_3$, 150 MHz) δ 154.2, 138.9, 133.7, 128.3, 123.7, 110.4, 70.4, 54.8, 16.9, 13.1.

1,1-Diisopropyl-4-methyl-1,3-dihydrobenzo[c][1,2]oxasilole **1h**:



1h

The synthesis of **1h** followed the synthesis of **1a** in smaller scale. Step 1: 2-methylbenzyl alcohol (1.22 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (120 °C, 0.1 mmHg) to afford **1b** (1.4 g, 60 % yield, 2 steps) as a colorless oil.

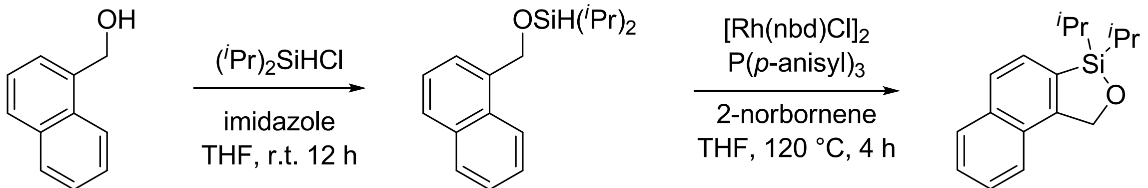
^{1}H NMR (CDCl$_3$, 400MHz) δ 7.49 (d, *J* = 7.3 Hz, 1H), 7.34-7.25 (m, 2H), 5.17 (s, 2H), 2.30 (s, 3H), 1.36-1.28 (m, 2H), 1.15-1.09 (m, 12H).

^{13}C NMR (CDCl$_3$, 150 MHz) δ 149.1, 131.4, 130.6, 129.5, 126.8, 71.8, 18.1, 17.0, 13.1.

DART-MS m/z cald for $C_{14}H_{23}OSi$ [M+H]$^+$: 235.15182, found: 235.15219

IR (KBr, cm^{-1}) ν: 2944, 284, 1462, 1211, 1074, 1049, 989, 881, 778, 694.

3,3-Diisopropyl-1,3-dihydronaphtho[2,1-c][1,2]oxasilole **1i**:



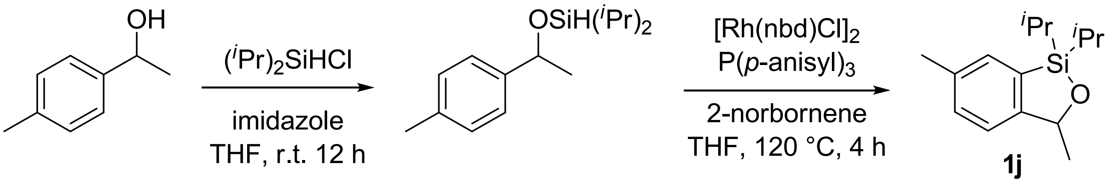
1i

The synthesis of **1i** followed the synthesis of **1a** in smaller scale. Step 1: 1-naphthalenemethanol (1.58 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by column chromatography (EtOAc:*n*-Hexane = 5:95) followed by Kugelrohr distillation (200 °C, 0.1 mmHg) to afford **1i** (1.7 g, 63% yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[1]

^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.94 - 7.92 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.73-7.71 (m, 1H), 7.64-7.62 (m, 1H), 7.57-7.54 (m, 2H), 5.61 (s, 2H), 1.34-1.29 (m, 2H), 1.08-1.04 (m, 12H).

^{13}C NMR (CDCl$_3$, 150 MHz) δ 148.3, 134.0, 129.3, 128.6, 127.9, 127.9, 127.1, 126.5, 126.2, 122.9, 71.9, 17.1, 17.0, 13.2.

1,1-Diisopropyl-3,6-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1j**:



1j

The synthesis of **1j** followed the synthesis of **1a** in smaller scale. Step 1: 1-(4-methylphenyl)ethanol (1.36 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) followed by column chromatography (EtOAc:*n*-Hexane = 5:95) to afford **1j** (1.0 g, 40% yield, 2 steps) as a colorless oil.

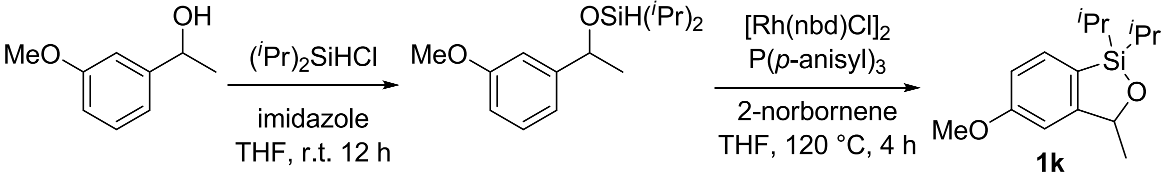
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 5.30 (q, *J* = 6.3 Hz, 1H), 2.39 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.26-1.15 (m, 2H), 1.07-0.96 (m, 12H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 152.5, 135.9, 132.3, 131.8, 130.6, 121.8, 78.1, 24.9, 21.2, 17.4, 17.3, 17.0, 17.0, 13.2, 12.5.

DART-MS m/z cald for $C_{15}H_{25}OSi$ $[M+H]^+$: 249.16747, found: 249.16632

IR (KBr, cm^{-1}) ν: 2946, 2865, 1464, 1085, 925, 880, 792, 670, 635, 494.

<u>1,1-Diisopropyl-5-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole **1k**:</u>



The synthesis of **1k** followed the synthesis of **1a** in smaller scale. Step 1: 1-(3-methoxyphenyl)ethanol (1.50 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), $[Rh(nbd)Cl]_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) followed by column chromatography (EtOAc:*n*-Hexane = 5:95) to afford **1k** (1.58 g, 60% yield, 2 steps) as a colorless oil.

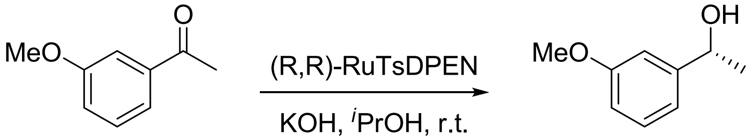
^{1}H NMR ($CDCl_3$, 400MHz) δ 7.45 (d, *J* = 8.2 Hz, 1H), 6.87 (dd, *J* = 2.1, 8.0 Hz, 1H), 6.73 (s, 1H), 5.28 (q, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.22-1.17 (m, 2H), 1.06-0.97 (m, 12H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 161.3, 157.4, 133.0, 122.4, 113.5, 107.2, 78.1, 55.1, 24.8, 17.3, 17.2, 17.0, 16.9, 13.2, 12.5.

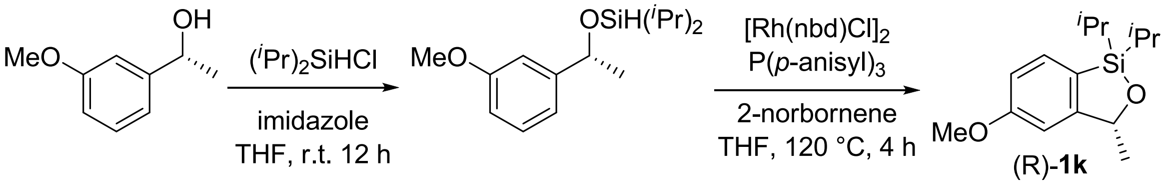
DART-MS m/z cald for $C_{15}H_{25}O_2Si$ $[M+H]^+$: 265.16238, found: 265.16109

IR (KBr, cm^{-1}) ν: 2945, 2864, 1600, 1465, 1306, 1239, 1071, 881, 786, 677.

(R)-1,1-Diisopropyl-5-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (R)-**1k**:

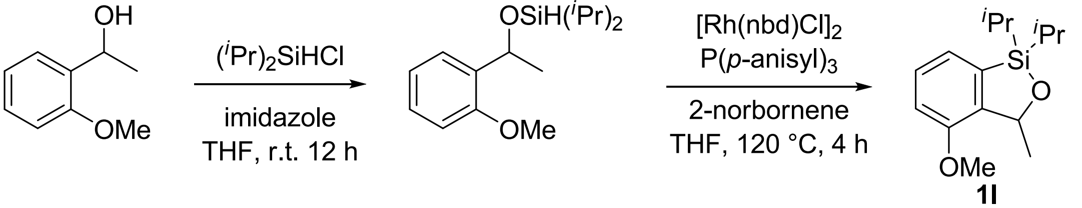


Synthesis of chiral alcohol: In a 300 mL 3 neck round bottom flask was charged (R,R)-RuTsDPEN (127 mg, 0.2 mmol). An argon balloon was attached and isopropanol (200 mL) was added followed by 3'-methoxyacetophenone (3.0 g, 20 mmol) and a solution of KOH (28 mg) in isopropanol (20 mL). The reaction was stirred at room temperature for 3 days, then quenched with HCl (1N, 1 mL) and the solvent was removed. Brine (50 mL) was added and the mixture was extracted to EtOAc. Removal of solvent followed by column chromatography afforded the chiral alcohol (2 g, 66%) with 94% ee (HPLC, OD-H, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min).



The chiral alcohol was then used for the synthesis of (R)-**1k** following the same procedure for the synthesis of **1k**. Yield: 1.7 g (65%) colorless oil.

1,1-Diisopropyl-4-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole **1l**:



The synthesis of **1l** followed the synthesis of **1a** in smaller scale. Step 1: 1-(2-methoxyphenyl)ethanol (1.50 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (^{i}Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36

mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) followed by column chromatography (EtOAc:*n*-Hexane = 5:95) to afford **1l** (2.0 g, 76% yield, 2 steps) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.29-7.25 (m, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.38 (q, *J* = 6.3 Hz, 1H), 3.82 (s, 3H), 1.53 (d, *J* = 6.4 Hz, 3H), 1.25-0.87 (m, 14H).

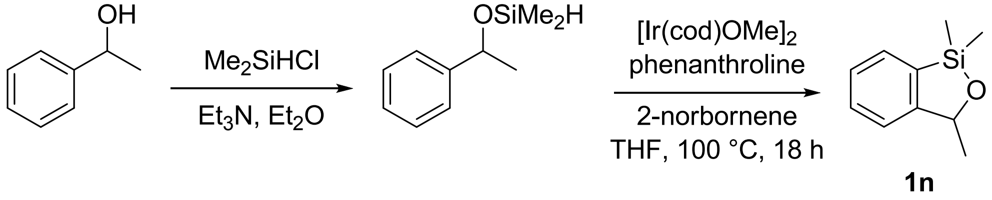
^{13}C NMR ($CDCl_3$, 101MHz) δ 154.4, 142.9, 133.8, 128.5, 123.7, 111.1, 77.2, 54.8, 23.4, 17.4, 17.4, 17.0, 13.2, 12.6.

DART-MS m/z cald for $C_{15}H_{25}O_2Si$ $[M+H]^+$: 265.16238, found: 265.16170

IR (KBr, cm^{-1}) ν: 2943, 2866, 1568, 1464, 1255, 1078, 1053, 1024, 927, 880, 803, 685.

*Synthesis of benzoxasiloles **1n-w**[2]*

1,1,3-Trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1n**:



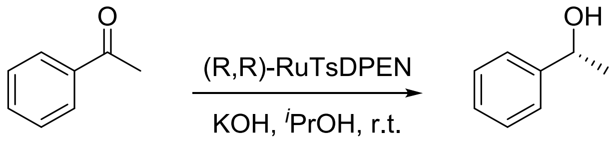
Step 1: In a 200 mL 2 neck round bottom flask equipped with a 20 mL dropping funnel and an argon balloon, to the solution of $ClMe_2SiH$ (2.8 g, 3.3 mL, 30 mmol) in Et_2O (70 mL) at 0 °C was added dropwise a solution of 1-phenylethanol (2.44 g, 20 mmol), Et_3N (4.0 g, 40 mmol) in Et_2O (20 mL). A white precipitate appeared immediately. The mixture was stirred at 0 °C for 20 mins and at room temperature for 16 h. Then, it was diluted with Et_2O (50 mL), washed quickly with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. Et_2O was then removed under reduced pressure to afford the silyl ether which was directly used for the next step.

Step 2: Inside and argon glovebox, a 100 mL Schlenck tube was successively charged with a solution of the silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), $[Ir(cod)(OMe)]_2$ (60 mg, 0.092 mmol) and phenanthroline (48 mg, 0.25 mmol). The flask was sealed, taken out of glovebox, stirred at room temperature for 1h and 100 °C for 16 h upon which ^{1}H NMR analysis showed full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified using Kugelrohr distillation (125-130 °C, 40 mmHg) to afford **1n** (2.6 g, 73 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[3]

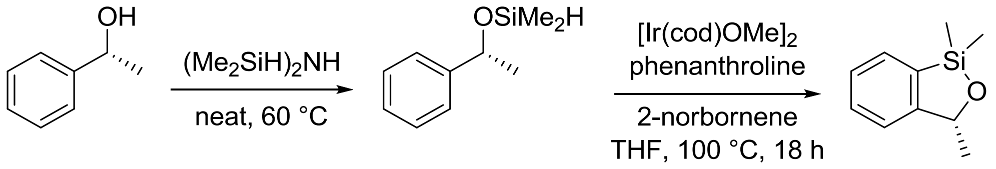
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.34 (q, *J* = 6.6 Hz, 1H), 1.52 (d, *J* = 6.9 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.3, 135.0, 130.8, 129.6, 126.9, 122.1, 77.8, 25.2, 1.6, 0.4.

(R)-1,1,3-Trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (R)-**1n**:



The chiral alcohol was prepared via asymmetric transfer hydrogenation as described in the synthesis of (R)-**1k**. Yield: 1.6 g (66%) colorless oil, 94% ee (HPLC: OD-H, ^{i}PrOH/*n*-Hexane = 2:98, 1 mL/min).



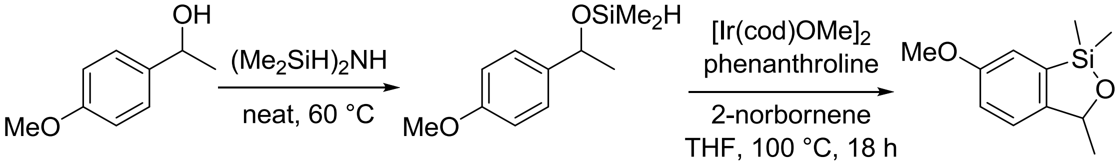
(R)-**1n**

Step 1: The chiral alcohol (1.22 g, 10 mmol) was treated with $(Me_2SiH)_2NH$ (1.14 mL, 6.6 mmol) at 60 °C overnight. Excess silylating reagent was removed under reduced pressure.

Step 2: Inside and argon glovebox, a 100 mL Schlenck tube was successively charged with a solution of the silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), $[Ir(cod)(OMe)]_2$ (30 mg, 0.046 mmol) and phenanthroline (24 mg, 0.125 mmol). The flask was sealed, taken out of glovebox, stirred at room temperature for 1h and 100 °C for

16 h upon which ^{1}H NMR analysis showed full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified using Kugelrohr distillation to afford (R)-**1n** (1.25 g, 70% yield, 2 steps) as a colorless oil.

6-Methoxy-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1n**:



1o

The synthesis of **1o** followed the synthesis of (R)-**1m**. Step 1: 1-(4-methoxyphenyl)ethanol (1.50 g, 10 mmol), $(Me_2SiH)_2NH$ (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), $[Ir(cod)(OMe)]_2$ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) to afford **1o** (1.2 g, 57% yield, 2 steps) as a colorless oil.

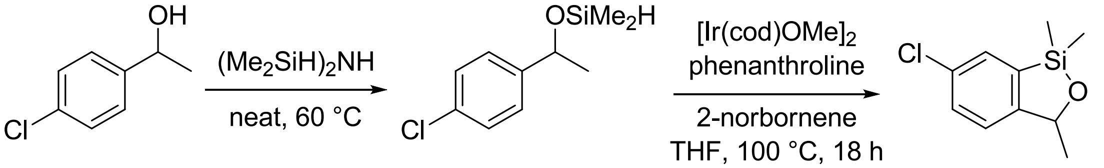
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.99-6.96 (m, 1H), 5.30 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 1.50 (d, *J* = 6.4 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 146.5, 136.6, 123.1, 116.6, 114.3, 77.4, 55.4, 25.4, 1.5, 0.3.

DART-MS m/z cald for $C_{11}H_{17}O_2Si$ $[M+H]^+$: 209.09978, found: 209.09951

IR (KBr, cm^{-1}) ν: 2968, 1471, 1286, 1228, 1082, 927, 880, 823, 789.

6-Chloro-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1p**:



1p

The synthesis of **1p** followed the synthesis of (R)-**1m**. Step 1: 1-(4-chlorophenyl)ethanol (1.56 g, 10 mmol), $(Me_2SiH)_2NH$ (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), $[Ir(cod)(OMe)]_2$ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (110 °C, 0.1 mmHg) afford **1p** (1.6 g, 76% yield, 2 steps) as a colorless oil.

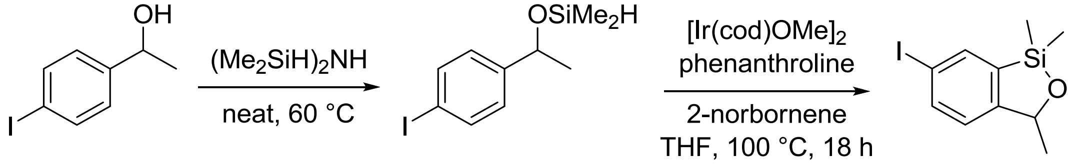
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 1.8, 8.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 5.30 (q, *J* = 6.4 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 137.7, 133.1, 130.5, 129.7, 123.6, 77.5, 25.2, 1.4, 0.3.

DART-MS m/z cald for $C_{10}H_{14}ClOSi$ $[M+H]^+$: 213.05024, found: 213.05015.

IR (KBr, cm^{-1}) ν: 2972, 2871, 1451, 1254, 1091,928, 791.

6-Iodo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1q**



1q

The synthesis of **1q** followed the synthesis of (R)-**1m** in a smaller scale. Step 1: 1-(4-iodophenyl)ethanol (1.24 g, 5 mmol), $(Me_2SiH)_2NH$ (0.57 mL, 3.3 mmol). Step 2: silyl ether in THF (5 mL), 2-norbornene (0.57 g, 6 mmol) in THF (5 mL), $[Ir(cod)(OMe)]_2$ (15 mg, 0.023 mmol) and phenanthroline (12 mg, 0.063 mmol). The crude mixture was purified by Kugelrohr distillation (130-140 °C, 0.1 mmHg) afford **1q** (0.9 g, 60% yield, 2 steps) as a colorless oil.

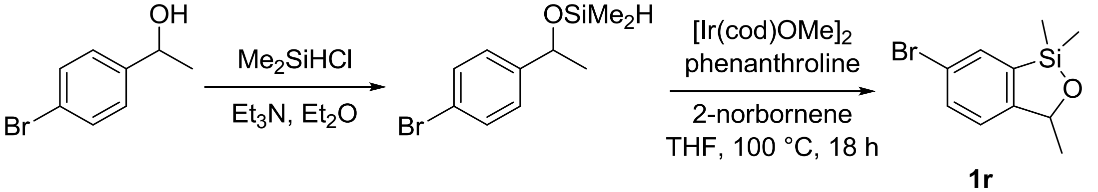
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 8.2, 1H), 5.30-5.27 (m, 1H), 1.48 (d, *J* = 6.4 Hz, 3H), 0.41 (s, 3H), 0.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 139.6, 138.8, 138.3, 124.3, 93.5, 77.5, 25.1, 1.5, 0.3.

DART-MS m/z cald for $C_{10}H_{14}IOSi$ $[M+H]^+$: 304.98586, found: 304.98595

IR (KBr, cm^{-1}) ν: 2975, 2869, 1254, 1084, 1022, 927, 826, 790, 747.

6-Bromo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1r**:



1r

The synthesis of **1r** followed the synthesis of **1m**. Step 1: 1-(4-bromophenyl)ethanol (4.0 g, 20 mmol), $ClMe_2SiH$ (2.8 g, 3.3 mL, 30 mmol), Et_3N (4 g, 40 mmol), Et_2O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), $[Ir(cod)(OMe)]_2$ (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (125-130 °C, 0.1 mmHg) to afford **1r** (3.4 g, 66% yield, 2 steps) as a colorless oil.

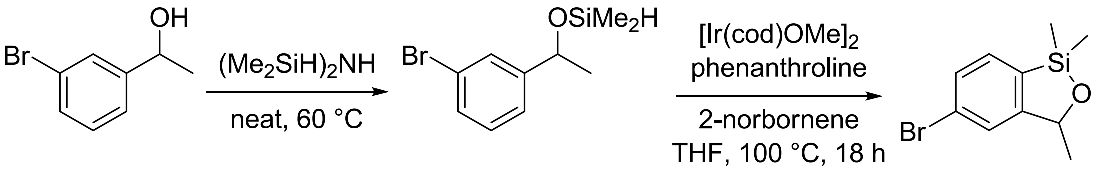
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.28 (q, *J* = 6.4 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ = 153.0, 138.3, 133.5, 132.5, 124.0, 121.5, 77.5, 25.1, 1.5, 0.3.

DART-MS m/z cald for $C_{10}H_{14}BrOSi$ $[M+H]^+$: 256.99973, found: 256.99873

IR (KBr, cm^{-1}) ν: 2971, 2869, 1254, 1084, 1023, 928, 857, 827, 791, 420.

5-Bromo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1s**:



1s

The synthesis of **1s** followed the synthesis of (R)-**1m**. Step 1: 1-(3-bromophenyl)ethanol (2.0 g, 10 mmol), $(Me_2SiH)_2NH$ (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), $[Ir(cod)(OMe)]_2$ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) afford **1s** (1.6 g, 62% yield, 2 steps) as a colorless oil.

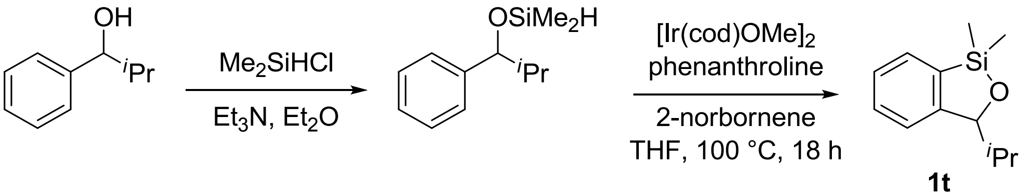
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.37 (m, 3H), 5.29 (q, J = 6.7 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H), 0.41 (s, 3H), 0.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 133.8, 132.3, 130.1, 125.5, 124.5, 77.3, 25.1, 1.5, 0.3.

DART-MS m/z cald for $C_{10}H_{14}BrOSi$ $[M+H]^+$: 256.99973, found: 256.99966

IR (KBr, cm^{-1}) ν: 2971, 2875, 1254, 1190, 1088, 1025, 931, 857, 824, 789.

3-Isopropyl-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1t**



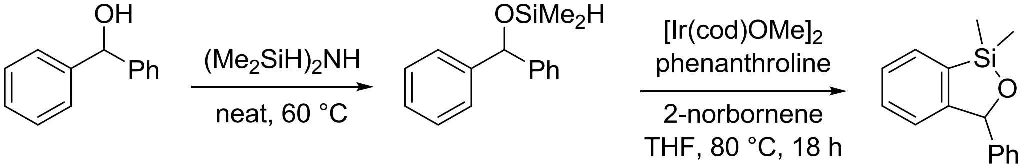
1t

The synthesis of **1s** followed the synthesis of **1m**. Step 1: 2-methyl-1-phenylpropan-1-ol (3.0 g, 20 mmol), $ClMe_2SiH$ (2.8 g, 3.3 mL, 30 mmol), Et_3N (4 g, 40 mmol), Et_2O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), $[Ir(cod)(OMe)]_2$ (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (90 °C, 0.1 mmHg) to afford **1t** (2.6 g, 63% yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, J = 7.3 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 5.18 (s, 1H), 2.14-2.11 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H), 0.60 (d, J = 6.9 Hz, 3H), 0.42 (s, 3H), 0.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 136.2, 130.7, 129.5, 126.8, 122.2, 86.3, 34.4, 20.3, 14.8, 0.8, 0.7.

1,1-Dimethyl-3-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole **1u**:



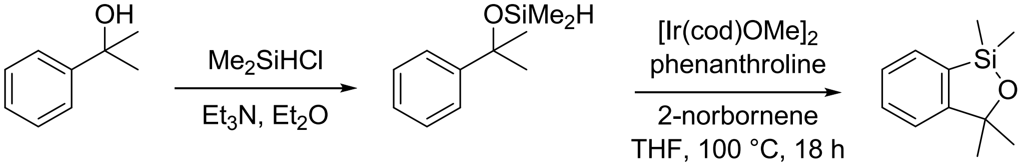
1u

The synthesis of **1u** followed the synthesis of (R)-**1m** with slight modification. Step 1: benzhydrol (1.84 g, 10 mmol), $(Me_2SiH)_2NH$ (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), $[Ir(cod)(OMe)]_2$ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The reaction was heated at 80 °C. The crude mixture was purified by Kugelrohr distillation (140 °C, 0.1 mmHg) afford **1u** (1.4 g, 58% yield, 2 steps) as a white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[3]

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62-7.61 (m, 1H), 7.33-7.26 (m, 7H), 7.03-7.02 (m, 1H), 6.16 (s, 1H), 0.53 (s, 3H), 0.45 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.4, 143.7, 135.1, 130.6, 129.8, 128.5, 127.8, 127.1, 127.1, 123.7, 84.0, 1.2, 0.5.

1,1,3,3-Tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1w**



1w

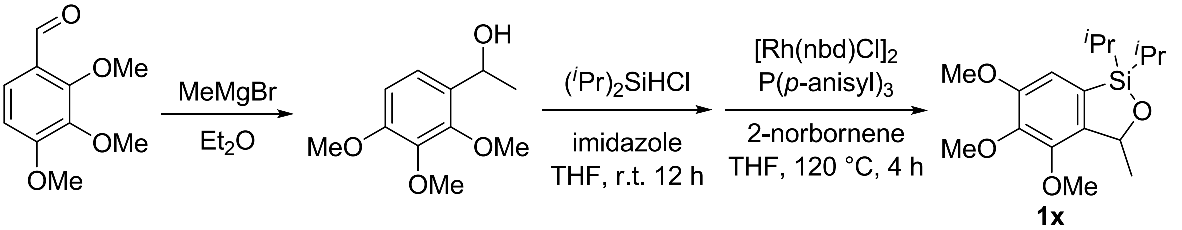
The synthesis of **1w** followed the synthesis of **1m**. Step 1: 2-phenyl-2-propanol (2.72 g, 20 mmol), $ClMe_2SiH$ (2.8 g, 3.3 mL, 30 mmol), Et_3N (4 g, 40 mmol), Et_2O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), $[Ir(cod)(OMe)]_2$ (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (140 °C, 40 mmHg) to afford **1w** (2.3 g, 60% yield, 2 steps) as a white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[3]

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.43-7.40 (m, 1H), 7.33-7.29 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1 H), 1.55 (s, 6 H), 0.40 (s, 6 H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 157.9, 134.5, 130.7, 129.7, 126.8, 122.1, 83.4, 32.1, 1.2.

*Synthesis of **1x-y***

1,1-Diisopropyl-4,5,6-trimethoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole **1x**:



Synthesis of 1-(2,3,4-trimethoxyphenyl)ethanol: To a solution of the 2,3,4-trimethoxybenzaldehyde (2.9 g, 15 mmol) in Et_2O (10 mL) was added MeMgBr (3 M in Et_2O, 6.3 mL) dropwise. The mixture was then heated to reflux for 2 h, cooled to room temperature and quenched with saturated NH_4Cl solution. The mixture was extracted with Et_2O (3 x 20 mL). The combined organic phase was washed with $NaHCO_3$, brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The alcohol was obtained after column chromatography. Yield 2.2 g (69%) colorless oil.

The synthesis of **1x** followed the synthesis of **1a** in smaller scale. Step 1: 1-(2,3,4-trimethoxyphenyl)ethanol (2.12 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and $(^i\text{Pr})_2\text{SiHCl}$ (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), $[\text{Rh(nbd)Cl}]_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(*p*-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (170°C, 0.1 mmHg) to afford **1x** (1.7 g, 52% yield, 2 steps) as a colorless oil.

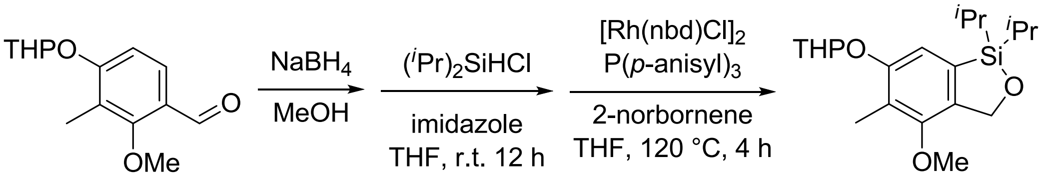
^{1}H NMR ($CDCl_3$, 600 MHz) δ 6.73 (s, 1H), 5.34 (q, *J* = 6.2 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.23-1.11 (m, 2H), 1.08 (dd, *J* = 3.1, 7.2 Hz, 6H), 0.97 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 153.5, 148.4, 143.4, 140.5, 127.0, 109.0, 60.7, 60.4, 56.2, 24.3, 17.4, 17.4, 17.0, 17.0, 13.2, 12.6.

DART-MS m/z cald for $C_{17}H_{29}O_4Si$ $[M+H]^+$: 325.18351, found: 325.18327

IR (KBr, cm^{-1}) ν: 2942, 2865, 1588, 1557, 1468, 1398, 1296, 1238, 1193, 1120, 1093, 1050, 1022

<u>1,1-Diisopropyl-4-methoxy-5-methyl-6-(tetrahydro-2H-pyran-2-yloxy)-1,3-dihydrobenzo [c][1,2]oxasilole **1x**:</u>



1y

The aldehyde starting material was prepared according to literature.[4]

Reduction of the aldehyde: A 50 mL round bottom flask was charged with the aldehyde (2.5 g, 10 mmol) and MeOH (20 mL) and cooled to 0 °C in an ice-water bath. $NaBH_4$ (760 mg, 20 mmol) was added in portions. After the addition was completed, the reaction was stirred at room temperature overnight before quenching with acetone. The solvent was removed and water (30 mL) was added and the mixture was extracted to EtOAc (3 x 15 mL). The combined organic solvent was washed with brine (2 x 20 mL), dried over Na_2SO_4. Removal of the solvent afforded the benzyl alcohol which was directly used in the next step.

The synthesis of **1y** followed the synthesis of **1a** in smaller scale. Step 1: imidazole (1.36 g, 10 mmol), THF (20 mL) and $(^iPr)_2SiHCl$ (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), $[Rh(nbd)Cl]_2$ (28 mg, 0.06 mmol) in THF (1 mL) and $P(p\text{-anisyl})_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by column chromatography to afford **1y** (2.7 g, 74% yield, 3 steps) as a slight yellow oil.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.04 (s, 1H), 5.44 (br. s., 1H), 5.14 (s, 2H), 3.94 (t, *J* = 10.7 Hz, 1H), 3.74 (s, 3H), 3.63-3.62 (m, 1H), 2.23 (s, 3H), 2.06-2.03 (m, 1H), 1.91-1.89 (m, 2H), 1.74-1.62 (m, 3H), 1.24-1.18 (m, 2H), 1.04-0.99 (m, 12H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.8, 153.5, 136.0, 130.8, 122.3, 112.7, 96.7, 70.0, 62.0, 60.0, 30.7, 25.3, 18.9, 17.0, 17.0, 17.0, 16.9, 13.1, 13.1, 9.2.

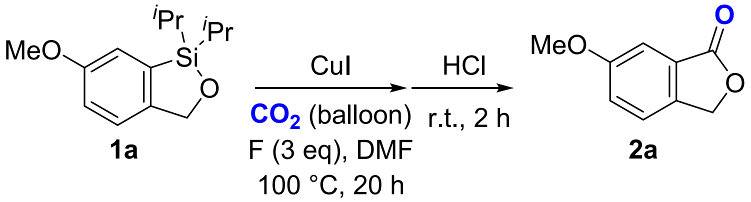
DART-MS m/z cald for $C_{20}H_{31}O_4Si$ $[M-H]^+$: 363.19916, found: 363.20035

IR (KBr, cm^{-1}) ν: 2943, 2864, 1461, 1403, 1280, 1125, 1089, 1052, 1020, 961, 880, 787, 673.

Part II: Optimization and Control Experiments

*Experimental Procedure for the reaction of **1a** and CO_2 (Table 1):* In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (7.6 mg, 0.04 mmol) and CsF (182 mg, 1.2 mmol). The tube was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (1.6 mL) and **1a** (100 mg, 0.4 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down, the reaction mixture was diluted with H_2O (5 mL), acidified using HCl 1N (4 mL), stirred for another 2 h and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR in $CDCl_3$ using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The results were shown in Table 1.

Screening different fluoride salts:



Entry	Fluoride	Yield(%)[a]
1	CsF	67
2	AgF	n.d.
3	KF	45
4	$KF.2H_2O$	n.d.
5	TBAT[b]	28

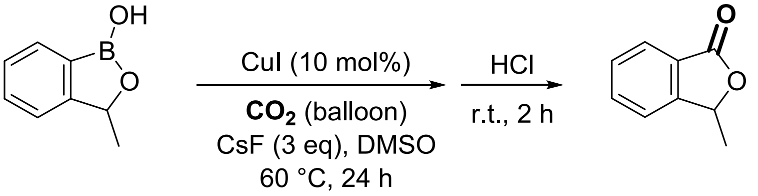
[a] Yields were determined by ^1H NMR analysis

[b] Tetrabutylammonium difluorotriphenylsilicate.

Control Experiments for the carboxylation of $PhSiMe_3$ and $PhSi(OMe)_3$: In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (10 mg, 0.05 mmol) and

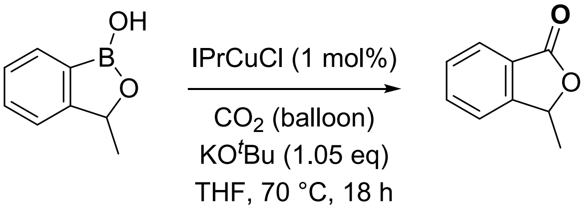
CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (2 mL) and $PhSiMe_3$ (75 mg, 0.5 mmol) or $PhSi(OMe)_3$ were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down to 0 °C in an ice-water bath, the reaction mixture was diluted with H_2O (5 mL), acidified using HCl 1N (2 mL) and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR in $CDCl_3$ using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The reaction using $PhSi(OMe)_3$ yielded benzoic acid (45%) while the reaction of $PhSiMe_3$ did not.

Control Experiments for the carboxylation of benzoxaboroles



In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (10 mg, 0.05 mmol), CsF (228 mg, 1.5 mmol) and the substrate (75 mg, 0.5 mmol). The tube was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (2 mL) was added. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down to 0 °C in an ice-water bath, the reaction mixture was diluted with H_2O (5 mL), acidified using HCl 1N (2 mL), stirred for another 2 h and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude mixture was analyzed by ^1H NMR in $CDCl_3$ using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The desired phthalide was not detected.

Control Experiments for the carboxylation of benzoxaboroles under reported condition:

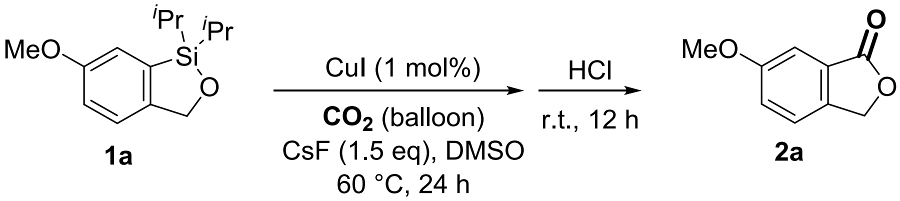


To a 10 mL 2-neck tube was added the substrate (74 mg, 0.5 mmol) and IPrCuCl (2.4 mg, 0.005 mmol). THF (2 mL) was then added, followed by a solution of KO^{t}Bu (60 mg, 0.525 mmol) in THF (0.5 mL). A CO_2 balloon was attached and the mixture was stirred at 70 °C for 18 h. The work-up was followed the above procedure. The desired phthalide was not detected.

Part III: Substrate Scope for the Carboxylation of Benzoxasiloles

*Carboxylation of substrate **1a-m***

6-Methoxyisobenzofuran-1(3H)-one **2a**:

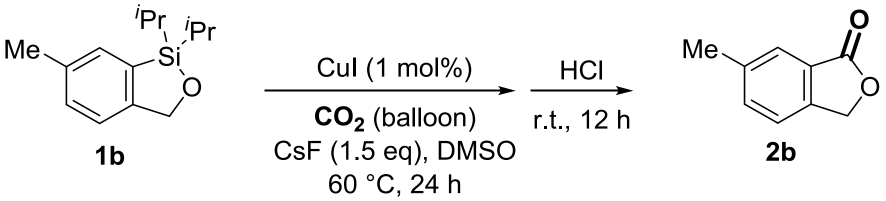


In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with CuI (2 mg, 0.01 mmol) and CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (4 mL) and **1a** (250 mg, 1 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H_2O (5 mL), acidified using HCl 1N (8 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The pure product was obtained using pTLC in DCM (the use of DCM as the eluent was neccessary to separate the product from small amount of alcohol, the use of EtOAc:*n*-Hexane system was not effective). Yield: 134 mg (82%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5a]

^{1}H NMR ($CDCl_3$, 600MHz) δ 7.37 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.25-7.23 (m, 1H), 5.26 (s, 2H), 3.87 (s, 3H).

^{13}C NMR ($CDCl_3$ 151MHz) δ 171.1, 160.6, 138.8, 127.0, 123.0, 122.9, 107.5, 69.5, 55.7.

6-Methylisobenzofuran-1(3H)-one **2b**:

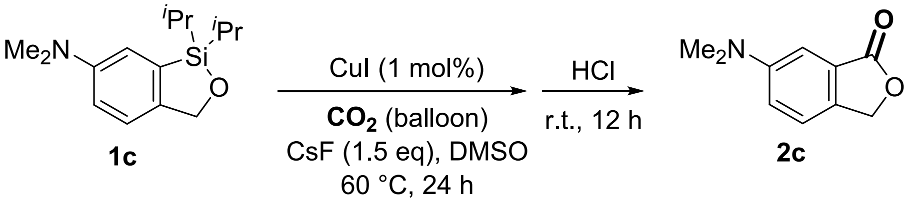


The synthesis of **2b** from **1b** (234 mg, 1 mmol) followed the synthesis of **2a**. Yield 114 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5b]

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.69 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.38-7.36 (m, 1H), 5.27 (s, 2H), 2.46 (s, 3H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 171.2, 143.8, 139.2, 135.1, 125.8, 125.6, 121.7, 69.5, 21.2.

6-(Dimethylamino)isobenzofuran-1(3H)-one **2c**:

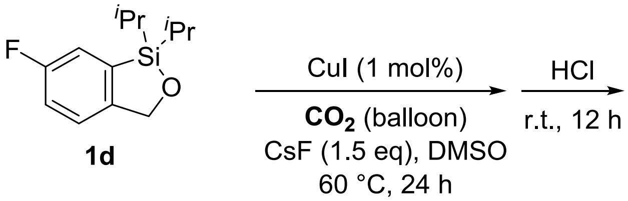


The synthesis of **2c** from **1c** (263 mg, 1 mmol) followed the synthesis of **2a** with slight modification. After the acidic quenching, the reaction was basified with NaOH 1N until pH > 10 before extraction. Yield 124 mg (72%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5c]

^{1}**H NMR** (CDCl$_3$, 600 MHz) δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 2.3 Hz, 1H), 7.04 (dd, *J* = 2.3, 8.7 Hz, 1H), 5.22 (s, 2H), 3.01 (s, 6H).

^{13}**C NMR** (CDCl$_3$, 150 MHz) δ 172.1, 151.2, 133.9, 126.6, 122.3, 118.9, 106.9, 69.5, 40.6.

6-Fluoroisobenzofuran-1(3H)-one **2d**:



The synthesis of **2d** from **1d** (238 mg, 1 mmol) followed the synthesis of **2a**. Yield 117 mg (77%) white solid. M.p: 109-111 °C.

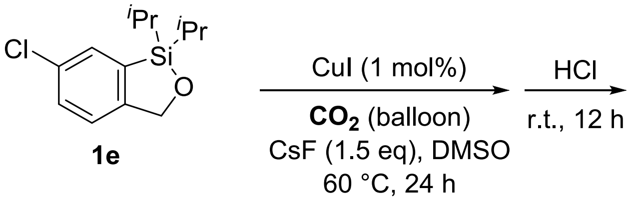
^{1}**H NMR** (CDCl$_3$, 400MHz) δ 7.56 (dd, *J* = 2.3, 7.3 Hz, 1H), 7.49 (dd, *J* = 4.4, 8.5 Hz, 1H), 7.43-7.38 (m, 1H), 5.31 (s, 2H).

^{13}**C NMR** (CDCl$_3$, 101MHz) δ 169.9 (d, *J* = 4.8 Hz), 163.0 (d, *J* = 246 Hz), 141.9 (d, *J* = 2.0 Hz), 127.7 (d, *J* = 8.6 Hz), 123.8 (d, *J* = 8.6 Hz), 122.0 (d, *J* = 24 Hz), 112.0 (d, *J* = 23 Hz), 69.4.

DART-MS m/z cald for $C_8H_6O_2F$ [M+H]$^+$: 153.03518, found: 153.03564

IR (KBr, cm^{-1}) ν: 2355, 1763, 1626, 1493, 1463, 1363, 1311, 1269, 1244, 1195, 1112, 1045.

6-Chloroisobenzofuran-1(3H)-one **2e**:

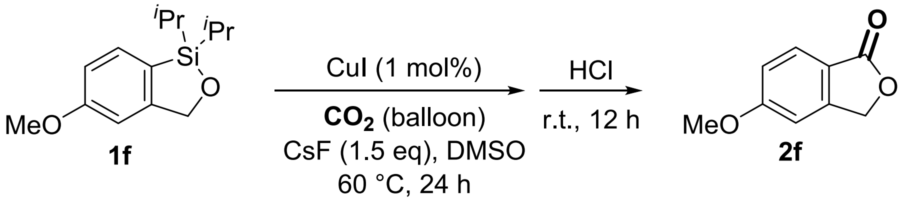


The synthesis of **2e** from **1e** (255 mg, 1 mmol) followed the synthesis of **2a**. Yield 135 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5b]

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.86 (s, 1H), 7.65 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 5.31 (s, 2H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 169.6, 144.6, 135.3, 134.3, 127.5, 125.6, 123.4, 69.4.

<u>5-Methoxyisobenzofuran-1(3H)-one **2f**:</u>

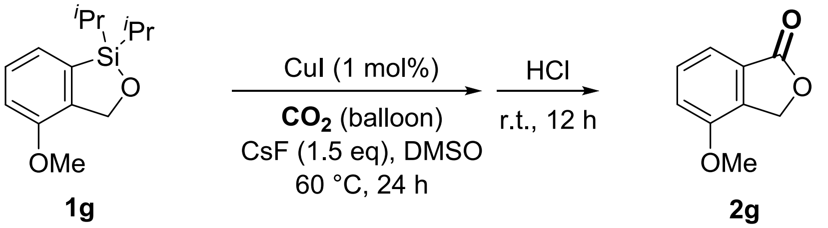


The synthesis of **2f** from **1f** (250 mg, 1 mmol) followed the synthesis of **2a**. Yield 110 mg (68%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5b]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 5.25 (s, 2H), 3.90 (s, 3H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 164.7, 149.3, 127.2, 118.0, 116.5, 106.0, 69.1, 55.8.

<u>4-Methoxyisobenzofuran-1(3H)-one **2g**:</u>

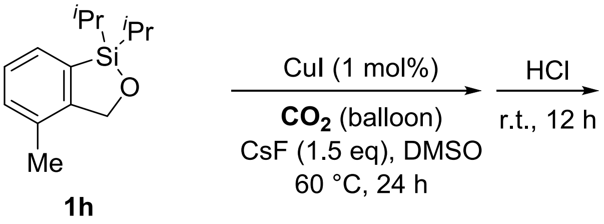


The synthesis of **2g** from **1g** (250 mg, 1 mmol) followed the synthesis of **2a**. Yield 124 mg (76%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5d]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.48-7.47 (m, 2H), 7.11-7.09 (m, 1H), 5.24 (s, 2H), 3.91 (s, 3H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.1, 154.2, 134.9, 130.7, 127.3, 117.1, 114.7, 68.0, 55.5.

4-Methylisobenzofuran-1(3H)-one **2h**:

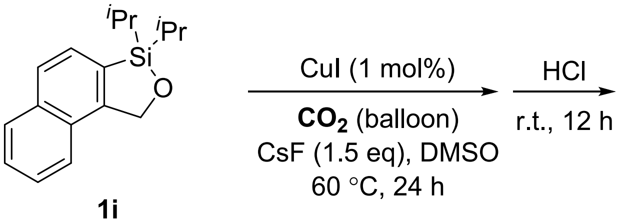


The synthesis of **2h** from **1h** (234 mg, 1 mmol) followed the synthesis of **2a**. Yield 114 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5e]

^{1}H NMR ($CDCl_3$ 400MHz) δ 7.73 (d, *J* = 6.9 Hz, 1H), 7.45-7.41 (m, 2H), 5.24 (s, 2H), 2.36 (s, 3H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 171.4, 145.4, 134.6, 132.3, 129.2, 125.3, 123.0, 69.0, 17.3.

Naphtho[1,2-c]furan-3(1H)-one **2i**:



The synthesis of **2i** from **1i** (270 mg, 1 mmol) followed the synthesis of **2a**, but use CuI (20 mg, 0.1 mmol). Yield 117 mg (64%) white solid. M.p 122-125 °C

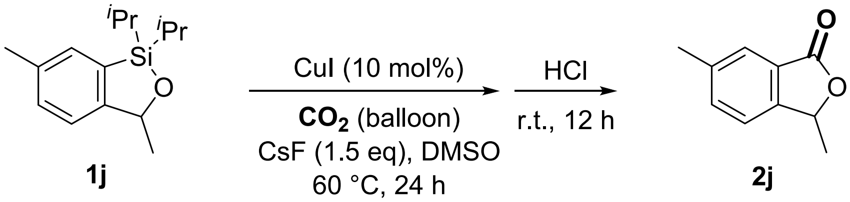
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.72 - 7.64 (m, 2H), 5.60 (s, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.6, 146.9, 135.8, 130.0, 129.2, 129.1, 127.8, 126.7, 123.4, 123.0, 120.4, 69.0.

DART-MS m/z cald for $C_{12}H_9O_2$ $[M+H]^+$: 185.06025, found: 185.06043

IR (KBr, cm^{-1}) ν: 3050, 1752, 1633, 1593, 1521, 1456, 1395, 1338, 1252, 1083, 1019.

3,6-Dimethylisobenzofuran-1(3H)-one **2j**:



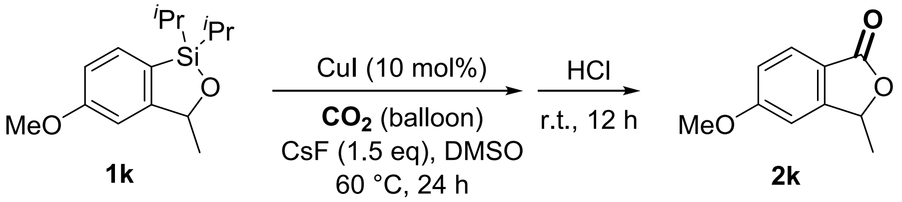
1j **2j**

The synthesis of **2j** from **1j** (248 mg, 1 mmol) followed the synthesis of **2a**, but use CuI (20 mg, 0.1 mmol). Yield 133 mg (82%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR (CDCl$_3$, 400MHz) δ 7.69 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 5.53 (q, *J* = 6.4 Hz, 1H), 2.47 (s, 3H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (CDCl$_3$, 101MHz) δ 170.6, 148.6, 139.3, 135.1, 125.9, 125.6, 121.2, 77.6, 21.2, 20.5.

5-Methoxy-3-methylisobenzofuran-1(3H)-one **2k**:



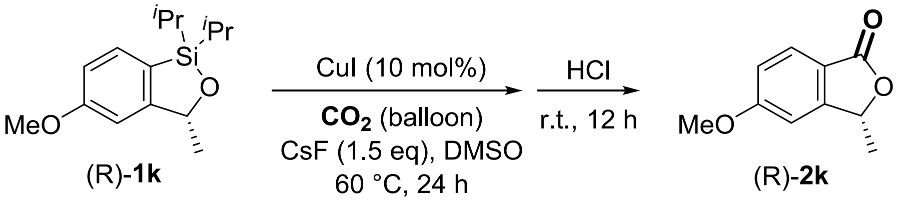
1k **2k**

The synthesis of **2k** from **1k** (278 mg, 1 mmol) followed the synthesis of **2a**, but use CuI (20 mg, 0.1 mmol). Yield 148 mg (83%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR (CDCl$_3$, 400MHz) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.02-7.00 (m, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 5.47 (q, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 1.60 (d, *J* = 6.4 Hz, 3H).

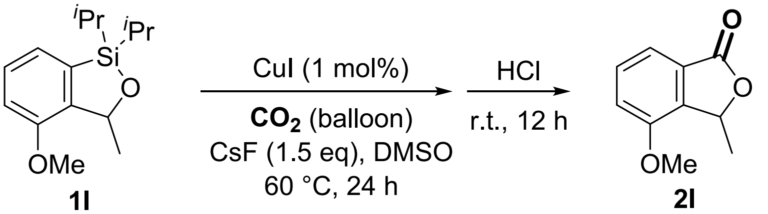
^{13}C NMR (CDCl$_3$, 101MHz) δ 170.1, 164.7, 153.9, 127.1, 118.0, 116.2, 105.6, 77.0, 55.8, 20.3.

(R)-5-Methoxy-3-methylisobenzofuran-1(3H)-one (R)-**2k**:



Yield 142 mg (80%) yellow solid, 94% ee (HPLC, OD-H, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min).

4-Methoxy-3-methylisobenzofuran-1(3H)-one **2l**:



The synthesis of **2l** from **1l** (278 mg, 1 mmol) followed the synthesis of **2a**. Yield 140 mg (79%) white solid. M.p. 115-117 °C

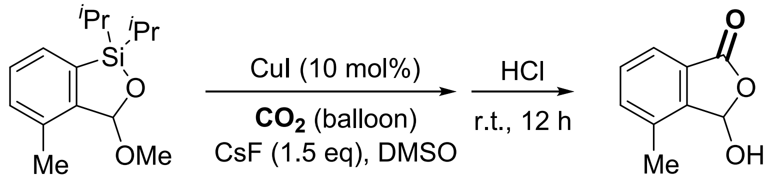
^{1}H NMR (CDCl$_3$, 400MHz) δ 7.48-7.43 (m, 2H), 7.10 (dd, *J* = 1.8, 6.9 Hz, 1H), 5.54 (q, *J* = 6.4 Hz, 1H), 3.91 (s, 3H), 1.64 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (CDCl$_3$, 101 MHz) δ 170.4, 154.2, 138.9, 130.8, 127.5, 117.0, 114.9, 77.0, 55.5, 19.0.

DART-MS m/z cald for $C_{10}H_{11}O_3$ $[M+H]^+$: 179.07082, found: 179.07108

IR (KBr, cm^{-1}) ν: 2987, 2939, 2841, 1757, 1607, 1490, 1445, 1357, 1357, 1308, 1274, 1187, 1118, 1047.

3-Hydroxy-4-methylisobenzofuran-1(3H)-one **2m**:



1m **2m**

The synthesis of **2m** from **1m** (264 mg, 1 mmol)[1b] followed the synthesis of **2a**, with slight modification. The acidification step was conducted at 0 °C using HCl 2N (6 mL). PTLC was run using EtOAc:*n*-Hexane (1:1) as eluent. Yield 110 mg (68%) white solid. M.p. 123-126 °C

^{1}H NMR (CD_3OD, 600MHz) δ 7.64-7.62 (m, 1H), 7.47-7.44 (m, 2H), 6.59 (s, 1H), 4.36 (s, 1H), 2.44 (s, 3H).

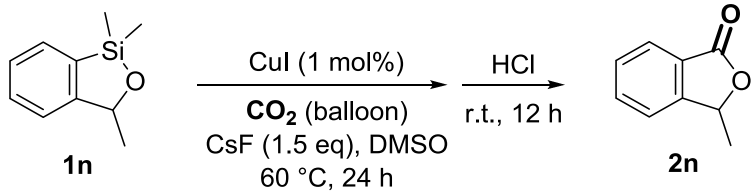
^{13}C NMR (CD_3OD, 151MHz) δ 171.5, 146.9, 137.0, 136.3, 131.9, 128.1, 123.3, 99.7, 17.3.

DART-MS m/z cald for $C_9H_9O_3$ $[M+H]^+$: 165.05517, found: 165.05589

IR (KBr, cm^{-1}) ν: 3358, 2959, 1747, 1602, 1485, 1433, 1357, 1310, 1261, 1206, 1103, 1063, 1032.

*Carboxylation of substrate **1n-w***

3-Methylisobenzofuran-1(3H)-one **2n**:



1n **2n**

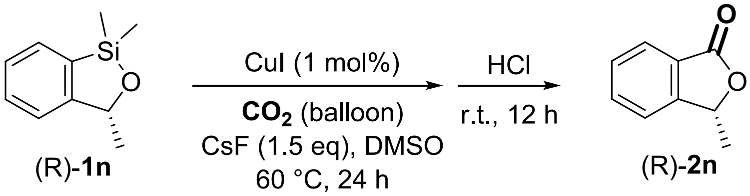
In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with CuI (2 mg, 0.01 mmol) and CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (4 mL) and **1n** (178 mg, 1 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H_2O

(20 mL), NaOH 1N (4 mL), stirred for 1 h and washed with Et_2O (3 x 10 mL). The aqueous phase was acidified using HCl 1N (12 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford pure **2n**. Yield: 112 mg (76%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, *J* = 7.3 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 5.58 (q, *J* = 6.6 Hz, 1H), 1.65 (d, *J* = 6.9 Hz, 3H).

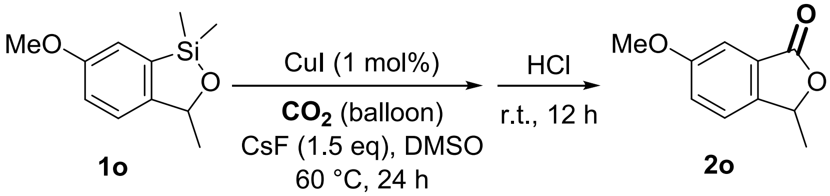
^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 151.2, 134.0, 129.0, 125.8, 125.7, 121.5, 77.7, 20.4.

(R)-3-Methylisobenzofuran-1(3H)-one (R)-**2n**:



Yield 113 mg (76%) yellow solid, 94% ee (HPLC, OJ, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min).

6-Methoxy-3-methylisobenzofuran-1(3H)-one **2o**:

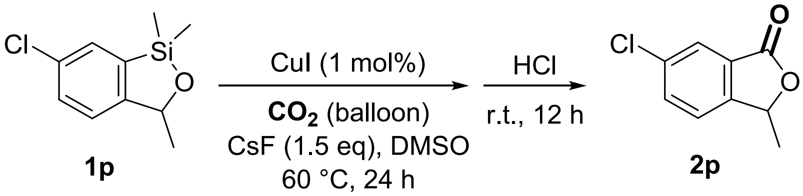


The synthesis of **2o** from **1o** (208 mg, 1 mmol) followed the synthesis of **2n**. Yield 134 mg (75%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5h]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.31 (m, 2H), 7.24-7.22 (m, 1H), 5.52 (q, *J* = 6.6 Hz, 1H), 3.86 (s, 3H), 1.60 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6, 160.6, 143.7, 127.1, 122.9, 122.4, 107.4, 77.6, 55.7, 20.5.

6-Chloro-3-methylisobenzofuran-1(3H)-one **2p**:

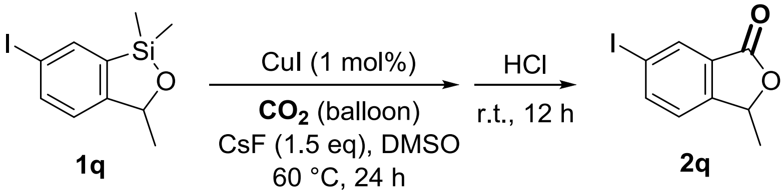


The synthesis of **2p** from **1b** (212 mg, 1 mmol) followed the synthesis of **2n**. Yield 152 mg (84%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 1.8, 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 5.56 (q, *J* = 6.9 Hz, 1H), 1.64 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 149.3, 135.4, 134.3, 127.6, 125.6, 122.9, 77.6, 20.3.

6-Iodo-3-methylisobenzofuran-1(3H)-one **2q**:



The synthesis of **2q** from **1q** (304 mg, 1 mmol) followed the synthesis of **2a**. Yield 195 mg (72%) white solid. M.p. 142-145 °C

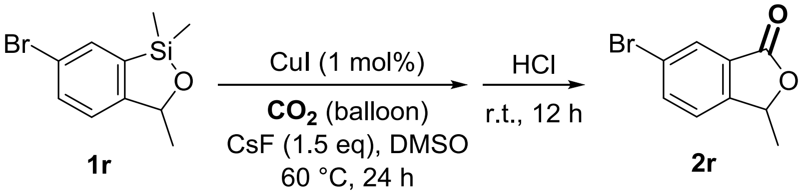
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (br. s., 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.52 (q, *J* = 6.9 Hz, 1H), 1.62 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 150.4, 142.7, 134.6, 128.0, 123.3, 93.9, 77.7, 20.2.

DART-MS m/z cald for $C_9H_8IO_2$ $[M+H]^+$: 274.95690, found: 274.95773

IR (KBr, cm^{-1}) ν: 2362, 1756, 1196.

6-Bromo-3-methylisobenzofuran-1(3H)-one **2r**:

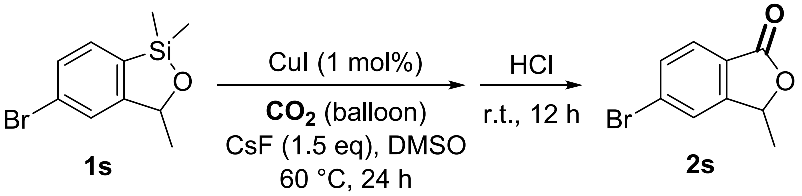


The synthesis of **2r** from **1r** (257 mg, 1 mmol) followed the synthesis of **2n**, but further purification by pTLC (EtOAc:*n*-Hexane = 4:6) was required for isolation of pure **2r**. Yield 170 mg (75%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5g]

^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.01 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 5.54 (q, *J* = 6.9 Hz, 1H), 1.63 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz) δ 168.8, 149.7, 137.1, 128.6, 127.8, 123.2, 123.0, 77.6, 20.2.

5-Bromo-3-methylisobenzofuran-1(3H)-one **2s**:



The synthesis of **2s** from **1s** (257 mg, 1 mmol) followed the synthesis of **2a**. Yield 160 mg (70%) white solid. M.p. 109 °C

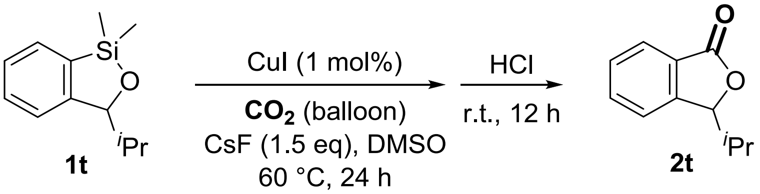
^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.76-7.74 (m, 1H), 7.67-7.65 (m, 1H), 7.61 (s, 1H), 5.54 (q, *J* = 6.9 Hz, 1H), 1.64 (d, *J* = 6.9 Hz, 4H).

^{13}C NMR (CDCl$_3$, 100 MHz) δ 169.4, 152.8, 132.7, 129.2, 127.0, 125.1, 124.7, 77.1, 20.2.

DART-MS m/z cald for $C_9H_8BrO_2$ $[M+H]^+$: 226.97077, found: 226.97038

IR (KBr, cm^{-1}) ν: 2361, 1750, 1335, 1051.

3-Isopropylisobenzofuran-1(3H)-one **2t**:

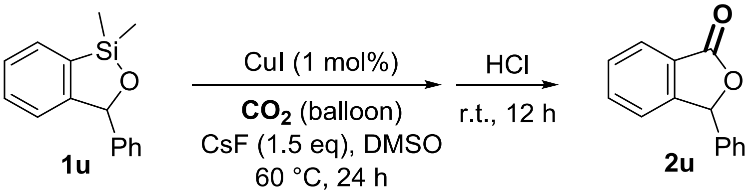


The synthesis of **2p** from **1p** (204 mg, 1 mmol) followed the synthesis of **2n**. Yield 130 mg (74%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 7.3 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 5.38 (d, J = 3.7 Hz, 1H), 2.33-2.25 (m, 1H), 1.13 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 6.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8, 148.8, 133.8, 129.0, 126.7, 125.6, 122.1, 85.6, 32.3, 18.7, 15.6.

3-Phenylisobenzofuran-1(3H)-one **2u**:

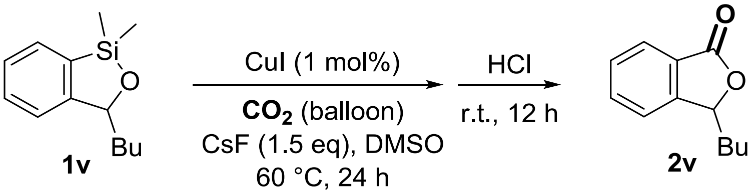


In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with CuI (2 mg, 0.01 mmol), **1u** (240 mg, 1 mmol) and DMSO (4 mL). CsF (228 mg, 1.5 mmol) was added and the tube was taken out and attached to a CO_2 balloon using a three-way stopcock. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H_2O (20 mL), NaOH 1N (4 mL), stirred for 1 h and washed with Et_2O (3 x 10 mL). The aqueous phase was acidified using HCl 1N (12 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H_2O (2 x 15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Pure **2u** was obtained after pTLC using EtOAc:n-Hexane 1:1. Yield: 147 mg (70%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.95 (d, *J*= 7.9 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.37-7.32 (m, 3H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.28-7.26 (m, 2H), 6.40 (s, 1H).

^{13}C NMR (CDCl$_3$, 125 MHz) δ 170.5, 149.6, 136.3, 134.3, 129.3, 129.2, 128.9, 126.9, 125.6, 125.5, 122.8, 82.7.

3-Butylisobenzofuran-1(3H)-one **2v**:

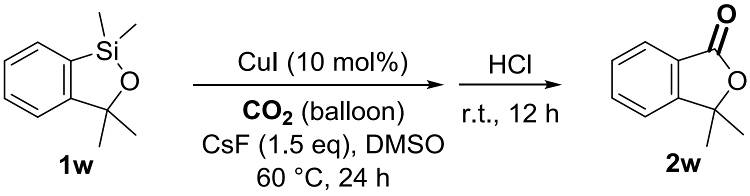


The synthesis of **2v** from **1v** (220 mg, 1 mmol)[3] followed the synthesis of **2n**. Yield 162 mg (85%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.[5f]

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 5.48 (dd, *J* = 7.7, 4.3 Hz, 1H), 2.09-2.02 (m, 1H), 1.81-1.74 (m, 1H), 1.53-1.34 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (CDCl$_3$, 125 MHz) δ 170.7, 150.1, 133.9, 129.0, 126.1, 125.7, 121.7, 81.4, 34.4, 26.9, 22.4, 13.8.

3,3-Dimethylisobenzofuran-1(3H)-one **2w**:

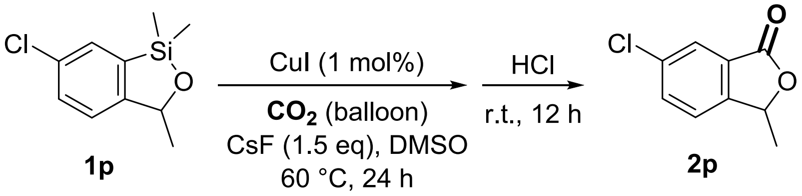


The synthesis of **2w** from **1w** (192 mg, 1 mmol) followed the synthesis of **2n**, with slight modification. CuI (20 mg, 0.1 mmol) was used and **1w** was dissolved in small amount of DMSO before being added to the reaction mixture. Yield 95 mg (59%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[5i]

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.86 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.68-7.64 (m, 1H), 7.52-7.48 (m, 1H), 7.42-7.39 (m, 1H), 1.66 (s, 6H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 169.8, 154.9, 134.1, 128.9, 125.7, 125.2, 120.6, 85.4, 27.3.

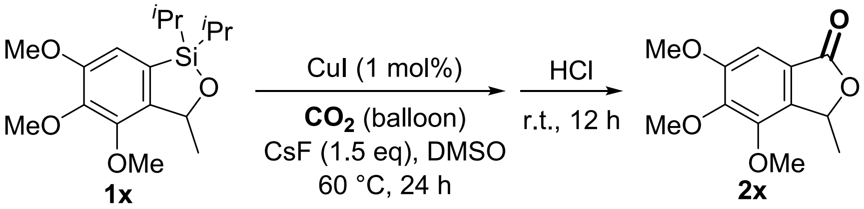
Part IV: Gram-Scale Synthesis of 2p



In an argon glove box, a flame-dried 100 mL two neck flask was charged with CuI (9 mg, 0.048 mmol) and CsF (1.09 g, 7.2 mmol). The flask was taken out and attached to a vacuum line and a CO_2 balloon using a three-way stopcock. After three evacuation-CO_2 refill cycles was conducted, DMSO (20 mL) and **1p** (1.02 g, 4.8 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H_2O (50 mL), NaOH 1N (20 mL), stirred for 1 h and washed with Et_2O (3 x 30 mL). The aqueous phase was acidified using HCl 1N (60 mL), stirred for another 12 h and extracted to EtOAc (3 x 25 mL). The combined organic phase was washed with H_2O (3 x 50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford crude **2p** (almost pure). The crude was further purified using column chromatography (EtOAc:*n*-Hexane = 3:7). Yield: 670 mg (77%) yellow oil.

Part V: Synthesis of Natural Products 4, 5 and 6

4,5,6-Trimethoxy-3-methylisobenzofuran-1(3H)-one **2w**:



The synthesis of **2w** from **1w** (324 mg, 1 mmol) followed the synthesis of **2a**, with slight modification. **1w** was dissolved in a small amount of DMSO before being added to the reaction mixture. Yield 139 mg (58%) yellow oil.

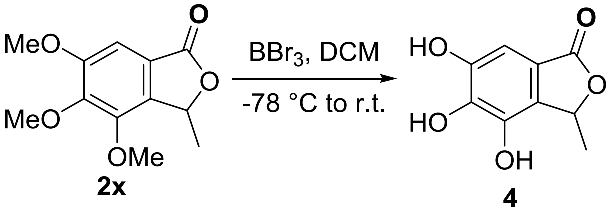
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (s, 1H), 5.49 (q, *J* = 6.2 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 1.62 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.2, 155.5, 147.5, 146.8, 136.6, 121.0, 102.5, 76.3, 61.0, 60.8, 56.3, 19.6.

DART-MS m/z cald for $C_{12}H_{15}O_5$ $[M+H]^+$: 239.09195, found: 239.09226

IR (KBr, cm^{-1}) ν: 2941, 1761, 1614, 1478, 1421, 1341, 1253, 1196, 1116, 1074, 1041.

4,5,6-Trihydroxy-3-methylisobenzofuran-1(3H)-one **4**:

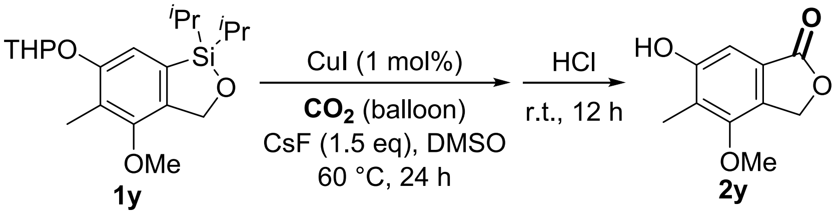


In a 20 mL 2-neck tube, attached with an argon balloon, was charged **2x** (120 mg, 0.5 mmol) and DCM (2 mL). The solution was cooled to -78 °C in a dry ice-acetone bath. Then, BBr_3 (1 M solution in DCM, 2.3 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 minutes and at room temperature for 3 h. After that, it was again cooled to -78 °C and carefully quenched with saturated $NaHCO_3$ (1 mL), diluted with brine and extracted to EtOAc (3 x 15 mL). The combined organic solution was washed once with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford compound **6** as brown solid. Yield: 97 mg (quant.). This is a known compound and the spectroscopic data is in agreement with the literature.[6]

^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.89 (s, 1H), 9.38 (br. s., 1H), 9.31 (s, 1H), 6.69 (s, 1H), 5.46 (q, *J* = 6.4 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.2, 147.4, 139.9, 139.6, 130.6, 115.1, 101.5, 75.5, 19.4.

6-Hydroxy-4-methoxy-5-methylisobenzofuran-1(3H)-one **2x**:

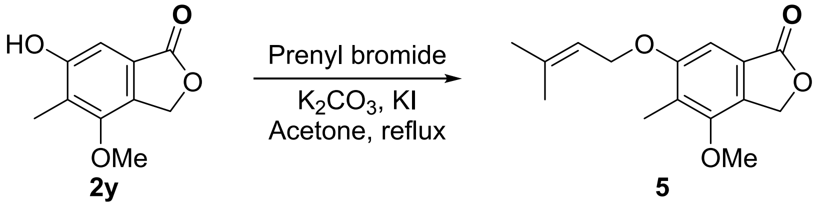


The synthesis of **2x** from **1x** (364 mg, 1 mmol) followed the synthesis of **2u**. Yield: 125 mg (65%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.[7]

^{1}H NMR (CD$_3$OD, 600 MHz) δ 6.93 (s, 1H), 5.47 (s, 2H), 3.91 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (CD$_3$OD, 150 MHz) δ 173.7, 159.3, 154.8, 127.8, 125.8, 124.9, 105.3, 70.2, 59.6, 9.8.

4-Methoxy-5-methyl-6-((3-methylbut-2-en-1-yl)oxy)isobenzofuran-1(3H)-one **4**:

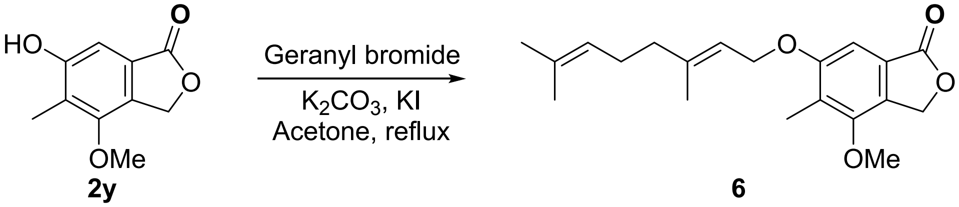


To a 10 mL 2-neck tube was added **2y** (97 mg, 0.5 mmol), K$_2$CO$_3$ (345 mg, 2.5 mmol) and KI (250 mg, 1.5 mmol). The tube was attached to an argon balloon. Acetone (1.5 mL) and prenyl bromide (223 mg, 1.5 mmol) was added *via* syringes. The reaction was refluxed for 24 h. Then, it was diluted to H$_2$O (10 mL) and extracted to EtOAc (3 x 15 mL). The combined organic solution was washed with brine, dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. Compound **5** was obtained as white solid after column chromatography. Yield: 130 mg (quant.). This is a known compound and the spectroscopic data is in agreement with the literature.[7]

^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.08 (s, 1H), 5.49 (br. s., 1H), 5.38 (s, 2H), 4.58 (d, J = 5.5 Hz, 2H), 3.89 (s, 3H), 2.21 (s, 3H), 1.80 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (CDCl$_3$, 150 MHz) δ 171.3, 159.2, 152.9, 138.2, 128.0, 125.7, 124.7, 119.2, 101.9, 68.2, 65.8, 59.3, 25.7, 18.3, 9.7.

(E)-6-((3,7-Dimethylocta-2,6-dien-1-yl)oxy)-4-methoxy-5-methylisobenzofuran-1(3H)-one **5** (Marilone C):



Following the above procedure, using geranyl bromide (325 mg, 1.5 mmol) instead of prenyl bromide, compound **5** was obtained as colorless oil after column chromatography. Yield: 130 mg (78%). This is a known compound and the spectroscopic data is in agreement with the literature.[8]

^{1}H NMR (Acetone-d$_6$, 600 MHz) δ 7.04 (s, 1H), 5.53-5.50 (m, 3H), 5.11 (t, J = 6.5 Hz, 1H), 4.71 (d, J = 6.2 Hz, 2H), 3.97 (s, 3H), 2.14-2.09 (m, 7H), 1.79 (s, 3H), 1.64 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (Acetone-d$_6$, 150 MHz) δ 171.2, 159.9, 154.0, 141.7, 132.2, 128.6, 126.0, 125.0, 124.8, 120.7, 102.2, 69.0, 66.6, 59.4, 40.2, 27.1, 25.9, 17.8, 16.8, 9.9.

Part VI: References

1. (a) Y. Hua, S. Jung, J. Roh and J. Jeon, *J. Org. Chem.*, 2015, **80**, 4661; (b) Y. Hua, P. Asgari, U. S. Dakarapu and J. Jeon, *Chem. Commun.*, 2015, **51**, 3778.

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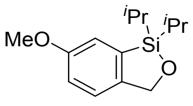
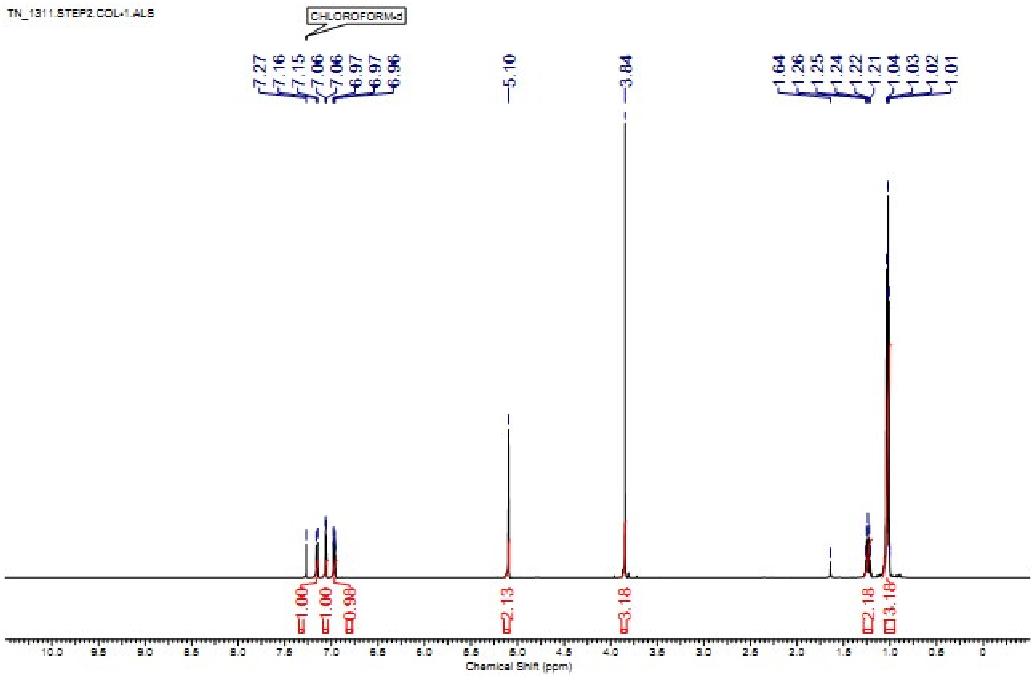
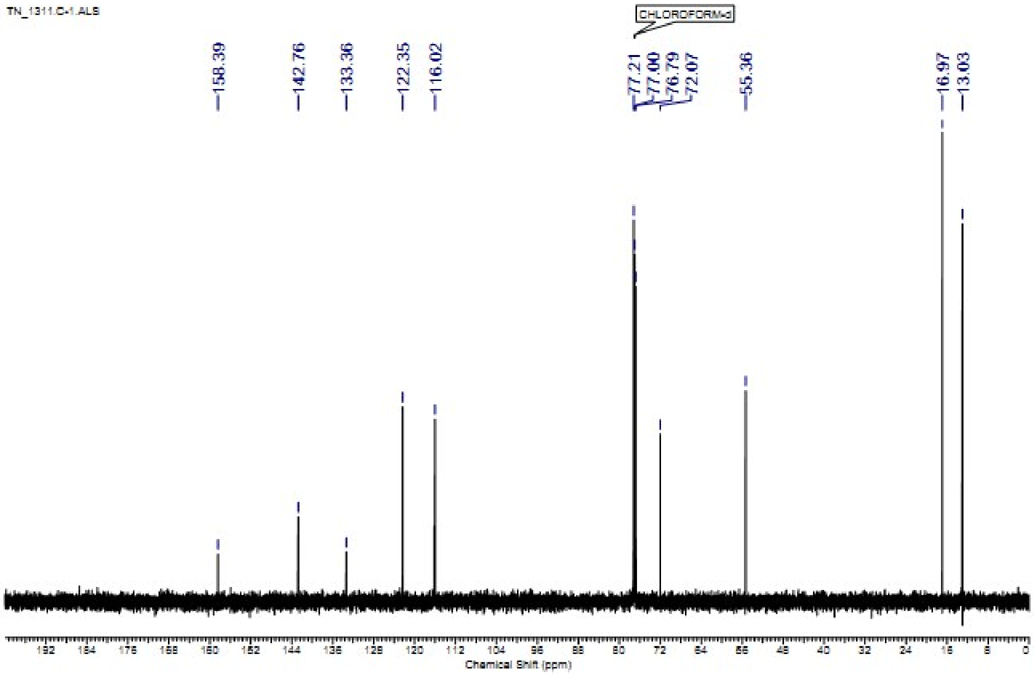
Part VII: NMR Spectra of Starting Materials and Products



1a

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13.03
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160
152
144
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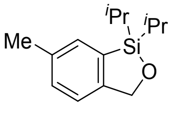
Chemical Shift (ppm)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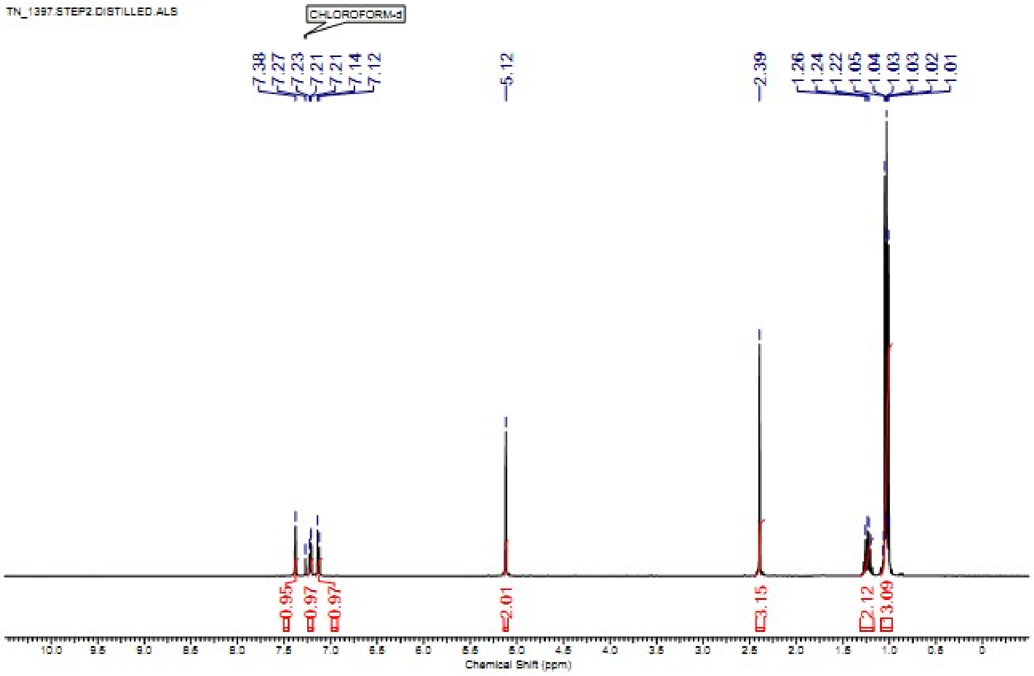
1b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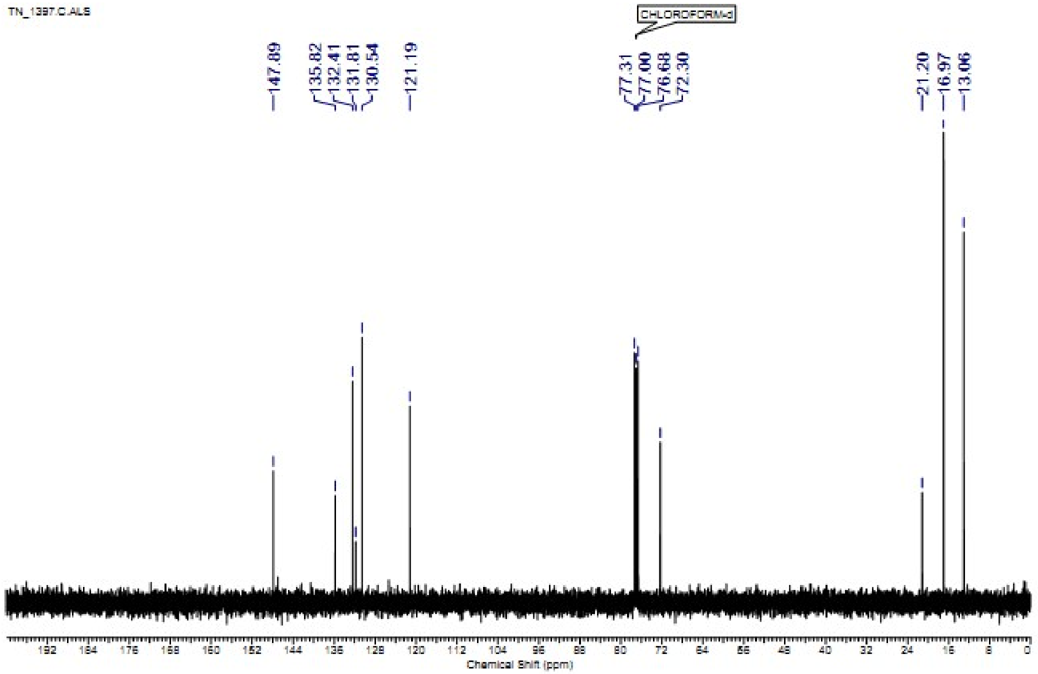
Chemical Shift (ppm)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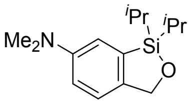
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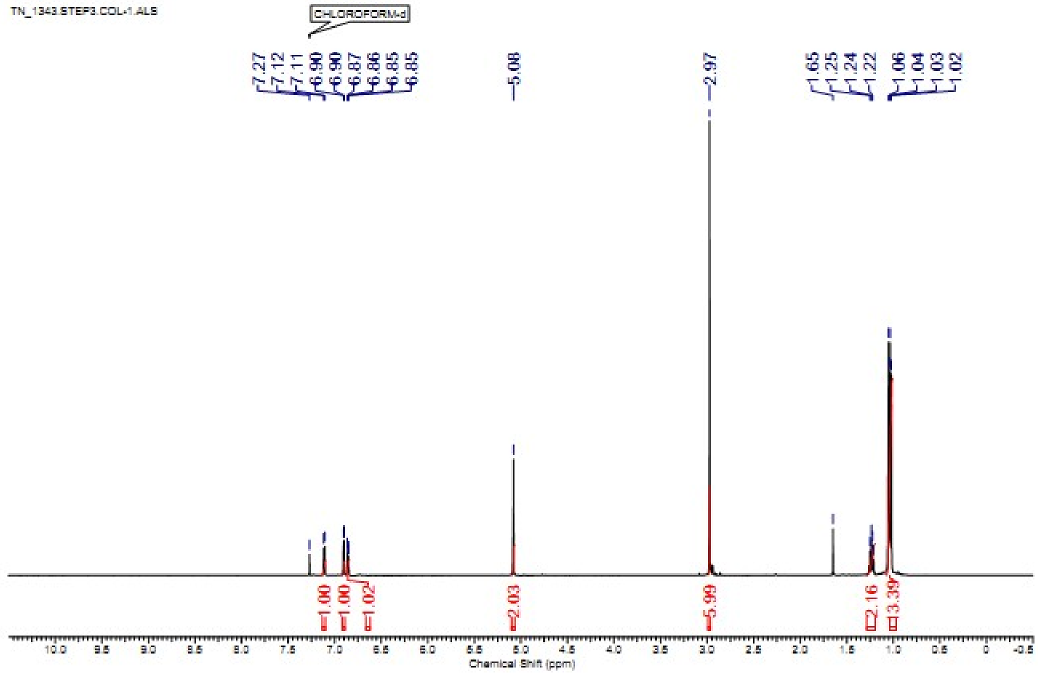
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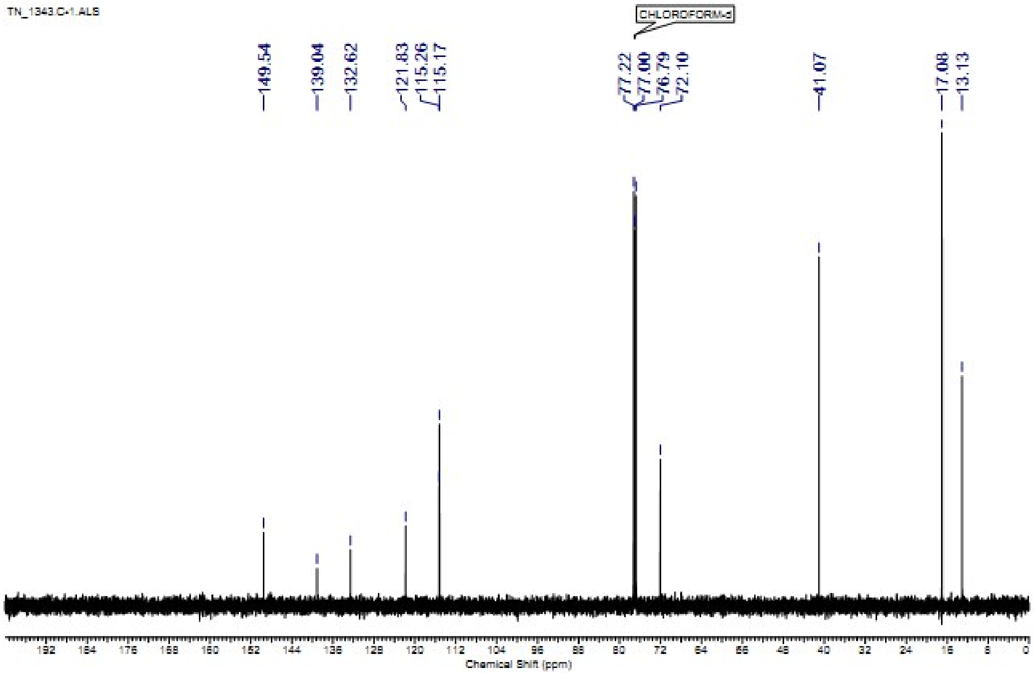
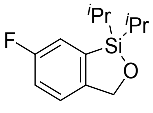
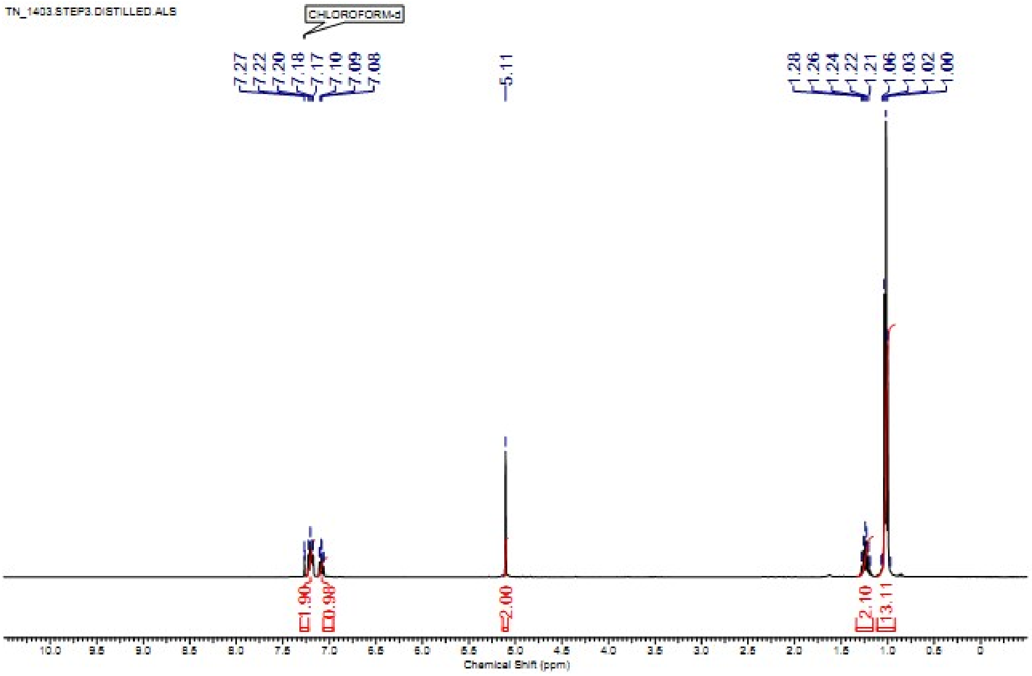
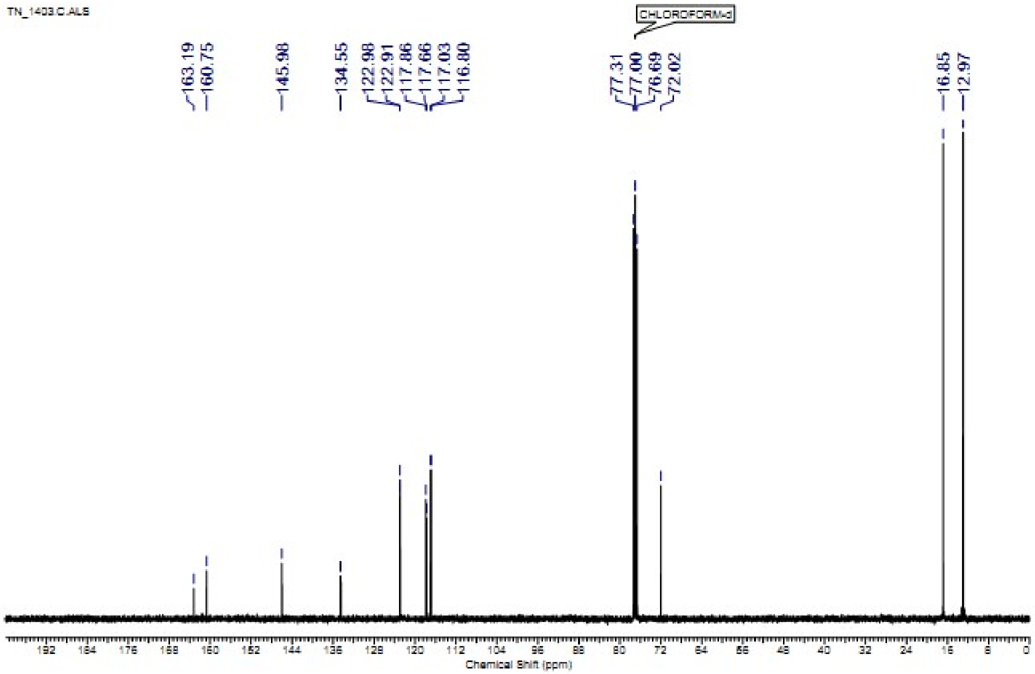
1.02
1.00
1.00
1.02
2.03
5.99
2.16
13.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

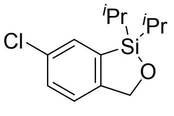

TN_1343.C-1.ALS
CHLOROFORM-d
149.54
139.04
132.62
121.83
115.26
115.17
77.22
77.00
76.79
72.10
41.07
17.08
13.13
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


F
^{i}Pr
^{i}Pr
Si
O

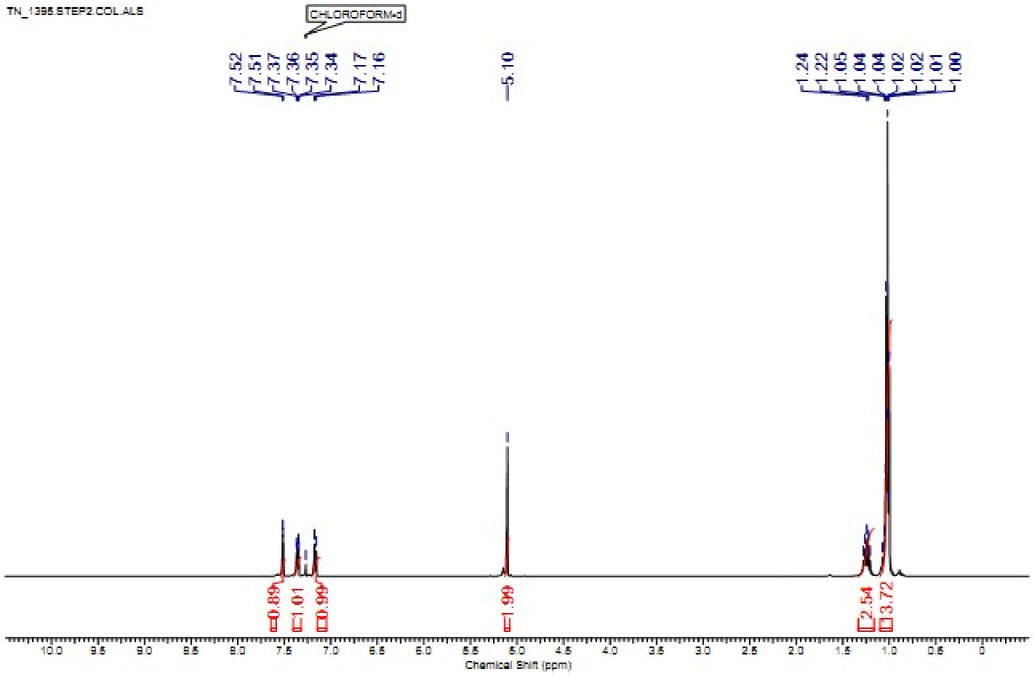
1d

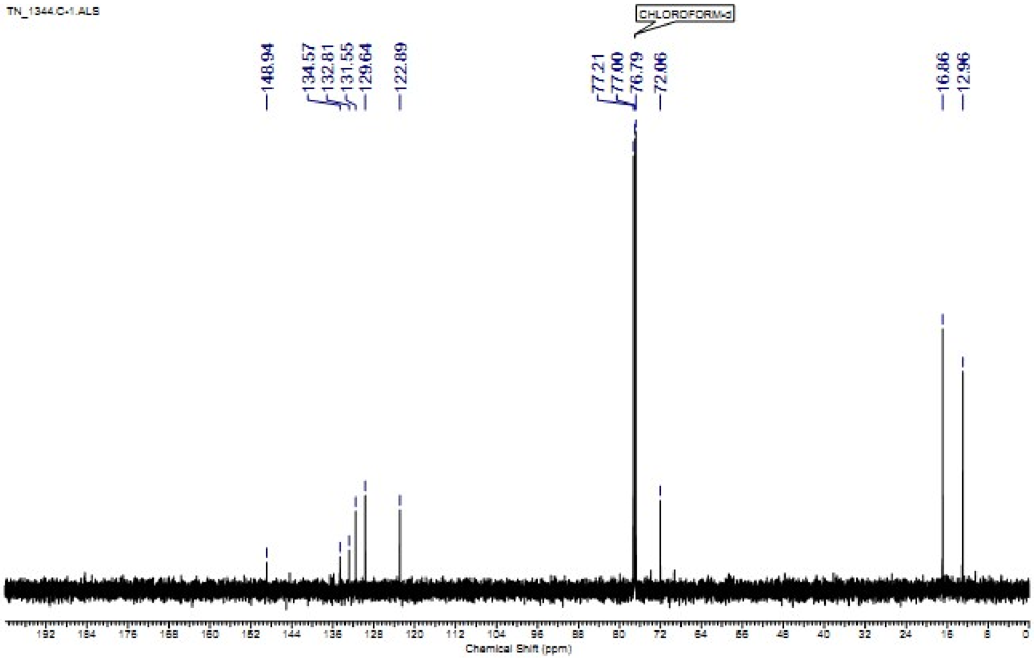

TN_1403.STEP3.DISTILLED.ALS
CHLOROFORM-d
7.27
7.22
7.20
7.18
7.17
7.10
7.09
7.08
5.11
1.28
1.26
1.24
1.22
1.21
1.06
1.03
1.02
1.00
1.90
0.98
2.00
2.10
13.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

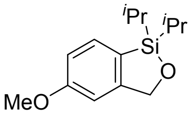

TN_1403.C.ALS
CHLOROFORM-d
163.19
160.75
145.98
134.55
122.98
122.91
117.86
117.66
117.03
116.80
77.31
77.00
76.69
72.02
16.85
12.97
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Cl
Si
O
^{i}Pr
^{i}Pr

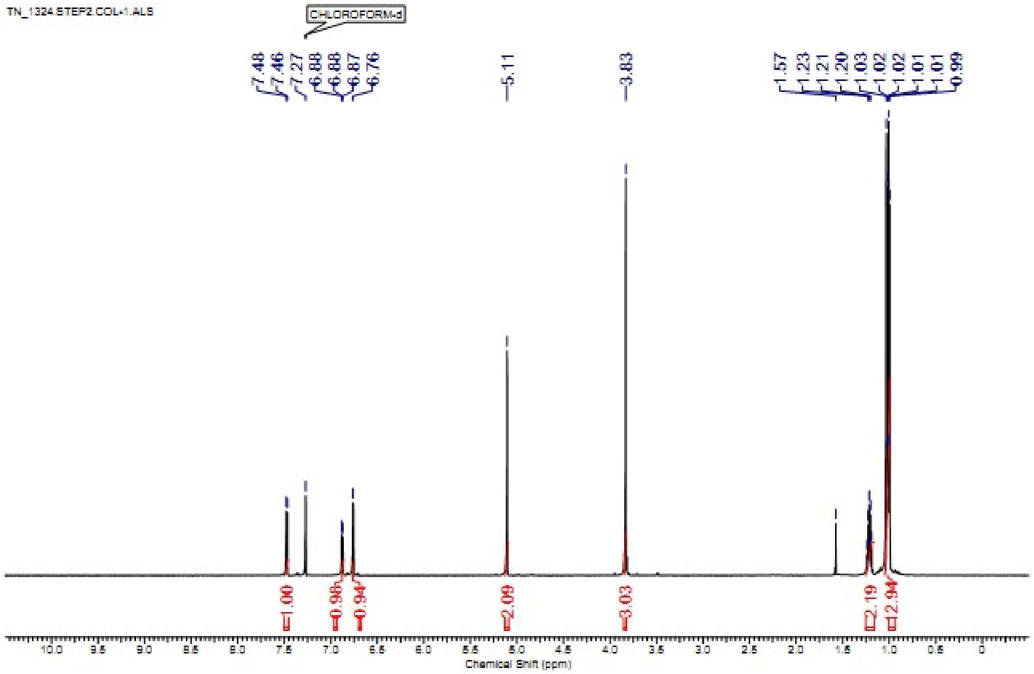
1e

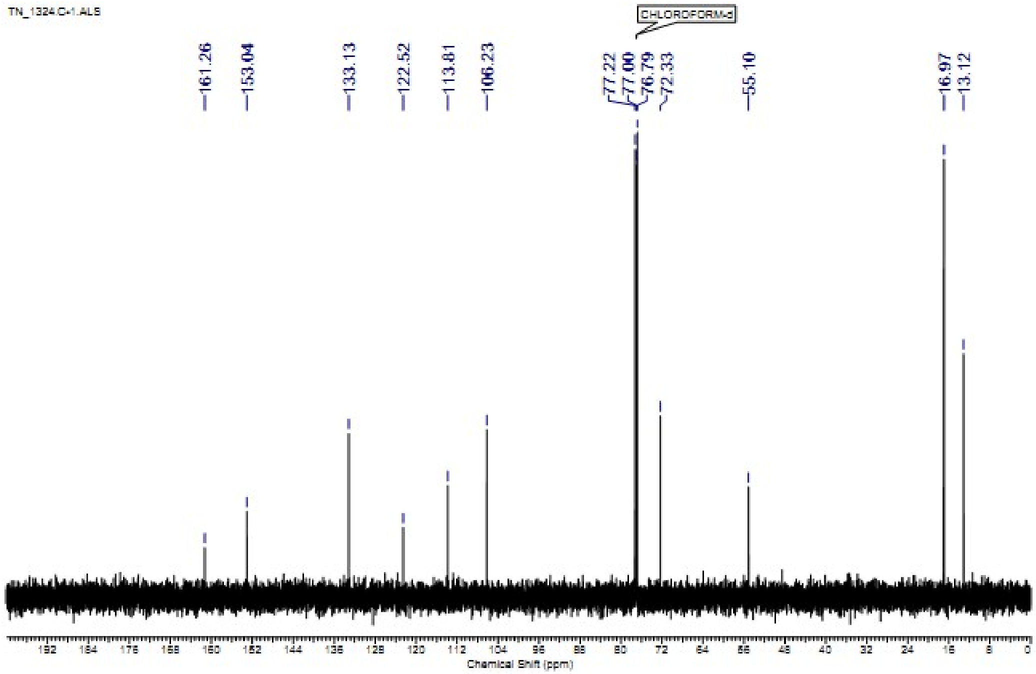

TN_1395.STEP2.COL.ALS
CHLOROFORM-d
7.52
7.51
7.37
7.36
7.35
7.34
7.17
7.16
5.10
1.24
1.22
1.05
1.04
1.04
1.02
1.02
1.01
1.00
0.89
1.01
0.99
1.99
2.54
3.72
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

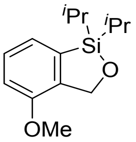

TN_1344.C-1.ALS
CHLOROFORM-d
148.94
134.57
132.81
131.55
129.64
122.89
77.21
77.00
76.79
72.06
16.86
12.96
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


iPr
iPr
Si
O
MeO

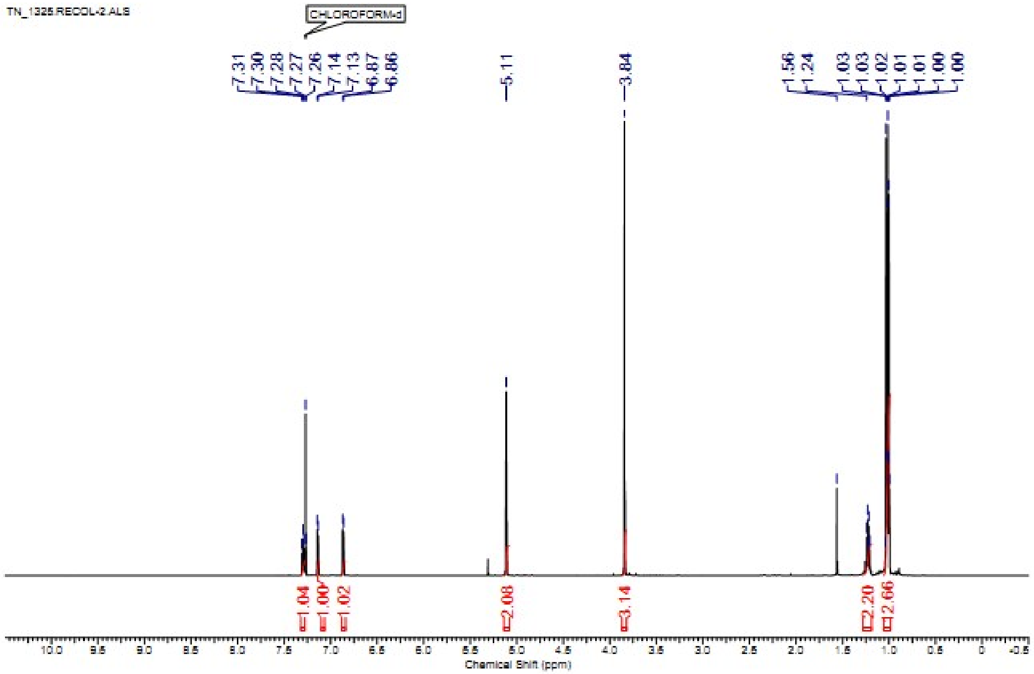
1f

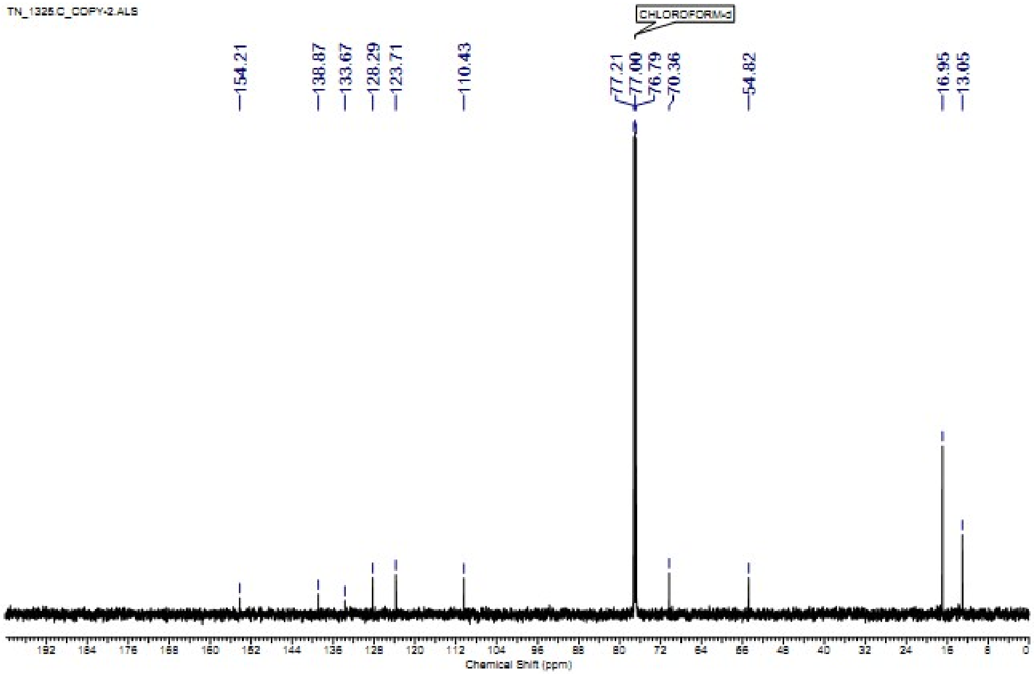

TN_1324.STEP2.COL-1.ALS
CHLOROFORM-d
7.48
7.46
7.27
6.88
6.88
6.87
6.76
5.11
3.83
1.57
1.23
1.21
1.20
1.03
1.02
1.01
0.99
1.00
0.98
0.94
2.09
3.03
2.19
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

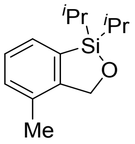

TN_1324.C-1.ALS
CHLOROFORM-d
161.26
153.04
133.13
122.52
113.81
106.23
77.22
77.00
76.79
72.33
55.10
16.97
13.12
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


iPr
iPr
Si
O
OMe

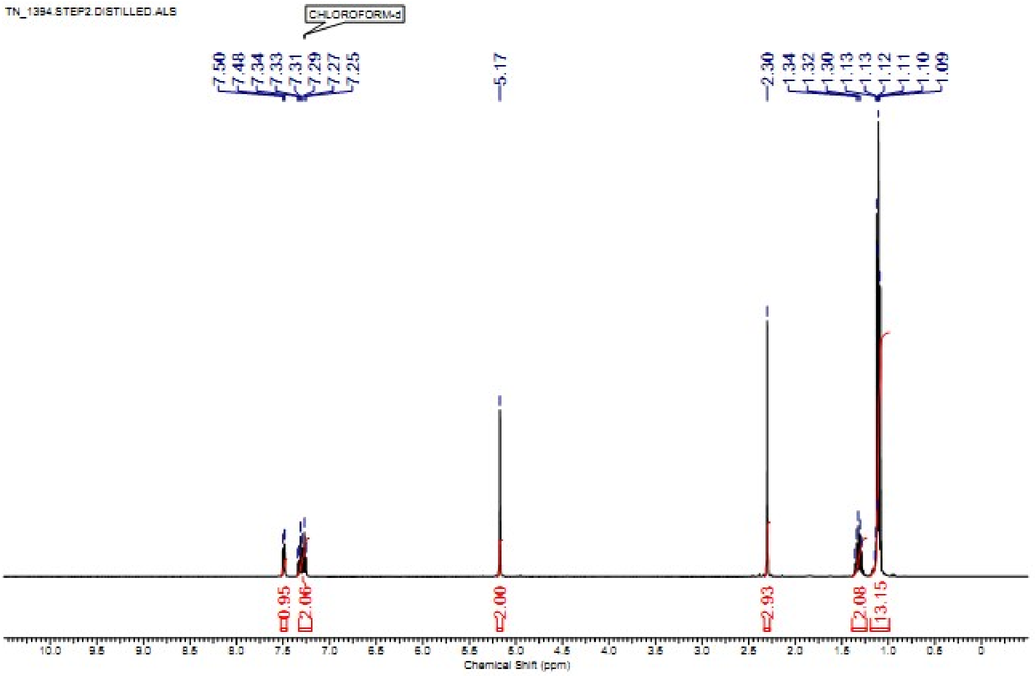
1g

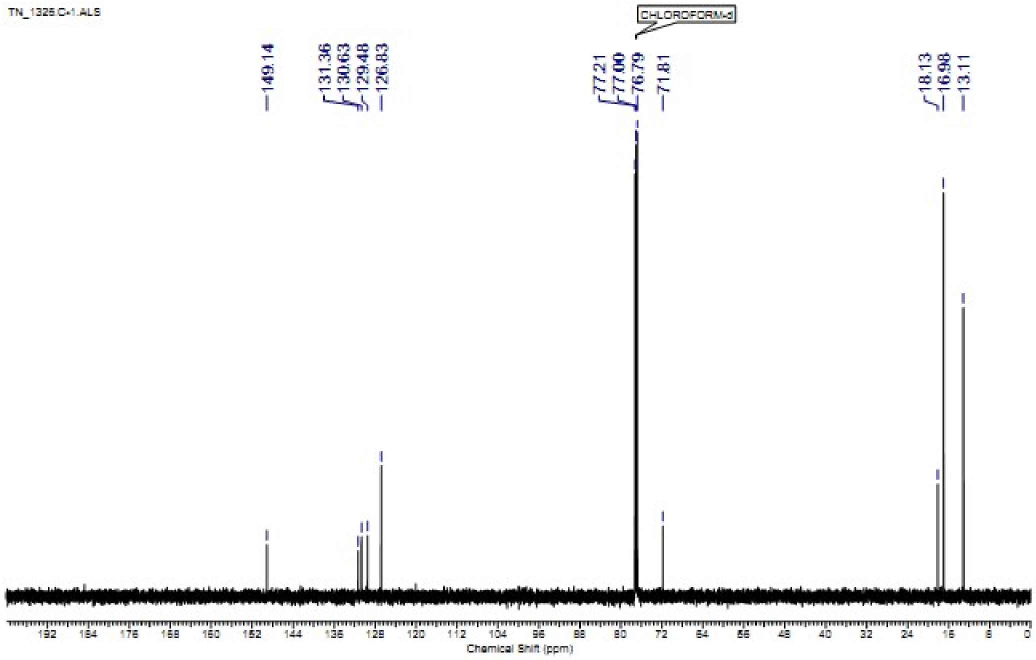

TN_1325.RECOL-2.ALS
CHLOROFORM-d
7.31
7.30
7.28
7.27
7.26
7.14
7.13
6.87
6.86
5.11
3.84
1.56
1.24
1.03
1.03
1.02
1.01
1.01
1.00
1.00
1.04
1.00
1.02
2.08
3.14
2.20
12.66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

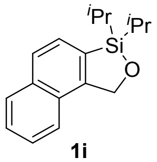

TN_1325.C_COPY-2.ALS
CHLOROFORM-d
154.21
138.87
133.67
128.29
123.71
110.43
77.21
77.00
76.79
70.36
54.82
16.95
13.05
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


^{i}Pr
^{i}Pr
Si
O
Me

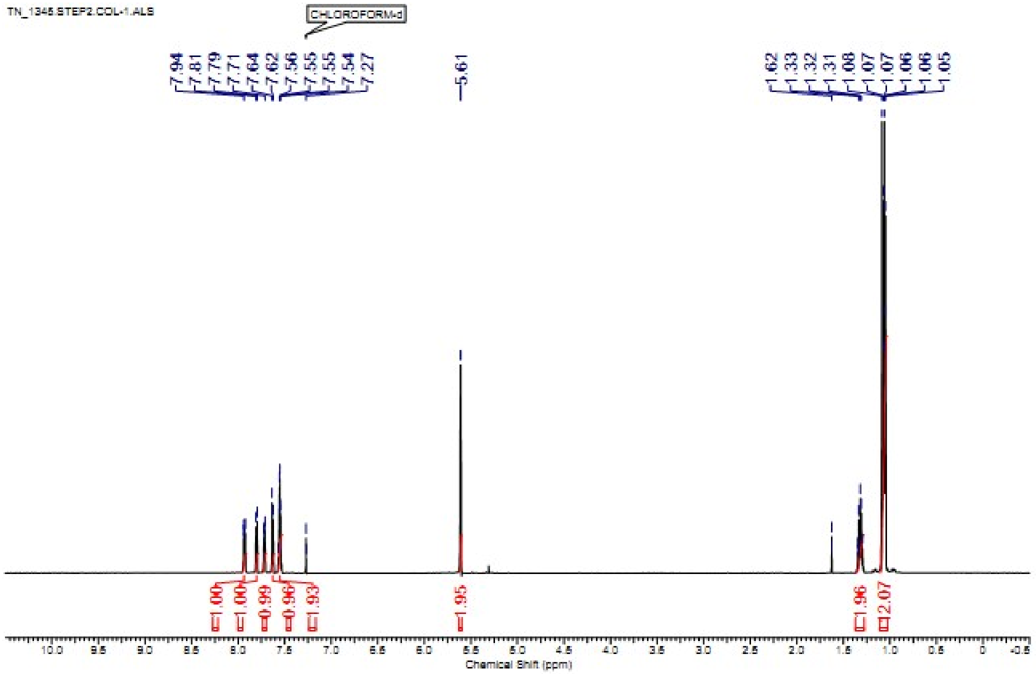
1i

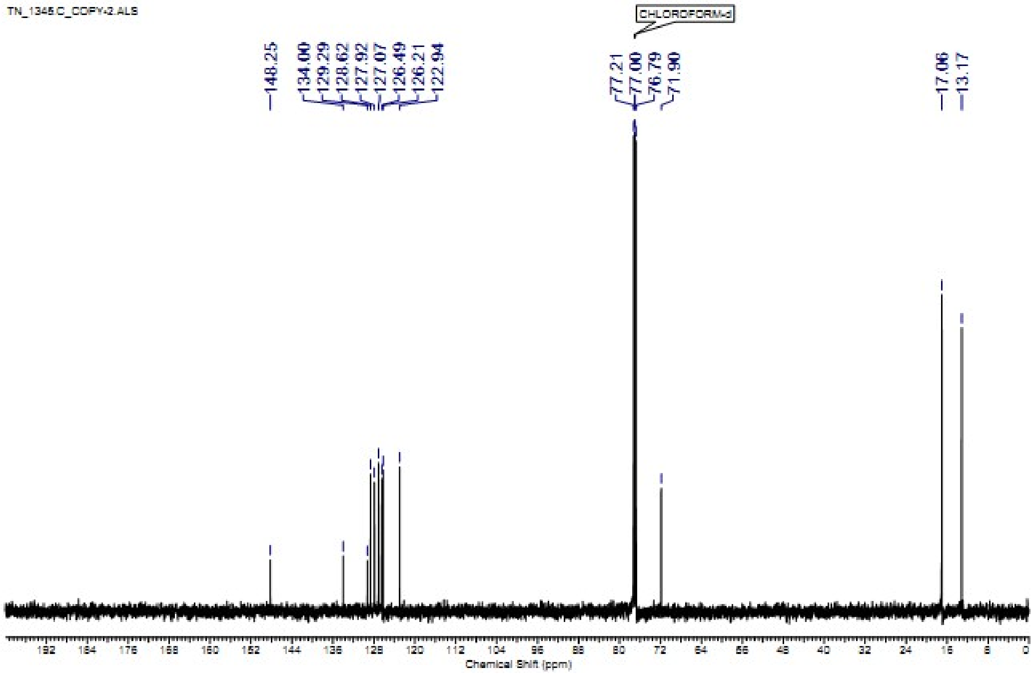

TN_1394.STEP2.DISTILLED.ALS
CHLOROFORM-d
7.50
7.48
7.34
7.33
7.31
7.29
7.27
7.25
5.17
2.30
1.34
1.32
1.30
1.13
1.13
1.12
1.11
1.10
1.09
0.95
2.06
2.00
2.93
2.08
13.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

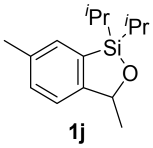

TN_1325.C-1.ALS
CHLOROFORM-d
149.14
131.36
130.63
129.48
126.83
77.21
77.00
76.79
71.81
18.13
16.98
13.11
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


iPr
iPr
Si
O

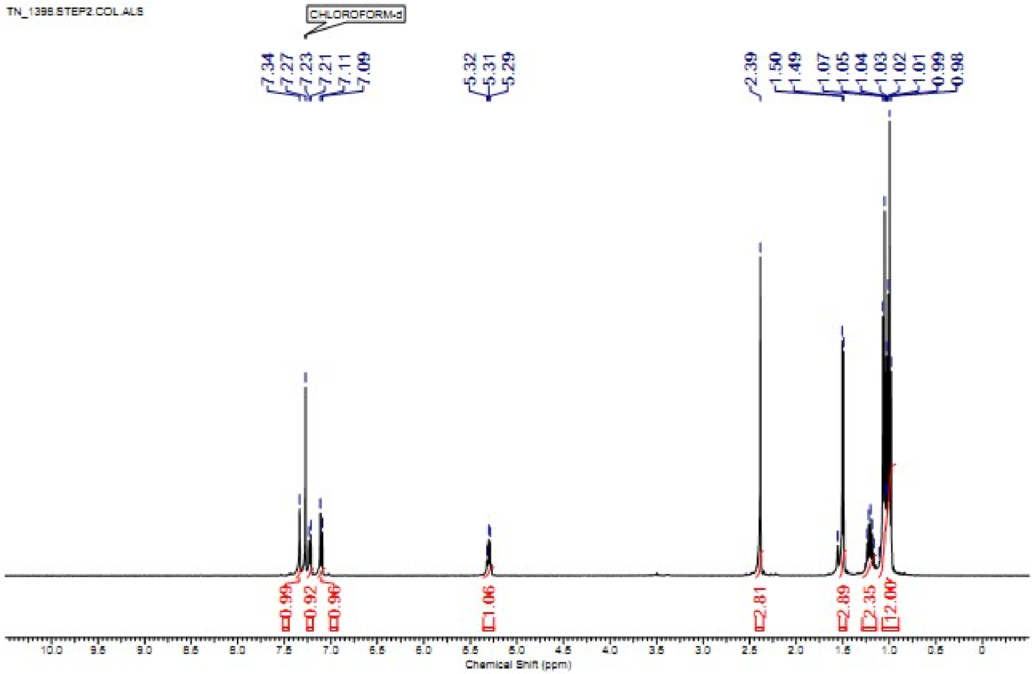
1i

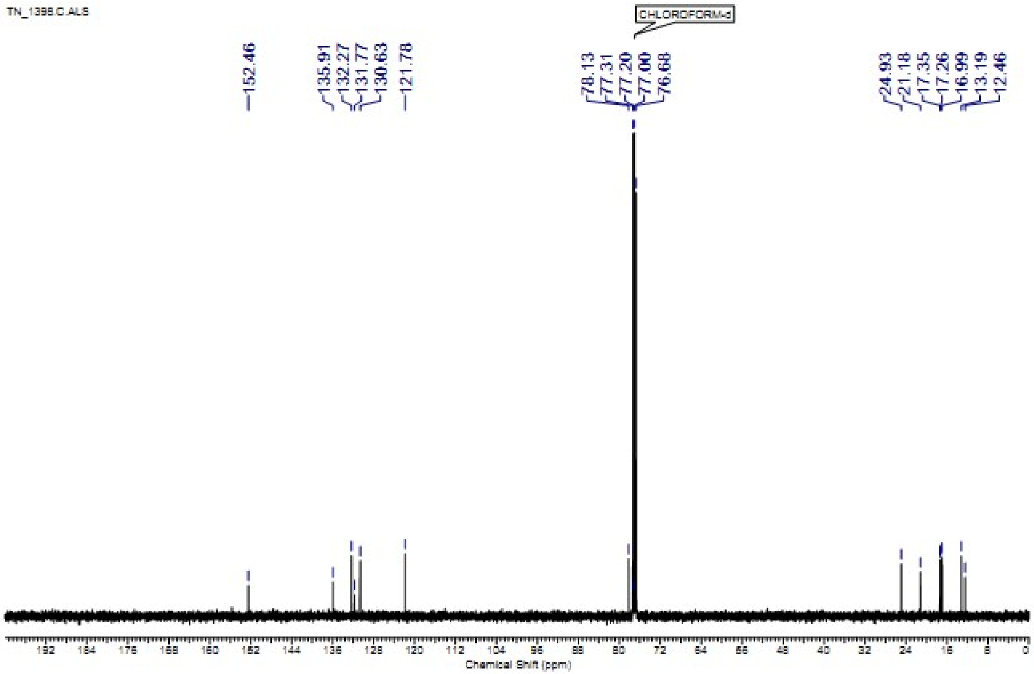

TN_1345.STEP2.COL-1.ALS
CHLOROFORM-d
7.94
7.81
7.79
7.71
7.64
7.62
7.56
7.55
7.55
7.54
7.27
5.61
1.62
1.33
1.32
1.31
1.08
1.07
1.07
1.06
1.06
1.05
1.00
1.00
0.99
0.96
1.93
1.95
1.96
12.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

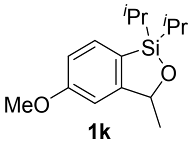

TN_1345.C_COPY-2.ALS
CHLOROFORM-d
148.25
134.00
129.29
128.62
127.92
127.07
126.49
126.21
122.94
77.21
77.00
76.79
71.90
17.06
13.17
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


iPr
iPr
Si
O

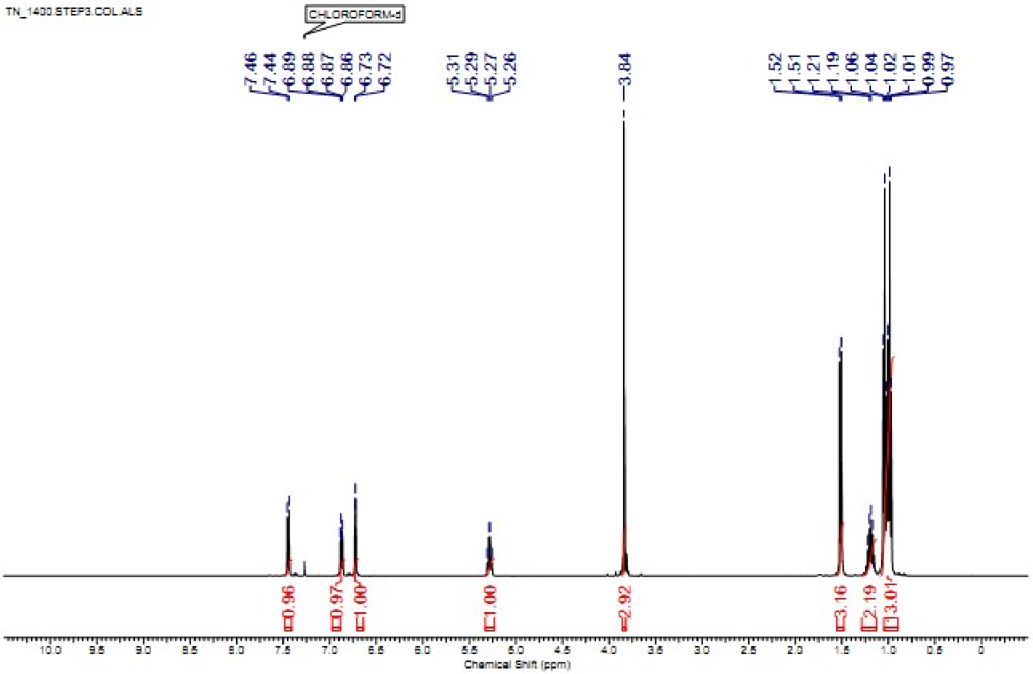
1j

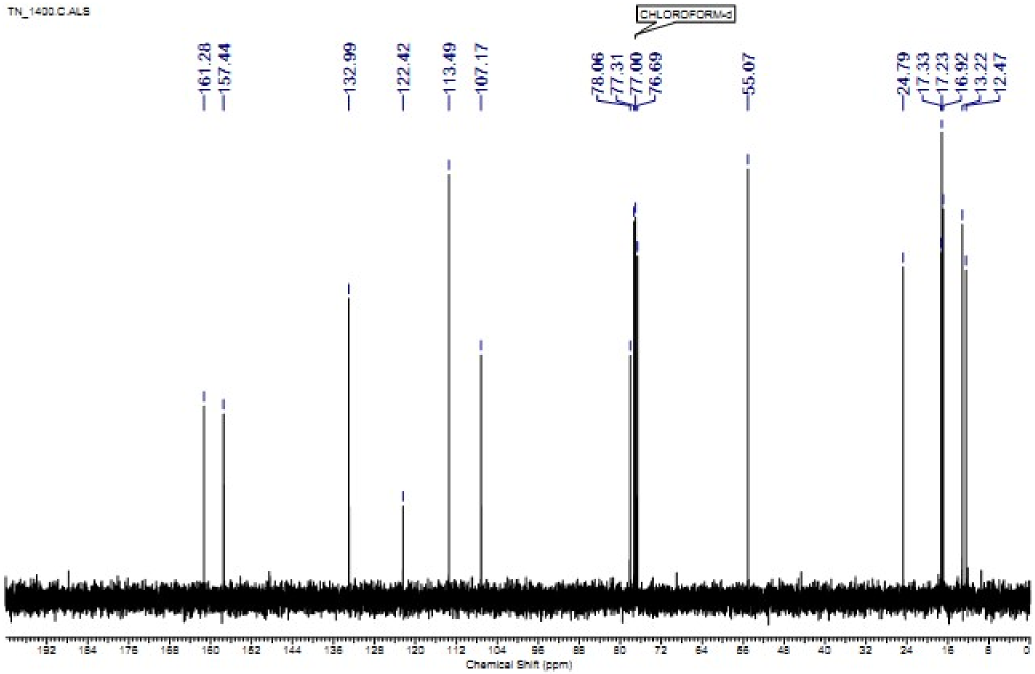

TN_1398.STEP2.COL.ALS
CHLOROFORM-d
7.34
7.27
7.23
7.21
7.11
7.09
5.32
5.31
5.29
2.39
1.50
1.49
1.07
1.05
1.04
1.03
1.02
1.01
0.99
0.98
0.99
0.92
0.96
1.06
2.81
2.89
2.35
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

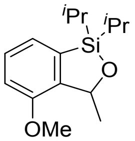

TN_1399.C.ALS
CHLOROFORM-d
152.46
135.91
132.27
131.77
130.63
121.78
78.13
77.31
77.20
77.00
76.68
24.93
21.18
17.35
17.26
16.99
13.19
12.46
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


^{i}Pr
^{i}Pr
Si
O
MeO

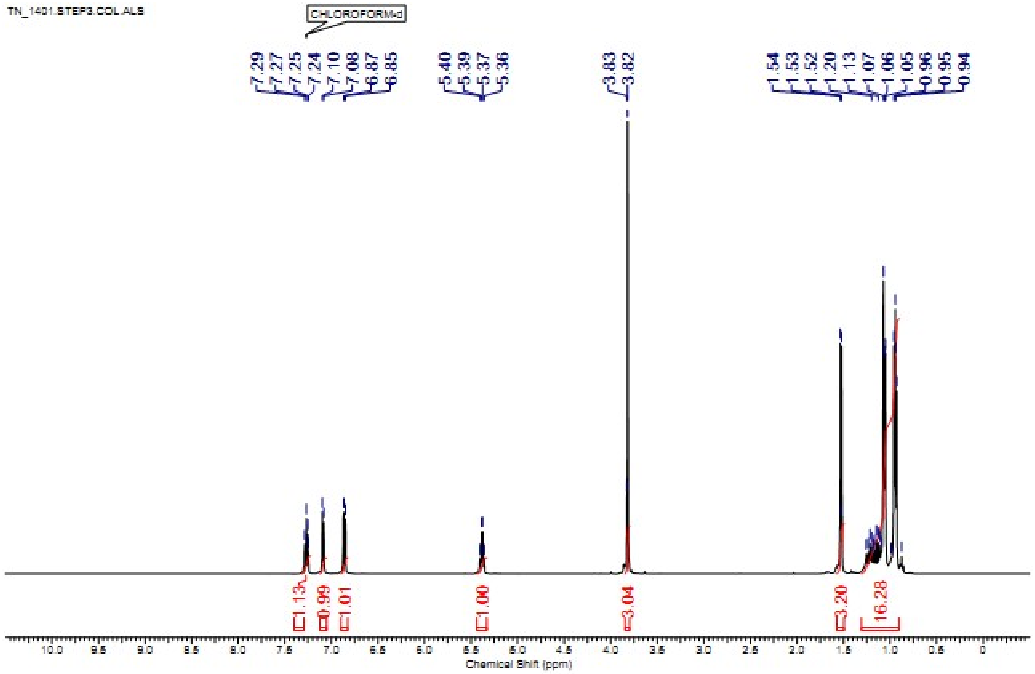
1k

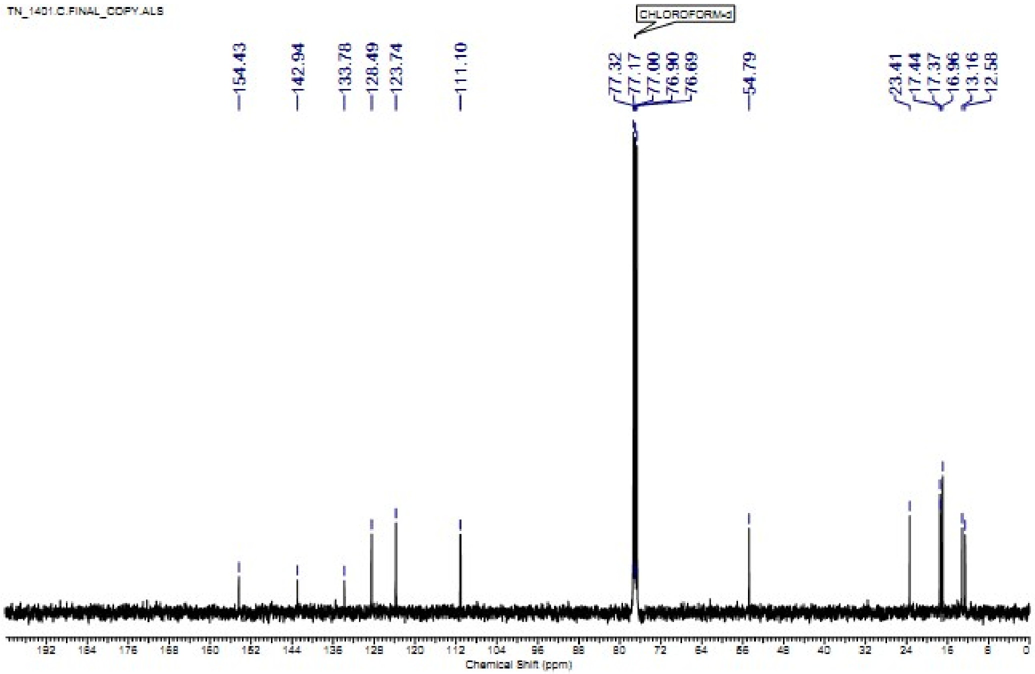

TN_1400.STEP3.COL.ALS
CHLOROFORM-d
7.46
7.44
6.89
6.88
6.87
6.86
6.73
6.72
5.31
5.29
5.27
5.26
3.84
1.52
1.51
1.21
1.19
1.06
1.04
1.02
1.01
0.99
0.97
0.96
0.97
1.00
1.00
2.92
3.16
2.19
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

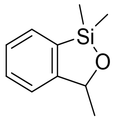

TN_1400.C.ALS
CHLOROFORM-d
161.28
157.44
132.99
122.42
113.49
107.17
78.06
77.31
77.00
76.69
55.07
24.79
17.33
17.23
16.92
13.22
12.47
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


^{i}Pr
^{i}Pr
Si
O
OMe

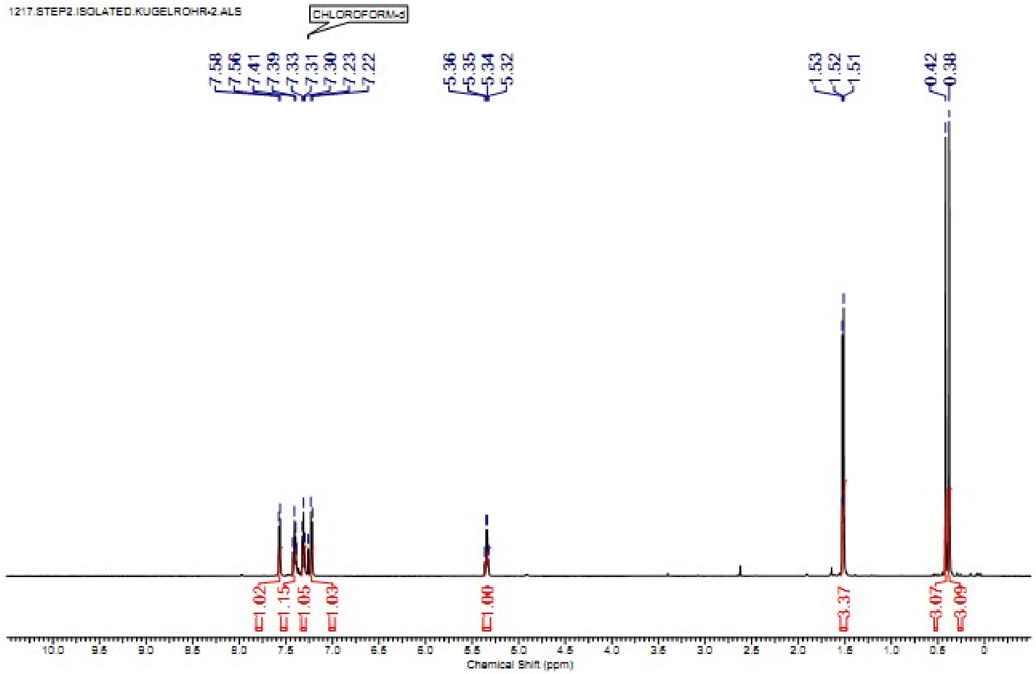
1l

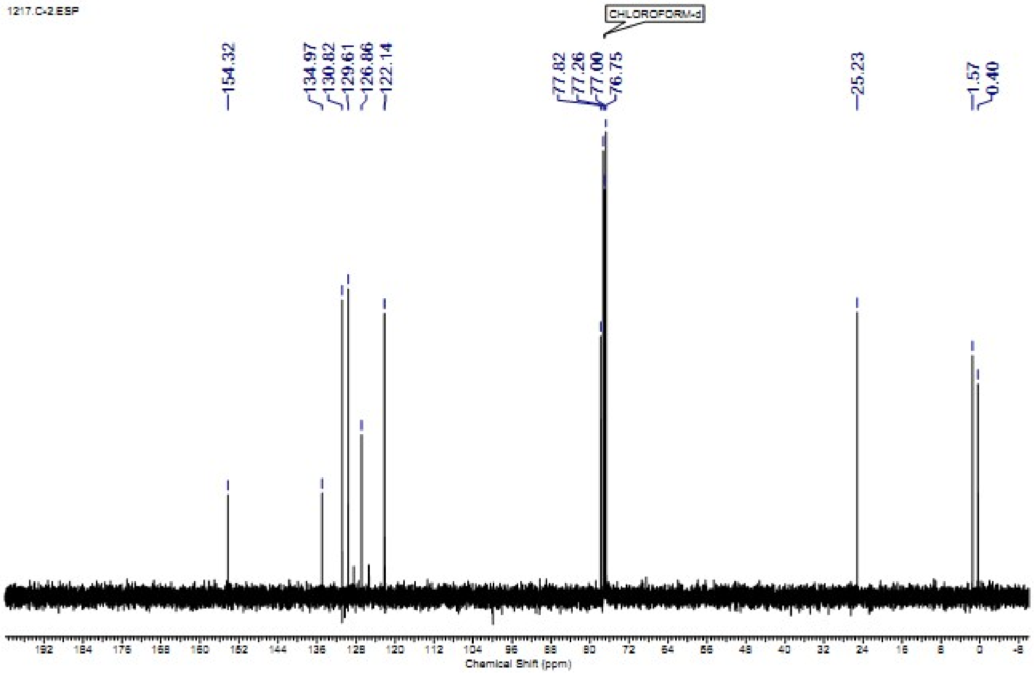

TN_1401.STEP3.COL.ALS
CHLOROFORM-d
7.29
7.27
7.25
7.24
7.10
7.08
6.87
6.85
5.40
5.39
5.37
5.36
3.83
3.82
1.54
1.53
1.52
1.20
1.13
1.07
1.06
1.05
0.96
0.95
0.94
1.13
0.99
1.01
1.00
3.04
3.20
16.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

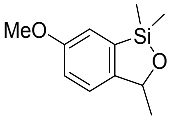

TN_1401.C.FINAL_COPY.ALS
CHLOROFORM-d
154.43
142.94
133.78
128.49
123.74
111.10
77.32
77.17
77.00
76.90
76.69
54.79
23.41
17.44
17.37
16.96
13.16
12.58
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


Si
O

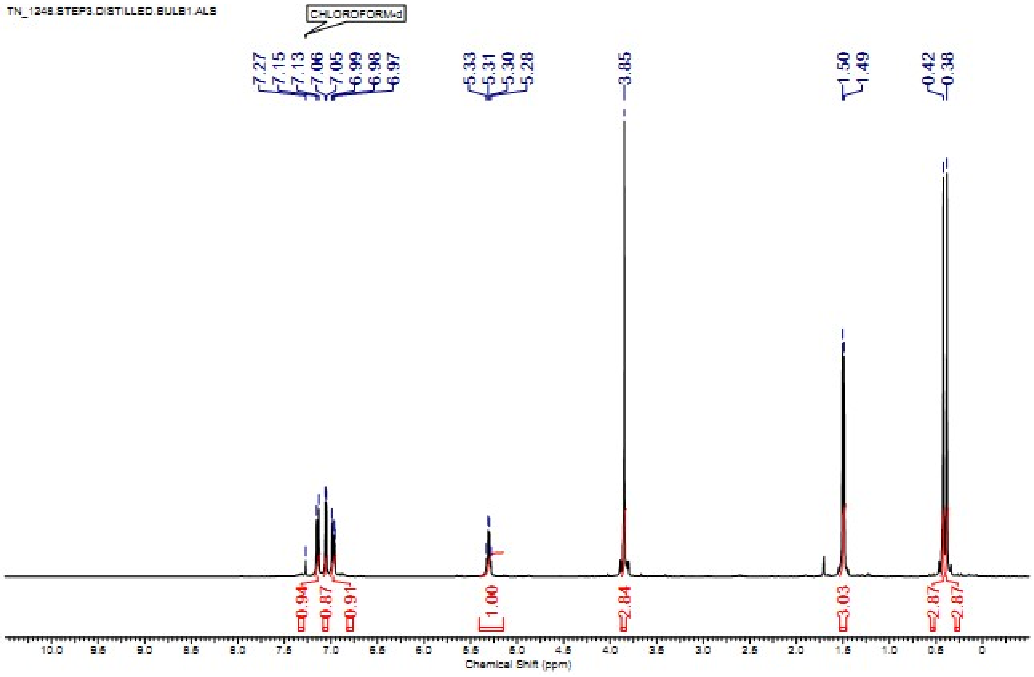
1n

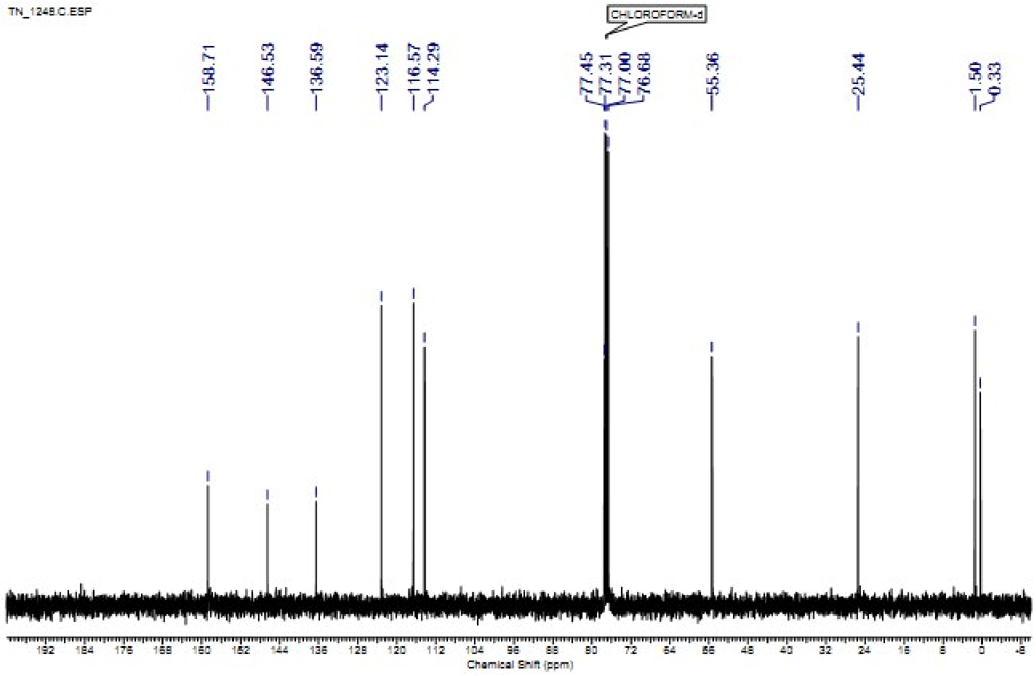

1217.STEP2.ISOLATED.KUGELROHR-2.ALS
CHLOROFORM-d
7.58
7.56
7.41
7.39
7.33
7.31
7.30
7.23
7.22
5.36
5.35
5.34
5.32
1.53
1.52
1.51
0.42
0.38
1.02
1.15
1.05
1.03
1.00
3.37
3.07
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

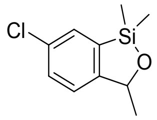

1217.C-2.ESP
CHLOROFORM-d
154.32
134.97
130.82
129.61
126.86
122.14
77.82
77.26
77.00
76.75
25.23
1.57
0.40
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


MeO
Si
O

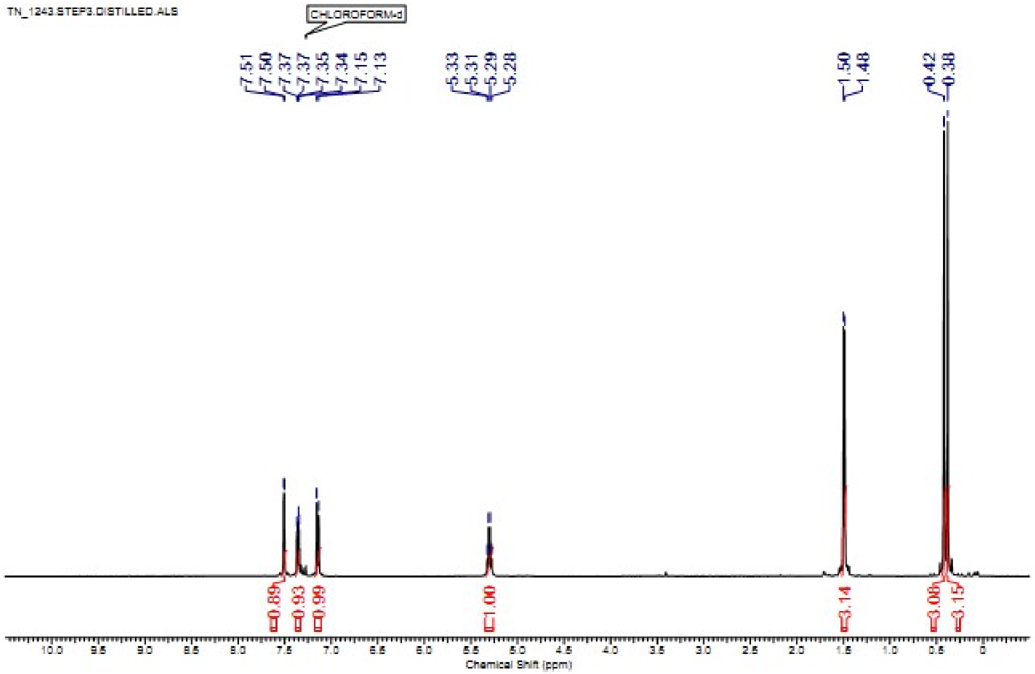
1o

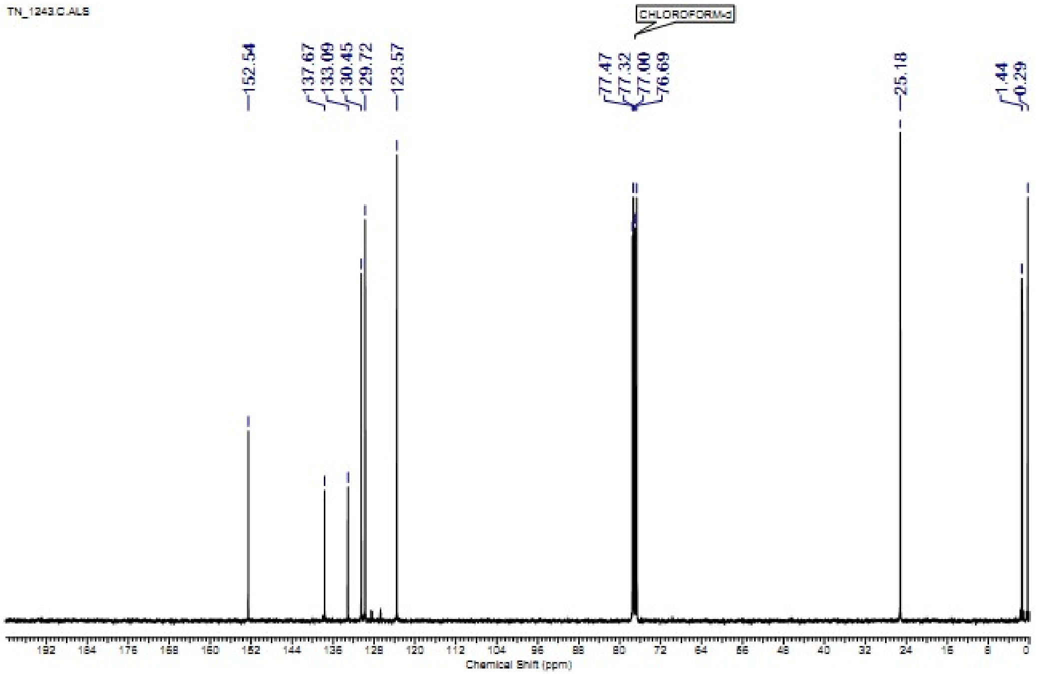

TN_1248.STEP3.DISTILLED.BULB1.ALS
CHLOROFORM-d
7.27
7.15
7.13
7.06
7.05
6.99
6.98
6.97
5.33
5.31
5.30
5.28
3.85
1.50
1.49
0.42
0.38
0.94
0.87
0.91
1.00
2.84
3.03
2.87
2.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

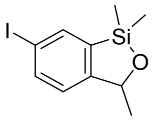

TN_1248.C.ESP
CHLOROFORM-d
158.71
146.53
136.59
123.14
116.57
114.29
77.45
77.31
77.00
76.68
55.36
25.44
1.50
0.33
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


Cl
Si
O

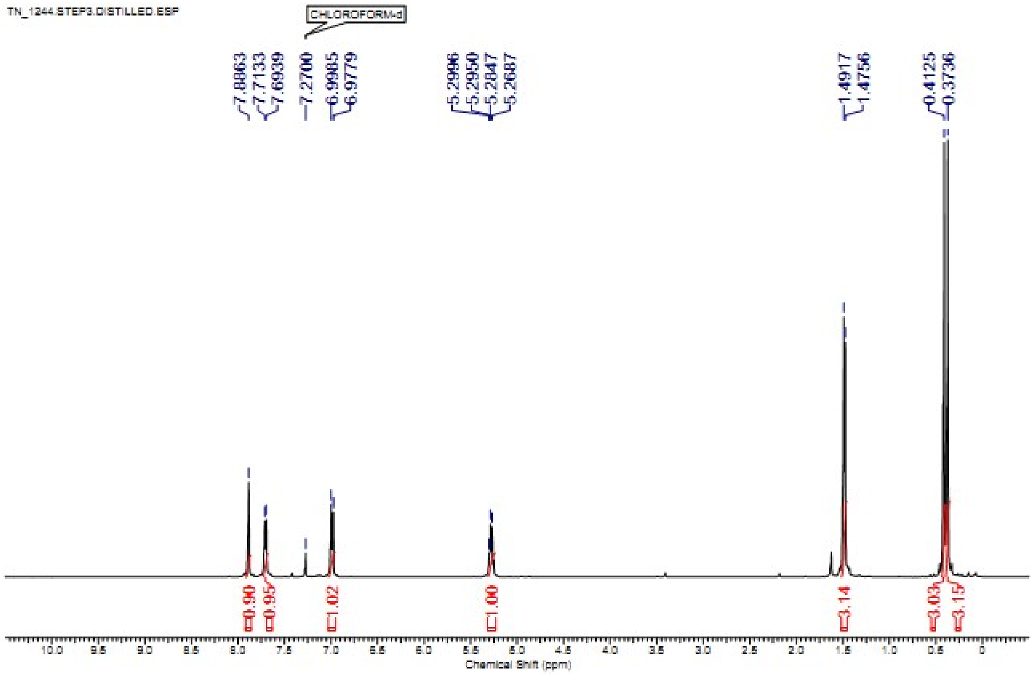
1p

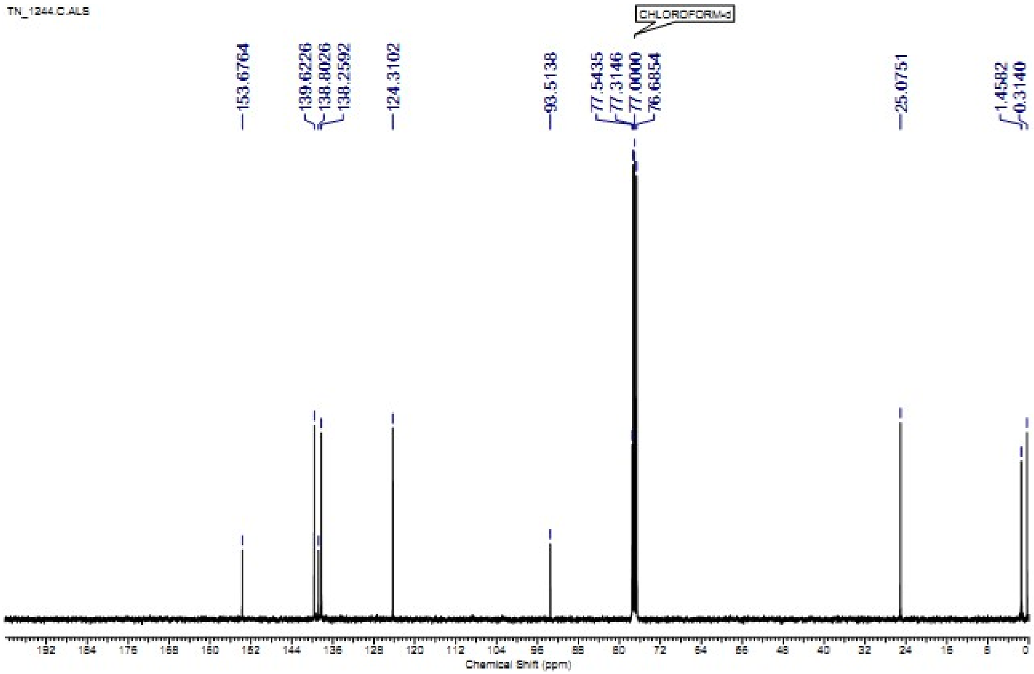

TN_1243.STEP3.DISTILLED.ALS
CHLOROFORM-d
7.51
7.50
7.37
7.37
7.35
7.34
7.15
7.13
5.33
5.31
5.29
5.28
1.50
1.48
0.42
0.38
0.89
0.93
0.99
1.00
3.14
3.08
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

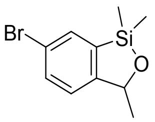

TN_1243.C.ALS
CHLOROFORM-d
152.54
137.67
133.09
130.45
129.72
123.57
77.47
77.32
77.00
76.69
25.18
1.44
0.29
Chemical Shift (ppm)


I
Si
O

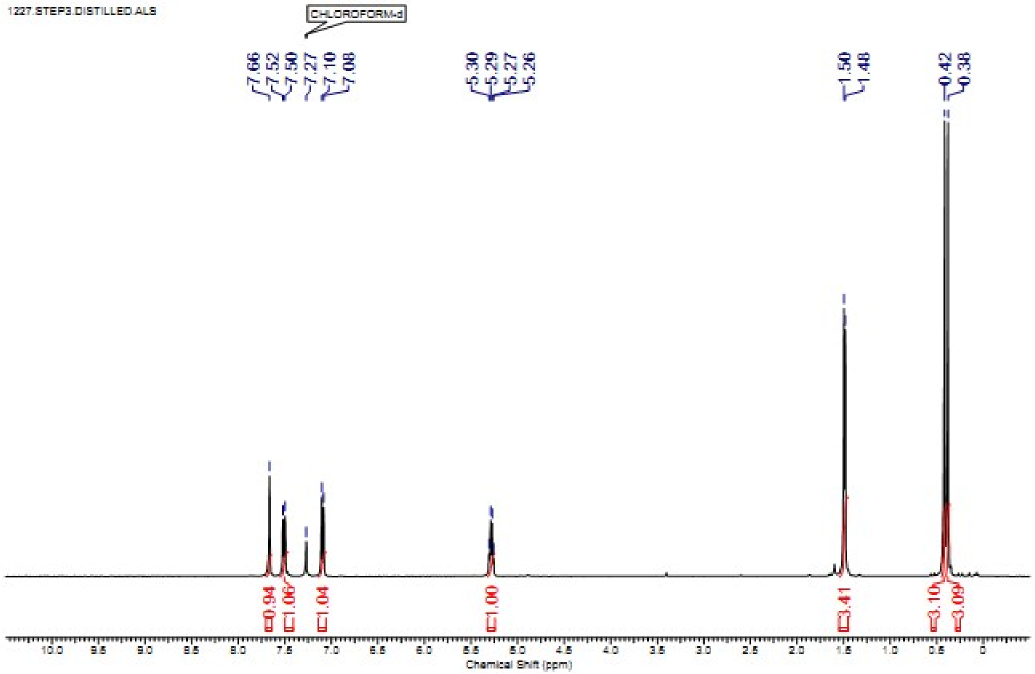
1q

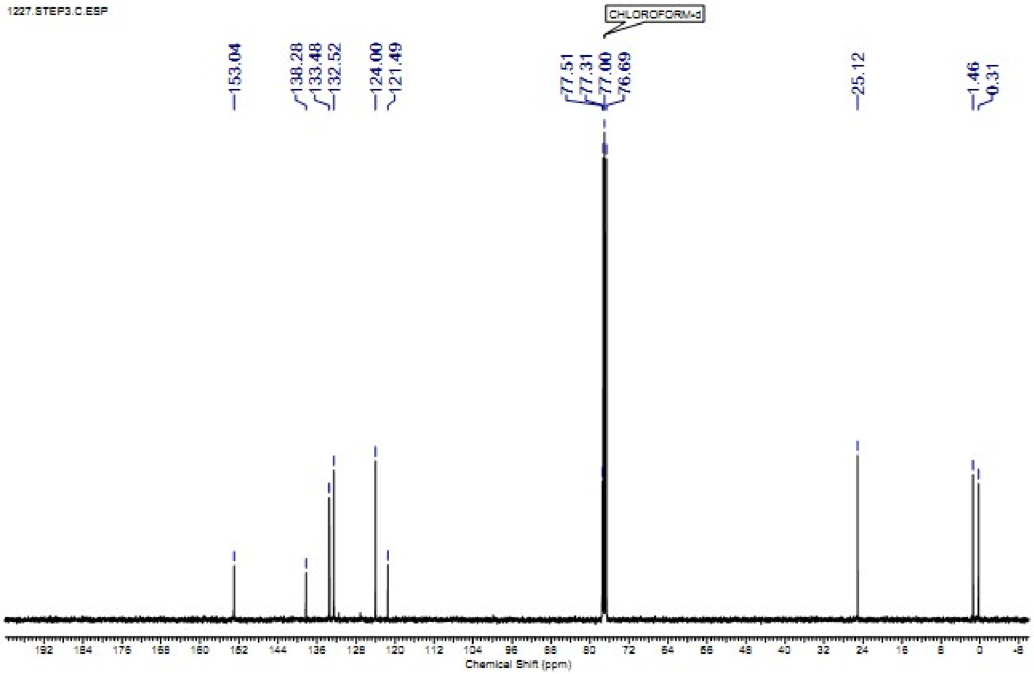

TN_1244.STEP3.DISTILLED.ESP
CHLOROFORM-d
7.8863
7.7133
7.6939
7.2700
6.9985
6.9779
5.2996
5.2950
5.2847
5.2687
1.4917
1.4756
0.4125
0.3736
0.90
0.95
1.02
1.00
3.14
3.03
3.15
Chemical Shift (ppm)

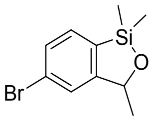

TN_1244.C.ALS
CHLOROFORM-d
153.6764
139.6226
138.8026
138.2592
124.3102
93.5138
77.5435
77.3146
77.0000
76.6854
25.0751
1.4582
0.3140
Chemical Shift (ppm)


Br
Si
O

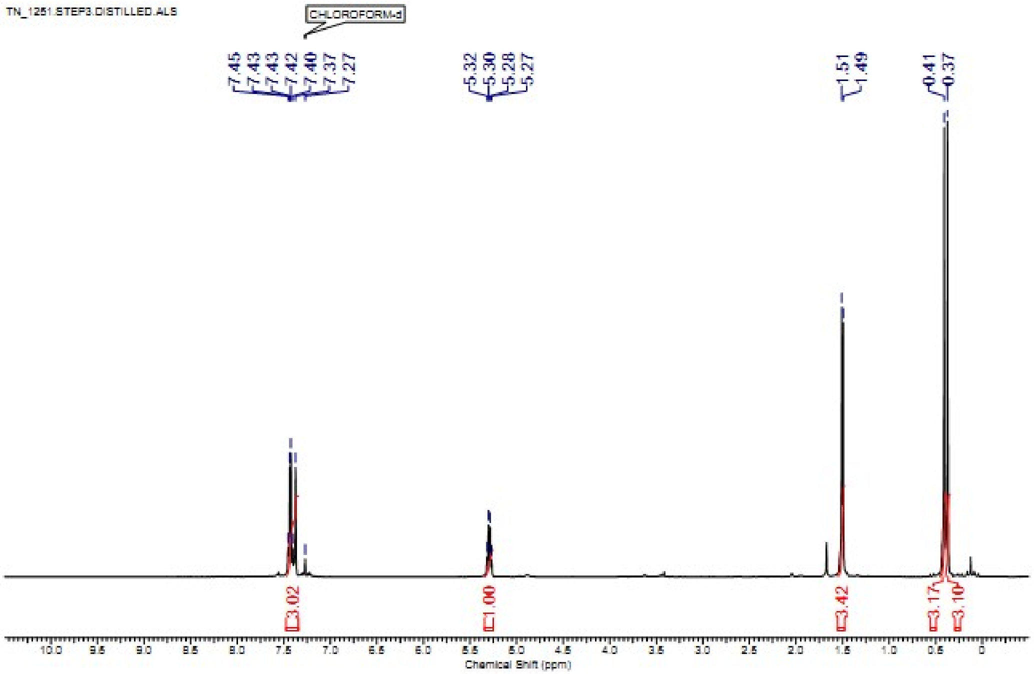
1r

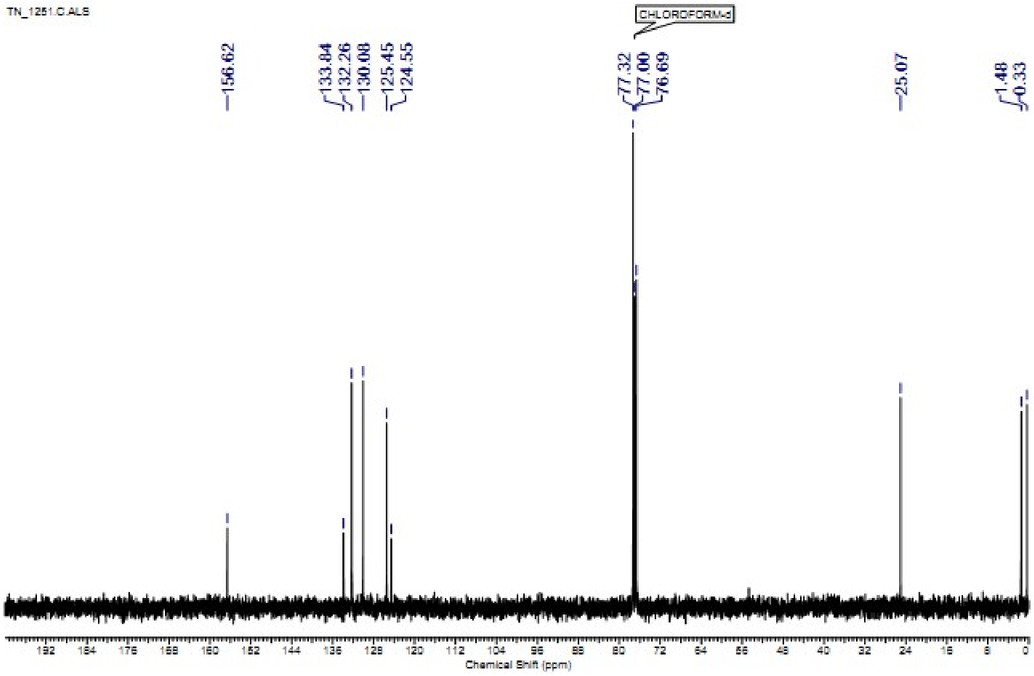

1227.STEP3.DISTILLED.ALS
CHLOROFORM-d
7.66
7.52
7.50
7.27
7.10
7.08
5.30
5.29
5.27
5.26
1.50
1.48
0.42
0.38
0.94
1.06
1.04
1.00
3.41
3.10
3.09
Chemical Shift (ppm)

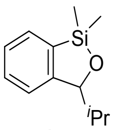

1227.STEP3.C.ESP
CHLOROFORM-d
153.04
138.28
133.48
132.52
124.00
121.49
77.51
77.31
77.00
76.69
25.12
1.46
0.31
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


Si
O
Br

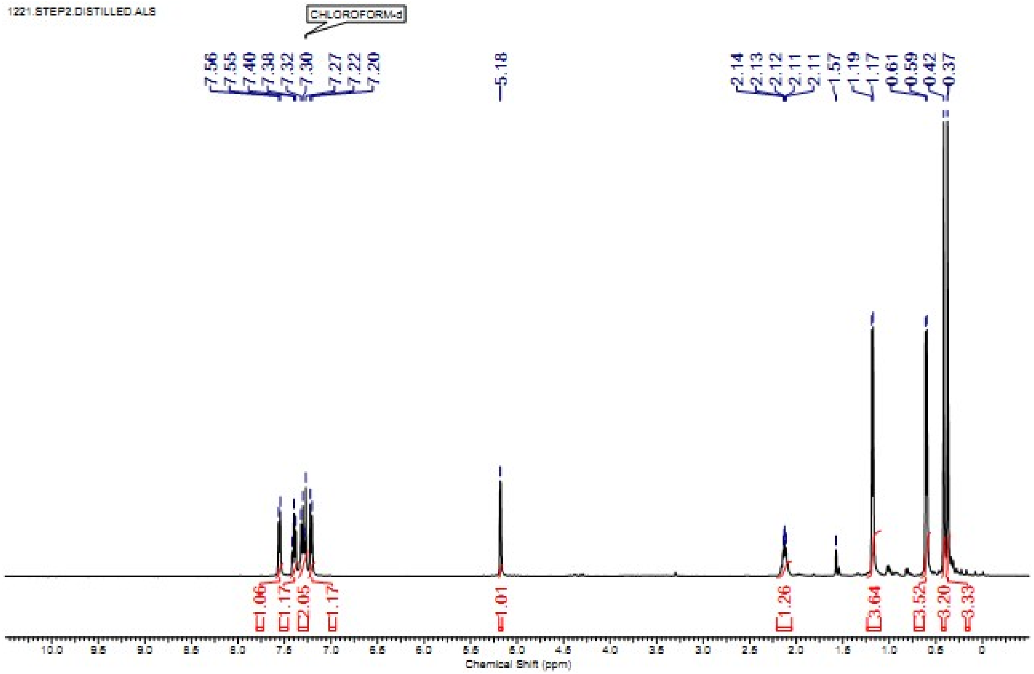
1s

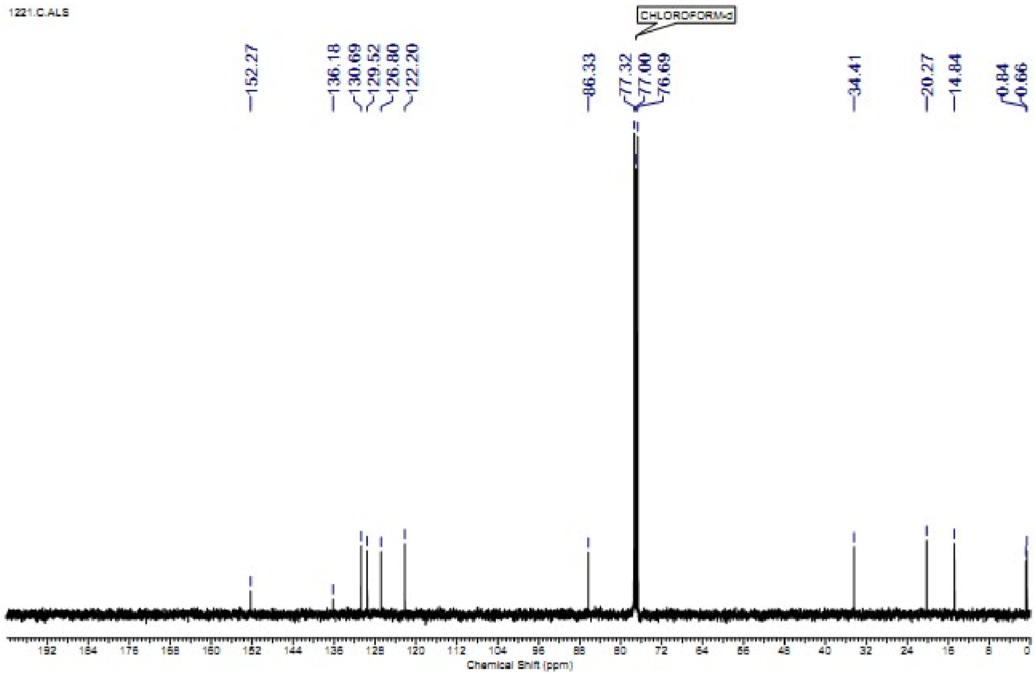

TN_1251.STEP3.DISTILLED.ALS
CHLOROFORM-d
7.45
7.43
7.43
7.42
7.40
7.37
7.27
5.32
5.30
5.28
5.27
1.51
1.49
0.41
0.37
3.02
1.00
3.42
3.17
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

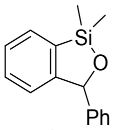

TN_1251.C.ALS
CHLOROFORM-d
156.62
133.84
132.26
130.08
125.45
124.55
77.32
77.00
76.69
25.07
1.48
0.33
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


Si
O
iPr

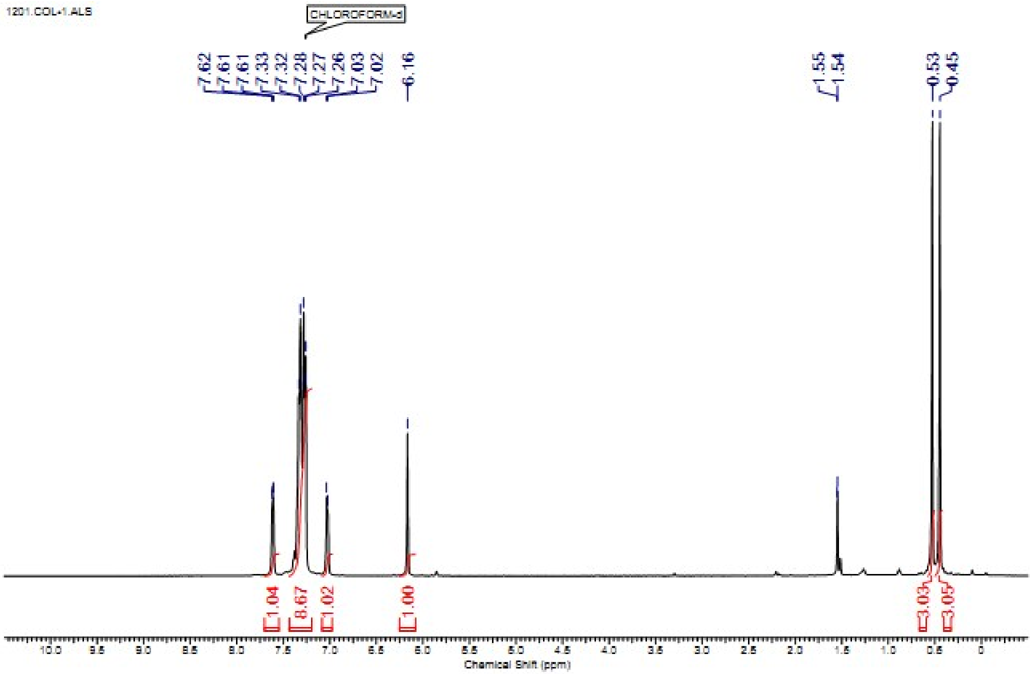
1t

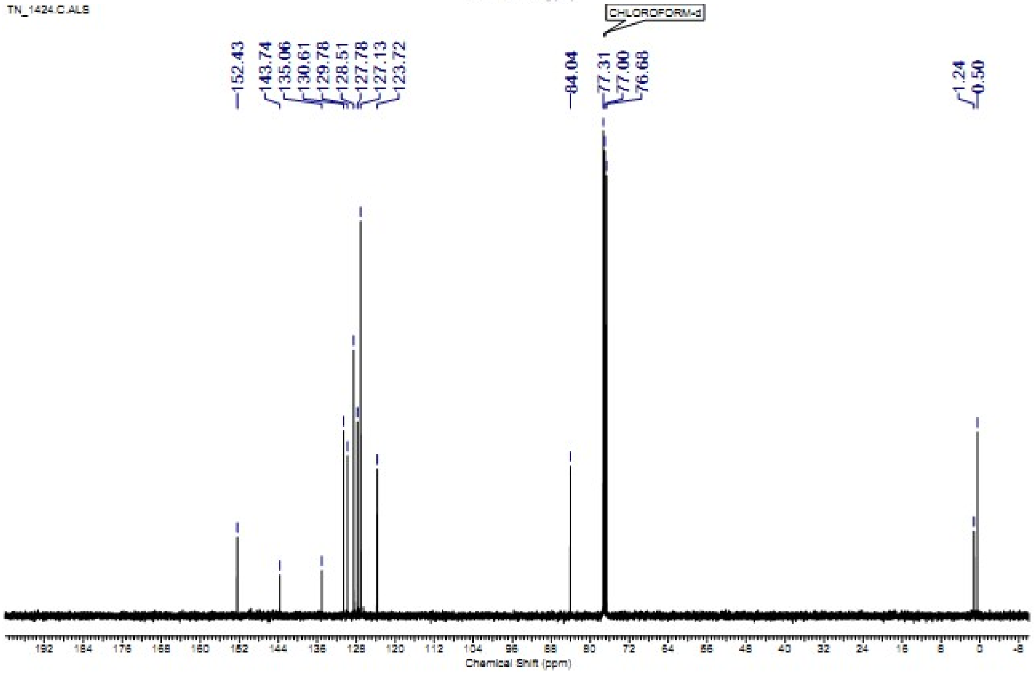

1221.STEP2.DISTILLED.ALS
CHLOROFORM-d
7.56
7.55
7.40
7.38
7.32
7.30
7.27
7.22
7.20
5.18
2.14
2.13
2.12
2.11
2.11
1.57
1.19
1.17
0.61
0.59
0.42
0.37
1.06
1.17
2.05
1.17
1.01
1.26
3.64
3.52
3.20
3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

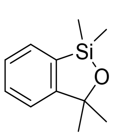

1221.C.ALS
CHLOROFORM-d
152.27
136.18
130.69
129.52
126.80
122.20
86.33
77.32
77.00
76.69
34.41
20.27
14.84
0.84
0.66
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Si
O
Ph

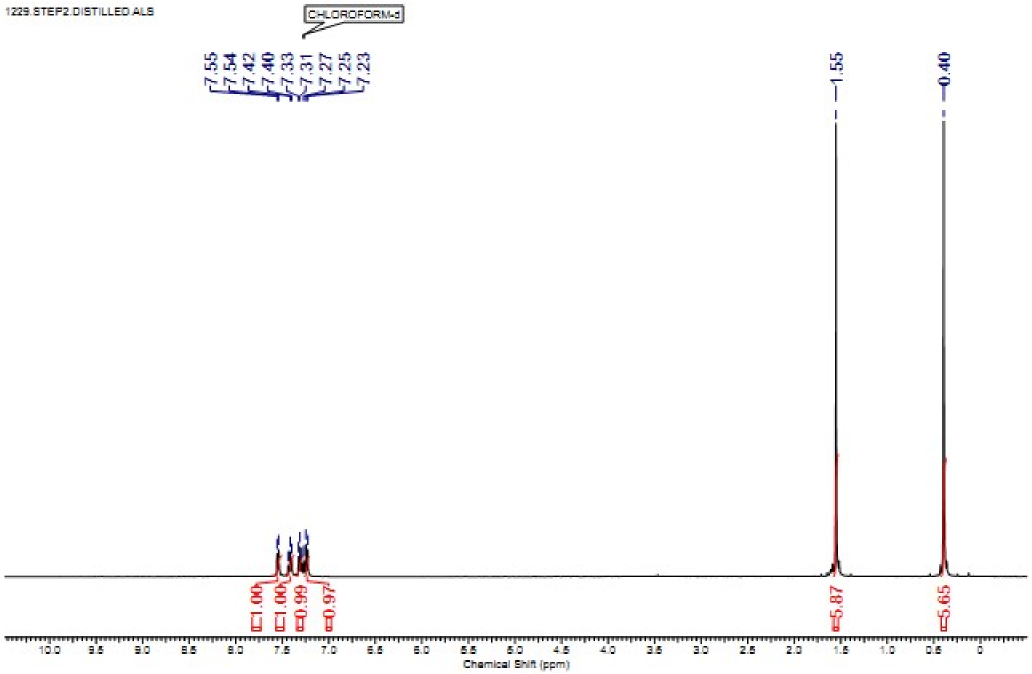
1u

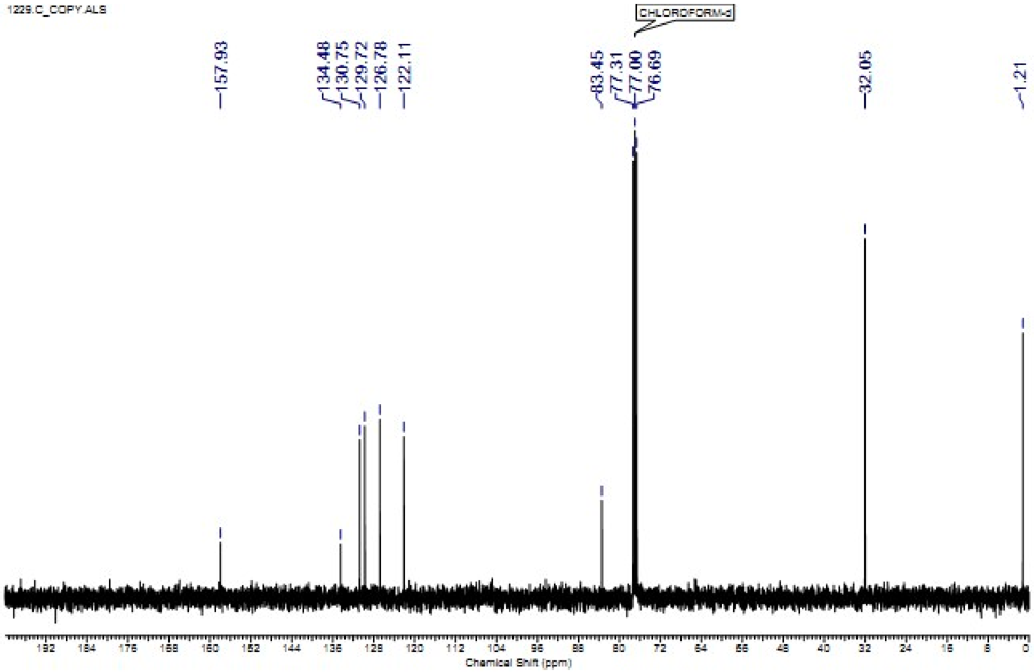

1201.COL-1.ALS
CHLOROFORM-d
7.62
7.61
7.61
7.33
7.32
7.28
7.27
7.26
7.03
7.02
6.16
1.55
1.54
0.53
0.45
1.04
8.67
1.02
1.00
3.03
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

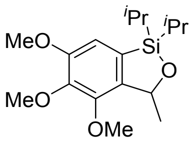

TN_1424.C.ALS
CHLOROFORM-d
152.43
143.74
135.06
130.61
129.78
128.51
127.78
127.13
123.72
84.04
77.31
77.00
76.68
1.24
0.50
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


Si
O

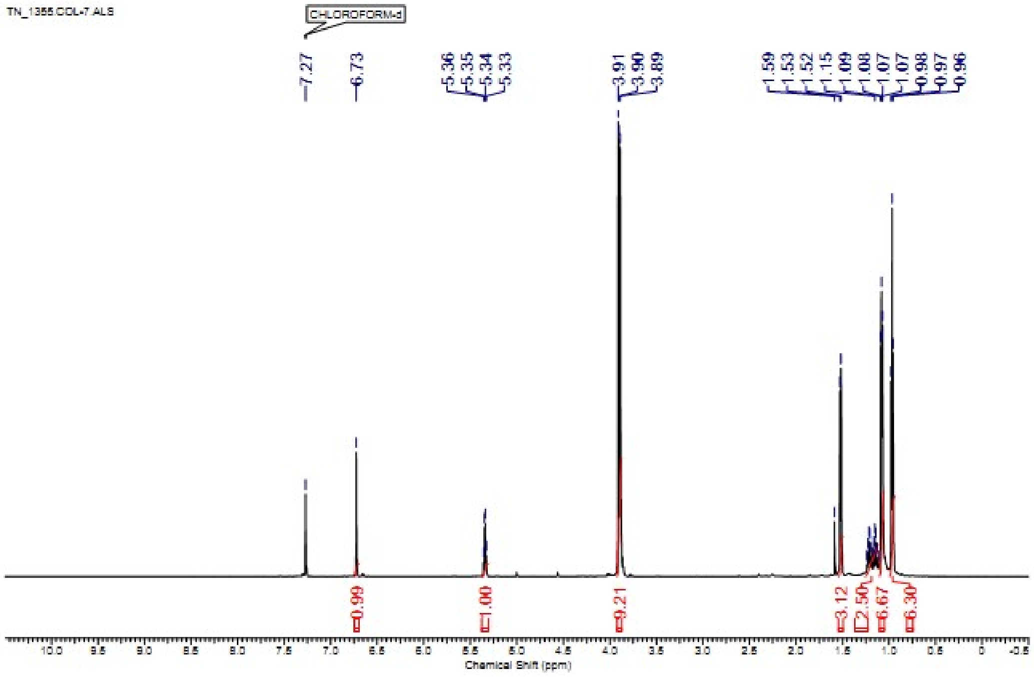
1w

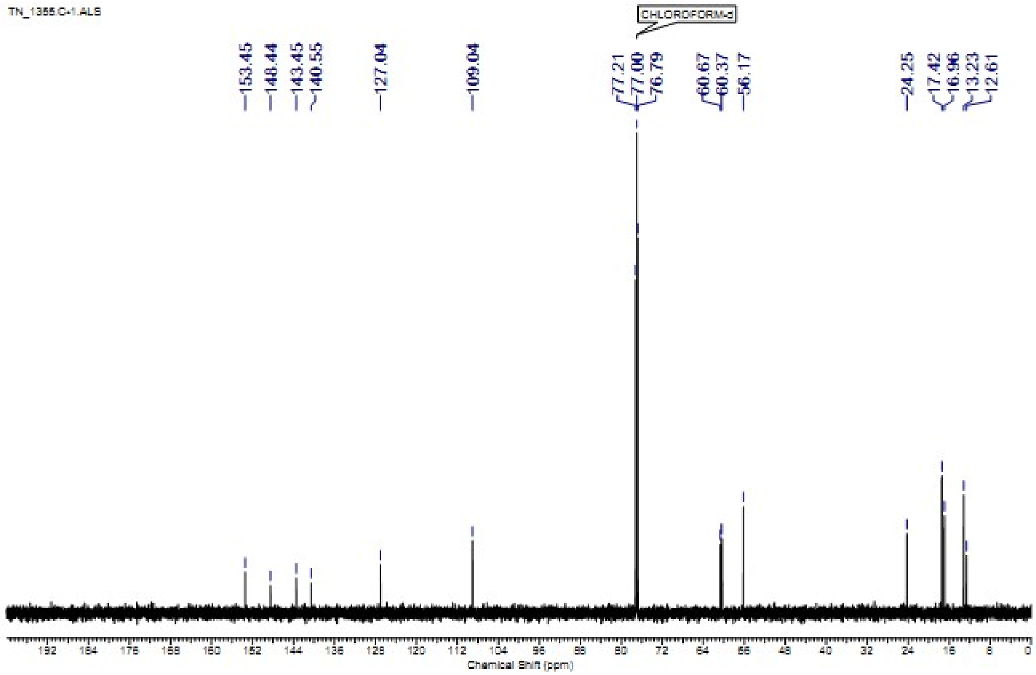

1229.STEP2.DISTILLED.ALS
CHLOROFORM-d
7.55
7.54
7.42
7.40
7.33
7.31
7.27
7.25
7.23
1.55
0.40
1.00
1.00
0.99
0.97
5.87
5.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

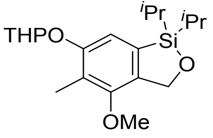

1229.C_COPY.ALS
CHLOROFORM-d
157.93
134.48
130.75
129.72
126.78
122.11
83.45
77.31
77.00
76.69
32.05
1.21
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


iPr
iPr
Si
O
MeO
MeO
OMe

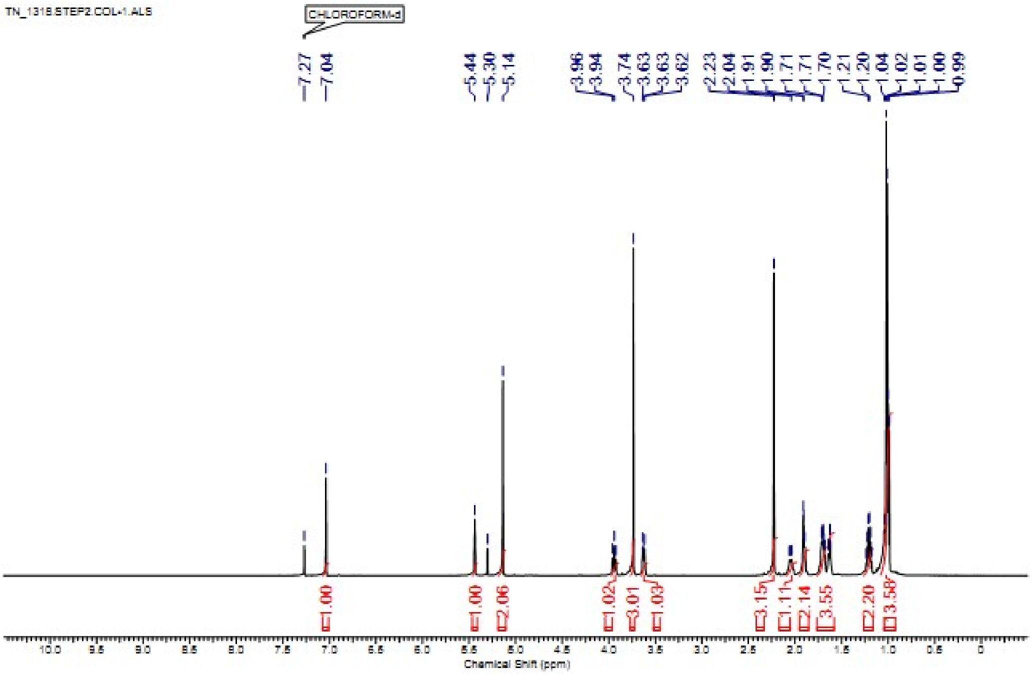
1x

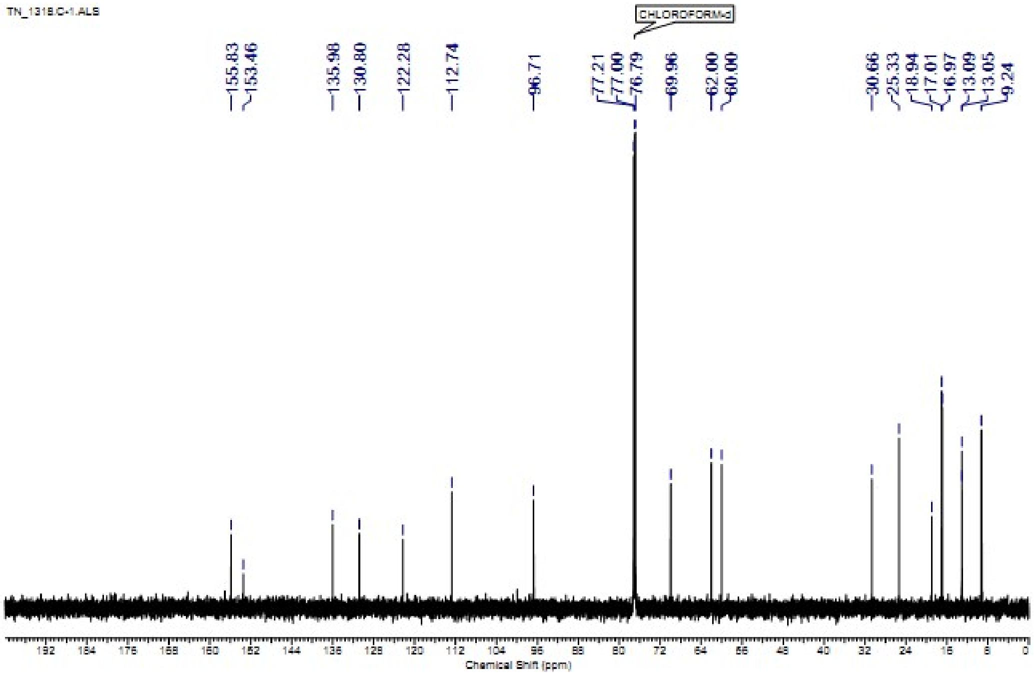

TN_1355.CDL-7.ALS
CHLOROFORM-d
7.27
6.73
5.36
5.35
5.34
5.33
3.91
3.90
3.89
1.59
1.53
1.52
1.15
1.09
1.08
1.07
1.07
0.98
0.97
0.96
0.99
1.00
9.21
3.12
2.50
6.67
6.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

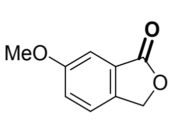

TN_1355.C-1.ALS
CHLOROFORM-d
153.45
148.44
143.45
140.55
127.04
109.04
77.21
77.00
76.79
60.67
60.37
56.17
24.25
17.42
16.96
13.23
12.61
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


THPO
iPr
iPr
Si
O
OMe

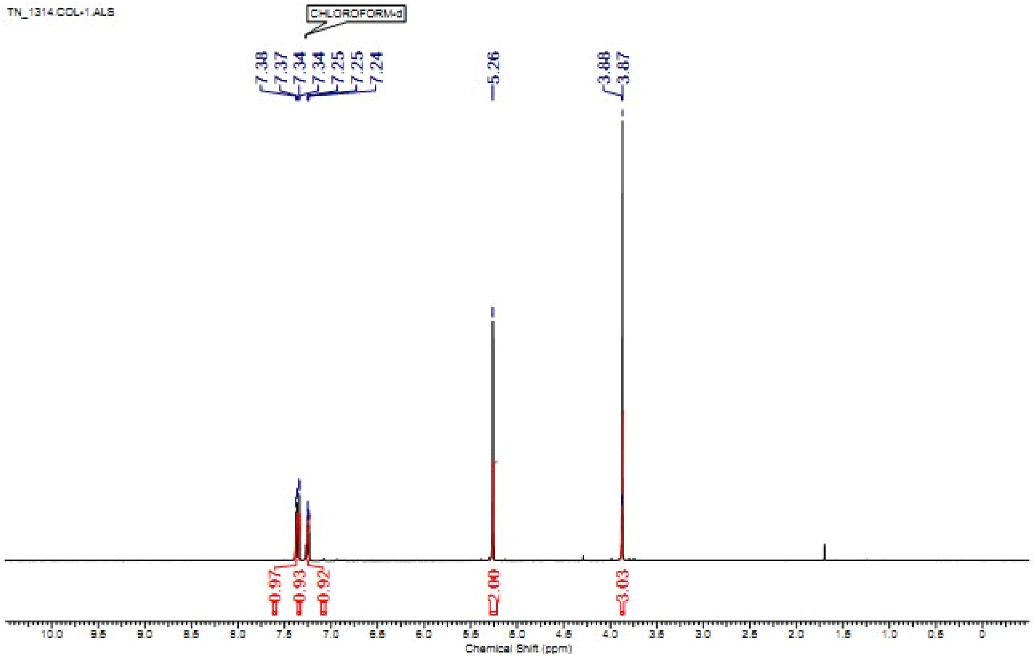
1y

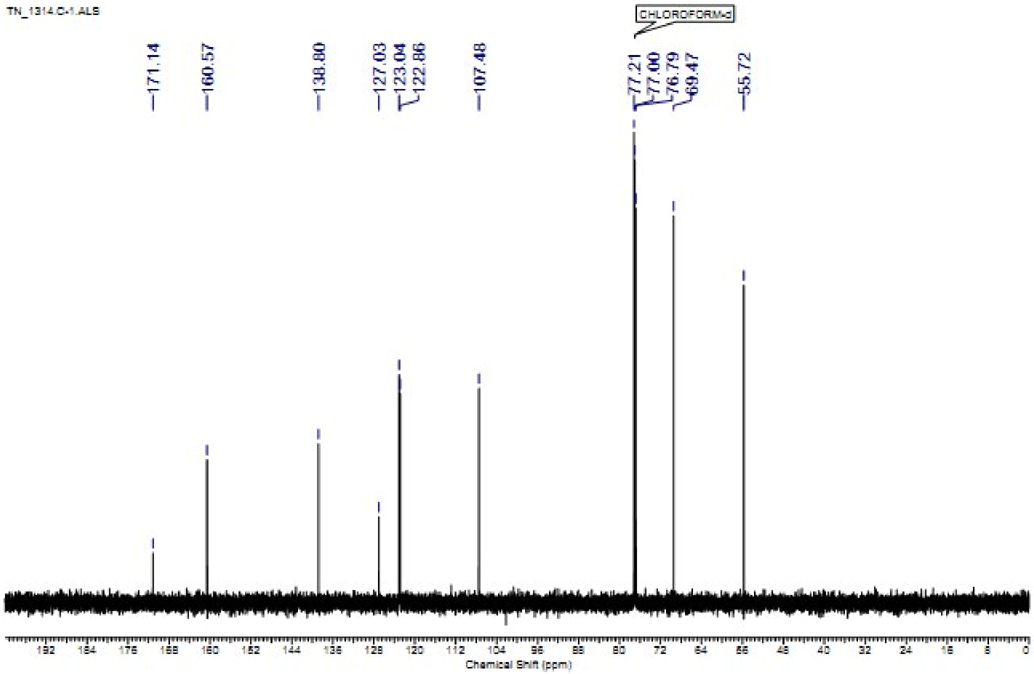

TN_1318.STEP2.COL-1.ALS
CHLOROFORM-d
7.27
7.04
5.44
5.30
5.14
3.96
3.94
3.74
3.63
3.63
3.62
2.23
2.04
1.91
1.90
1.71
1.71
1.70
1.21
1.20
1.04
1.02
1.01
1.00
0.99
1.00
1.00
2.06
1.02
3.01
1.03
3.15
1.11
2.14
3.55
2.20
3.58
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

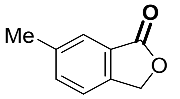

TN_1318.C-1.ALS
CHLOROFORM-d
155.83
153.46
135.98
130.80
122.28
112.74
96.71
77.21
77.00
76.79
69.96
62.00
60.00
30.66
25.33
18.94
17.01
16.97
13.09
13.05
9.24
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


MeO
O
O

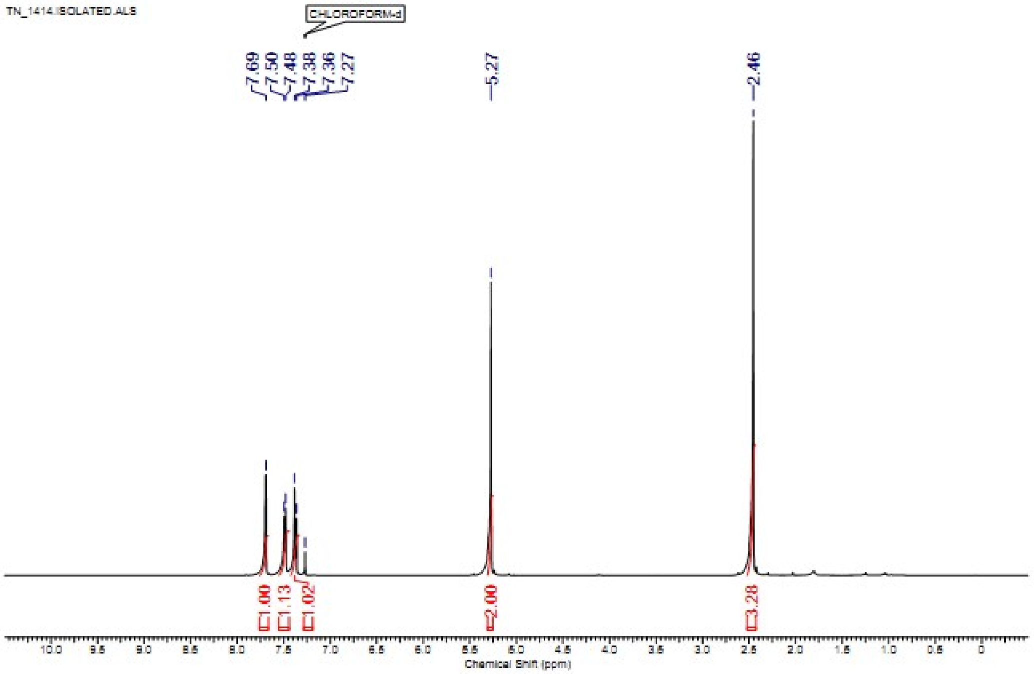
2a

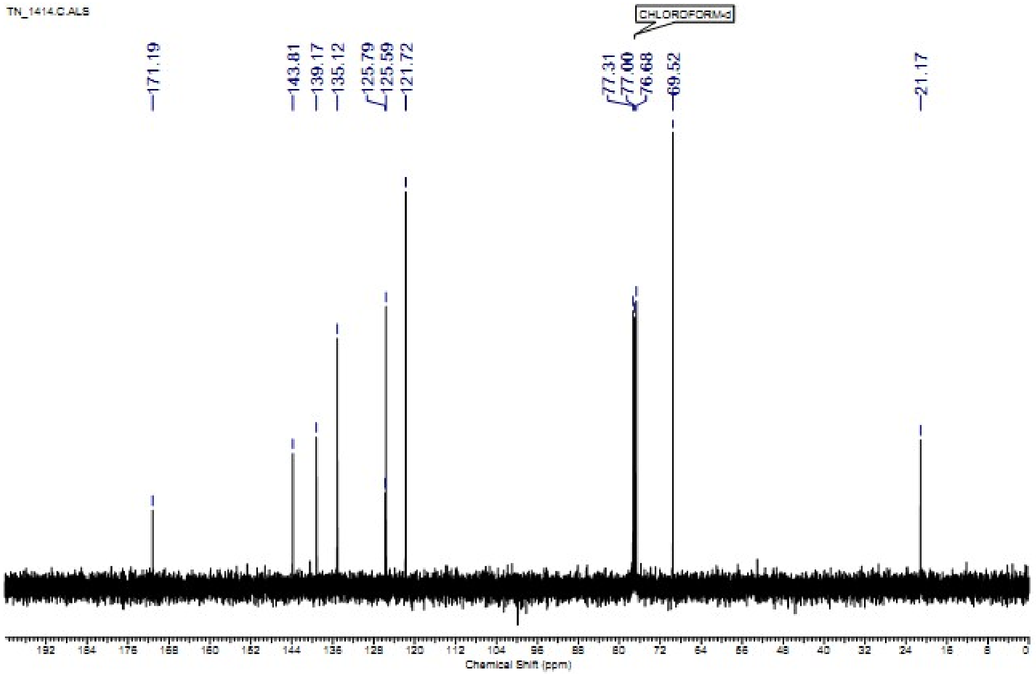

TN_1314.COL-1.ALS
CHLOROFORM-d
7.38
7.37
7.34
7.34
7.25
7.25
7.24
5.26
3.88
3.87
0.97
0.93
0.92
2.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

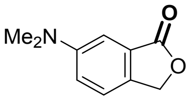

TN_1314.C-1.ALS
CHLOROFORM-d
171.14
160.57
138.80
127.03
123.04
122.86
107.48
77.21
77.00
76.79
69.47
55.72
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Me
O
O

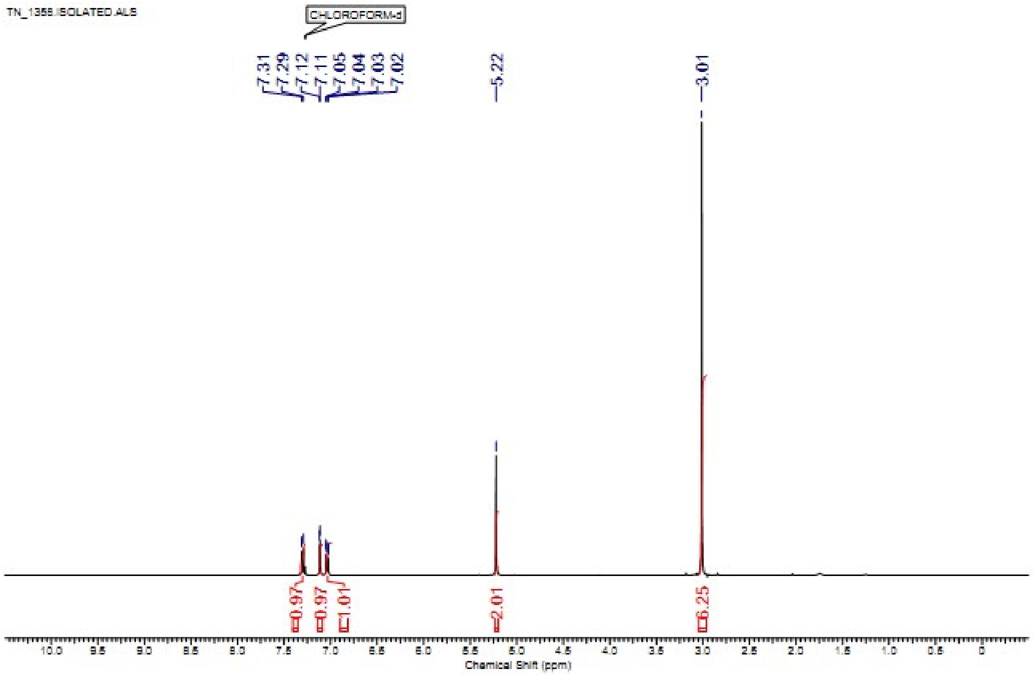
2b

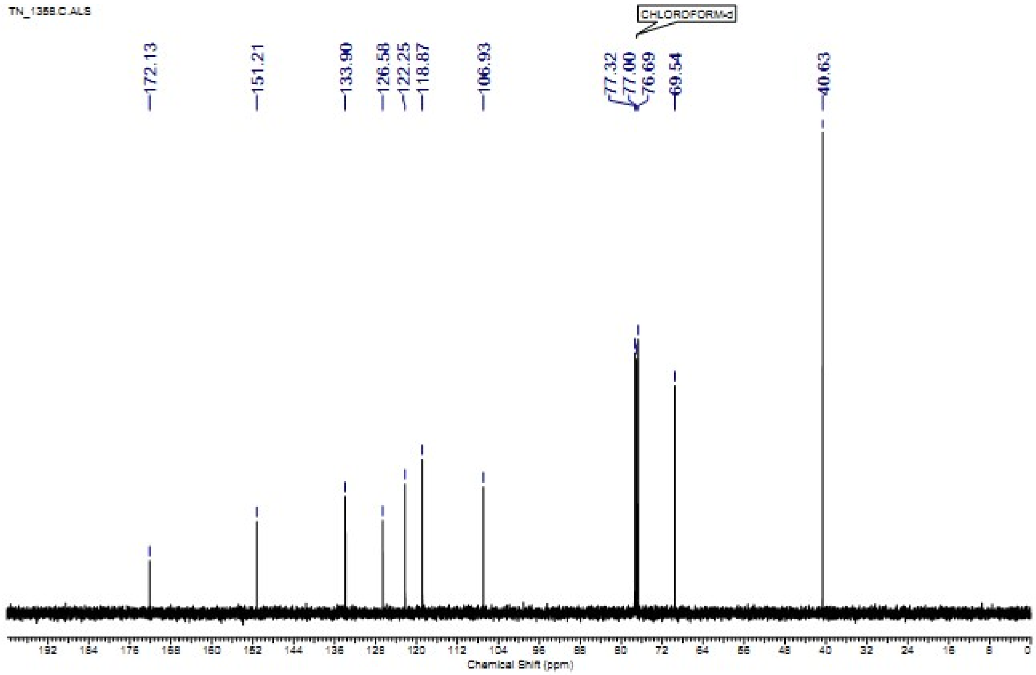

TN_1414.ISOLATED.ALS
CHLOROFORM-d
7.69
7.50
7.48
7.38
7.36
7.27
5.27
2.46
1.00
1.13
1.02
2.00
3.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

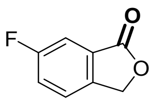

TN_1414.C.ALS
CHLOROFORM-d
171.19
143.81
139.17
135.12
125.79
125.59
121.72
77.31
77.00
76.68
69.52
21.17
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Me2N
O
O

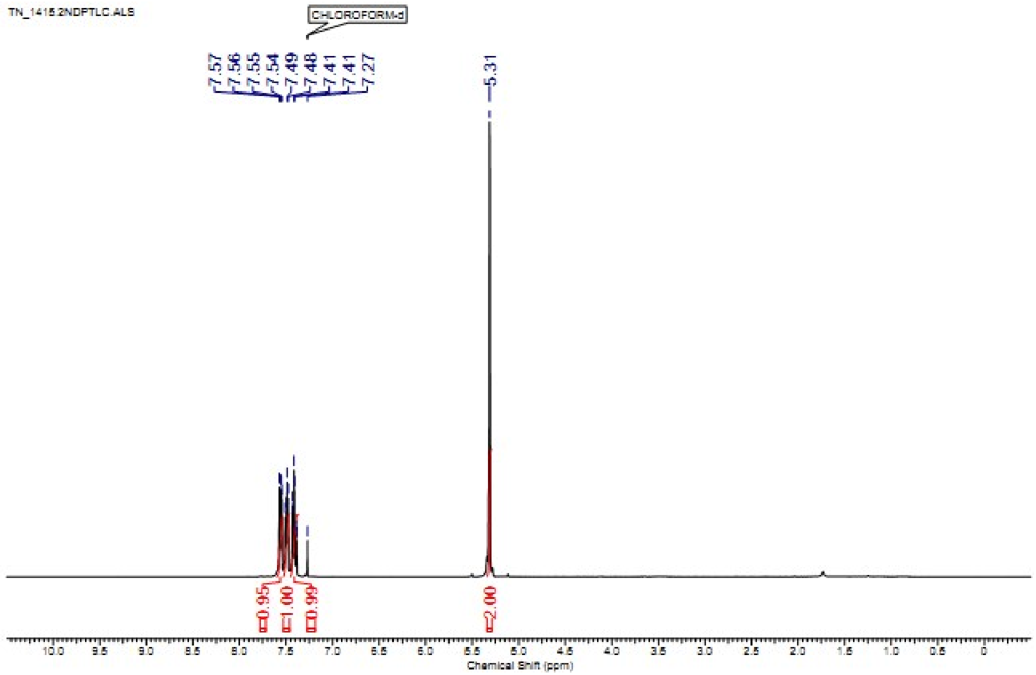
2c

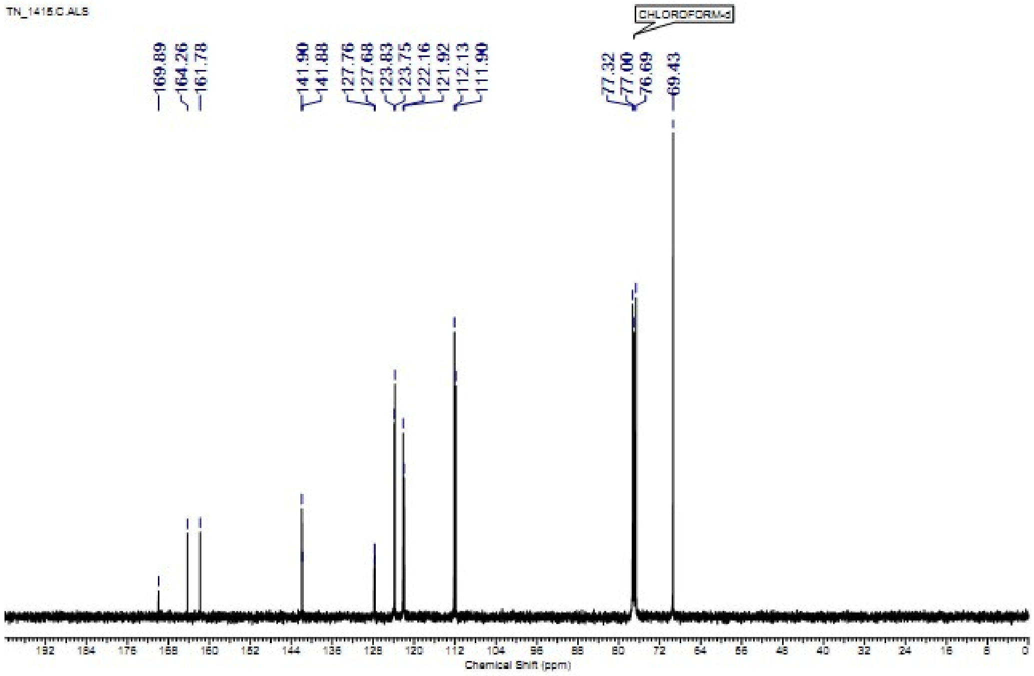

TN_1358 ISOLATED.ALS
CHLOROFORM-d
7.31
7.29
7.12
7.11
7.05
7.04
7.03
7.02
5.22
3.01
0.97
0.97
1.01
2.01
6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

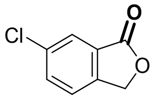

TN_1358.C.ALS
CHLOROFORM-d
172.13
151.21
133.90
126.58
122.25
118.87
106.93
77.32
77.00
76.69
69.54
40.63
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


F
O
O

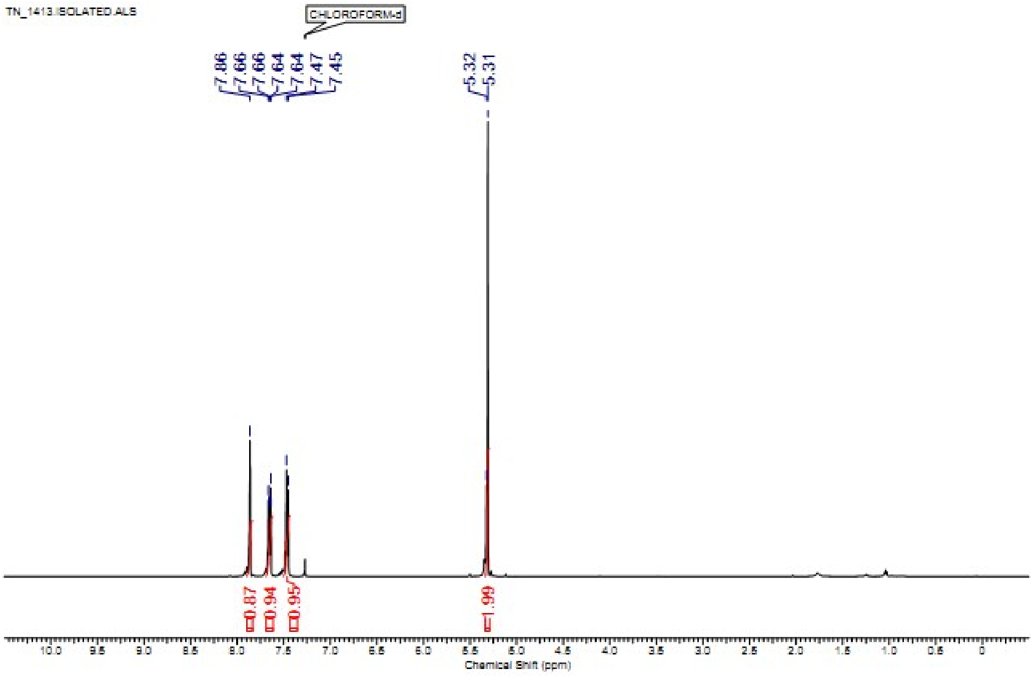
2d

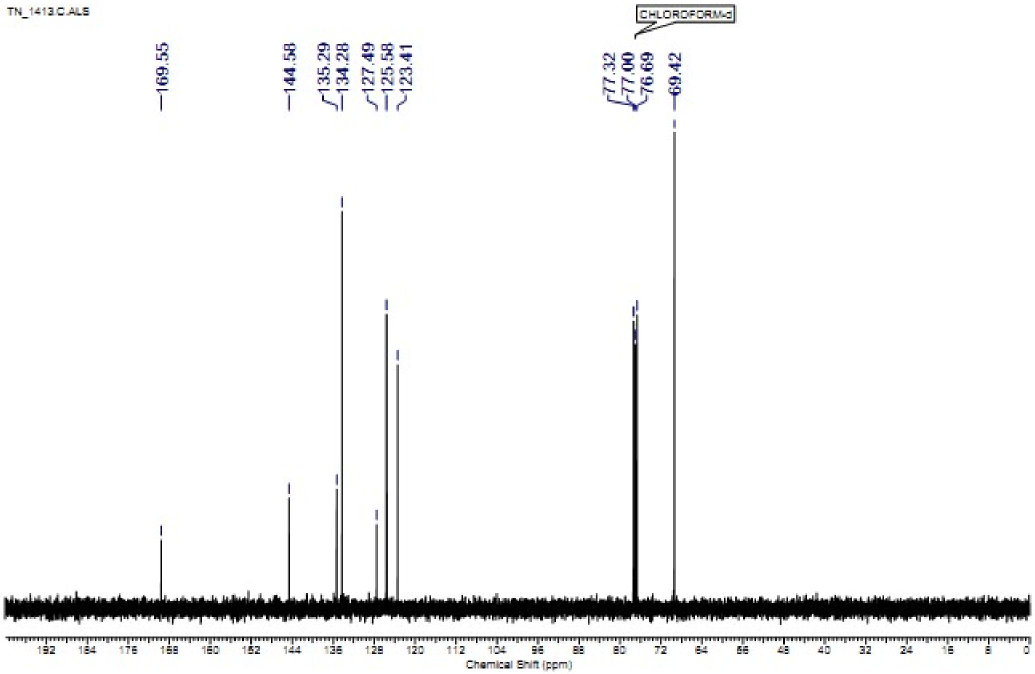

TN_1415.2NDPTLC.ALS
CHLOROFORM-d
7.57
7.56
7.55
7.54
7.49
7.48
7.41
7.41
7.27
5.31
0.95
1.00
0.99
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

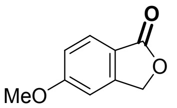

TN_1415.C.ALS
CHLOROFORM-d
169.89
164.26
161.78
141.90
141.88
127.76
127.68
123.83
123.75
122.16
121.92
112.13
111.90
77.32
77.00
76.69
69.43
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Cl
O
O

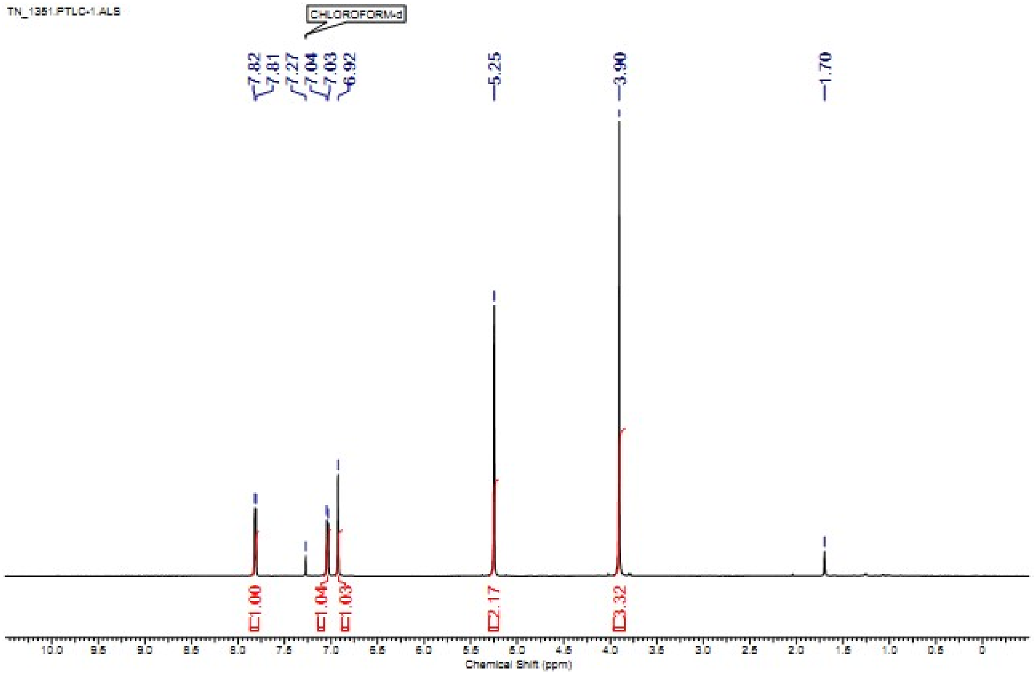
2e

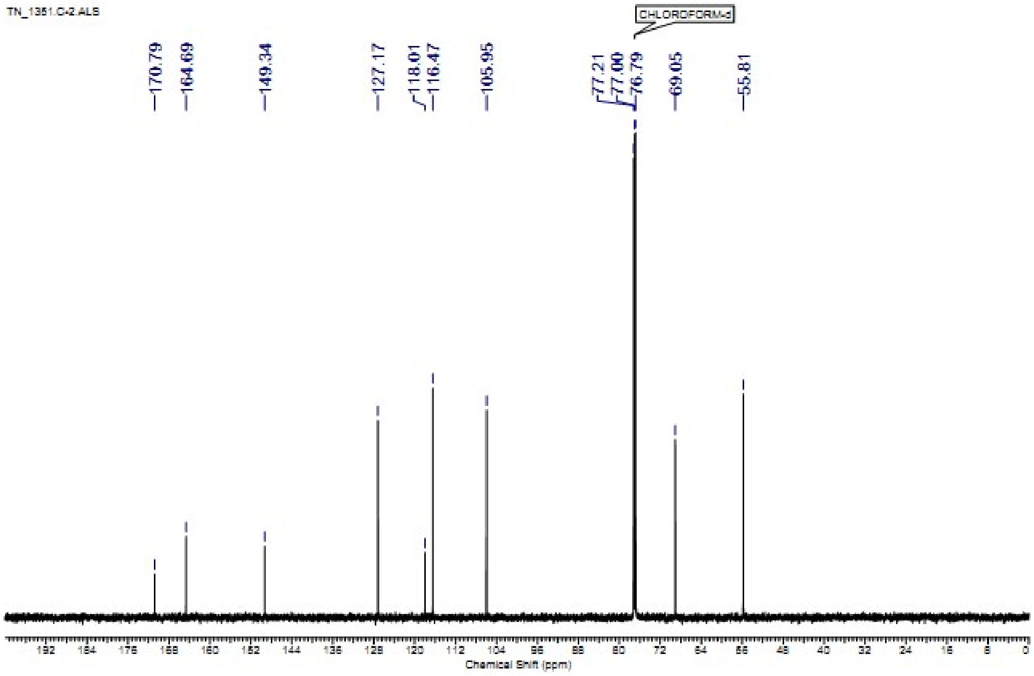

TN_1413.ISOLATED.ALS
CHLOROFORM-d
7.86
7.66
7.66
7.64
7.64
7.47
7.45
5.32
5.31
0.87
0.94
0.95
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

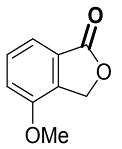

TN_1413.C.ALS
CHLOROFORM-d
169.55
144.58
135.29
134.28
127.49
125.58
123.41
77.32
77.00
76.69
69.42
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
MeO

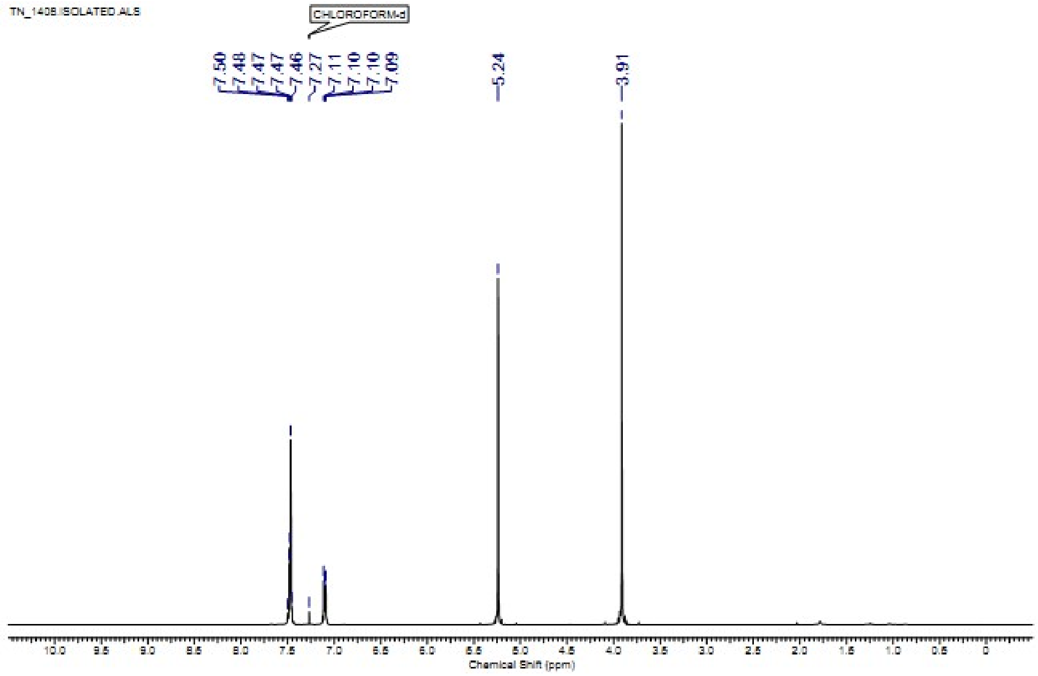
2f

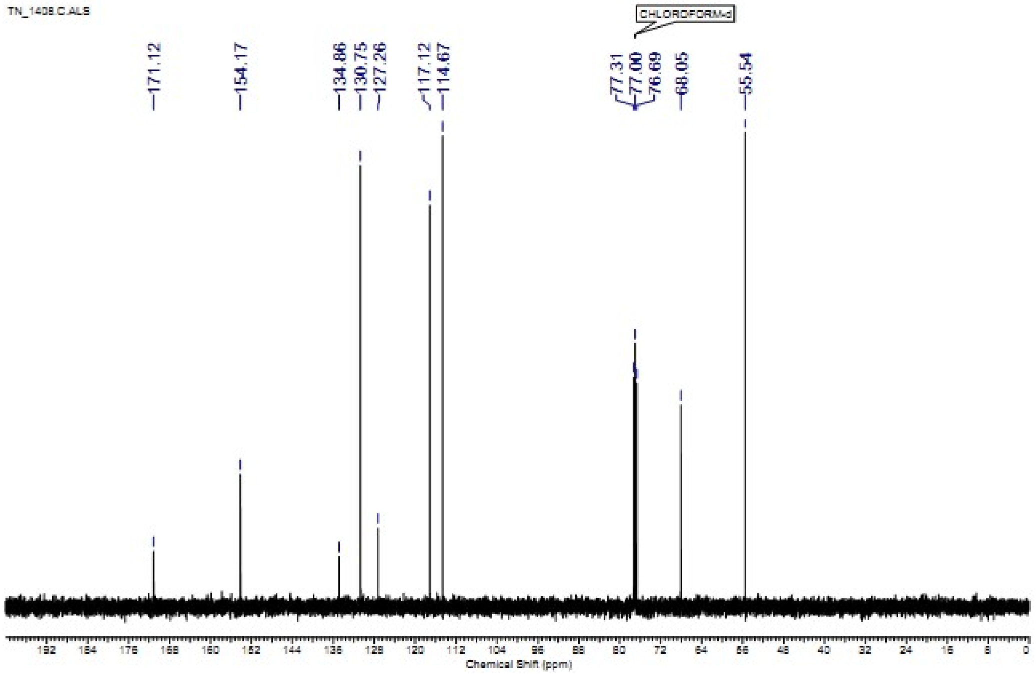

TN_1351.PTLC-1.ALS
CHLOROFORM-d
7.82
7.81
7.27
7.04
7.03
6.92
5.25
3.90
1.70
1.00
1.04
1.03
2.17
3.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

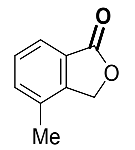

TN_1351.C-2.ALS
CHLOROFORM-d
170.79
164.69
149.34
127.17
118.01
116.47
105.95
77.21
77.00
76.79
69.05
55.81
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
OMe

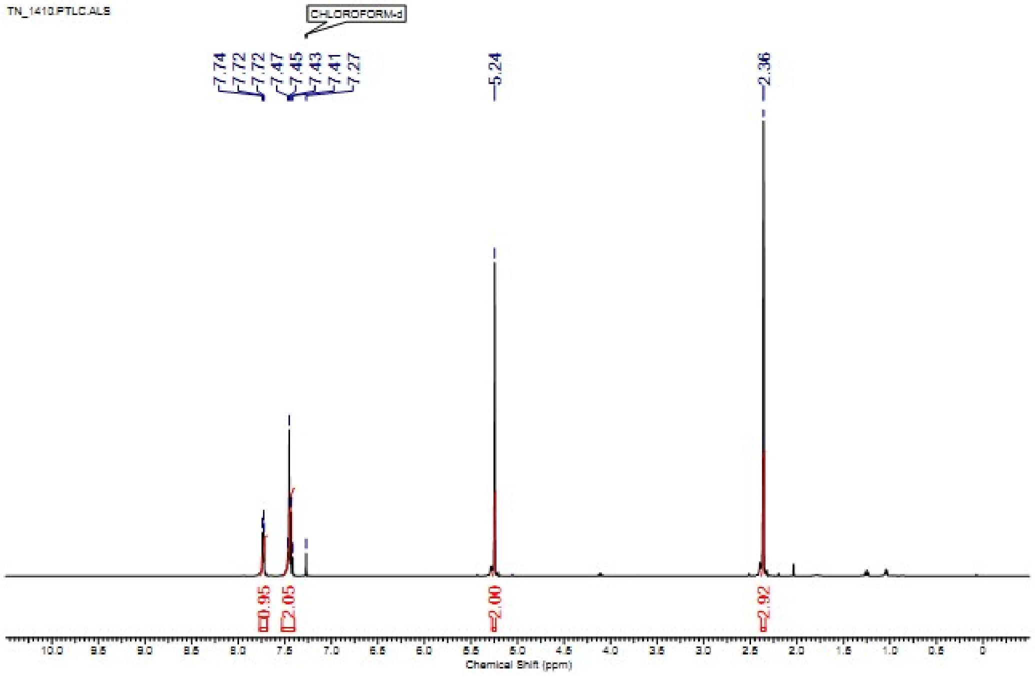
2g

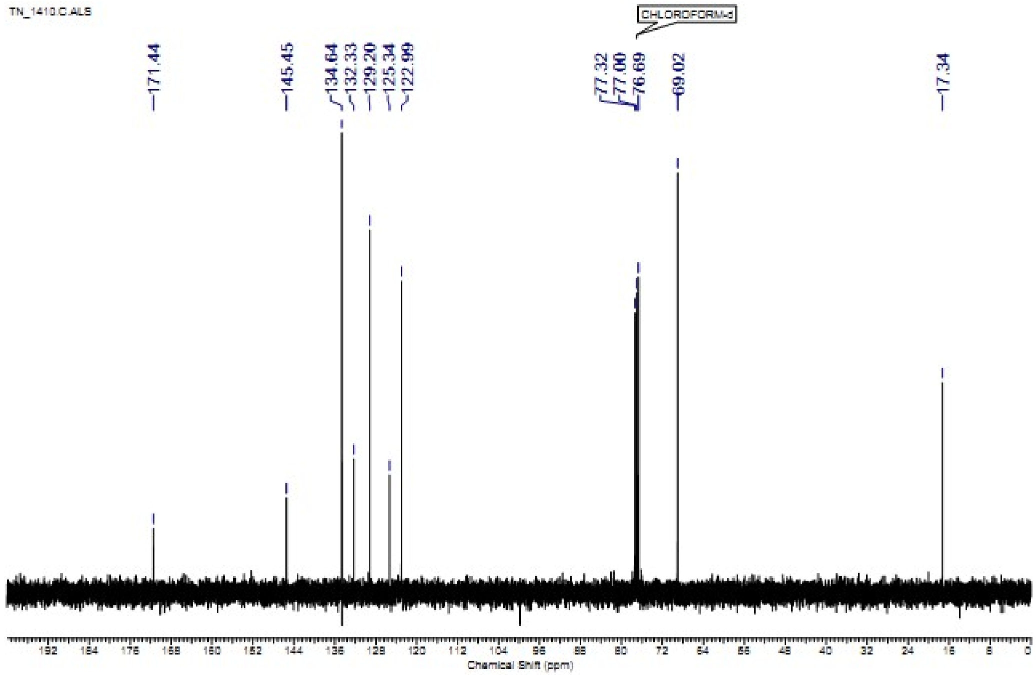

TN_1408.ISOLATED.ALS
CHLOROFORM-d
7.50
7.48
7.47
7.47
7.46
7.27
7.11
7.10
7.10
7.09
5.24
3.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

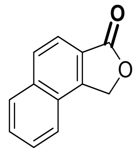

TN_1408.C.ALS
CHLOROFORM-d
171.12
154.17
134.86
130.75
127.26
117.12
114.67
77.31
77.00
76.69
68.05
55.54
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
Me

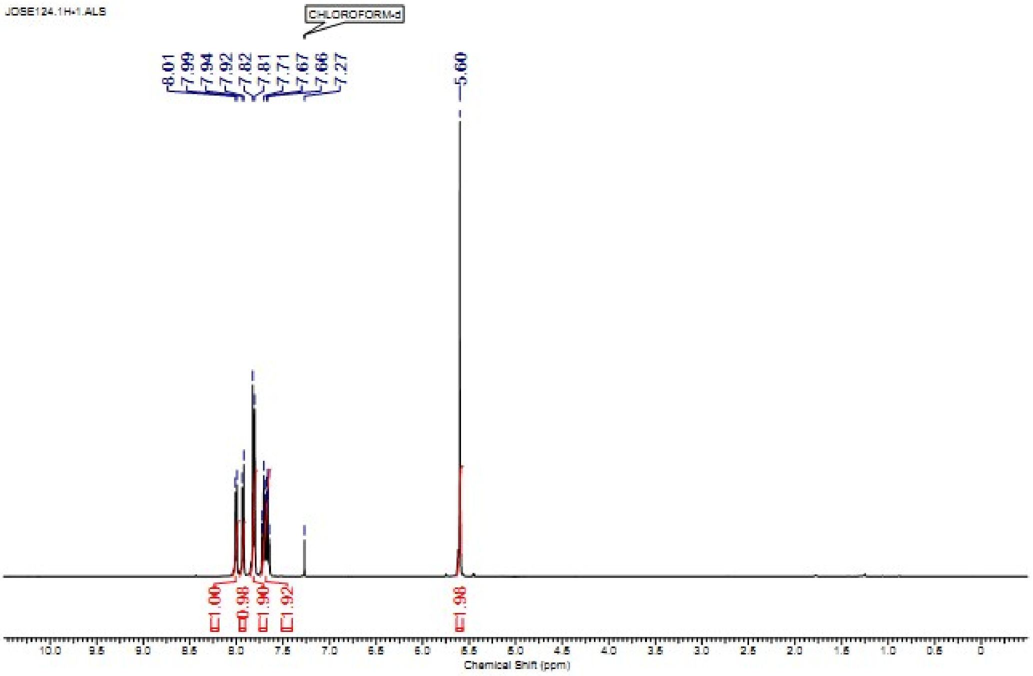
2h

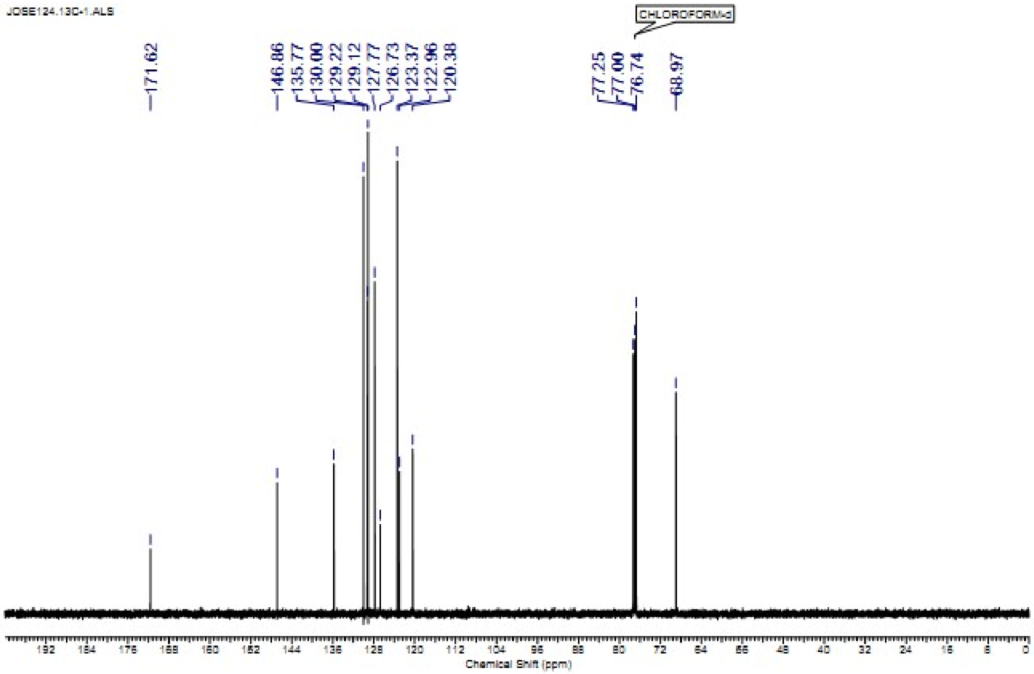

TN_1410.PTLC.ALS
CHLOROFORM-d
7.74
7.72
7.72
7.47
7.45
7.43
7.41
7.27
5.24
2.36
0.95
2.05
2.00
2.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

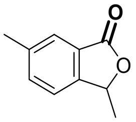

TN_1410.C.ALS
CHLOROFORM-d
171.44
145.45
134.64
132.33
129.20
125.34
122.99
77.32
77.00
76.69
69.02
17.34
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O

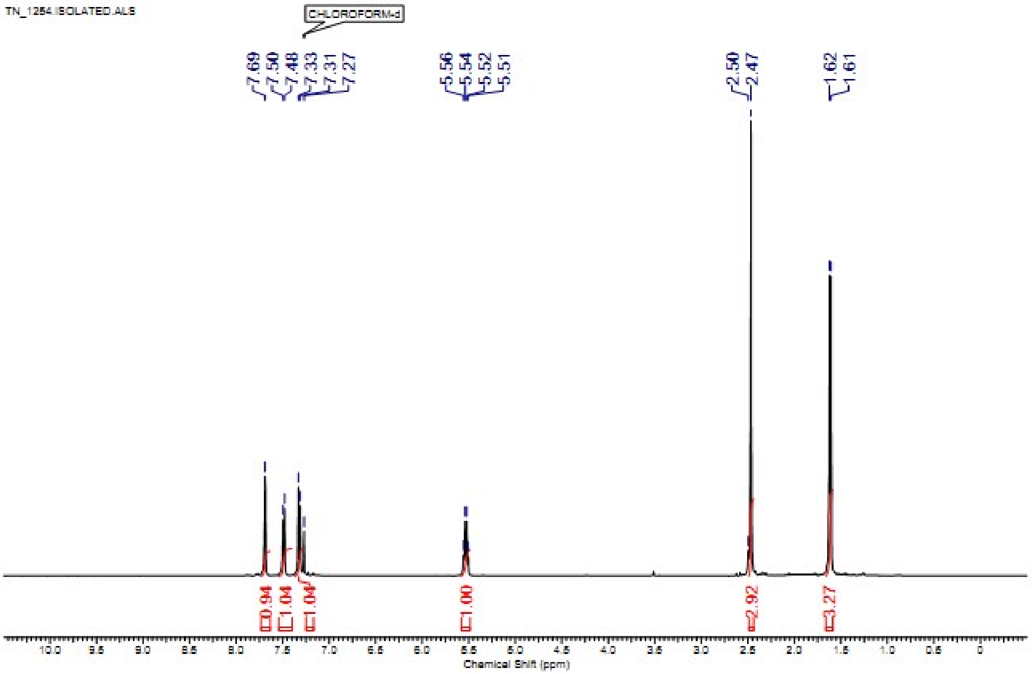
2i

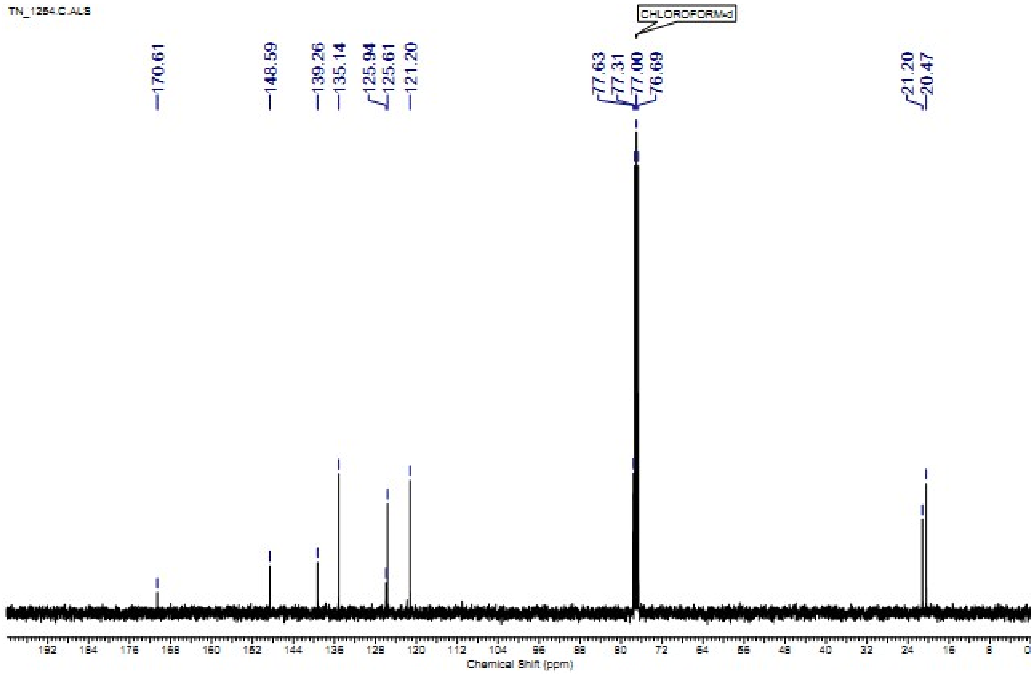

JOSE124.1H-1.ALS
CHLOROFORM-d
8.01
7.99
7.94
7.92
7.82
7.81
7.71
7.67
7.66
7.27
5.60
1.00
0.98
1.90
1.92
1.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

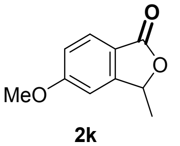

JOSE124.13C-1.ALS
CHLOROFORM-d
171.62
146.86
135.77
130.00
129.22
129.12
127.77
126.73
123.37
122.96
120.38
77.25
77.00
76.74
68.97
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O

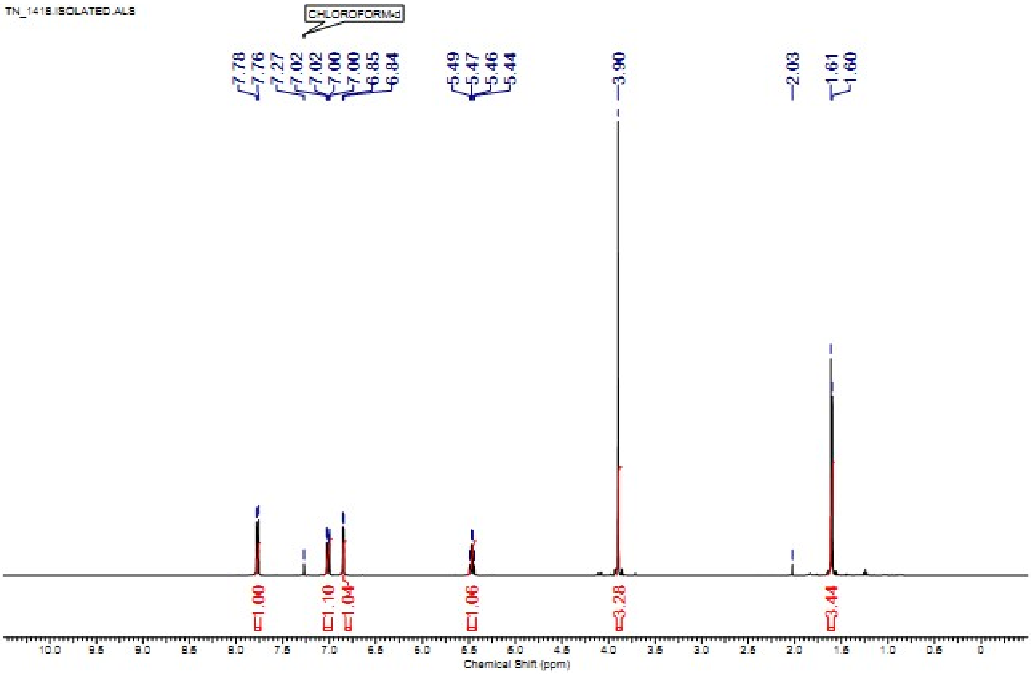
2j

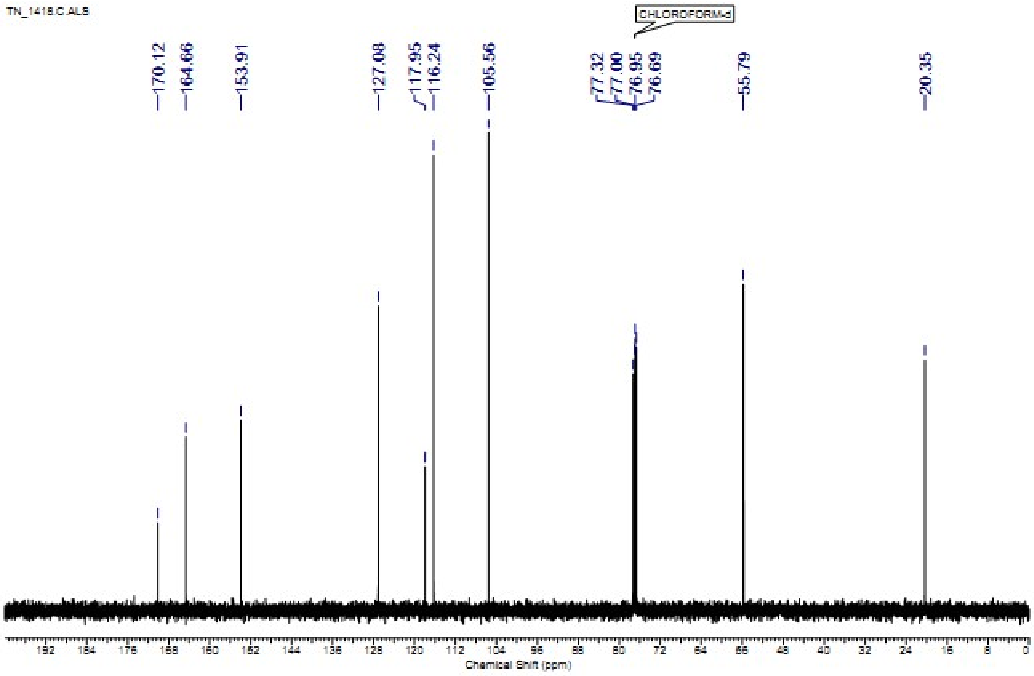

TN_1254.ISOLATED.ALS
CHLOROFORM-d
7.69
7.50
7.48
7.33
7.31
7.27
5.56
5.54
5.52
5.51
2.50
2.47
1.62
1.61
0.94
1.04
1.04
1.00
2.92
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

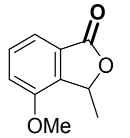

TN_1254.C.ALS
CHLOROFORM-d
170.61
148.59
139.26
135.14
125.94
125.61
121.20
77.63
77.31
77.00
76.69
21.20
20.47
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
MeO

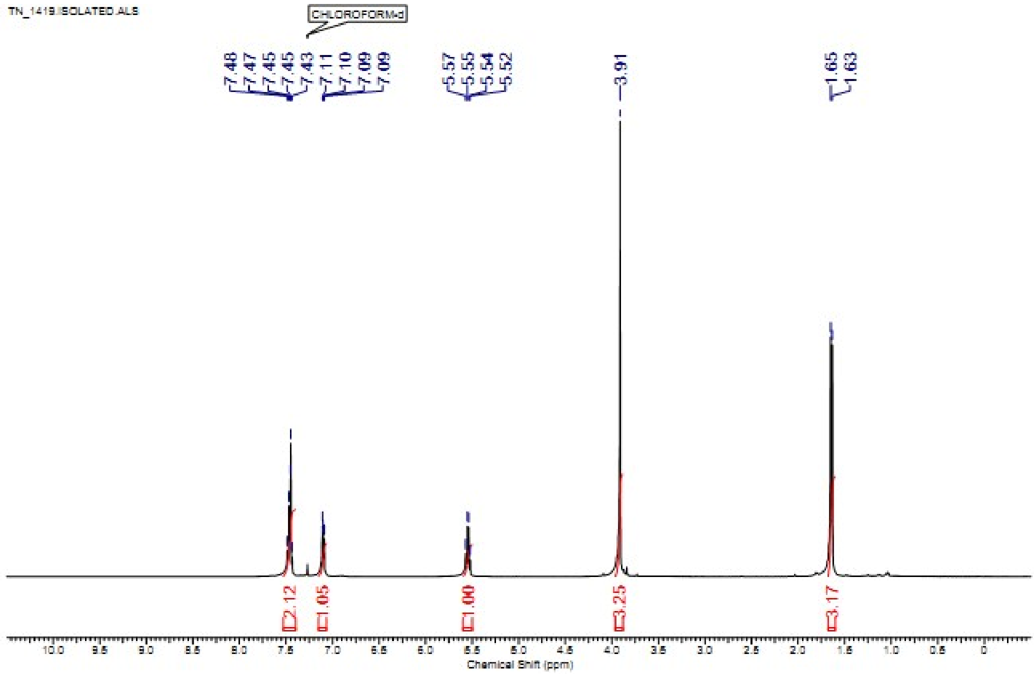
2k

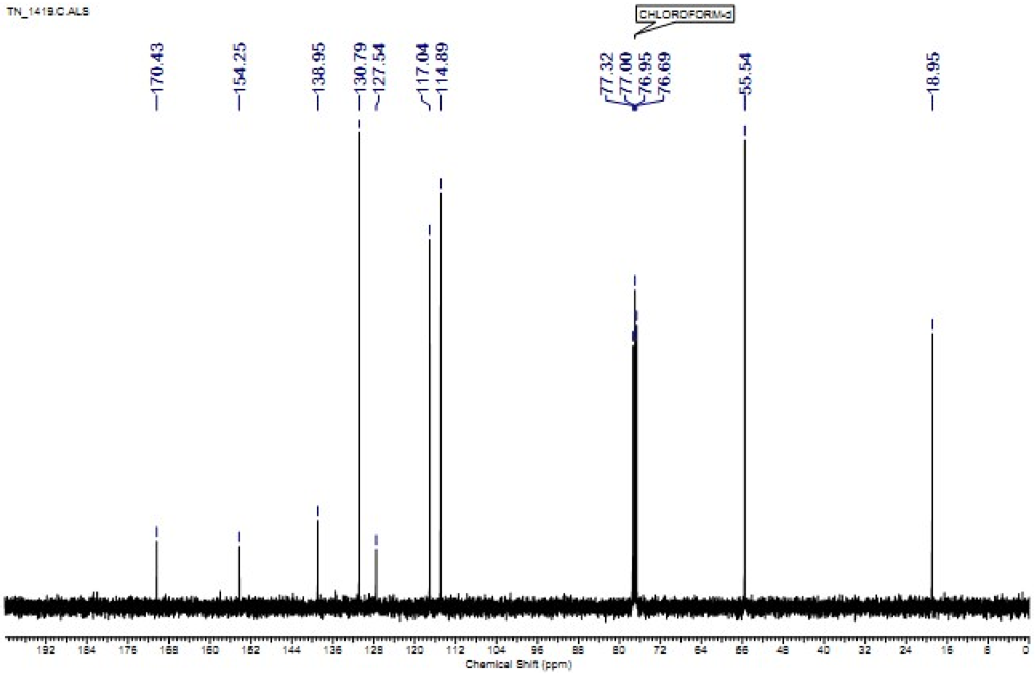

TN_141S.ISOLATED.ALS
CHLOROFORM-d
7.78
7.76
7.27
7.02
7.02
7.00
7.00
6.85
6.84
5.49
5.47
5.46
5.44
3.90
2.03
1.61
1.60
1.00
1.10
1.04
1.06
3.28
3.44
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

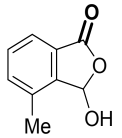

TN_141S.C.ALS
CHLOROFORM-d
170.12
164.66
153.91
127.08
117.95
116.24
105.56
77.32
77.00
76.95
76.69
55.79
20.35
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
OMe

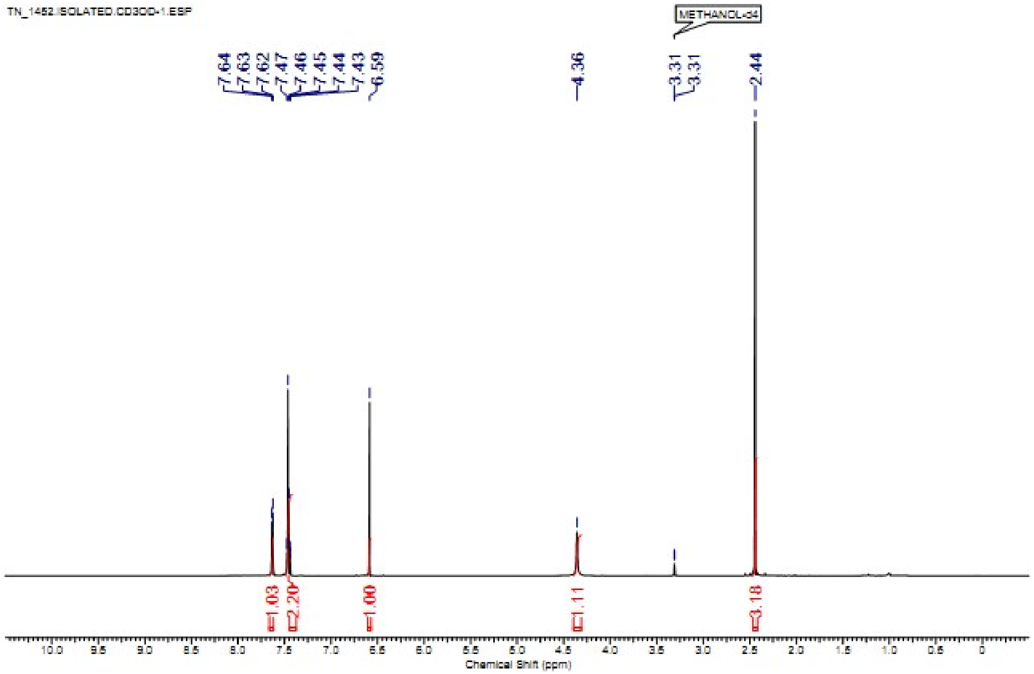
2l

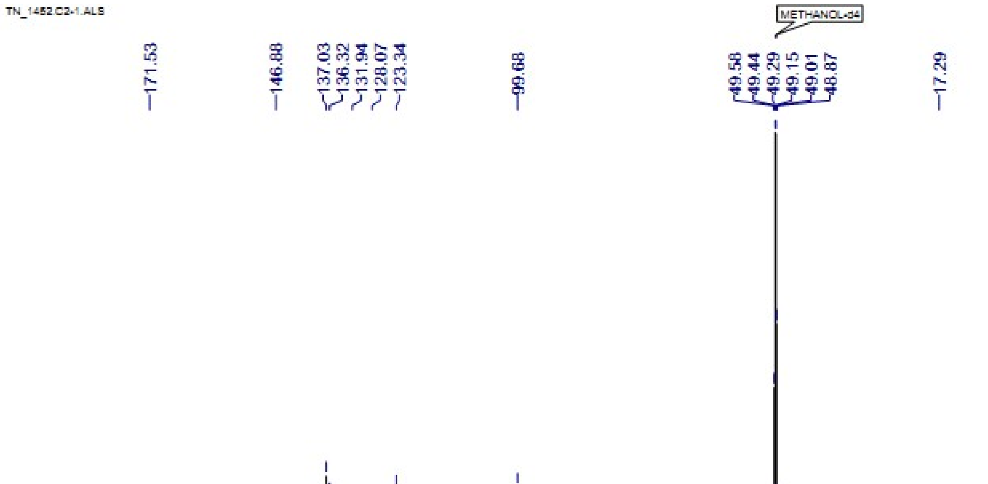

TN_1419.ISOLATED.ALS
CHLOROFORM-d
7.48
7.47
7.45
7.45
7.43
7.11
7.10
7.09
7.09
5.57
5.55
5.54
5.52
3.91
1.65
1.63
2.12
1.05
1.00
3.25
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

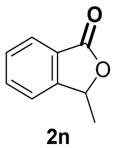

TN_1419.C.ALS
CHLOROFORM-d
170.43
154.25
138.95
130.79
127.54
117.04
114.89
77.32
77.00
76.95
76.69
55.54
18.95
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


O
O
Me
OH

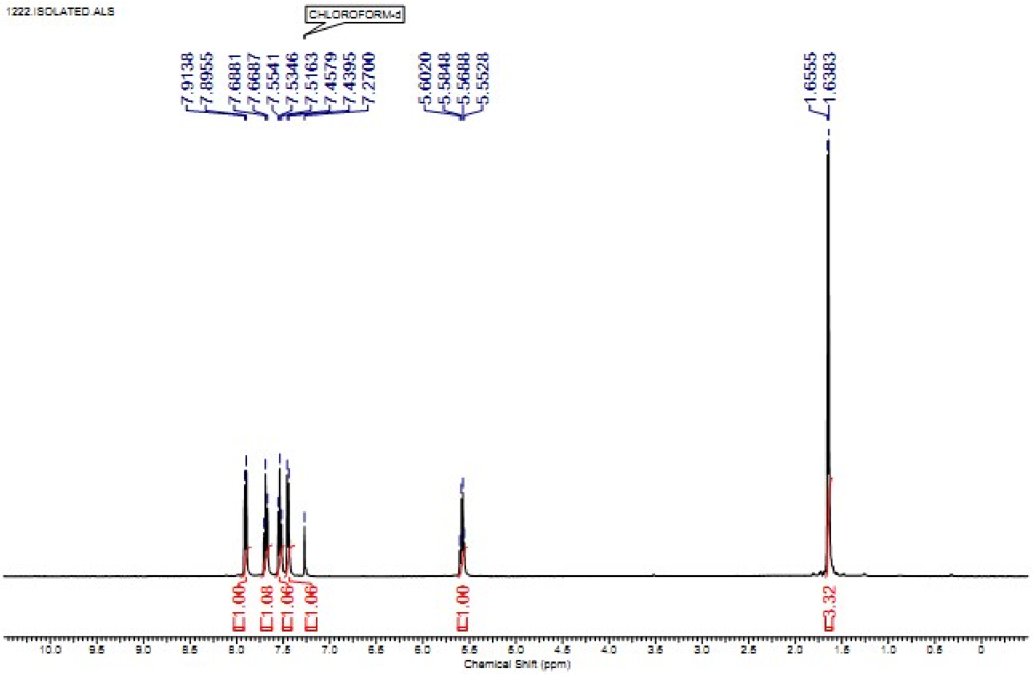
2m

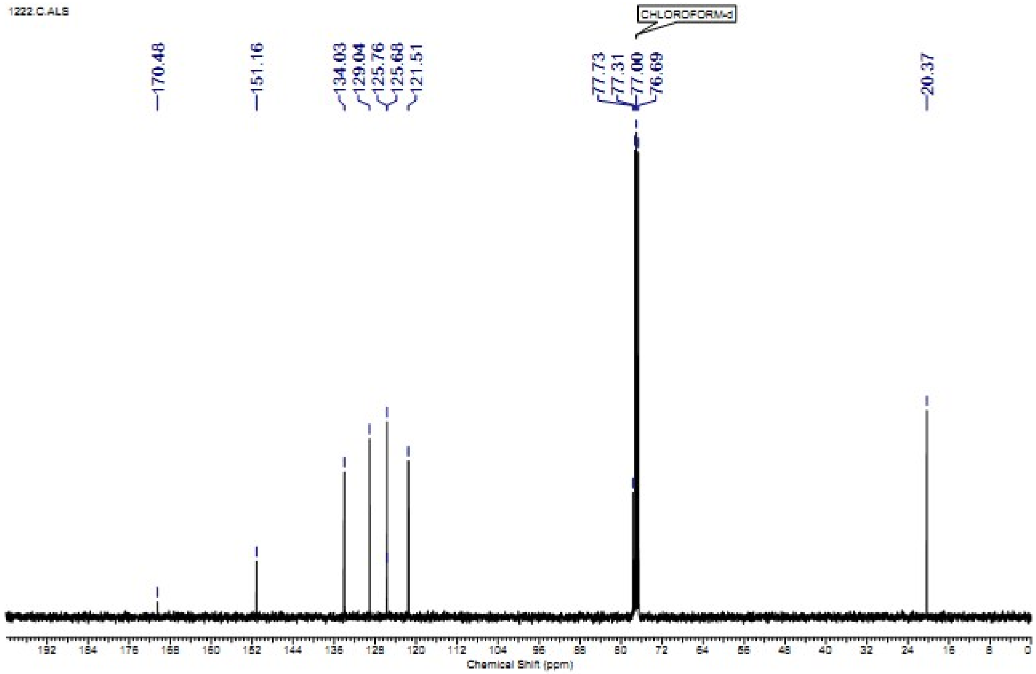

TN_1452.ISOLATED.CD3OD-1.ESP
METHANOL-d4
7.64
7.63
7.62
7.47
7.46
7.45
7.44
7.43
6.59
4.36
3.31
3.31
2.44
1.03
2.20
1.00
1.11
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

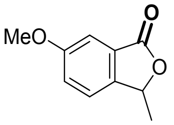

TN_1452.C2-1.ALS
METHANOL-d4
171.53
146.88
137.03
136.32
131.94
128.07
123.34
99.68
49.58
49.44
49.29
49.15
49.01
48.87
17.29
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O

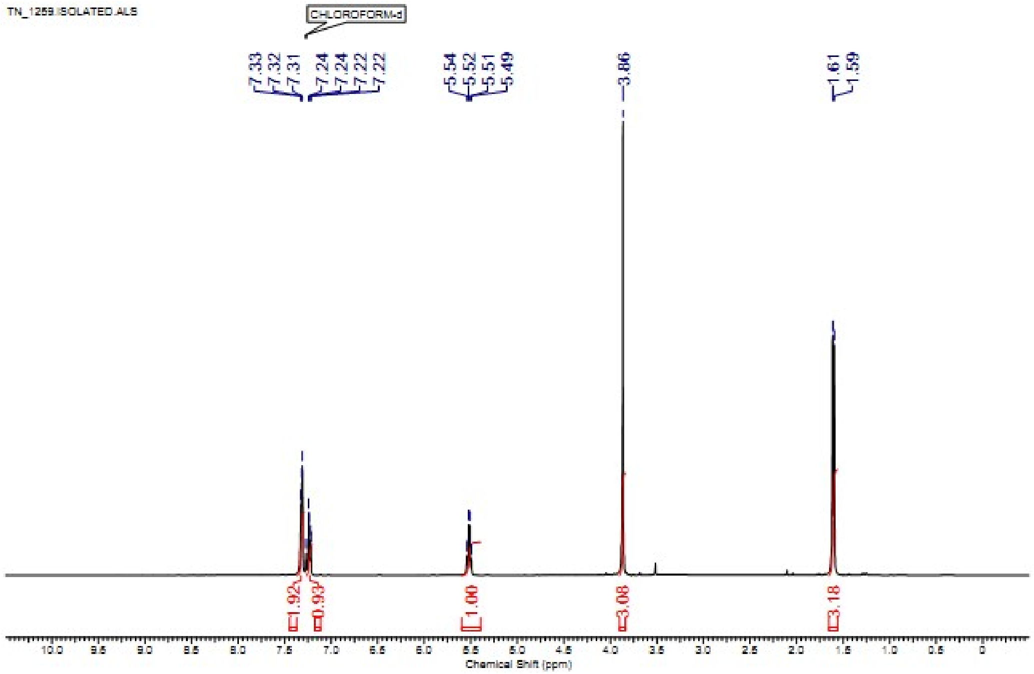
2n

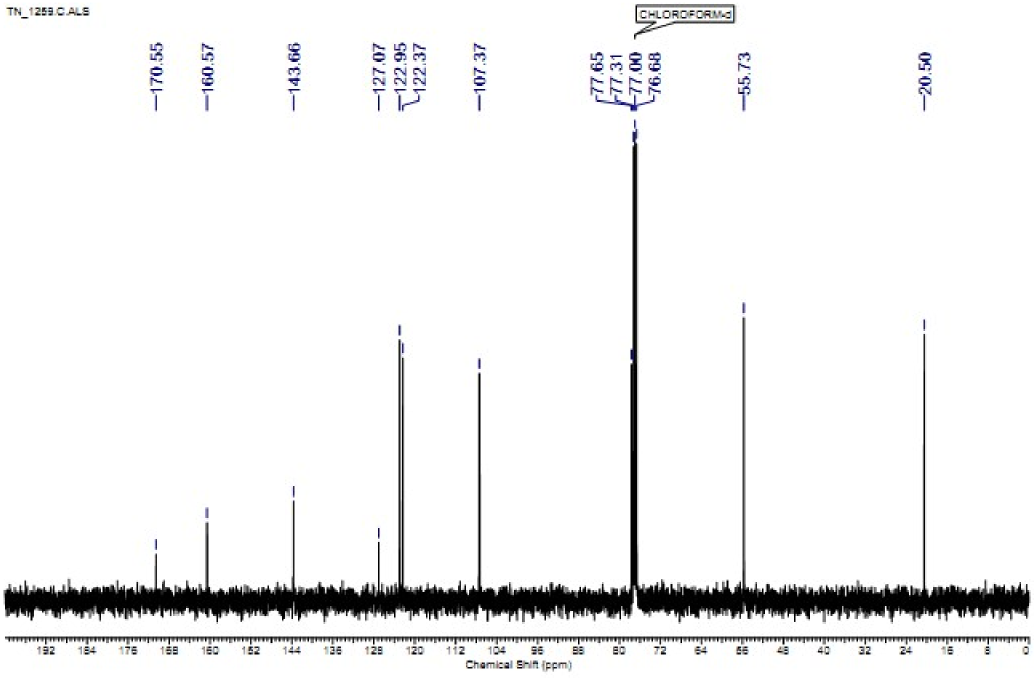

1222.ISOLATED.ALS
CHLOROFORM-d
7.9138
7.8955
7.6881
7.6687
7.5541
7.5346
7.5163
7.4579
7.4395
7.2700
5.6020
5.5848
5.5688
5.5528
1.6555
1.6383
1.00
1.08
1.06
1.06
1.00
3.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

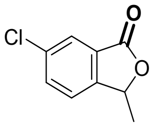

1222.C.ALS
CHLOROFORM-d
170.48
151.16
134.03
129.04
125.76
125.68
121.51
77.73
77.31
77.00
76.69
20.37
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


MeO
O
O

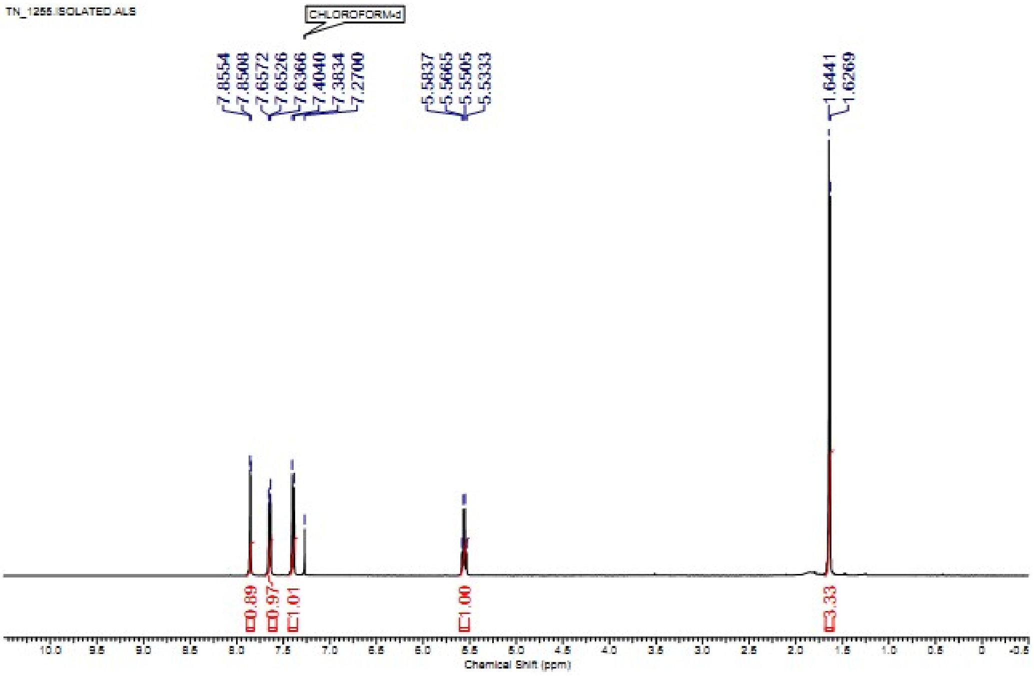
2o

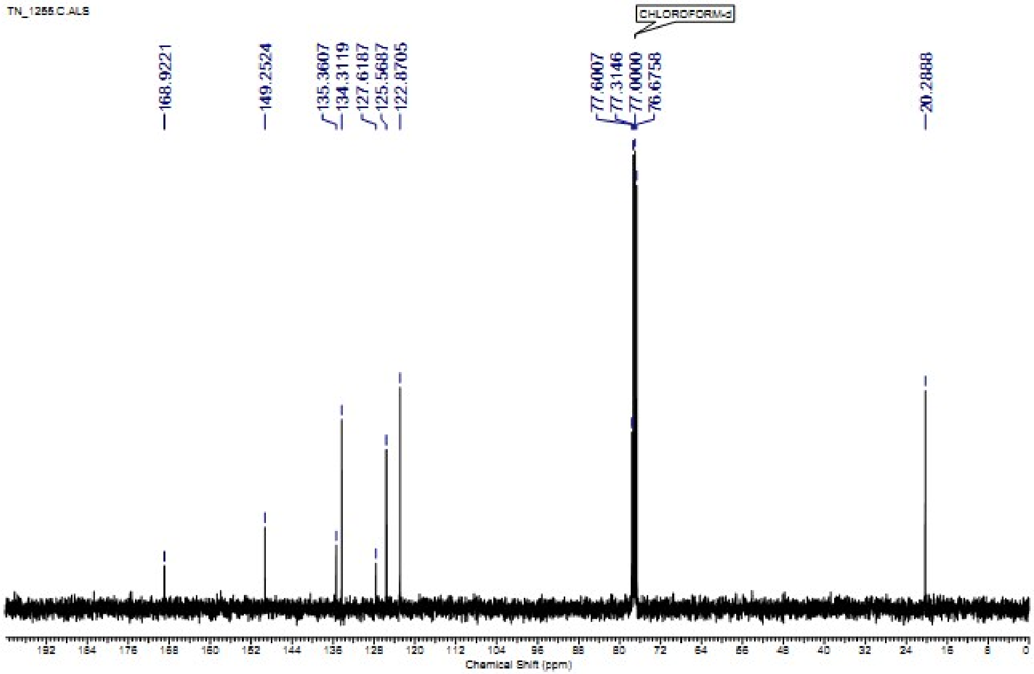

TN_1259.ISOLATED.ALS
CHLOROFORM-d
7.33
7.32
7.31
7.24
7.24
7.22
7.22
5.54
5.52
5.51
5.49
3.86
1.61
1.59
1.92
0.93
1.00
3.08
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

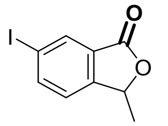

TN_1259.C.ALS
CHLOROFORM-d
170.55
160.57
143.66
127.07
122.95
122.37
107.37
77.65
77.31
77.00
76.68
55.73
20.50
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Cl
O
O

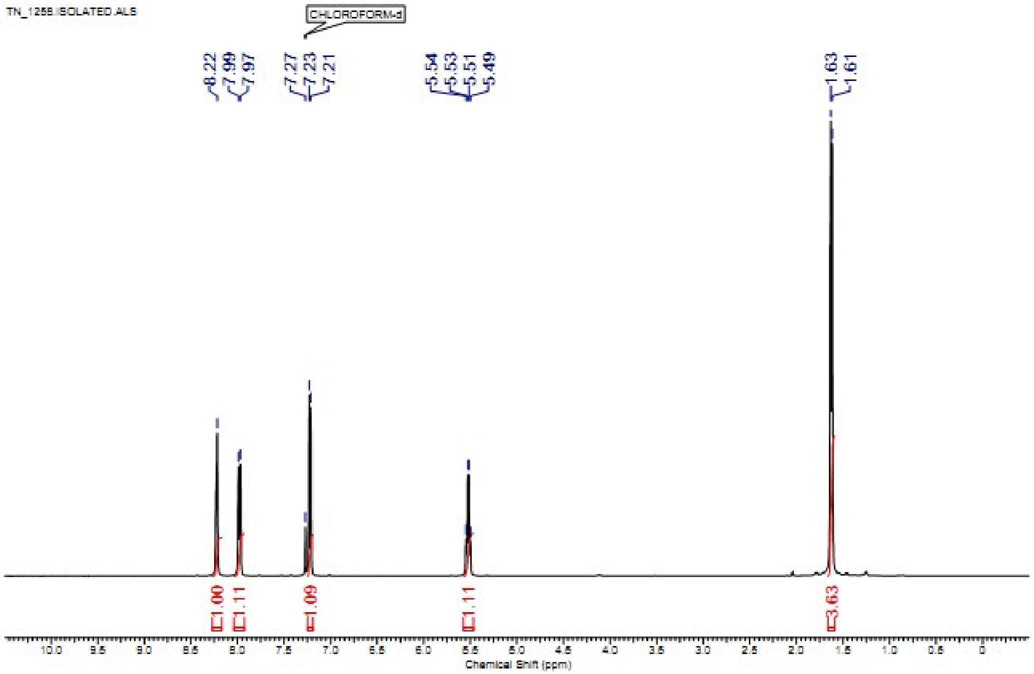
2p

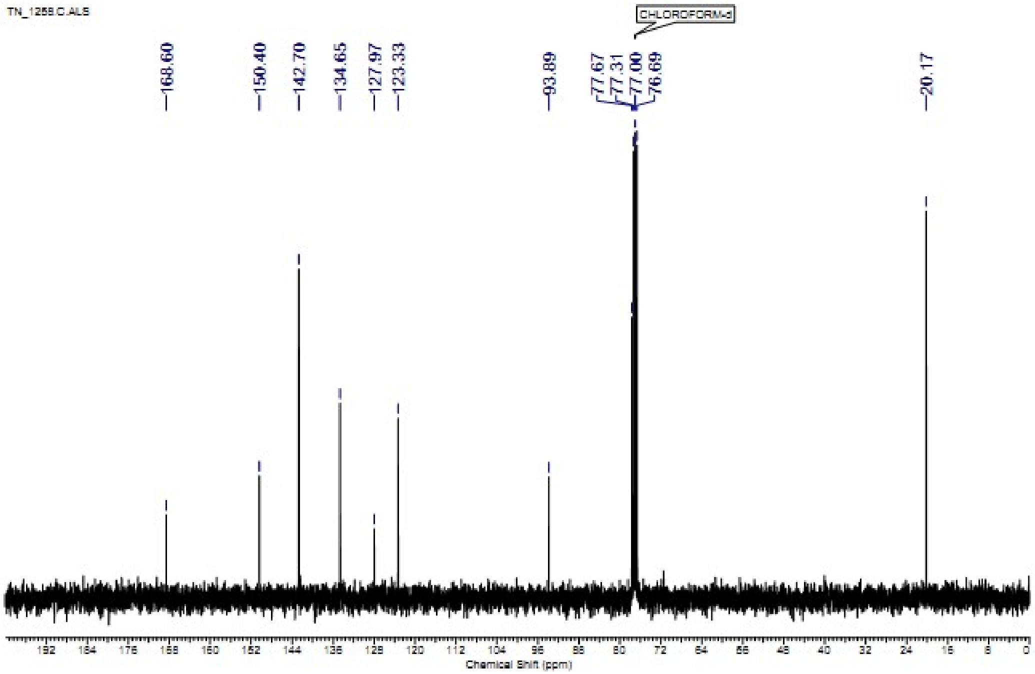

TN_1255.ISOLATED.ALS
CHLOROFORM-d
7.8554
7.8508
7.6572
7.6526
7.6366
7.4040
7.3834
7.2700
5.5837
5.5665
5.5505
5.5333
1.6441
1.6269
0.89
0.97
1.01
1.00
3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

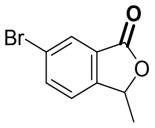

TN_1255.C.ALS
CHLOROFORM-d
168.9221
149.2524
135.3607
134.3119
127.6187
125.5687
122.8705
77.6007
77.3146
77.0000
76.6758
20.2888
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


I
O
O

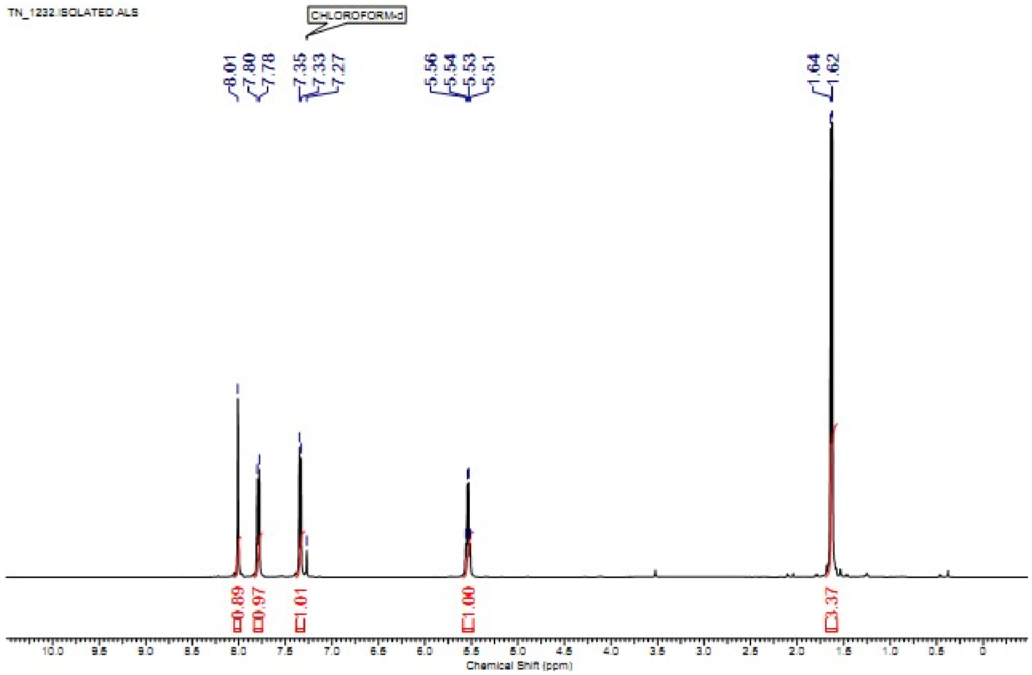
2q

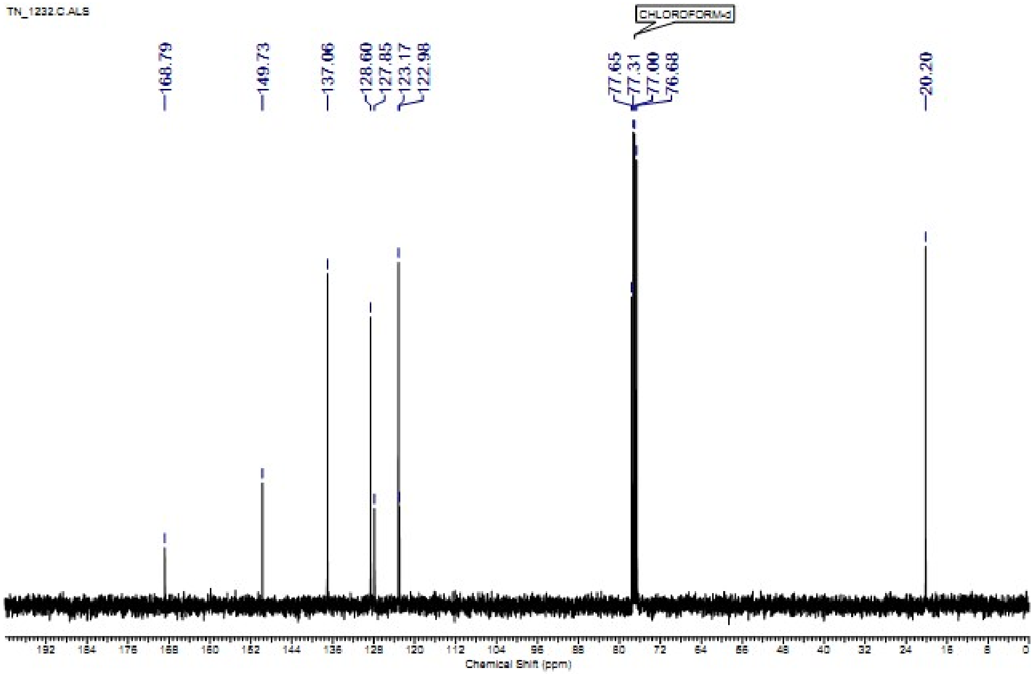

TN_1258 ISOLATED.ALS
CHLOROFORM-d
8.22
7.99
7.97
7.27
7.23
7.21
5.54
5.53
5.51
5.49
1.63
1.61
1.00
1.11
1.09
1.11
3.63
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

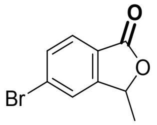

TN_1258.C.ALS
CHLOROFORM-d
168.60
150.40
142.70
134.65
127.97
123.33
93.89
77.67
77.31
77.00
76.69
20.17
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


Br
O
O

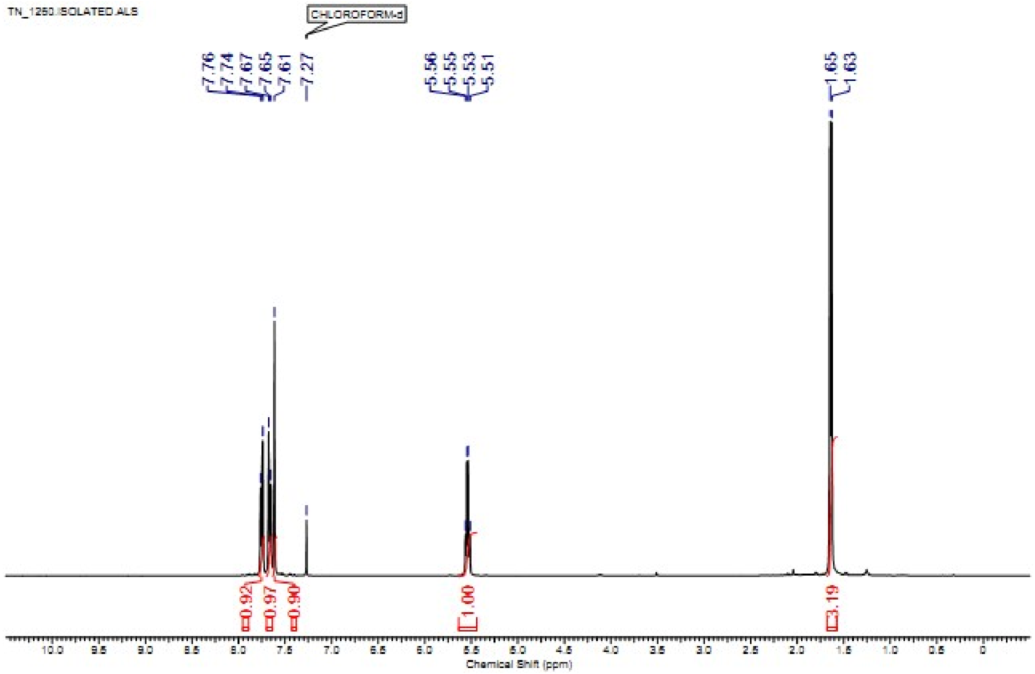
2r

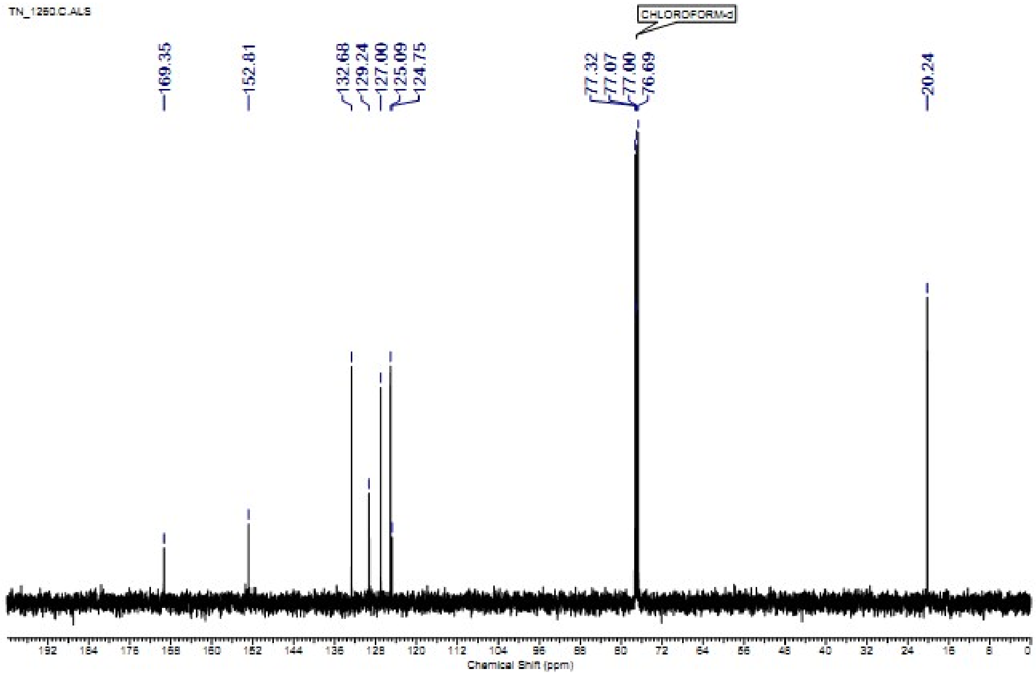

TN_1232 ISOLATED.ALS
CHLOROFORM-d
8.01
7.80
7.78
7.35
7.33
7.27
5.56
5.54
5.53
5.51
1.64
1.62
0.89
0.97
1.01
1.00
3.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

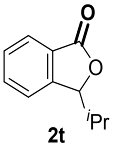

TN_1232 C.ALS
CHLOROFORM-d
168.79
149.73
137.06
128.60
127.85
123.17
122.98
77.65
77.31
77.00
76.68
20.20
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
Br

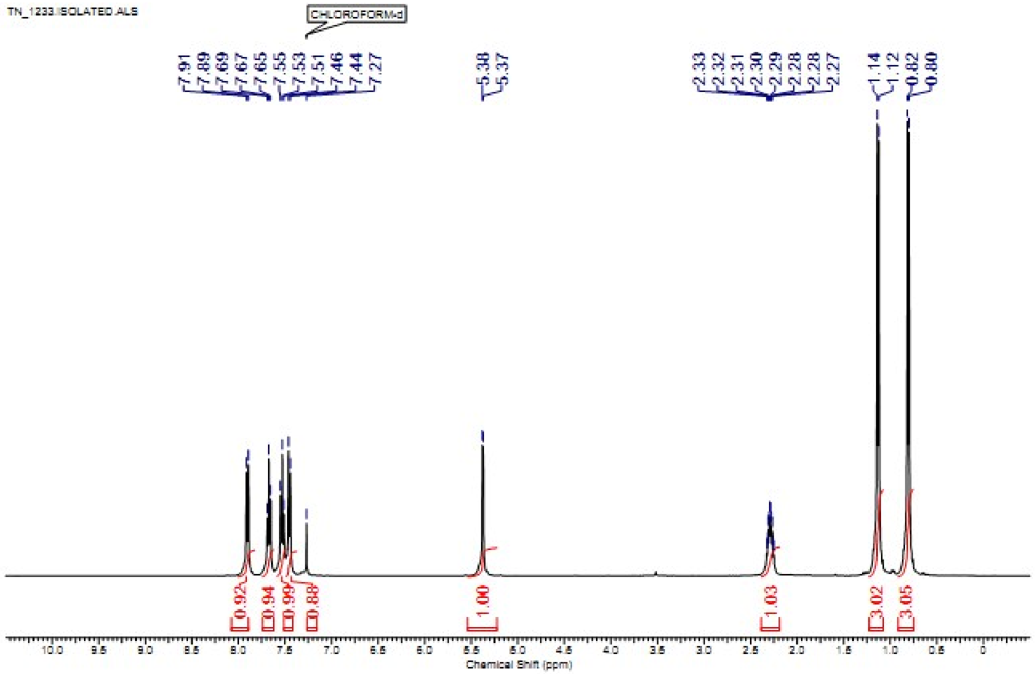
2s

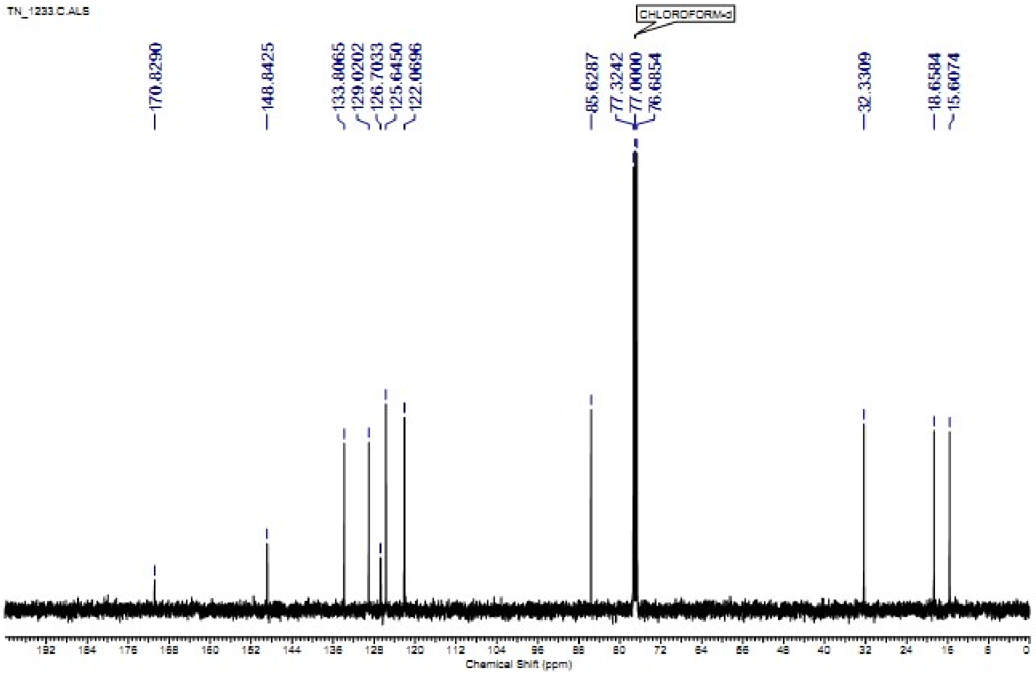

TN_1250.ISOLATED.ALS
CHLOROFORM-d
7.76
7.74
7.67
7.65
7.61
7.27
5.56
5.55
5.53
5.51
1.65
1.63
0.92
0.97
0.90
1.00
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

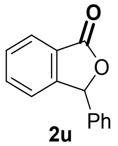

TN_1250.C.ALS
CHLOROFORM-d
169.35
152.81
132.68
129.24
127.00
125.09
124.75
77.32
77.07
77.00
76.69
20.24
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


O
O
^{i}Pr

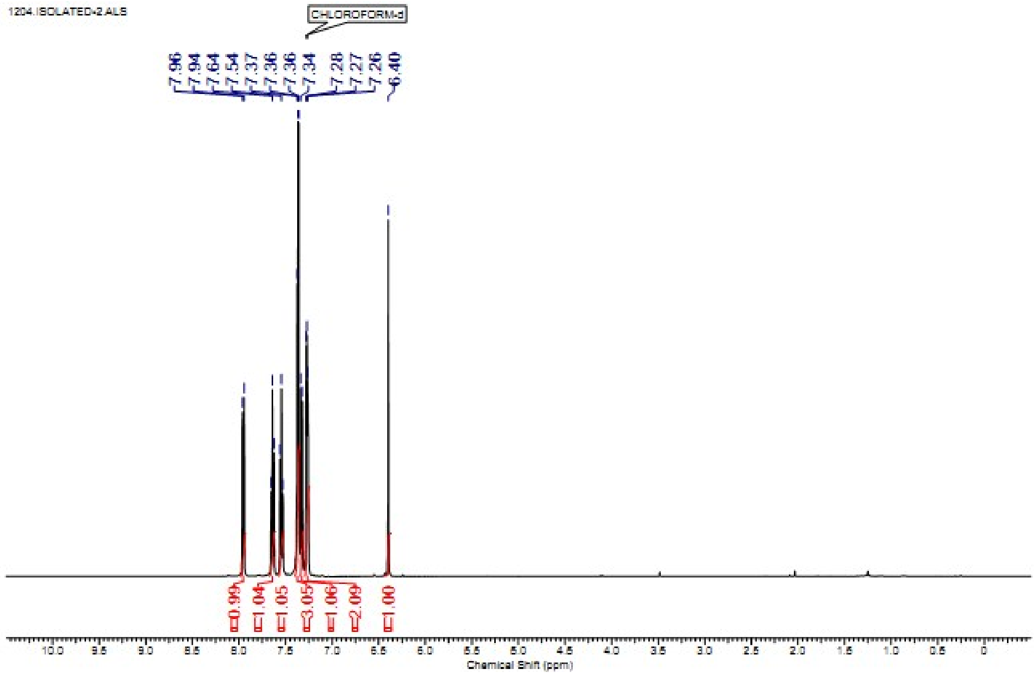
2t

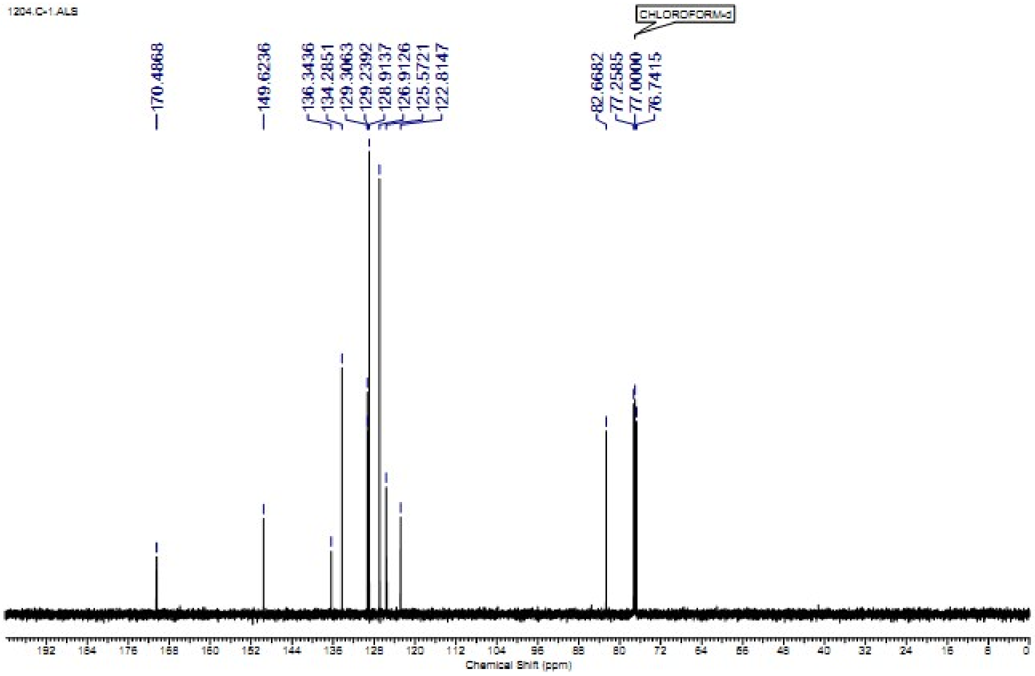

TN_1233.ISOLATED.ALS
CHLOROFORM-d
7.91
7.89
7.69
7.67
7.65
7.55
7.53
7.51
7.46
7.44
7.27
5.38
5.37
2.33
2.32
2.31
2.30
2.29
2.28
2.28
2.27
1.14
1.12
0.82
0.80
0.92
0.94
0.99
0.88
1.00
1.03
3.02
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

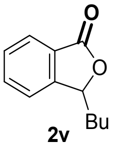

TN_1233.C.ALS
CHLOROFORM-d
170.8290
148.8425
133.8065
129.0202
126.7033
125.6450
122.0696
85.6287
77.3242
77.0000
76.6854
32.3309
18.6584
15.6074
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
Ph

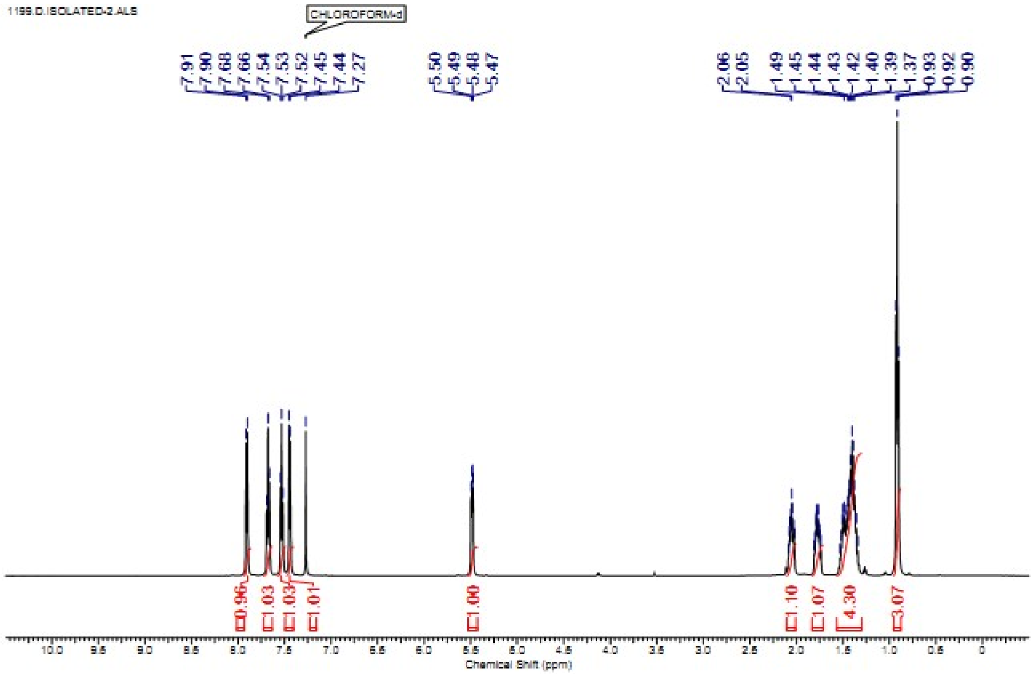
2u

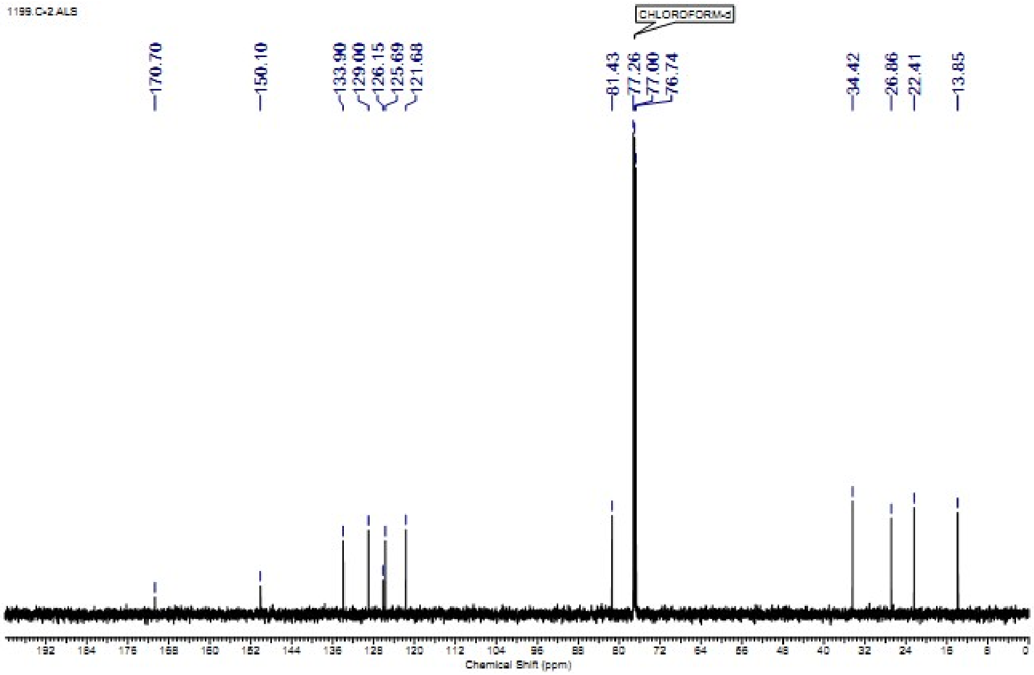

1204.ISOLATED-2.ALS
CHLOROFORM-d
7.96
7.94
7.64
7.54
7.37
7.36
7.36
7.34
7.28
7.27
7.26
6.40
0.99
1.04
1.05
3.05
1.06
2.09
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

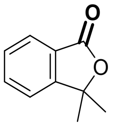

1204.C-1.ALS
CHLOROFORM-d
170.4868
149.6236
136.3436
134.2851
129.3063
129.2392
128.9137
126.9126
125.5721
122.8147
82.6682
77.2585
77.0000
76.7415
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O
Bu

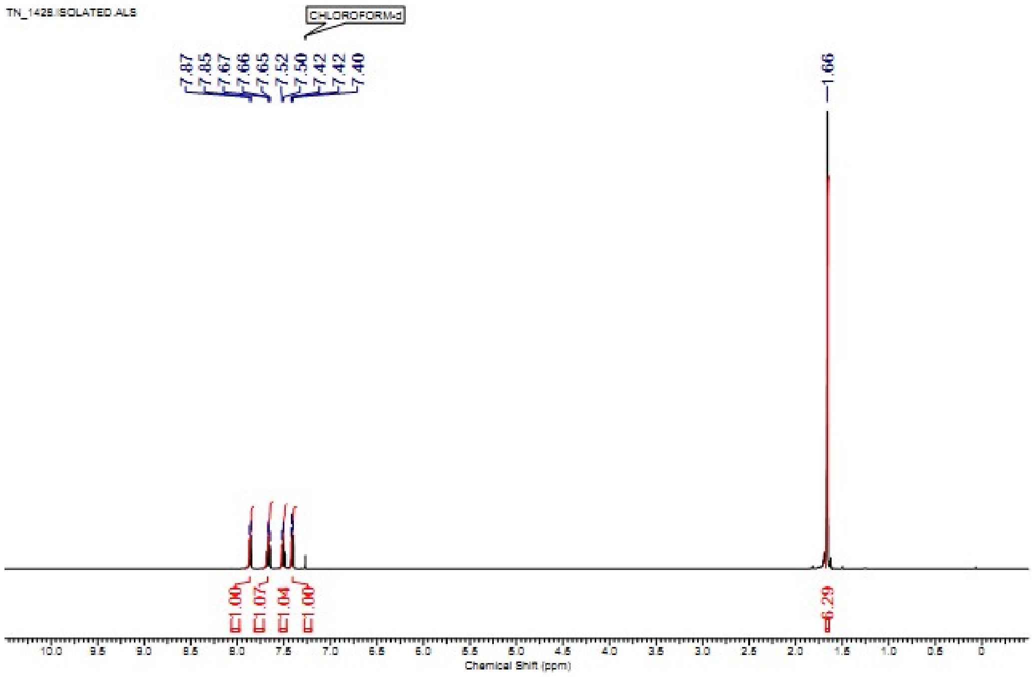
2v

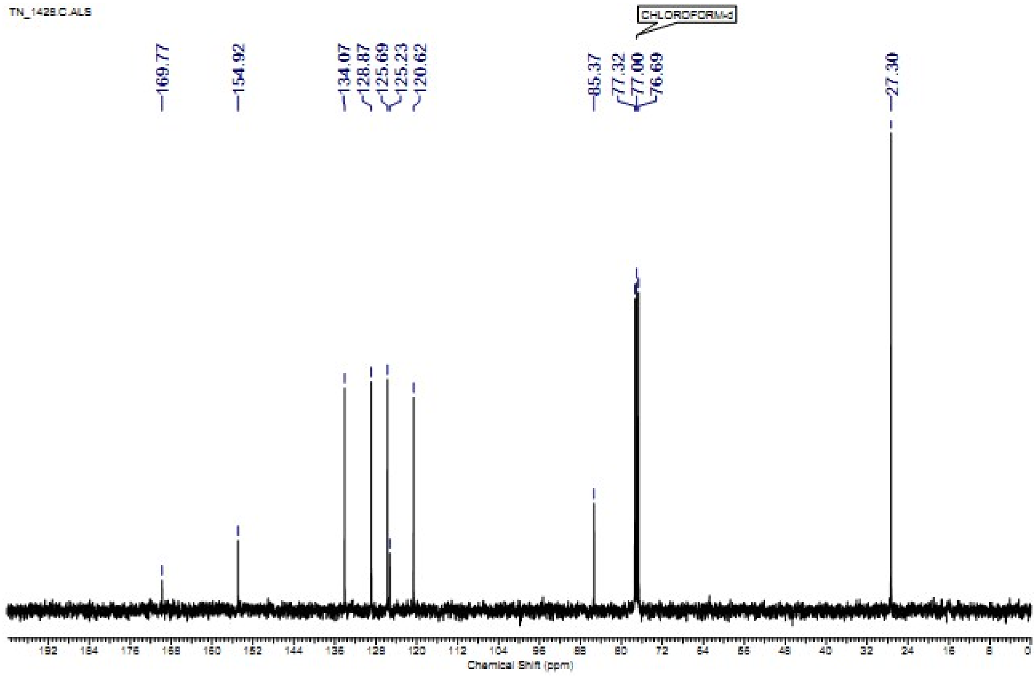

1199.D.ISOLATED-2.ALS
CHLOROFORM-d
7.91
7.90
7.68
7.66
7.54
7.53
7.52
7.45
7.44
7.27
5.50
5.49
5.48
5.47
2.06
2.05
1.49
1.45
1.44
1.43
1.42
1.40
1.39
1.37
0.93
0.92
0.90
0.96
1.03
1.03
1.01
1.00
1.10
1.07
4.30
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

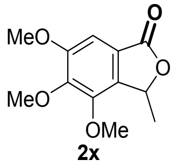

1199.C-2.ALS
CHLOROFORM-d
170.70
150.10
133.90
129.00
126.15
125.69
121.68
81.43
77.26
77.00
76.74
34.42
26.86
22.41
13.85
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
O

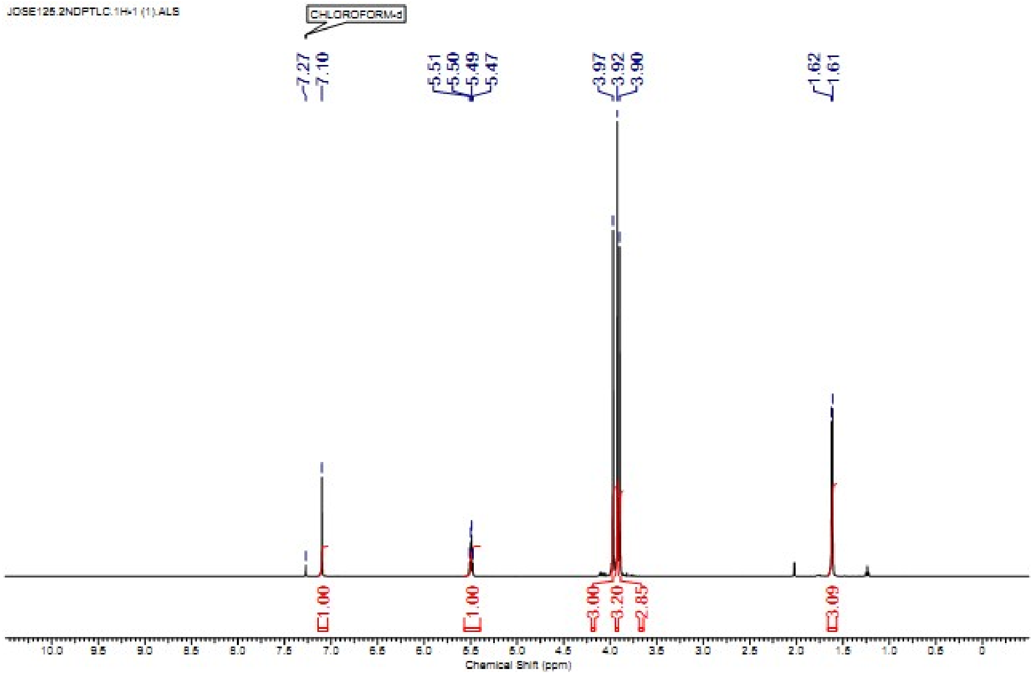
2w

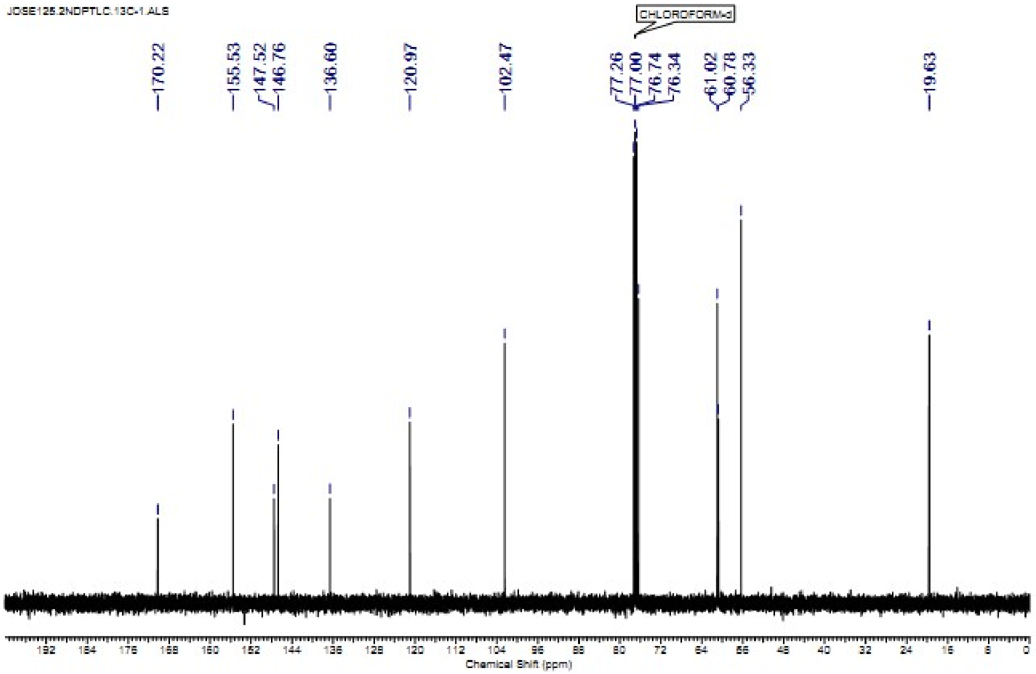

TN_1428.ISOLATED.ALS
CHLOROFORM-d
7.87
7.85
7.67
7.66
7.65
7.52
7.50
7.42
7.42
7.40
1.66
1.00
1.07
1.04
1.00
6.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

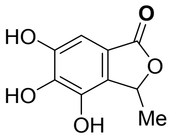

TN_1428.C.ALS
CHLOROFORM-d
169.77
154.92
134.07
128.87
125.69
125.23
120.62
85.37
77.32
77.00
76.69
27.30
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O
MeO
O
MeO
OMe

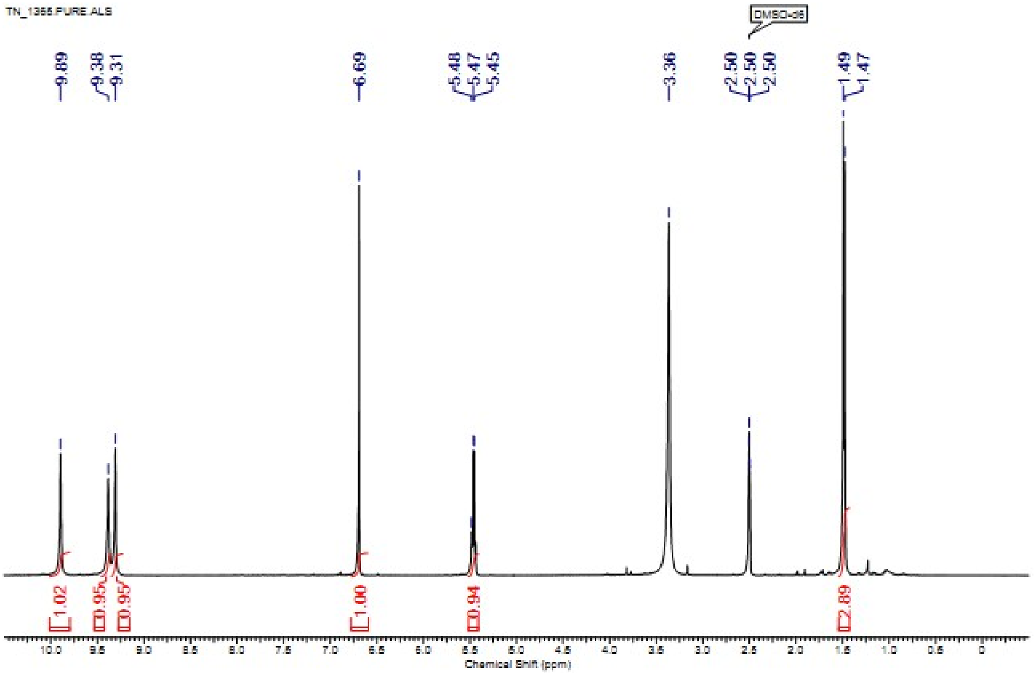
2x

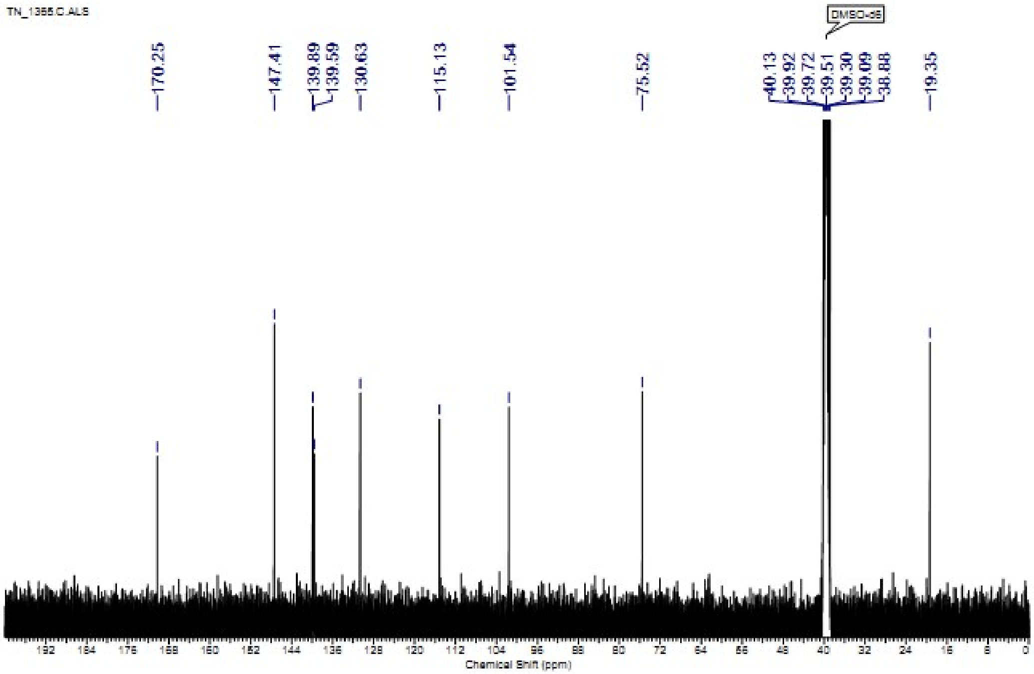

JOSE125.2NDPTLC.1H-1 (1).ALS
CHLOROFORM-d
7.27
7.10
5.51
5.50
5.49
5.47
3.97
3.92
3.90
1.62
1.61
1.00
1.00
3.00
3.20
2.85
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

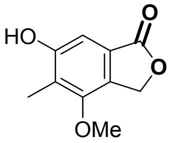

JOSE125.2NDPTLC.13C-1.ALS
CHLOROFORM-d
170.22
155.53
147.52
146.76
136.60
120.97
102.47
77.26
77.00
76.74
76.34
61.02
60.78
56.33
19.63
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


O
HO
O
HO
OH
Me

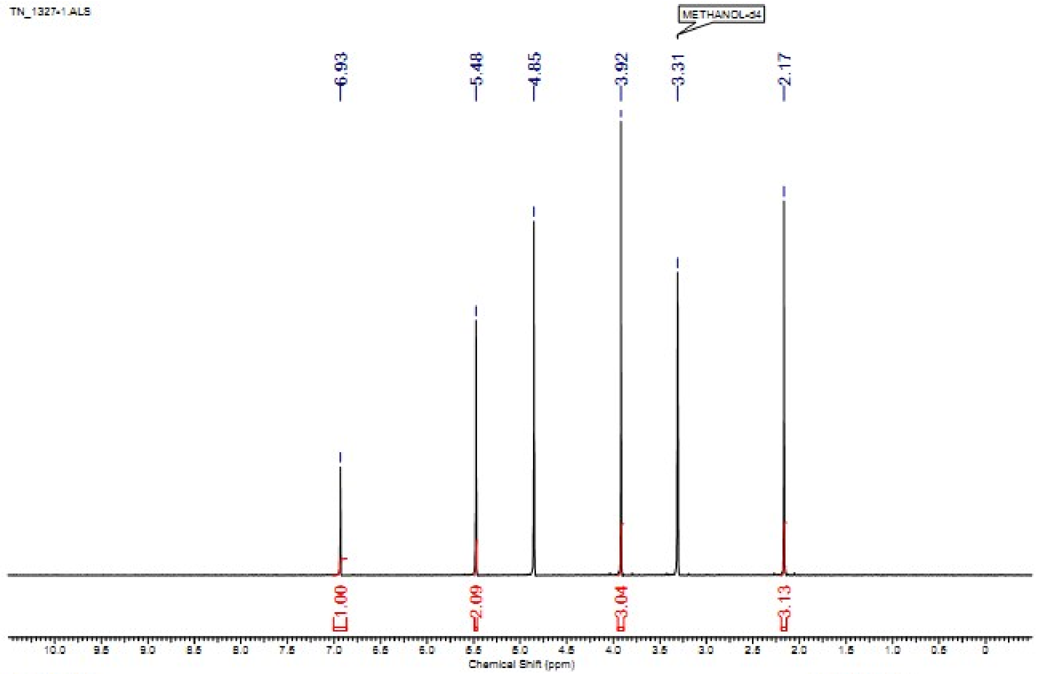
4

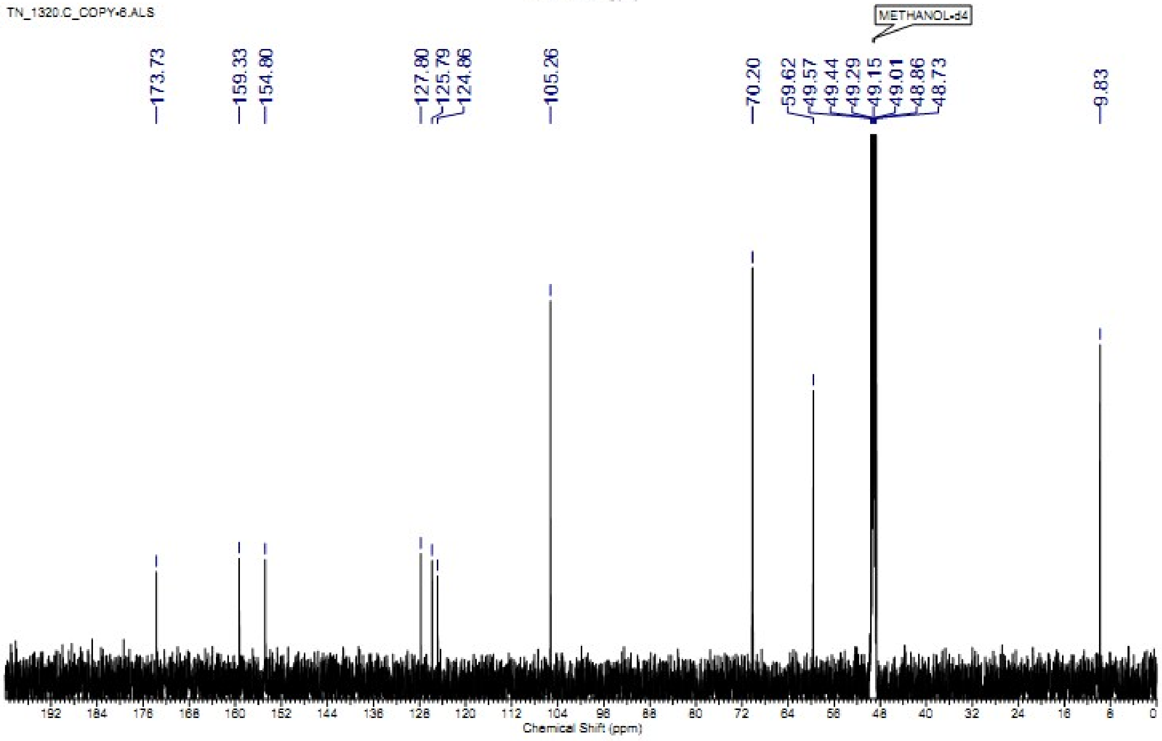

TN_1355.PURE.ALS
DMSO-d6
9.89
9.38
9.31
6.69
5.48
5.47
5.45
3.36
2.50
2.50
2.50
1.49
1.47
1.02
0.95
0.95
1.00
0.94
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

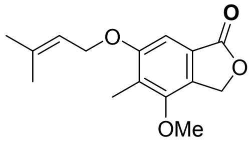

TN_1355.C.ALS
DMSO-d6
170.25
147.41
139.89
139.59
130.63
115.13
101.54
75.52
40.13
39.92
39.72
39.51
39.30
39.09
38.88
19.35
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


HO
O
O
OMe

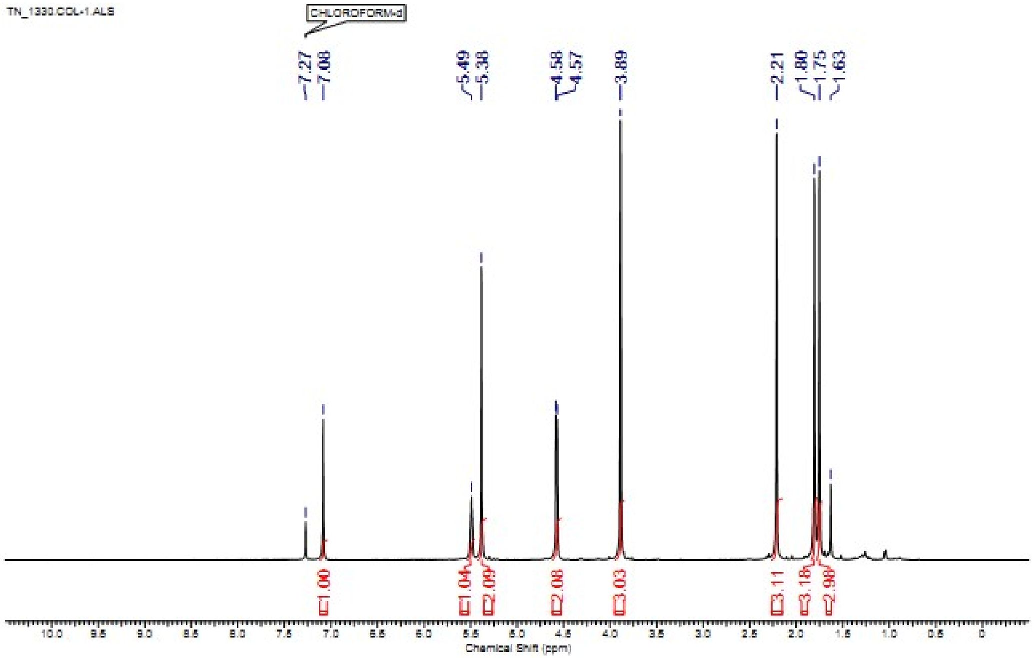
2y

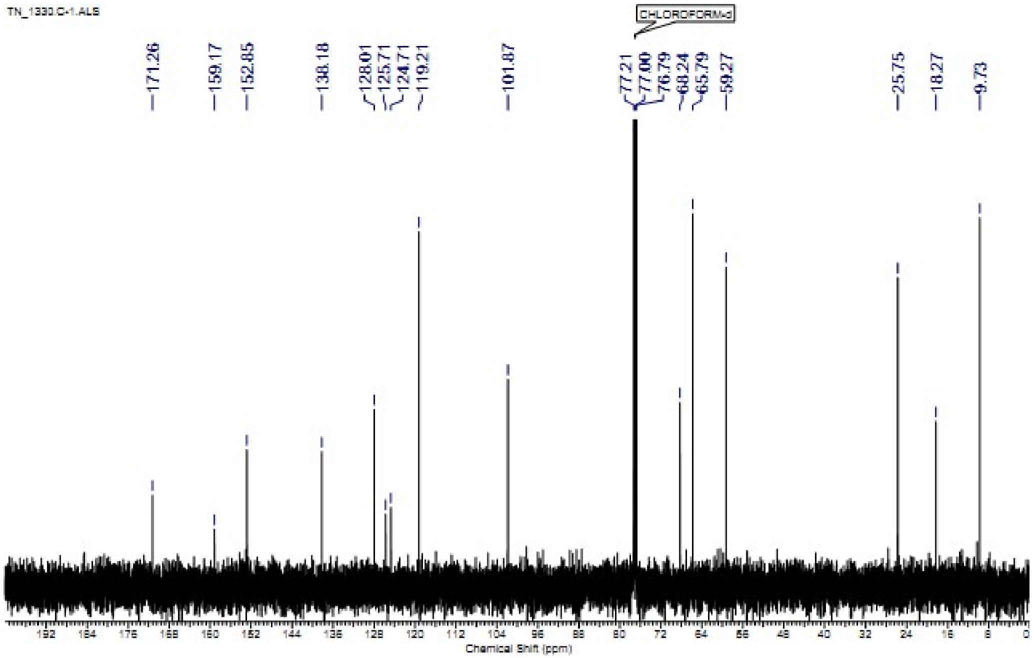

TN_1327-1.ALS
METHANOL-d4
6.93
5.48
4.85
3.92
3.31
2.17
1.00
2.09
3.04
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

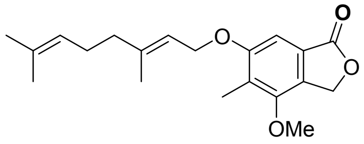

TN_1320.C_COPY-6.ALS
METHANOL-d4
173.73
159.33
154.80
127.80
125.79
124.86
105.26
70.20
59.62
49.57
49.44
49.29
49.15
49.01
48.86
48.73
9.83
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


O
O
O
OMe

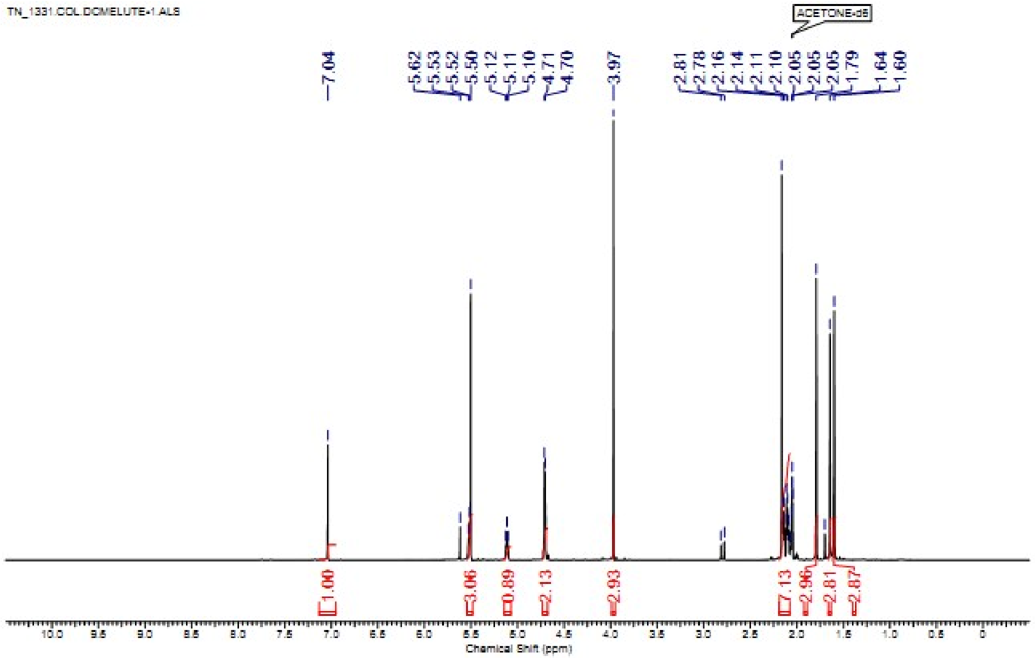
5

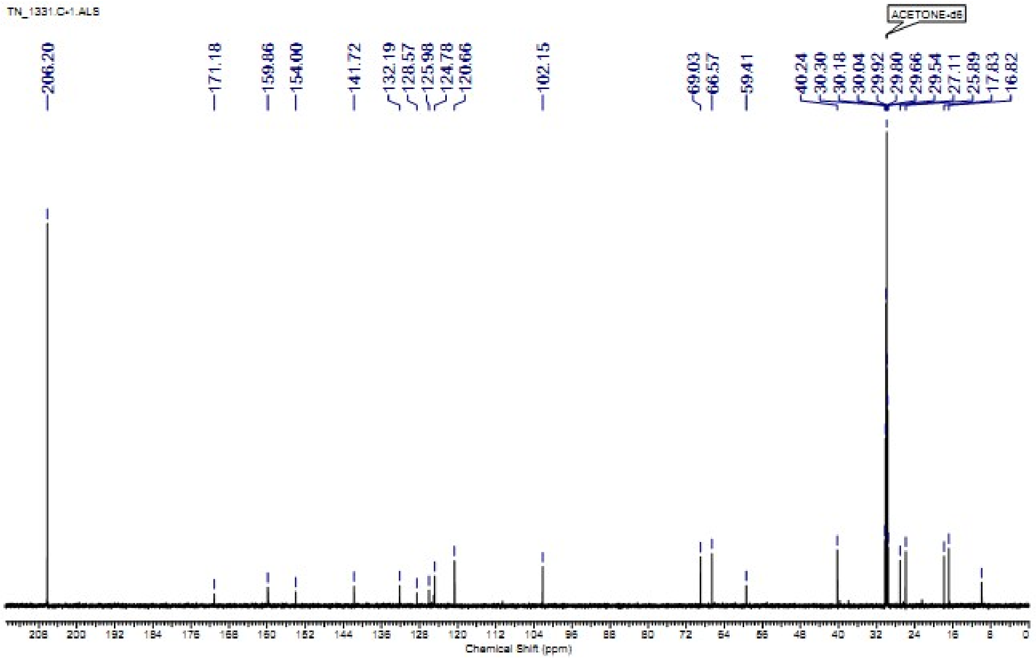

TN_1330.CDL-1.ALS
CHLOROFORM-d
7.27
7.08
5.49
5.38
4.58
4.57
3.89
2.21
1.80
1.75
1.63
1.00
1.04
2.09
2.08
3.03
3.11
3.18
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


TN_1330.C-1.ALS
CHLOROFORM-d
171.26
159.17
152.85
138.18
128.01
125.71
124.71
119.21
101.87
77.21
77.00
76.79
68.24
65.79
59.27
25.75
18.27
9.73
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

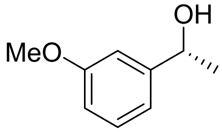

O
O
O
OMe

6


TN_1331.COL.DCMELUTE-1.ALS
ACETONE-d6
7.04
5.62
5.53
5.52
5.50
5.12
5.11
5.10
4.71
4.70
3.97
2.81
2.78
2.16
2.14
2.11
2.10
2.05
2.05
2.05
1.79
1.64
1.60
1.00
3.06
0.89
2.13
2.93
7.13
2.96
2.81
2.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

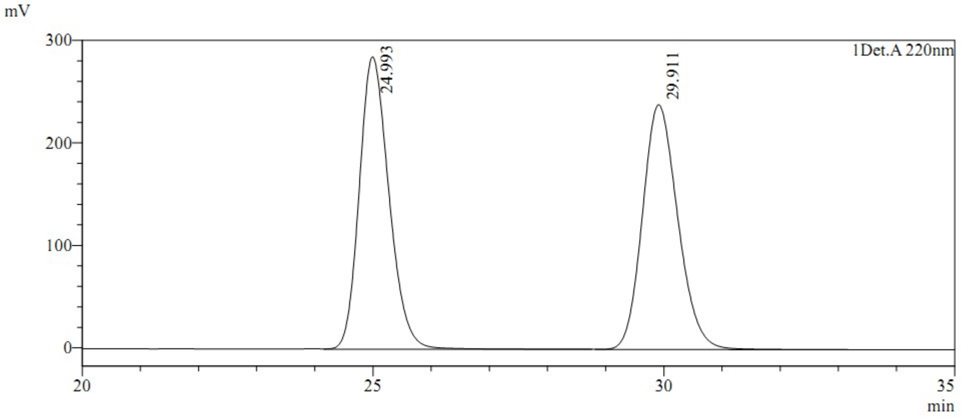

TN_1331.C-1.ALS
ACETONE-d6
206.20
171.18
159.86
154.00
141.72
132.19
128.57
125.98
124.78
120.66
102.15
69.03
66.57
59.41
40.24
30.30
30.18
30.04
29.92
29.80
29.66
29.54
27.11
25.89
17.83
16.82
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

Part VIII: HPLC Traces of Chiral Alcohols and Phthalides



HPLC condition: OD-H, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min, t_1 = 24.993, t_2 = 29.911

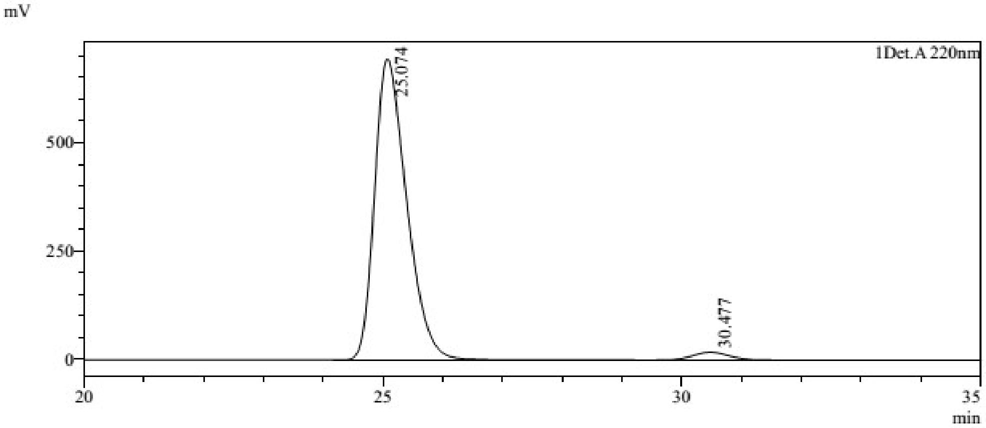
HPLC chart of racemic alcohol



Det.A 220nm

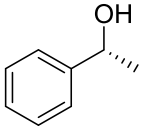
Peak#	Ret. Time	Area	Height	Area%
1	24.993	10119073	285245	49.996
2	29.911	10120787	238889	50.004

HPLC chart of chiral alcohol



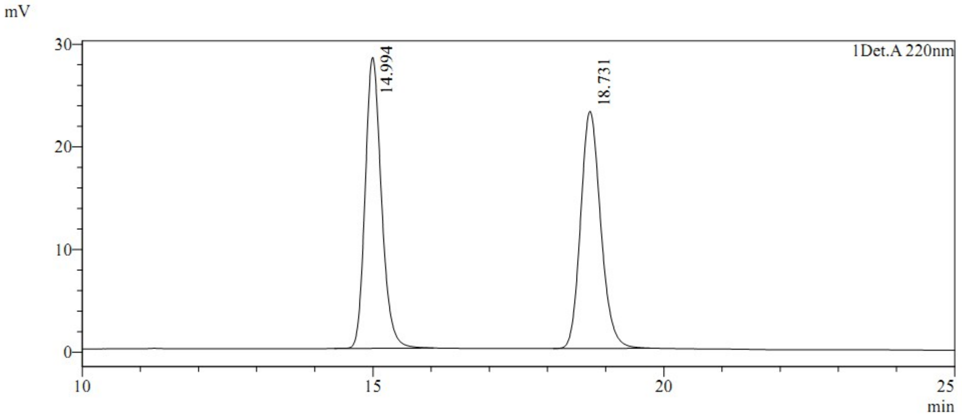
Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	25.074	25983680	694049	97.083
2	30.477	780680	18248	2.917



HPLC condition: OD-H, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min, t_1 = 14.994, t_2 = 18.731

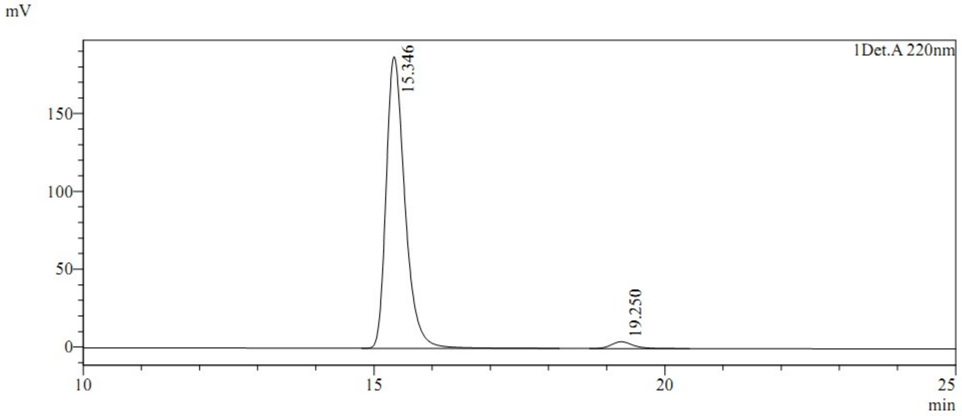
HPLC chart of racemic alcohol:



Det.A 220nm

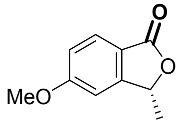
Peak#	Ret. Time	Area	Height	Area%
1	14.994	551402	28339	49.827
2	18.731	555225	23085	50.173

HPLC chart of chiral alcohol



Det.A 220nm

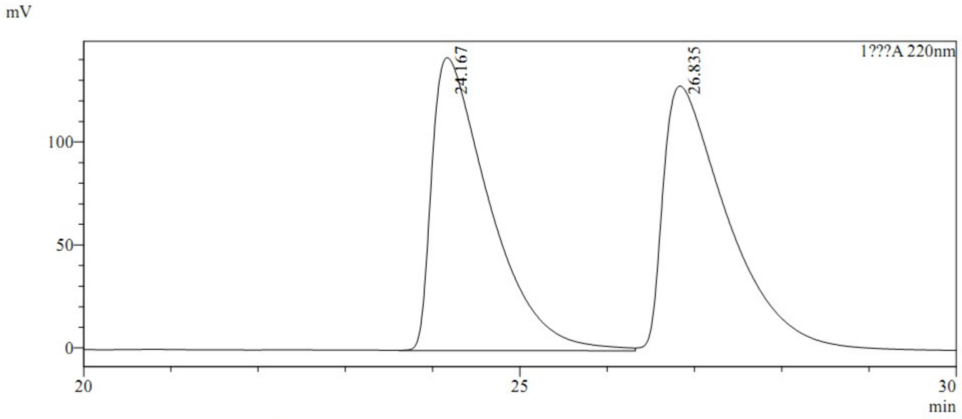
Peak#	Ret. Time	Area	Height	Area%
1	15.346	4207920	187356	97.370
2	19.250	113660	4352	2.630



(R)-**2k**

HPLC Condition: OD-H, ^{i}PrOH:*n*-Hexane = 2:98, 1 mL/min, t_1 = 24.167, t_2 = 26.835

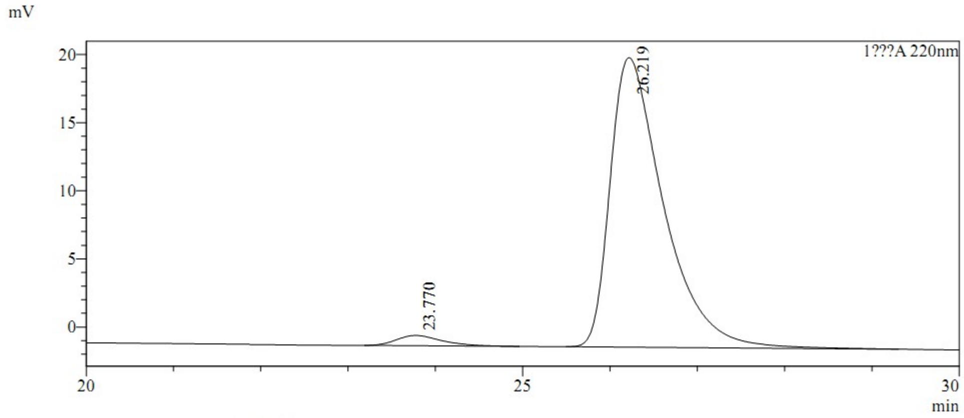
HPLC chart of racemic phthalide:



???A 220nm

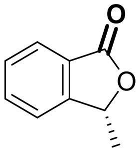
Peak#	Ret. Time	Area	Height	Area%
1	24.167	6564842	142225	49.365
2	26.835	6733773	128662	50.635

HPLC chart of chiral phthalide:



???A 220nm

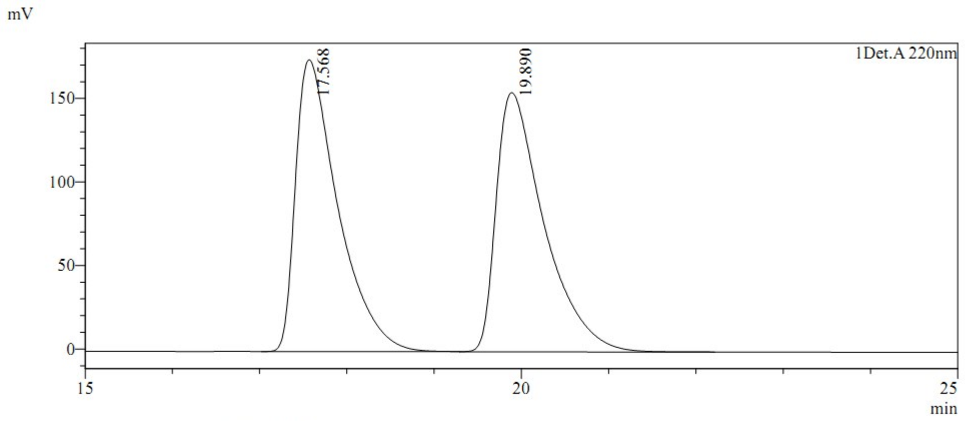
Peak#	Ret. Time	Area	Height	Area%
1	23.770	27122	748	2.905
2	26.219	906473	21259	97.095



(R)-**2n**

HPLC Condition: OD-H, ^{i}PrOH:n-Hexane = 2:98, 1 mL/min, t_1 = 24.167, t_2 = 26.835

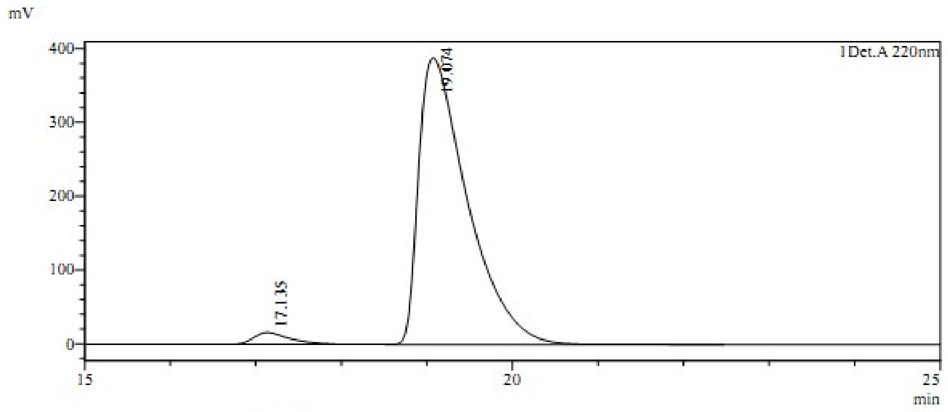
HPLC chart of racemic phthalide:



Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	17.568	5894453	174681	50.002
2	19.890	5893886	155044	49.998

HPLC chart of chiral phthalide:



Det.A 220nm

Peak#	Ret. Time	Area	Height	Area%
1	17.135	484483	16177	3.049
2	19.074	15405299	388113	96.951