Iron(II)-Catalyzed Intermolecular Amino-Oxygenation of Olefins through the N–O Bond Cleavage of Functionalized Hydroxylamines

Deng-Fu Lu, Cheng-Liang Zhu, Zhen-Xin Jia, and Hao Xu*

Department of Chemistry, Georgia State University, Atlanta GA 30303, United States

Supporting Material

A. General Information

B. Catalyst and Amination Reagent Discovery for the Iron-Catalyzed Olefin Amino-Oxygenation

a. Synthesis of New Olefin Amino-Oxygenation Reagents

b. Synthesis of Nitrogen-Based Tri-dentate Ligands

c. Catalyst Discovery for the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

C. Procedures for the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

D. Procedures for the Iron-Catalyzed Asymmetric Olefin Amino-Oxygenation

E. Mechanistic Studies of the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

F. References

G. NMR Spectra

A. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma–Aldrich.

Materials. Commercial reagents were purchased from Sigma Aldrich, Fluka, EM Science, and Lancaster and used as received. All solvents were used after being freshly distilled unless otherwise noted.

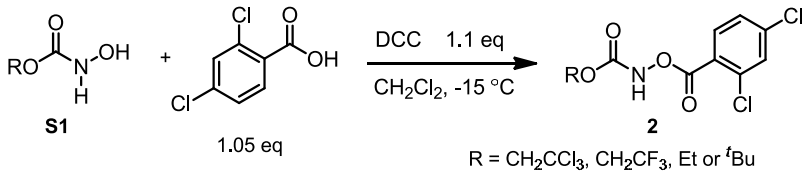
Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra， carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker UltraShield-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CHCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.0). Chemical shifts for fluorine are reported in parts per million downfield and are referenced to the fluorine resonances of $CFCl_3$. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), and integration.

The mass spectroscopic data were obtained at the Georgia State University mass spectrometry facility using a Micromass Platform II single quadruple instrument. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}) and absorption strength (s = strong, m = medium, w = weak).

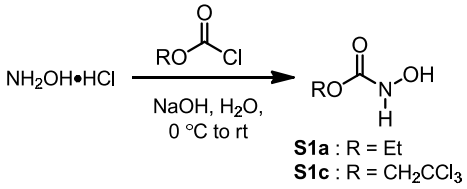
Abbreviations used: EtOH–ethanol, EtOAc–ethyl acetate, THF–tetrahydrofuran, MeOH–methanol, Et_2O–diethyl ether, CH_2Cl_2–dichloromethane, TEA–triethylamine, MeCN–acetonitrile, MS–molecular sieves, CDI–1,1′-carbonyldiimidazole, Troc–2,2,2-trichloroethoxycarbonyl, DCC–*N*,*N*′- dicyclohexylcarbodiimide, TLC–thin layer chromatography，Boc_2O–di-*tert*-butyl dicarbonate, DMAP−4-dimethylaminopyridine.

B. Catalyst and Amino-oxygenation Reagent Discovery for the Iron-Catalyzed Olefin Amino-oxygenation

a. Synthesis of New Amino-oxygenation Reagents



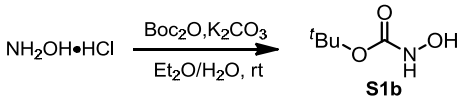
General procedure: To a 250 mL flame-dried round bottom flask equipped with a stir bar, an *N*-hydroxyl carbamate **S1** (20 mmol, 1.0 equiv), 2,4-dichlorobenzoic acid (4.01 g, 21 mmol) and anhydrous CH_2Cl_2 (80 mL) were added. The flask was cooled to -15 °C. DCC (4.53 g, 22 mmol, dissolved in 20 mL of anhydrous CH_2Cl_2) solution was then added drop-wise. The reaction mixture was stirred at the same temperature for additional 30 min until the *N*-hydroxyl carbamate was fully consumed (monitored by TLC). The white precipitate (*N*,*N*′-dicyclohexylurea) was removed by filtration and the filtrate was concentrated *in vacuo* and dissolved again in Et_2O (30 mL). The solution was cooled to -20 ^oC for 2 h and filtered again to remove additional precipitate. The organic layer was then concentrated *in vacuo* and the residue was recrystallized from hexanes and EtOAc to afford corresponding acyloxyl carbamate **2** as a white solid (yield 73–76%).



N-hydroxyl ethyl carbamate **S1a** and *N*-hydroxyl trichloroethyl carbamate **S1b** were prepared from hydroxylamine with the corresponding chloroformates according to a known procedure.[1]

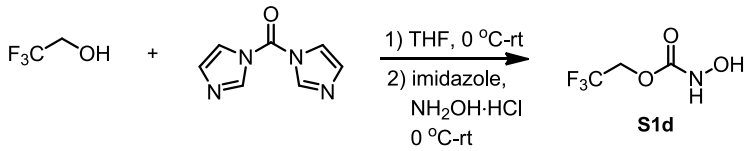
Hydroxylamine hydrochloride (13.9 g, 200 mmol) was added to aqueous solution of NaOH (1.5 M, 160 mL, 240 mmol). The solution was cooled to 0 °C and ethyl or 2,2,2-trichloroethyl chloroformate (38 mmol) was added drop-wise. Upon the completion of addition, the mixture was warmed up to room temperature and stirred for additional 2 h. The reaction was then acidified with aqueous HCl (6 M) till pH is around 4.5. Then the mixture was extracted with

Et_2O (200 mL × 3) and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo*, the *N*-hydroxyl carbamate was used directly without further purification.



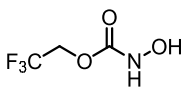
S1b

N-hydroxyl *tert*-butyl carbamate **S1b** was prepared from hydroxylamine hydrochloride with Boc_2O, according to a known procedure.[2] A suspension of $NH_2OH{\cdot}HCl$ (9.6 g, 0.14 mol, 1.5 equiv) and K_2CO_3 (7.2 g, 0.07 mol, 1.5 equiv) in Et_2O (60 mL) and H_2O (2 mL) was stirred for about 1 h at room temperature with evolution of CO_2 gas. A solution of Boc_2O (20.0 g, 92 mmol) in Et_2O (40 mL) was then added drop-wise at 0 °C and the suspension was stirred at room temperature for 12 h. The organic phase was decanted and the solid was washed with Et_2O (30 mL × 2) and the organic layers were combined and concentrated. Recrystallization with a cyclohexane/toluene mixture afforded the desired product **S1b**.



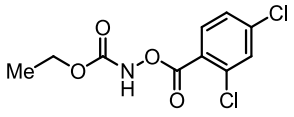
S1d

Procedure for the preparation of *N*-hydroxyl trifluoroethyl carbamate (**S1d**): To a flame-dried 100 mL round bottom flask equipped with a stir bar was added CDI (1.78 g, 11 mmol) in anhydrous THF (30 mL). The flask was cooled to 0 °C and trifluoroethanol (0.72 mL, 10 mmol) was added drop-wise. The mixture was stirred for additional 1 h at room temperature and then $NH_2OH{\cdot}HCl$ (1.04 g, 15 mmol) and imidazole (0.82g, 12 mmol) were added in one portion. The reaction was monitored by TLC, until the starting material disappeared (about 1 h). Then the mixture was filtered and concentrated *in vacuo*. The residue was dissolved in EtOAc (40 mL) and washed with aqueous HCl (1 M, 20 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product **S1d** as colorless oil (1.35g, 85% yield), which can be used directly for next step.



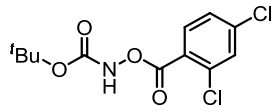
S1d

2,2,2-Trifluoroethyl hydroxycarbamate (S1d): IR ν_{max} (neat)/cm^{-1}: 3291 (m), 2982 (w), 1730 (s), 1487 (m), 1444 (m), 1252 (s), 1128 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (brs, 1H), 6.18 (brs, 1H), 4.56 (q, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 122.6 (q, *J* = 277.3 Hz), 61.5 (q, *J* = 37.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.41 (t, *J* = 7.6 Hz); HRMS (ESI, m/z): calcd for $C_3H_3F_3NO_3^-$, [M - H^+], 158.0071, found 158.0061.



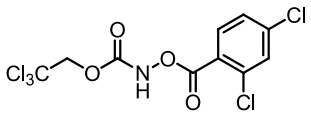
2a

Ethyl (2,4-dichlorobenzoyl)oxycarbamate (2a): compound **2a** was obtained by the acylation of *N*-hydroxyl ethyl carbamate **S1a** according to the general procedure as a white solid (73% yield, m.p. 71–73 °C). IR ν_{max} (neat)/cm^{-1}: 3230 (m), 2982 (w), 1780 (s), 1709 (s), 1580 (m), 1496 (m), 1472 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 156.4, 139.9, 135.7, 132.8, 131.3, 127.3, 125.0, 63.1, 14.2; HRMS (ESI, m/z): calcd for $C_{10}H_8Cl_2NO_4^-$, [M - H^+], 275.9836, found 275.9836.



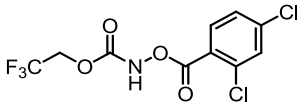
2b

***tert*-butyl (2,4-dichlorobenzoyl)oxycarbamate (2b)**: compound **2b** was obtained by the acylation of *N*-hydroxyl *tert*-butyl carbamate **S1b** according to the general procedure as a white solid (73% yield, m.p. 48–49 °C). IR ν_{max} (neat)/cm^{-1}: 3281 (w), 2977 (w), 1772 (m), 1732 (s), 1583 (m), 1469 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.53 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 155.4, 139.7, 135.6, 132.8, 131.2, 127.3, 125.1, 83.7, 28.0; HRMS (ESI, m/z): calcd for $C_{12}H_{12}Cl_2NO_4^-$, [M - H^+], 304.0149, found 304.0148.



2c

2,2,2-Trichloroethyl (2,4-dichlorobenzoyl)oxycarbamate (2c): compound **2c** was obtained by the acylation of *N*-hyroxyl trichloroethyl carbamate **S1c** according to the general procedure as a white solid (76% yield, m.p. 85–87 °C). IR ν_{max} (neat)/cm^{-1}: 3271 (m), 2957 (w), 1747 (s), 1583 (s), 1556 (w), 1469 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (br, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.55 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 4.86 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.5, 140.3, 136.0, 132.9, 131.4, 127.4, 124.3, 94.3, 75.3; HRMS (ESI, m/z): calcd for $C_{10}H_6Cl_5NNaO_4^+$, [M + Na^+], 401.8632, found 401.8615.

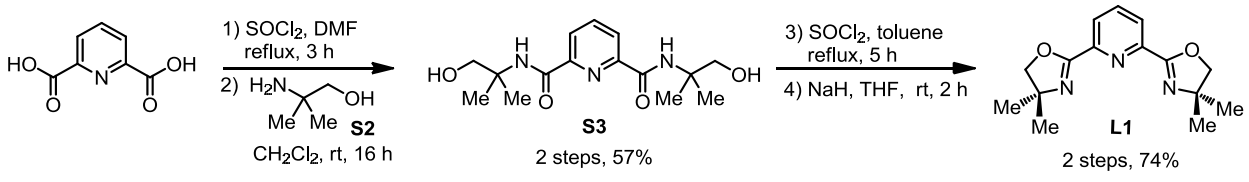


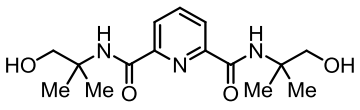
2d

2,2,2-Trifluoroethyl (2,4-dichlorobenzoyl)oxycarbamate (2d): compound **2d** was obtained by the acylation of *N*-hydroxyl trifluoroethyl carbamate **S1d** according to the general procedure as a white solid (74% yield, m.p. 80–81 °C). IR ν_{max} (neat)/cm^{-1}: 3230 (m), 2972 (w), 1783 (m), 1735 (s), 1583 (m), 1497 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 8.5, 1.9 Hz, 1H), 4.61 (q, *J* = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.4, 140.3, 136.0, 132.8, 131.5, 127.4, 124.2, 122.4 (q, *J* = 277.5 Hz), 62.1 (q, *J* = 37.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.10 (t, *J* = 8.2 Hz); HRMS (ESI, m/z): calcd for $C_{10}H_5Cl_2F_3NO_4^-$, [M - H^+], 329.9553, found 329.9552.

b. Synthesis of Nitrogen-Based Tri-dentate Ligands

Ligand **L1** was synthesized according to a modified literature procedure:[3]

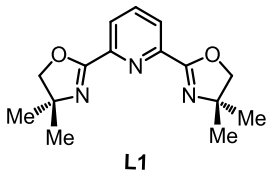



S3

To a 100 mL flame-dried flask charged with a stir bar and a reflux condenser was added 2,6-pyridinedicarboxylic acid (3.34 g, 20 mmol). After the flask was evacuated and backfilled with N_2 twice, $SOCl_2$ (30 ml) and DMF (0.2 mL) were added. The reaction was heated under a reflux condition for 3 h. Then the mixture was cooled to room temperature and concentrated *in vacuo* to

afford the 2,6-pyridinedicarbonyl dichloride as a white solid which can be used directly in the next step. Under N_2 atmosphere, to a solution of amino alcohol **S2** (6.23g, 70 mmol) and Et_3N (10.1g, 100 mmol) in CH_2Cl_2 (70 mL), were added 2,6-pyridinedicarbonyl dichloride in CH_2Cl_2 (30 mL) drop-wise at 0 °C. After the reaction mixture was stirred at room temperature for 16 h, the mixture was poured into an ice-water mixture (60 mL), which was then extracted with CH_2Cl_2 (60 mL × 3). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified through a silica gel flash column (hexanes/acetone: from 10:1 to 1:1) to afford product **S3** as a white solid (3.53 g, 57% yield for 2 steps), which is a known compound.[3]

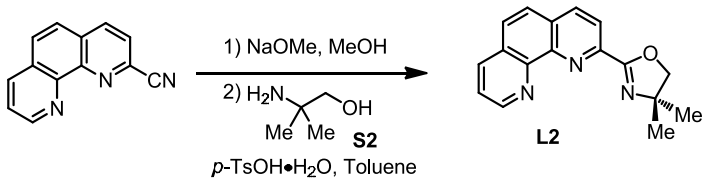
S3 (3.09 g, 10 mmol) was dissolved in toluene (40 mL) in a 100 mL flame-dried flask charged with a stir bar and a reflux condenser. $SOCl_2$ (7.14 g, 60 mmol) was added via a syringe and the mixture was heated under a reflux condition. The reaction was monitored with TLC. When the starting material disappeared, the reaction was cooled to 0 °C and quenched with saturated $NaHCO_3$ solution (30 mL). The organic layer was separated from the aqueous one which was then extracted with EtOAc (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was filtered through a short silica gel pad with EtOAc as an eluent and concentrated again. The obtained oil was dissolved in anhydrous THF (50 mL) under N_2 atmosphere and cooled to 0 °C. NaH (2 g, 50 mmol, 60% in mineral oil) was added to the solution portion-wise and the whole mixture was then warmed up to room temperature and monitored by TLC until the starting material was fully consumed. The reaction mixture was filtered through a Celite pad, concentrated and purified through a silica gel flash column (hexanes/acetone: from 20:1 to 2:1) to provide the ligand **L1** as a white solid (2.02 g, 74% yield for 2 steps).



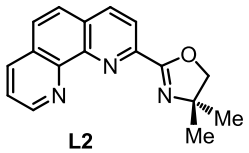
L1

2,6-Bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)pyridine (**L1**): ligand **L1** was further purified by recrystallization from a mixture of hexanes/EtOAc (9:1) as a colorless crystalline solid (m.p. 139–141 °C). IR ν_{max} (neat)/cm^{-1}: 3423 (w), 2967 (m), 2927 (w), 2896 (w), 1641 (s), 1573 (s), 1459 (s), 1365 (s), 1302 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.9 Hz, 2H), 7.87 (t, J =

7.9 Hz, 1H), 4.24 (s, 4H), 1.42 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 147.0, 137.1, 125.7, 79.8, 68.0, 28.4; HRMS (ESI, m/z): calcd for $C_{15}H_{20}N_3O_2^+$, [M + H^+], 274.1550, found 274.1554.

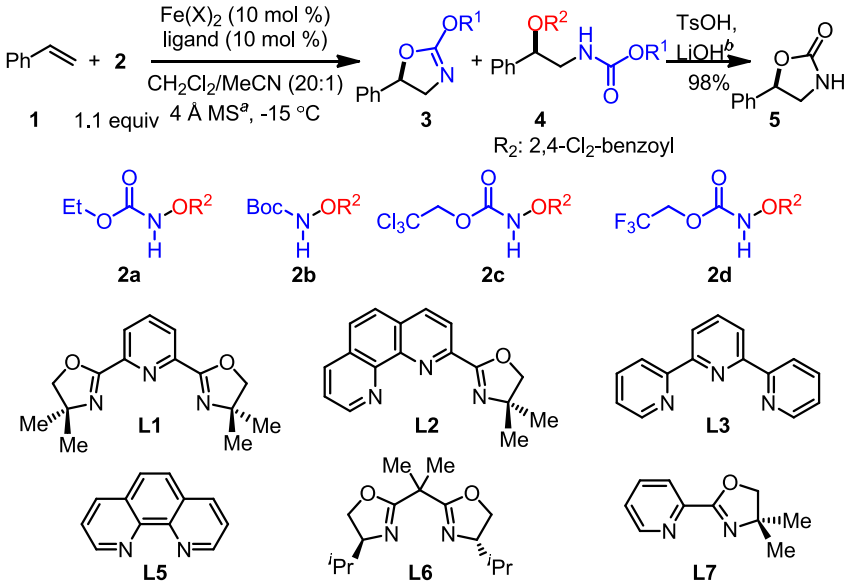


Ligand **L2** was synthesized from 2-cyanophenanthroline.[4] 2-Cyanophenanthroline (4.10g, 20 mmol) was dissolved in anhydrous methanol (60 mL) in a flame-dried flask equipped with a stir bar. NaOMe (108 mg, 2 mmol) was added to the reaction. The reaction mixture was stirred at room temperature and monitored with TLC until the starting material was fully consumed. The reaction was then quenched with acetic acid (0.22 mL) and the mixture was filtered and concentrated *in vacuo*. The residue was dissolved in toluene (100 mL) together with amino alcohol **S2** (1.87 g, 21 mmol) and *p*-TsOH·H_2O (380 mg, 2 mmol). The reaction mixture was then heated under a reflux condition with a Dean–Stark apparatus until the intermediate was consumed. After the reaction was cooled to room temperature, the solvent was removed *in vacuo* and the residue was purified through a silica gel flash column (hexanes/acetone: from 2:1 to 1:2) to afford **L2** as a white solid (3.6g, 65% yield).



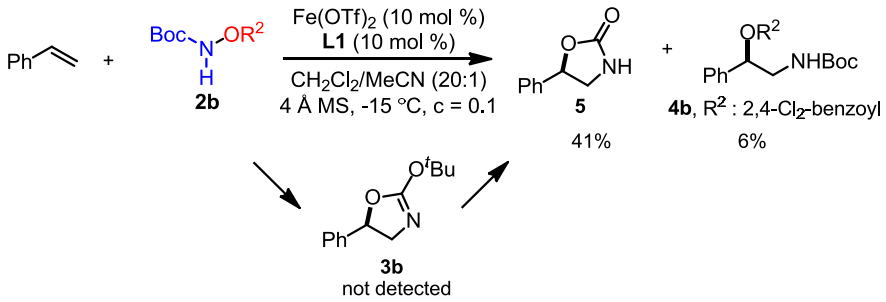
4,4-Dimethyl-2-(1,10-phenanthrolin-2-yl)-4,5-dihydrooxazole (**L2**): ligand **L2** was further purified by recrystallization from a hexanes/EtOAc mixture as a white solid (m.p. 106–108 °C).[4] IR ν_{max} (neat)/cm^{-1}: 3385 (m), 3223 (m), 2966 (w), 1646 (s), 1493 (m), 1400 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 4.3, 1.3 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.29 (d, *J* = 6.9 Hz, 1H), 7.86 (q, *J* = 8.8 Hz, 2H), 7.68 (dd, *J* = 8.1, 4.4 Hz, 1H), 4.34 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 150.4, 146.4, 145.9, 145.5, 136.6, 136.2, 129.4, 128.9, 128.0, 126.1, 123.4, 122.7, 79.8, 68.1, 28.5; HRMS (ESI, m/z): calcd for $C_{17}H_{16}N_3O^+$, [M + H^+], 278.1288, found 278.1289.

c. Catalyst Discovery for the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

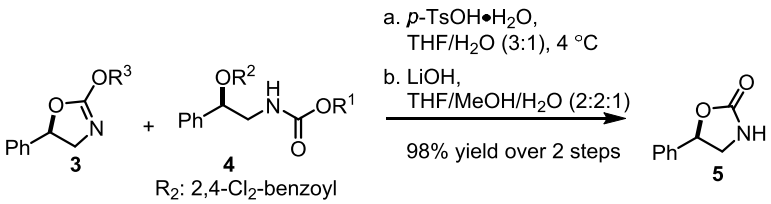


entry[b]	$Fe(X)_2$	ligand	2	conversion[c]	yield (3)[d]	yield (4)[d]	yield (5)[d]
1	$Fe(OTf)_2$	**L1**	**2a**	76%	51%	8%	57%
2	$Fe(OTf)_2$	**L1**	**2b**	69%	<5%[e]	6%	48%[e]
3	$Fe(OTf)_2$	**L1**	**2c**	>95%	71%	12%	82%
4	$Fe(OTf)_2$	**L1**	**2d**	>95%	63%	10%	72%
5	$Fe(OTf)_2$	**L2**	**2c**	67%	44%	14%	57%
6	$Fe(OTf)_2$	**L3**	**2c**	<5%	<5%	<5%	<5%
7	$Fe(OTf)_2$	**L4**	**2c**	<5%	<5%	<5%	<5%
8	$Fe(OTf)_2$	**L5**	**2c**	<5%	<5%	<5%	<5%
9	$Fe(OTf)_2$	**L6**	**2c**	<5%	<5%	<5%	<5%
10	$Fe(OTf)_2$	**L6**	**2c**	<5%	<5%	<5%	<5%
11	$Fe(NTf_2)_2$	**L1**	**2c**	>95%	62%	15%	76%
12	$FeCl_2$	**L1**	**2c**	<5%	<5%	<5%	<5%

[a]Molecular sieves were used to remove deleterious moisture. [b]Reactions were carried out under N_2 in 1 h and then quenched with saturated $NaHCO_3$ solution, unless stated otherwise. The crude mixture was first subjected to an acidic condition with TsOH (1.0 equiv) and then to a basic condition with LiOH (2.0 equiv) to afford **5**. [c]Conversion was measured by GC. [d]Isolated yield. [e]An oxazolidinone was isolated directly without the additional step (41% yield), see Supporting Information. OTf: trifluoromethanesulfonate, NTf_2: trifluoromethanesulfonimide.

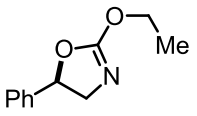


General procedure: To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added an iron salt (0.04 mmol) and a ligand (0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame-dried 3-dram vial (vial **B**) equipped with a stir bar were added freshly activated 4Å molecular sieves (50 mg) and the corresponding acyloxyl carbamate **2** (0.44 mmol). The vial was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (2.8 mL) was added. Both vials were degassed with brief evacuation and backfilling with N_2 twice. Subsequently, freshly distilled styrene (46 μL, 0.4 mmol) was added to vial **B** and the catalyst solution in vial **A** was added through a syringe pump over 15 min to vial **B** at -15 °C. The reaction was kept at this temperature for additional 45 min and quenched with saturated $NaHCO_3$ solution (2 mL). The organic layer was separated from the aqueous one, which was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was further purified through a silica gel flash column (hexanes/EtOAc as the eluent) to afford the amino-oxygenation products **3** and **4**.



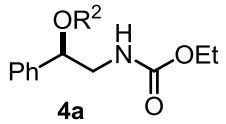
Alternatively, the crude mixture of **3** and **4** can be directly converted to **5** through a hydrolytic procedure (98% yield). The above mentioned crude product (a mixture of **3** and **4**) was dissolved in THF/H_2O (3:1) mixed solvent (3 mL) and cooled to 4 °C. After the addition of *p*-TsOH·H_2O (38 mg, 0.2 mmol), the reaction was stirred at the same temperature and monitored by TCL until **3** was consumed (ca. 1 h). The reaction mixture was then concentrated *in vacuo*, treated with saturated $NaHCO_3$ solution (2 mL) and extracted with EtOAc (2 mL× 3). The organic phase was

concentrated *in vacuo* and dissolved again in THF/MeOH/H_2O (2:2:1) mixture (3 mL). After addition of LiOH (12 mg, 0.5 mmol), the mixture was stirred at room temperature for 4 h and then quenched by aqueous HCl (1.0 M, 0.6 mL). After concentrated *in vacuo*, the aqueous phase was extracted with EtOAc (2 mL× 3). The combined organic layers were concentrated and purified by column. **5** was isolated through a silica gel flash column (hexanes/acetone: from 10:1 to 2:1) as a white solid (52.9 mg, 82% overall yield from styrene), which is a known compound.[5]



3a

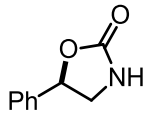
2-Ethoxy-5-phenyl-4,5-dihydrooxazole (**3a**): by following the general procedure, **3a** was obtained from the reaction of styrene **1** with **2a** and isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone : from 50:1 to 10:1) as colorless oil (39.0 mg, 51% yield). IR ν_{max} (neat)/cm^{-1}:2982 (w), 1666, 1406, 1378, 1327 (s), 1256 (s), 1047, 991, 920; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.31 (m, 5H), 5.62 (dd, *J* = 9.4, 7.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.23 (dd, *J* = 12.7, 9.5 Hz, 1H), 3.76 (dd, *J* = 12.7, 7.7 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 140.3, 128.8, 128.4, 125.6, 81.8, 66.7, 60.0, 14.4; HRMS (ESI, m/z): calcd for $C_{11}H_{14}NO_2^+$ [M + H^+], 192.1019, found 192.1010.



4a

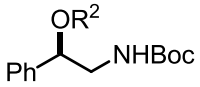
R^2 = 2,4-Cl_2-benzoyl

2-((Ethoxycarbonyl)amino)-1-phenylethyl 2,4-dichlorobenzoate (**4a**): by following the general procedure, **4a** was obtained from the reaction of styrene **1** with **2a** and isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (12.2 mg, 8% yield). IR ν_{max} (neat)/cm^{-1}: 3377 (w); 2977 (w), 1712 (s), 1583 (m), 1522 (m), 1239 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.48 – 7.30 (m, 6H), 6.09 (dd, *J* = 7.2, 3.7 Hz, 1H),4.96 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.84 – 3.57 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 156.5, 138.7, 137.1, 134.9, 132.9, 131.1, 128.8, 128.7, 128.1, 127.2, 126.6, 76.5, 61.1, 45.9, 14.6; HRMS (ESI, m/z): calcd for $C_{18}H_{16}Cl_2NO_4^-$ [M - H^+], 380.0462, found 380.0467.



5

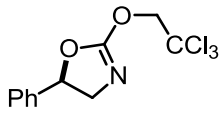
5-Phenyloxazolidin-2-one (**5**): by following the general procedure, **5** was directly obtained from the reaction of styrene **1** with **2b** and isolated through a silica gel flash column (hexanes/acetone: from 50:1 to 2:1) as a white solid (26.8 mg, 41% yield), which is a known compound.[5]



4b

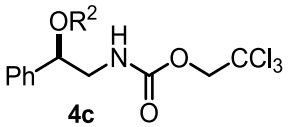
R^2 : 2,4-Cl_2-benzoyl

2-((*tert*-Butoxycarbonyl)amino)-1-phenylethyl 2,4-dichlorobenzoate (**4b**): by following the general procedure, **4a** was obtained from the reaction of styrene **1** with **2b** and isolated through a silica gel flash column (hexanes/acetone: from 50:1 to 10:1) as colorless oil (9.8 mg, 6% yield). IR ν_{max} (neat)/cm^{-1}: 3357 (w), 2972, 2927, 1709 (s), 1583 (m), 1509, 1365, 1277, 1239 (s), 1166 (m), 1100 (m) , 1065; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.48 – 7.30 (m, 6H), 6.08 (t, *J* = 6.0 Hz, 1H), 4.82 (brs, 1H), 3.81 – 3.54 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 155.7, 138.6, 137.3, 135.0, 132.9, 131.7, 128.8, 128.6, 128.1, 127.1, 126.6, 79.7, 76.6, 45.5, 28.3; HRMS (ESI, m/z): calcd for $C_{20}H_{21}Cl_3NO_4^-$, [M + Cl^-], 444.1, found 444.1.



3c

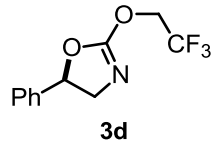
5-Phenyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (**3c**): by following the general procedure, **3c** was obtained from the reaction of styrene **1** with **2c** and isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (83.7 mg, 71% yield). IR ν_{max} (neat)/cm^{-1}: 2952 (w), 2881 (w), 1671 (s), 1396 (s), 1330 (s), 1249 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 5H), 5.74 (t, *J* = 8.2 Hz, 1H), 4.93 (dd, *J* = 16.4, 11.6 Hz, 2H), 4.27 (dd, *J* = 12.8, 9.6 Hz, 1H), 3.82 (dd, *J* = 12.9, 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 139.5, 128.9, 128.7, 125.7, 94.2, 83.2, 79.6, 59.7; HRMS (ESI, m/z): calcd for $C_{11}H_{11}Cl_3NO_2^+$ [M + H^+], 293.9850, found 293.9849.



4c

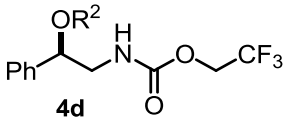
R^2 : 2,4-Cl_2-benzoyl

1-Phenyl-2-(((2,2,2-trichloroethoxy)carbonyl)amino)ethyl 2,4-dichlorobenzoate (**4c**): by following the general procedure, **4c** was obtained from the reaction of styrene **1** with **2c** and isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (23.3 mg, 12% yield). IR ν_{max} (neat)/cm^{-1}: 3347 (w), 2927 (m), 2851 (w), 1727 (s), 1585 (m), 1522 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.46 – 7.30 (m, 6H), 6.13 (dd, *J* = 7.7, 4.3 Hz, 1H), 5.29 (brs, 1H), 4.80 – 4.66 (m, 2H), 3.87 – 3.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 154.6, 138.8, 136.8, 134.9, 132.9, 131.1, 128.9, 128.8, 127.9, 127.2, 126.6, 95.4, 76.1, 74.6, 46.1; HRMS (ESI, m/z): calcd for $C_{18}H_{13}Cl_5NO_4^-$ [M - H^+], 481.9293, found 481.9289.



3d

5-Phenyl-2-(2,2,2-trifluoroethoxy)-4,5-dihydrooxazole (**3d**): by following the general procedure, **3d** was obtained from the reaction of styrene **1** with **2d** and isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (61.8 mg, 63% yield). IR ν_{max} (neat)/cm^{-1}: 2967 (w), 1679 (s), 1421, 1381, 1348, 1271 (s), 1257 (s), 1166 (s), 1100, 960; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 5H), 5.74 (t, *J* = 6.6 Hz, 1H), 4.68 (q, *J* = 8.2 Hz, 2H), 4.25 (dd, *J* = 12.9, 9.6 Hz, 1H), 3.80 (dd, *J* = 12.9, 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 139.4, 128.9, 128.7, 125.6, 122.5 (q, *J* = 277.5 Hz), 83.5, 66.23 (q, *J* = 37.1 Hz), 59.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.26 (t, *J* = 8.5 Hz); HRMS (ESI, m/z): calcd for $C_{11}H_{11}F_3NO_2^+$ [M + H^+], 246.0736, found 246.0726.



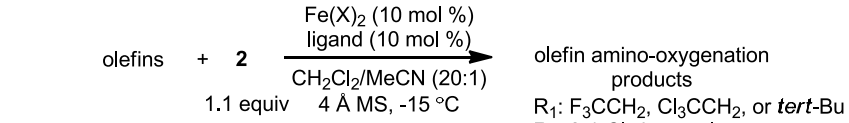
4d

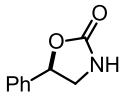
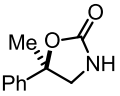
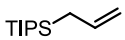
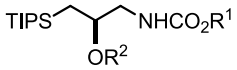
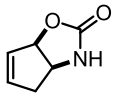
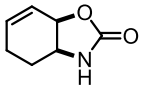
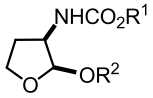
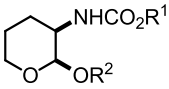
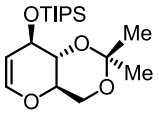
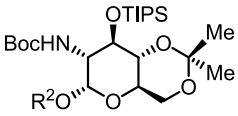
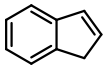
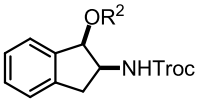
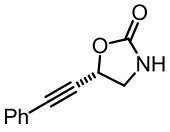
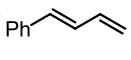
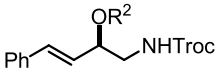
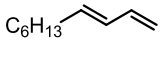
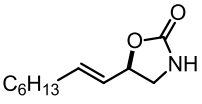
R^2 = 2,4-Cl_2-benzoyl

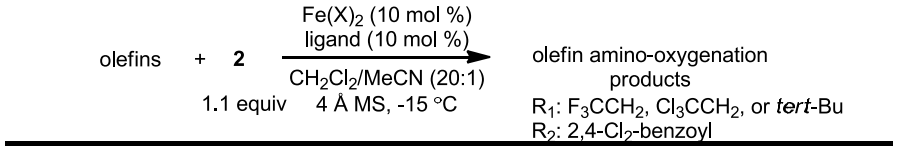
1-Phenyl-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)ethyl 2,4-dichlorobenzoate (**4d**): by following the general procedure, **4d** was obtained from the reaction of styrene **1** with **2d** and

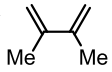
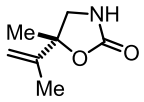
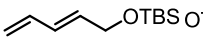
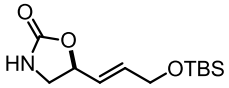
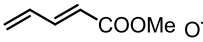
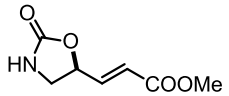
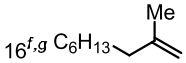
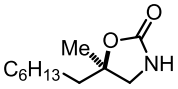
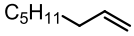
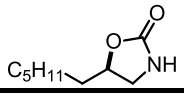
isolated through a silica gel flash column (hexanes (with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (17.4 mg, 10% yield). IR ν_{max} (neat)/cm^{-1}: 3362 (w), 1729 (s), 1585, 1540, 1378, 1279 (s), 1241 (s), 1166 (s), 1050, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.46 – 7.29 (m, 6H), 6.10 (dd, *J* = 7.6, 4.3 Hz, 1H), 5.25 (s, 1H), 4.54 – 4.38 (m, 2H), 3.84 – 3.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 154.5, 138.8, 136.7, 134.9, 132.9, 131.1, 128.9, 128.8, 127.8, 127.2, 126.5, 123.0 (q, *J* = 277.6 Hz), 76.1, 46.1, 61.03 (q, *J* = 36.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.29 (t, *J* = 8.5 Hz); HRMS (ESI, m/z): calcd for $C_{18}H_{13}Cl_2F_3NO_4^-$ [M - H^+], 434.0179, found 434.0173.

C. Procedures for the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

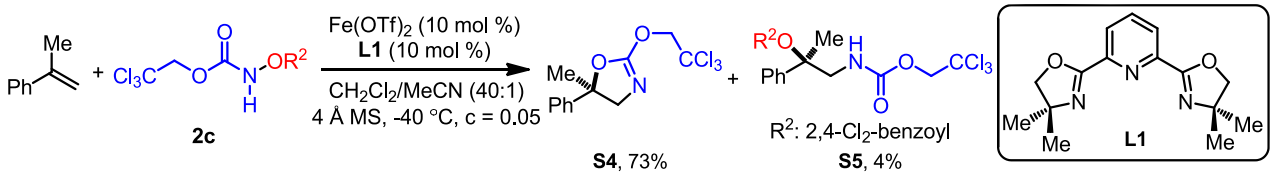


entry[a]	olefin	X	ligand	2	product	yield[b]
1[c,d]		OTf	**L1**	**2c**		82%
2[d,e]		OTf	**L1**	**2c**		75%
3		OTf	**L1**	**2d**		78%
4[f,g]		OTf	**L2**	**2b**	 *dr* > 20:1	61%
5[f,g]		OTf	**L2**	**2b**	 *dr* > 20:1	62%
6[e]		OTf	**L1**	**2d**	 *dr* > 20:1	72%
7[h]		OTf	**L1**	**2d**	 *dr* = 10:1	77%
8[h,i]		NTf_2	**L1**	**2b**	 *dr* > 20:1	63%
9[c,i]		NTf_2	**L1**	**2c**	 *dr* > 20:1	71%
10[d,j]		OTf	**L1**	**2c**		62%
11[c,k]		Cl+OTf	**L1**	**2c**		84%
12[f,g]		OTf	**L2**	**2b**		61%



entry[a]	olefin	X	ligand	2	product	yield[b]
13[f,g]		OTf	**L2**	**2b**		76%
14[f,g]		OTf	**L1**	**2b**		63%
15[f,g]		OTf	**L1**	**2b**		54%
16[f,g]		ClO_4	**L1**	**2b**		51%
17[d,l]		OTf	**L1**	**2c**		48%

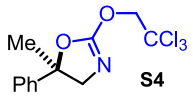
[a]Reactions were carried out under N_2 in 2 h, unless stated otherwise. [b]Isolated yield. [c]Reaction time: 1 h. [d]The crude mixture was treated with TsOH and then LiOH. [e]Reaction temperature: -40 °C. [f]Catalyst loading: 20 mol %; reaction temperature: 0 °C. [g]Reaction time: 12 h. [h]Reaction temperature: -30 °C. [i]$Fe(NTf_2)_2$ (15 mol %), **L1** (15 mol %). [j]Catalyst loading: 15 mol %. [k]$Fe(OTf)_2$ (2.5 mol %) and $FeCl_2$ (2.5 mol %) were used. [l]Catalyst loading: 30 mol %; reaction temperature: 0 °C; reaction time: 24 h.



α-Methylstyrene is commercially available and it was distilled before usage.

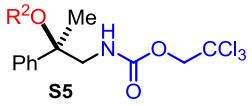
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (14.2 mg, 0.04 mmol) and **L1** (10.9 mg, 0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried vial (20 mL, vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and

2c (152.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (6.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, α-methylstyrene (62.3 μL, 0.48 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -40 °C. The reaction was kept stirring at the same temperature for another 1.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S4

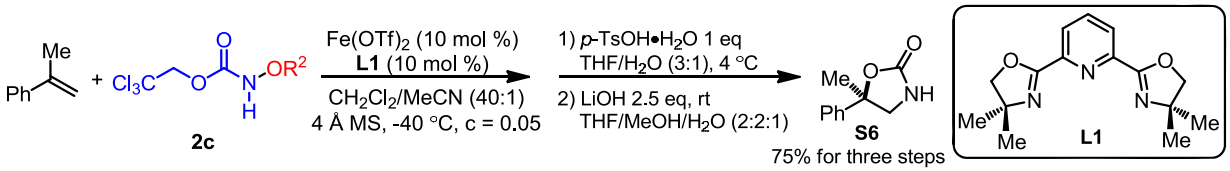
5-Methyl-5-phenyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (**S4**): compound **S4** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (90.1 mg, 73% yield); IR ν_{max} (neat)/cm^{-1}:2952 (w), 2876 (w), 1674 (w), 1393 (s), 1338 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 4.95 – 4.86 (m, 2H), 3.96 (q, J = 12.6 Hz, 2H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 144.4, 128.7, 127.7, 124.0, 89.5, 79.3, 65.5, 28.4; HRMS (ESI, m/z): calcd for $C_{12}H_{13}Cl_3NO_2^+$ [M + H^+], 308.0006, found 308.0004.



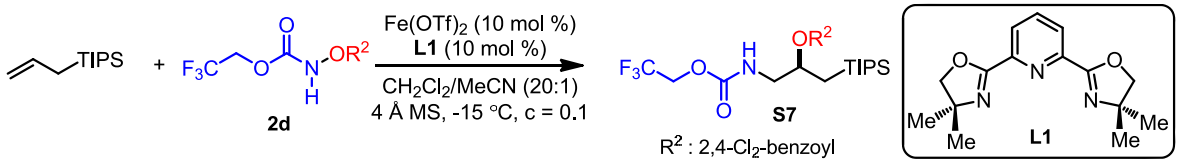
S5

R^2: 2,4-Cl_2-benzoyl

2-Phenyl-1-(((2,2,2-trichloroethoxy)carbonyl)amino)propan-2-yl 2,4-dichlorobenzoate (**S5**): compound **S5** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as a white foam (8.0 mg, 4% yield); IR ν_{max} (neat)/cm^{-1}: 3367 (w), 2947 (w), 1724 (d), 1583 (m), 1517 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 1.7 Hz, 1H), 7.47 – 7.31 (m, 6H), 5.41 (t, J = 6.0 Hz, 1H), 4.74 (dd, J = 32.6, 12.0 Hz, 2H), 3.84 (dd, J = 14.4, 7.6 Hz, 1H), 3.73 (dd, J = 14.3, 5.5 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.8, 141.0, 138.5, 134.3, 132.8, 131.0, 129.2, 128.7, 128.0, 127.3, 124.9, 95.5, 85.5, 74.6, 51.8, 22.1; calcd for $C_{19}H_{16}Cl_5NNaO_4^+$ [M + Na^+], 519.9414, found 519.9420.

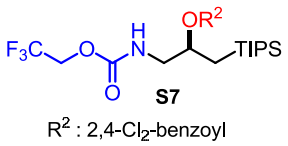


By following the typical hydrolysis procedure, above crude products can also be converted to corresponding oxazolidinone in good combined yield. Compound **S6** was isolated through a silica gel flash column (hexanes/acetone: from 10:1 to 2:1) as a white solid (53.2 mg, 75% yield), which is a known compound.[6]

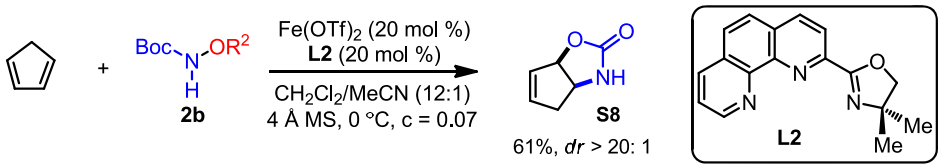


Allyl triisopropylsilane was prepared through a known procedure.[7]

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (14.2 mg, 0.04 mmol) and **L1** (10.9 mg, 0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2d** (146.1 mg, 0.44 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (2.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, allyl triisopropylsilane (79.4 mg, 0.40 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 1.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



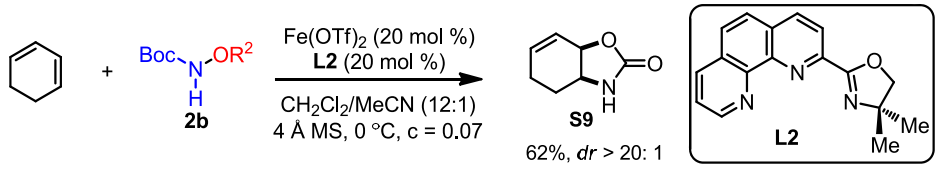
1-(((2,2,2-Trifluoroethoxy)carbonyl)amino)-3-(triisopropylsilyl)propan-2-yl 2,4-dichlorobenzoate (**S7**): compound **S7** was isolated through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as colorless oil (165.5 mg, 78% yield). IR ν_{max} (neat)/cm^{-1}: 3367 (w), 2942 (m), 2867 (m), 1727 (s), 1589 (m), 1527 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.45 (qd, *J* = 7.4, 2.9 Hz, 1H), 5.27 (brs, 1H), 4.57 – 4.35 (m, 2H), 3.67 (ddd, *J* = 14.3, 6.1, 3.0 Hz, 1H), 3.43 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.28 – 1.23 (m, 1H), 1.10 – 0.99 (m, 22H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 154.6, 138.4, 134.5, 132.4, 131.0, 128.5, 127.1, 123.0 (q, *J* = 277.6 Hz), 73.7, 61.0 (q, *J* = 36.5 Hz), 47.0, 18.7, 18.7, 13.3, 11.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.34 (t, *J* = 8.4 Hz); HRMS (ESI, m/z): calcd for $C_{22}H_{32}Cl_3F_3NO_4Si^-$, [M + Cl^-], 564.1124, found 564.1112.



Cyclopentadiene was freshly obtained *via* retro-Diels–Alder reaction by heating commercially available cyclopentadiene dimer above 150 °C.

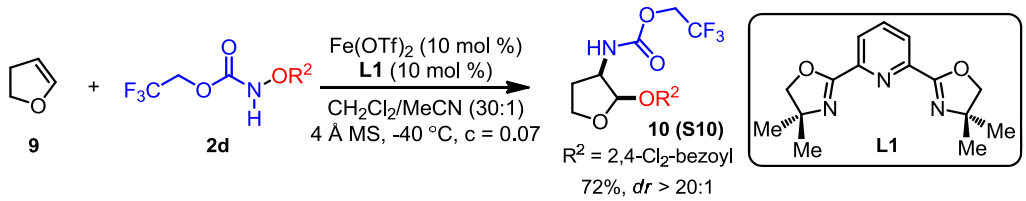
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L2** (22.2 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.5 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2b** (122.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, freshly distilled 1,3-cyclopentadiene (67.2 µL, 0.8 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and

concentrated *in vacuo*. Product **S8** was isolated through a silica gel flash column (hexanes/EtOAc: from 4:1 to 1:1) as a white solid (30.5 mg, 61% yield) which is a known compound.[8]



1,3-Cyclohexadiene is commercially available and distilled before usage.

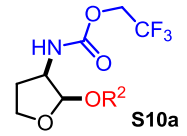
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L2** (22.2 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.5 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2b** (122.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, freshly distilled 1,3-cyclohexadiene (76.2 uL, 0.8 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. Product **S9** was isolated through a silica gel flash column (hexanes/EtOAc: from 4:1 to 1:1) as a white solid (34.5 mg, 62% yield), which is a known compound.[9]



2,3-Dihydrofuran **9** is commercially available and it was distilled before usage.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (14.2 mg, 0.04 mmol) and **L1** (10.9 mg, 0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2d** (132.8 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three

times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, 2,3-dihydrofuran (36.3 μL, 0.48 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -40 °C. The reaction was kept stirring at -40 °C for another 1.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S10a

R^2 = 2,4-Cl_2-bezoyl

3-(((2,2,2-Trifluoroethoxy)carbonyl)amino)tetrahydrofuran-2-yl 2,4-dichlorobenzoate (**S10a**): compound **S10a** was isolated through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as white solid (115.8 mg, 72% yield, m.p. 110−111 °C); IR ν_{max} (neat)/cm^{-1}: 3347 (w), 2972 (w), 2906 (w), 1724 (s), 1585 (m), 1530 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.40 – 7.31 (m, 1H), 6.44 (d, *J* = 4.3 Hz, 1H), 5.36 (d, *J* = 8.9 Hz, 1H), 4.59 – 4.35 (m, 3H), 4.24 (td, *J* = 9.3, 2.5 Hz, 1H), 4.07 (dd, *J* = 16.8, 8.7 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.08 – 1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 153.8, 139.0, 134.2, 133.2, 131.1, 128.1, 127.4, 122.9 (q, *J* = 277.5 Hz), 96.4, 67.5, 61.2 (q, *J* = 36.6 Hz), 53.5, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.25 (t, *J* = 8.4 Hz); HRMS (ESI, m/z): calcd for $C_{14}H_{12}Cl_2F_3NNaO_5^+$, [M + Na^+], 423.9937, found 423.9941.

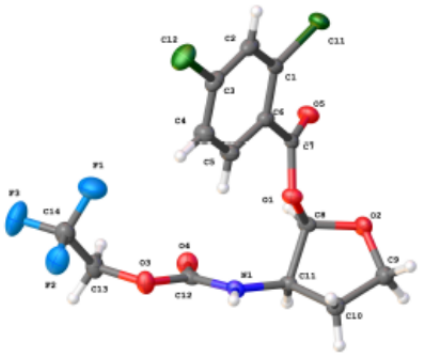
Determination of the Relative Stereochemistry of S10a

The relative stereochemistry of compound **S10a** was determined by *NOE* analysis of both diastereomers. The conclusion was further confirmed through X-ray structural analysis of **S10a**.

The crystal structure has been deposited in The Cambridge Crystallographic Data Centre as CCDC1014959.

Crystal Data and Experimental

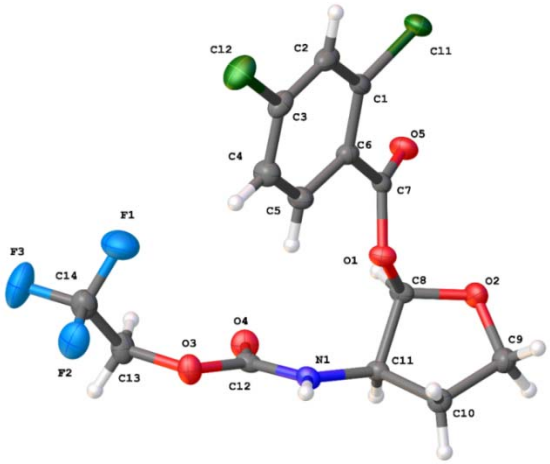
Crystal submitted by: Lu, D.
Structure solved by: Wieliczko, M.



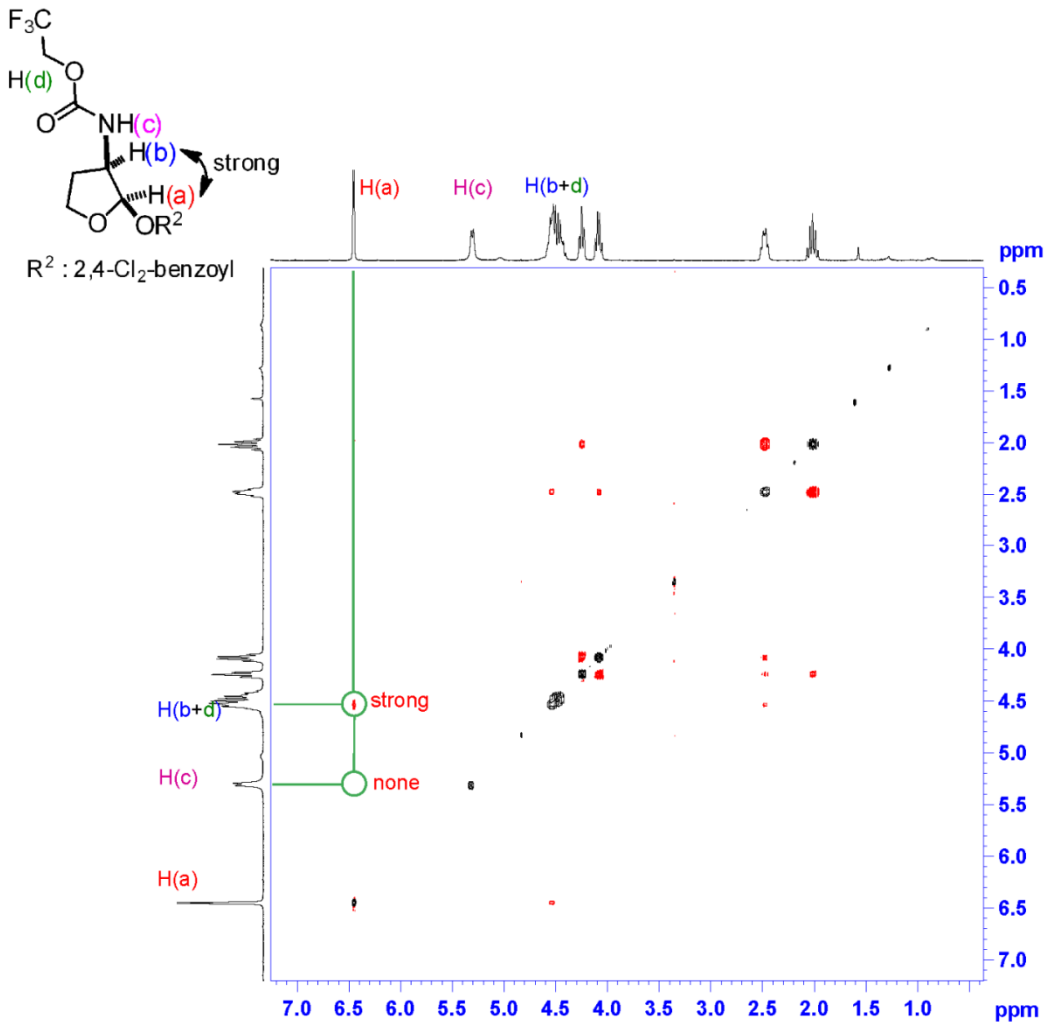
Crystal Data. $C_{14}H_{12}Cl_2F_3NO_5$, M = 402.15, triclinic, $P1$ (No. 1, a = 4.8784(8) Å, b = 10.6424(17) Å, c = 15.881(3) Å, α = 99.955°, β = 96.953°, γ = 90.633°, V = 805.7(2)Å^3, T = 110(2) K, Z = 2, μ(Mo Kα) = 0.462, 14822 reflections measured, 9669 unique (R_{int} = 0.0334) which were used in all calculations. The final wR_2 was 0.1238 (all data) and R_1 was 0.0495 ($I > 2\sigma(I)$).

Experimental. Single crystals of $C_{14}H_{12}Cl_2F_3NO_5$ (**A008_0m**) were recrystallised from DCM by slow evaporation. A suitable crystal (0.985 × 0.291 × 0.135mm^3) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 110(2) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program, using the Charge Flipping solution method. The model was refined with the ShelXL [3] refinement package using Least Squares minimisation.

Compound	A008_0m
CCDC	
Formula	$C_{14}H_{12}Cl_2F_3NO_5$
$D_{calc.}$/ g cm^{-3}	1.658
μ/ mm^{-1}	0.462
Formula Weight	402.15
Colour	colourless
Shape	plate
Size/mm^3	0.985 × 0.291 × 0.135
T/K	110(2)
Crystal System	triclinic
Space Group	$P1$
a/Å	4.8784(8)
b/Å	10.6424(17)
c/Å	15.881(3)
α/°	99.955(2)
β/°	96.953(2)
γ/°	90.633(2)
V/ Å^3	805.7(2)
Z	2
Θ_{min}/°	1.944
Θ_{max}/°	31.011
Measured Refl.	14822
Independent Refl.	9669
Reflections Used	8620
R_{int}	0.0334
Parameters	452
Restraints	3
Largest Peak Largest Peak	0.724
Deepest Hole	-0.279
GooF	1.041
wR_2(all data)	0.1238
wR_2	0.1187
R_1(all data)	0.0563
R_1	0.0495

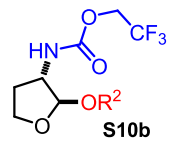


X-ray crystal structure of **S10a**



For the major (*syn*) diastereomer **S10a**, there is a strong *NOE* between H(a) and H(b) while there is no *NOE* observed between H(a) and NH(c). (Note: on ^{1}H NMR, H(b) and H(d) are partially overlapped and H(d) is in a distance away from H(a).

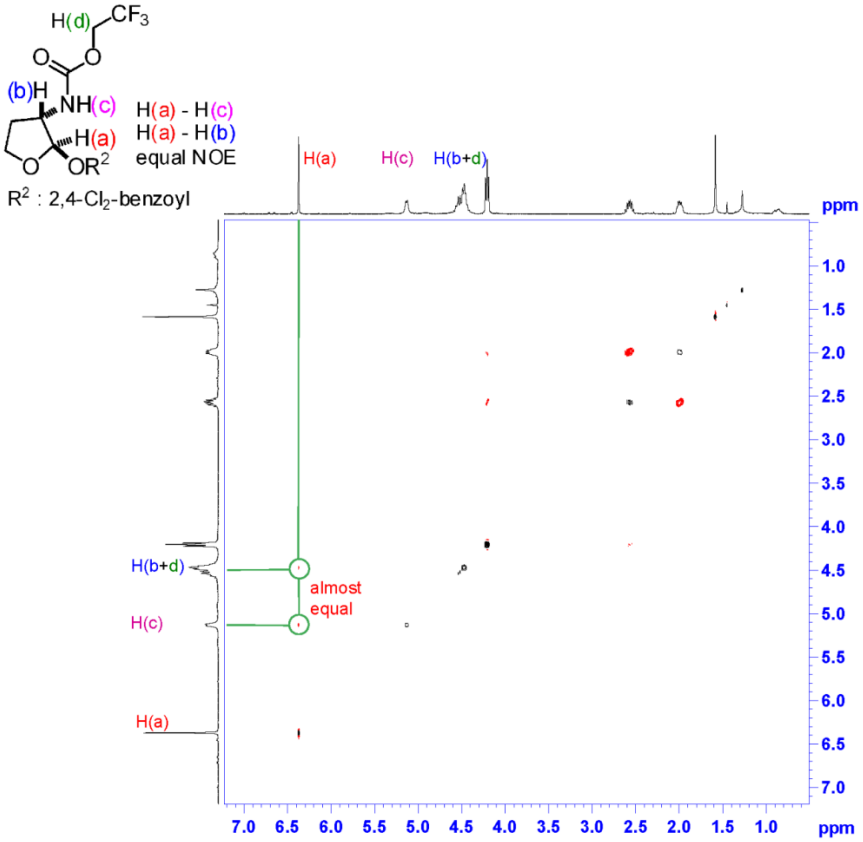
In order to further corroborate the *NOE* analysis, we carried out the reaction at an elevated temperature (room temperature) to obtain the minor diastereomer **S10b**. Note: the *dr* is 3.5:1 under this condition.



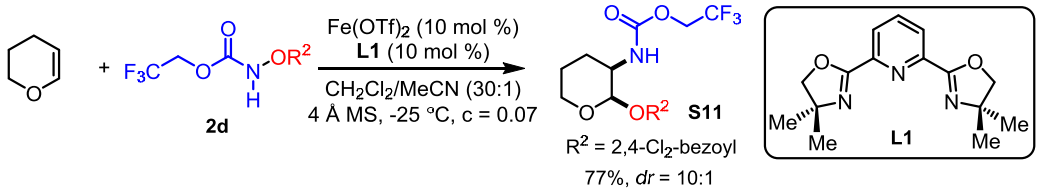
S10b

R^2 = 2,4-Cl_2-bezoyl

3-(((2,2,2-Trifluoroethoxy)carbonyl)amino)tetrahydrofuran-2-yl 2,4-dichlorobenzoate (**S10b**): the minor diastereomer **S10b** can be separated from the major diastereomer **S10a** through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as a white foam. IR ν_{max} (neat)/cm^{-1}: 3346 (w), 2972 (w), 2908 (w), 1723 (s), 1585 (m), 1534 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 1H), 7.50 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 6.37 (s, 1H), 5.13 (brd, J = 7.6 Hz, 1H), 4.63 – 4.35 (m, 3H), 4.27 – 4.14 (m, 2H), 2.65 – 2.50 (m, 1H), 2.09 – 1.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 153.6, 138.9, 135.0, 132.9, 131.1, 127.7, 127.1, 122.9 (q, J = 277.3 Hz), 101.4, 67.8, 61.2 (q, J = 37.0 Hz); 56.6, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.25 (t, J = 8.4 Hz); HRMS (ESI, m/z): calcd for $C_{14}H_{12}Cl_2F_3NNaO_5^+$, [M + Na^+], 423.9937, found 423.9936.

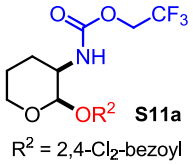


For the minor (*anti*) diastereomer **S10b** (*anti*), the *NOE*s between H(a)–H(b) and H(a)–NH(c) are almost identical.



3,4-Dihydro-2*H*-pyran is commercially available and distilled before usage.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (14.2 mg, 0.04 mmol) and **L1** (10.9 mg, 0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2d** (132.8 mg, 0.40 mmol). The vial was also evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, 3,4-dihydro-2*H*-pyran (43.8 μL, 0.48 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -25 °C. The reaction was kept stirring at the same temperature for another 1.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.

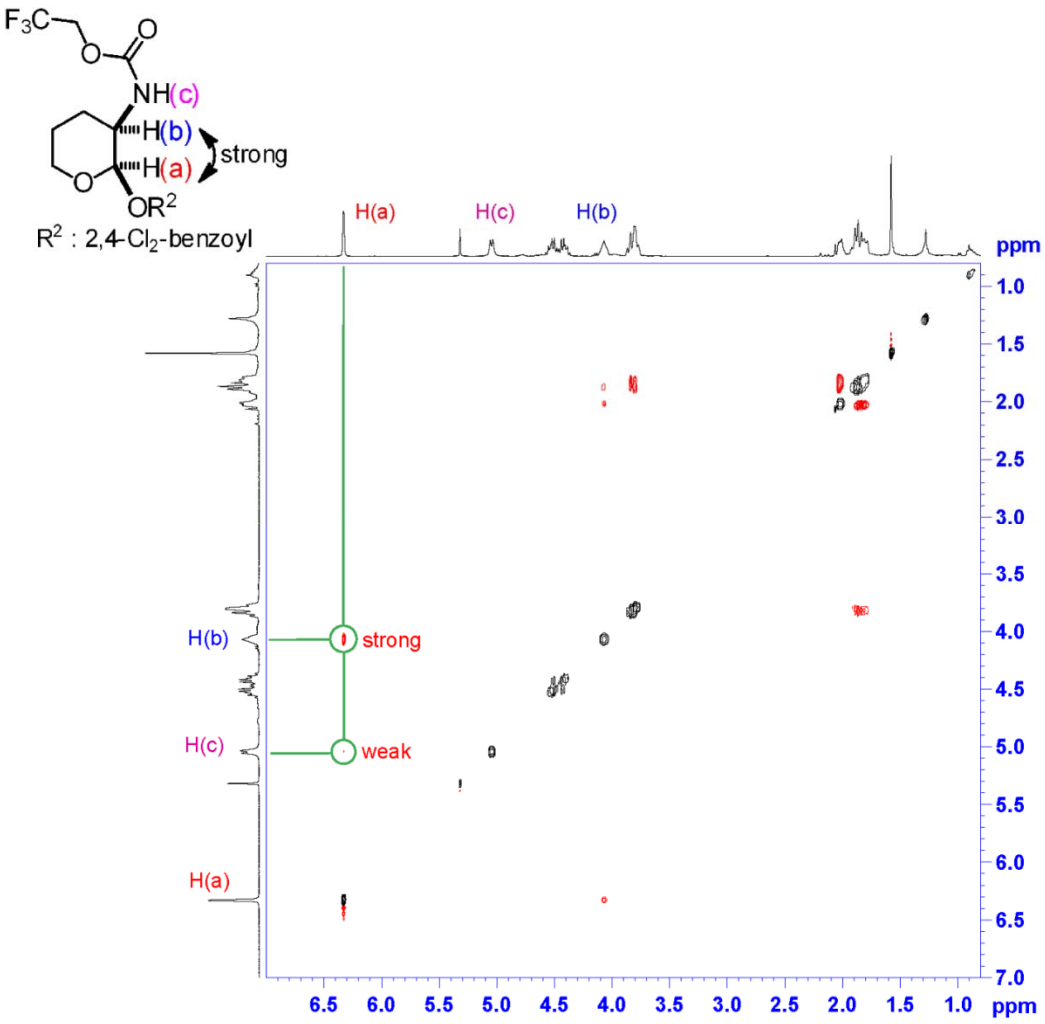


3-(((2,2,2-Trifluoroethoxy)carbonyl)amino)tetrahydro-2*H*-pyran-2-yl 2,4-dichlorobenzoate (**S11a**): compound **S11a** was isolated through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as colorless oil (128.2 mg, 77% yield, *dr* = 10:1). The pure major diastereomer can be obtained by another flash column. IR ν_{max} (neat)/cm^{-1}: 3347 (s), 2947 (w), 1724 (s), 1585 (m), 1530 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 5.06 (brd, *J* = 9.1 Hz, 1H), 4.59 – 4.34 (m, 2H), 4.11 – 4.00 (m, 1H), 3.89 – 3.73 (m, 2H), 2.05 – 1.96 (m, 1H), 1.94 – 1.76 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 153.7, 139.2, 134.5, 133.4, 131.2, 127.8, 127.4, 123.0 (q, *J* = 277.6 Hz), 93.2, 61.6, 60.9 (q, *J* = 36.6 Hz), 49.1, 25.3, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -

74.25 (t, J = 8.5 Hz); HRMS (ESI, m/z): calcd for $C_{15}H_{14}Cl_2F_3NNaO_5^+$, [M + Na^+], 438.0093, found 438.0084.

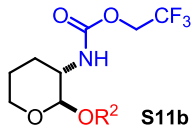
Determination of the Relative Stereochemistry of S11a/b

The relative stereochemistry of compound **S11a** and **S11b** were also determined through *NOE* analysis of both diastereomers.



For the major (*syn*) diastereomer **S11a**, there is a strong *NOE* between H(a) and H(b) while there is a weak *NOE* observed between H(a) and NH(c).

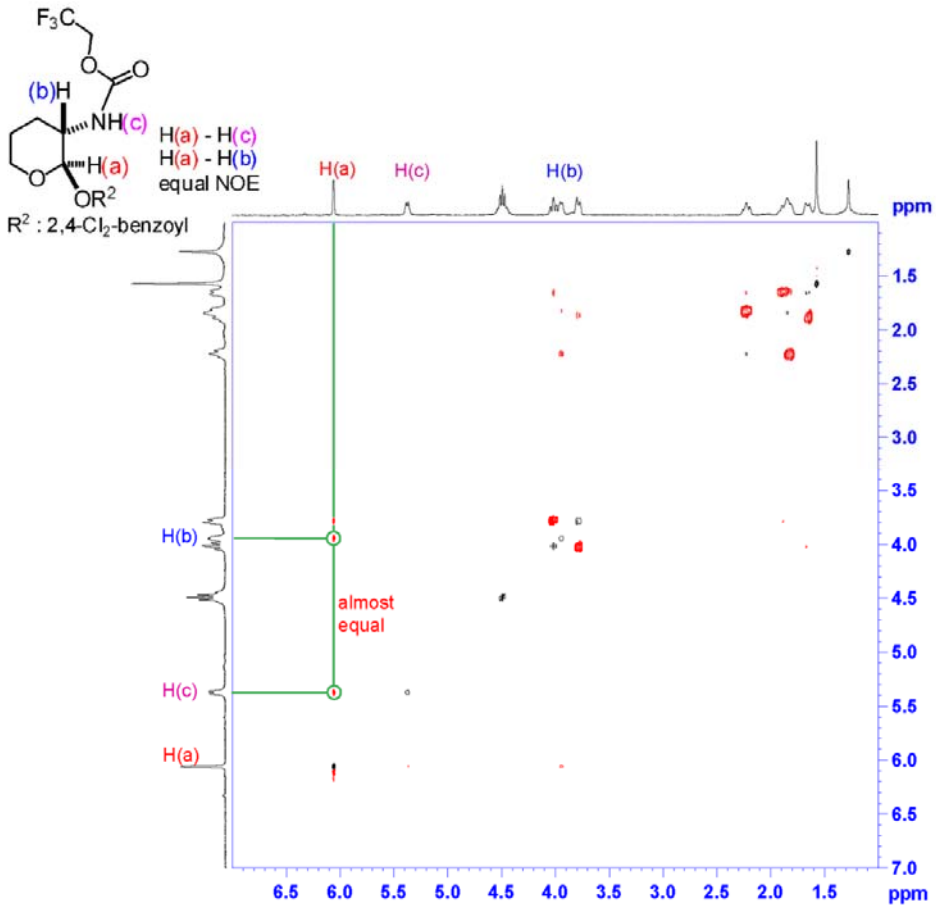
In order to further corroborate the *NOE* analysis, we carried out the reaction at an elevated temperature (room temperature) to obtain the minor diastereomer **S11b**. Note: the *dr* is 3:1 under this condition.



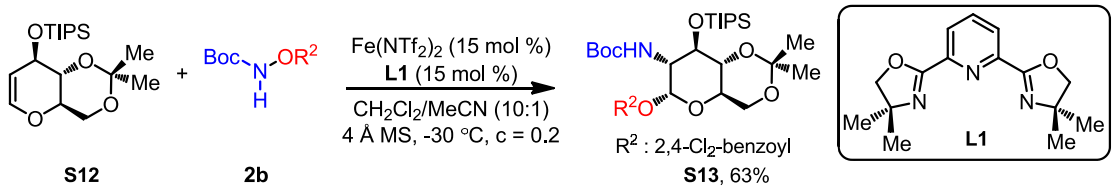
S11b

R^2 = 2,4-Cl_2-bezoyl

3-(((2,2,2-Trifluoroethoxy)carbonyl)amino)tetrahydro-2*H*-pyran-2-yl 2,4-dichlorobenzoate (**S11b**): the minor diastereomer **S11b** can be separated from the major diastereomer through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as a white foam. IR ν_{max} (neat)/cm^{-1}:3347 (s), 2949 (w), 1722 (s), 1586 (m), 1531 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.06 (s, 1H), 5.38 (d, *J* = 9.1 Hz, 1H), 4.56 – 4.40 (m, 2H), 4.02 (t, *J* = 11.2 Hz, 1H), 3.95 (s, 1H), 3.79 (d, *J* = 11.0 Hz, 1H), 2.22 (t, *J* = 11.9 Hz, 1H), 1.93 – 1.74 (m, 2H), 1.70 – 1.60 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 153.7, 139.1, 135.2, 133.2, 131.3, 127.4, 127.2, 123.0 (q, *J* = 277.3 Hz), 93.7, 62.8, 61.1 (q, *J* = 36.6 Hz), 48.0, 24.2, 20.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.25 (t, *J* = 8.4 Hz); HRMS (ESI, m/z): calcd for $C_{15}H_{14}Cl_2F_3NNaO_5^+$, [M + Na^+], 438.0093, found 438.0096.



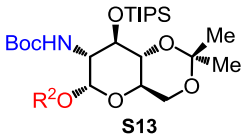
For the minor (*anti*) diastereomer **S11b**, the *NOE*s between H(a)–H(b) and H(a)–NH(c) are almost identical.



S12 **2b** **S13**, 63%

The D-glucal **S12** was protected based on a known two-step procedure.[10]

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(NTf_2)_2$ (36.9 mg, 0.06 mmol) and **L1** (16.4 mg, 0.06 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.8 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg), protected D-glucal **S12** (137.0 mg, 0.4 mmol) and **2b** (183.6 mg, 0.60 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (1.0 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -30 °C. The reaction was kept stirring at the same temperature for another 2.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.

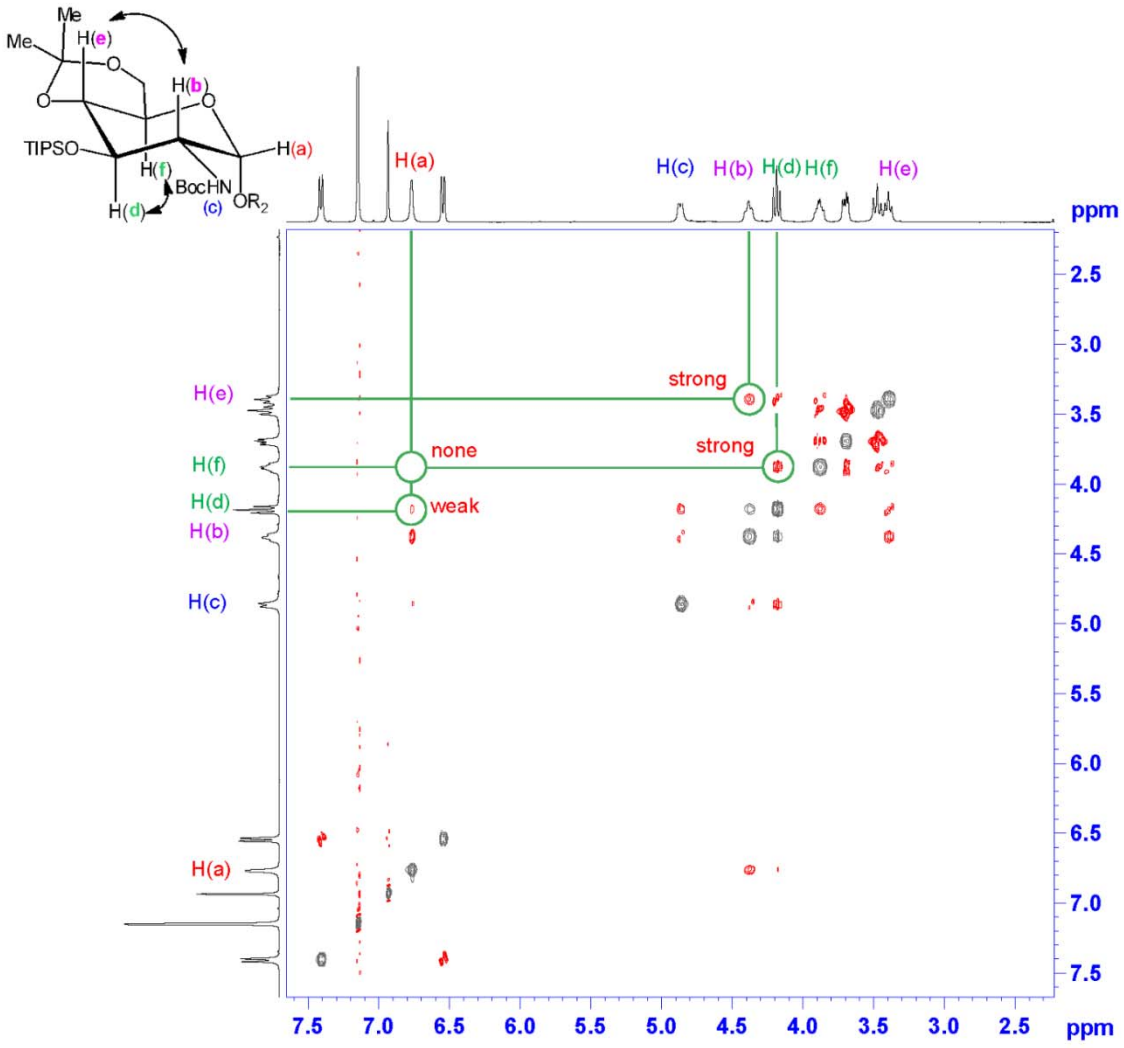


S13

R^2 : 2,4-Cl_2-benzoyl

(4a*R*,6*R*,7*R*,8*R*,8a*R*)-7-((*tert*-Butoxycarbonyl)amino)-2,2-dimethyl-8-((triisopropylsilyl)oxy)hexahydropyrano[3,2-*d*][1,3]dioxin-6-yl 2,4-dichlorobenzoate (**S13**): the product **S13** was isolated through a silica gel flash column (hexanes/ether: from 10:1 to 4:1) as colorless oil (163.5 mg, 63% yield). $[\alpha]_D^{20}$ = +88.4 (*c* 1.0, CH_2Cl_2); IR ν_{max} (neat)/cm^{-1}: 2942 (m), 2866 (m), 1724 (s), 1585, 1499, 1368, 1269, 1130 (s), 982 (s); ^1H NMR (400 MHz, C_6D_6) δ

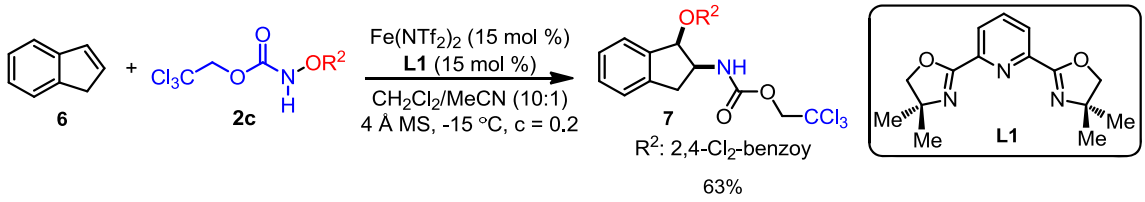
7.41 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 1.7 Hz, 1H), 6.77 (brd, J = 2.5 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 4.87 (d, J = 8.7 Hz, 1H), 4.38 (t, J = 8.2 Hz, 1H), 4.18 (t, J = 9.4 Hz, 1H), 3.88 (td, J = 10.1, 5.3 Hz, 1H), 3.70 (dd, J = 10.6, 5.1 Hz, 1H), 3.47 (t, J = 10.6 Hz, 1H), 3.39 (t, J = 9.3 Hz, 1H), 1.42 (s, 9H), 1.36 (s, 3H), 1.21 (d, J = 9.1 Hz, 21H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 155.0, 139.4, 134.5, 133.8, 131.3, 127.5, 99.7, 94.3, 80.0, 74.6, 71.3, 66.5, 62.0, 55.2, 28.9, 28.3, 18.8, 18.3, 18.2, 12.8; HRMS (ESI, m/z): calcd for $C_{30}H_{46}Cl_2NO_8Si^-$, [M - H^+], 646.2375, found 646.2352.



The stereochemistry of **S13** was determined through *NOE* analysis.

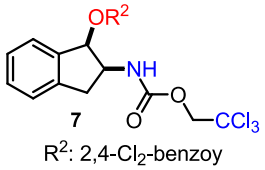
We observed strong *NOE*s between H(b) and H(e), as well as between H(d) and H(f). The results, together with the stereochemistry of the starting material, suggest that H(b) is at the axial

position. Additionally, we observed either no *NOE* or a very weak *NOE* between H(a) and H(f) or H(d), which indicates that H(a) is at the equatorial position; therefore, the stereochemical relationship between OR^2, NHBoc, and OTIPS are *syn*, *anti*.



Indene **6** is commercially available and it was distilled before usage.

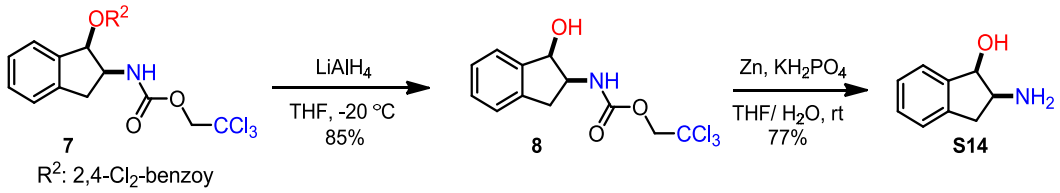
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(NTf_2)_2$ (36.9 mg, 0.06 mmol) and **L1** (16.4 mg, 0.06 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.8 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2c** (182.9 mg, 0.48 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (1.0 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then indene **6** (46.6 μL, 0.40 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



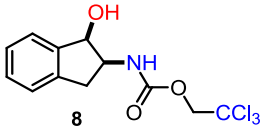
2-(((2,2,2-Trichloroethoxy)carbonyl)amino)-2,3-dihydro-1*H*-inden-1-yl 2,4-dichlorobenzoate (**7**): the product **7** was isolated through a silica gel flash column (hexanes/Acetone: from = 50:1 to 10:1) as a white solid (140.4 mg, 71% yield, m.p. 130−131 °C); IR ν_{max} (neat)/cm^{-1}: 3352 (w), 2952 (w), 1717 (w), 1853 (m), 1515 (m); ^1H NMR (400 MHz,

$CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.48 (s, 1H), 7.41 – 7.35 (m, 1H), 7.31 (d, *J* = 9.8 Hz, 3H), 6.35 (d, *J* = 5.5 Hz, 1H), 5.66 (d, *J* = 8.6 Hz, 1H), 4.93 – 4.66 (m, 3H), 3.38 (dd, *J* = 15.4, 7.4 Hz, 1H), 3.08 (dd, *J* = 15.5, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 154.2, 141.5, 138.7, 138.3, 134.3, 133.0, 131.0, 130.1, 128.4, 127.5, 127.2, 127.1, 125.0, 95.4, 77.9, 74.7, 53.8, 36.9; HRMS (ESI, m/z): calcd for $C_{19}H_{14}Cl_6NO_4^-$ [M + Cl^-], 529.9059, found 529.9054.

Product **7** has been converted to 2-amino-indanol **S14**, which is a known compound. Its relative stereochemistry was determined by comparing its NMR data with known compounds.[11,12]

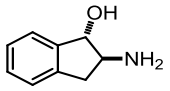
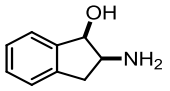
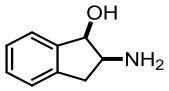


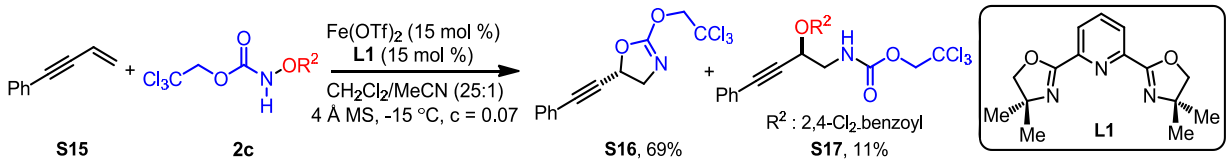
Compound **7** (99.5 mg, 0.20 mmol) was dissolved in anhydrous THF (3 mL) in a 10 mL flask equipped with a stir bar. The flask was cooled to -20 °C and then $LiAlH_4$ powder (15.2 mg, 0.4 mmol) was added in three portions. The reaction mixture was stirred at the same temperature and monitored by TLC. After about 20 to 30 min, the reaction was quenched with saturated NH_4Cl aqueous solution (1 mL) and aqueous HCl (1M, 2 mL) successively. The whole mixture was filtered through a short Celite pad and concentrated *in vacuo*. The resting aqueous phase was extracted with EtOAc (2 mL × 3) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified through a silica gel flash column (hexanes/EtOAc: from 6:1 to 2:1) to afford the *N*-Troc-2-aminoindanol **8** as a white solid (53.2 mg, 82% yield).



2,2,2-Trichloroethyl (1-hydroxy-2,3-dihydro-1H-inden-2-yl)carbamate (**8**): a white solid (m.p. 130−131 °C); IR ν_{max} (neat)/cm^{-1}: 3412 (m), 2952 (w), 1711 (s), 1507 (s), 1401 (m), 1242 (m), 1110 (m), 1012 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.1 Hz, 1H), 7.37 – 7.19 (m, 3H), 5.79 (d, *J* = 7.1 Hz, 1H), 5.06 (s, 1H), 4.74 (q, *J* = 12.0 Hz, 2H), 4.48 – 4.36 (m, 1H), 3.28 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.94 (dd, *J* = 15.8, 7.2 Hz, 1H), 2.17 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 141.8, 140.8, 129.5, 127.5, 125.3, 125.1, 95.5, 74.6, 74.6, 55.1, 36.7; HRMS (ESI, m/z): calcd for $C_{12}H_{11}Cl_3NO_3^-$ [M – H^+], 321.9810, found 321.9807.

The *N*-Troc protecting group was removed by treating **8** with Zn powder under a weakly acidic condition:[13] To a solution of **8** (0.15 mmol) and activated Zn powder (245 mg, 3.75 mmol) in THF (2.0 mL) at room temperature was added aqueous KH_2PO_4 (1 M, 0.4 mL). After being stirred for 1 h at room temperature, the mixture was filtrated through a Celite pad, concentrated and purified through a silica gel flash column ($CHCl_3$/MeOH : from 20:1 to 10:1), **S14** was obtained as a white solid (17.2 mg, 77% yield), which is determined to be *syn* by comparing its ^{1}H NMR data with ones from a known compound.[12]

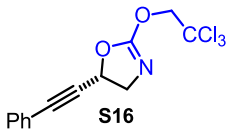
	 ***anti*-S14** (Literature Data) [12]	 ***syn*-S14** (Literature Data) [12]	 ***syn*-S14** (obtained through derivatization)
^{1}H NMR	7.60 – 7.15 (m, 4H), 4.82 (d, *J* = 6.5 Hz; 1H), 3.45 (dt, *J* = 8.0, 6.5 Hz; 1H), 3.25 (dd, *J* = 15.3, 8.0 Hz; 1H), 2.65 (dd, *J* = 15.3, 8.0 Hz, 1H), 2.0 (bs, 3H).	7.60 – 7.15 (m, 4H), 4.82 (d, *J* = 5.5 Hz; 1H), 3.75 (dt, *J* = 6.6, 5.5, 5.1 Hz; 1H), 3.15 (dd, *J* = 15.8, 6.6 Hz; 1H), 2.75 (dd, *J* = 15.8, 5.1 Hz; 1H), 2.15 (bs, 1H),	7.53 – 7.17 (m, 4H), 4.85 (d, *J* = 5.2 Hz, 1H), 3.73 (m, 1H), 3.14 (dd, *J* = 15.7, 6.4 Hz, 1H), 2.77 (dd, *J* = 15.7, 4.6 Hz, 1H), 1.98 (brs, 1H).



Enyne **S15** was synthesized according to a known procedure.[14]

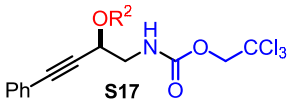
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (21.3 mg, 0.06 mmol) and **L1** (16.4 mg, 0.06 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.5 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-

dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2c** (152.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (6.2 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, enyne **S15** (61.5 mg, 0.48 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 1.5 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S16

5-(Phenylethynyl)-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (**S16**): compound **S16** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (87.9 mg, 69% yield). IR ν_{max} (neat)/cm^{-1}: 2952 (w), 2233 (w), 1674 (s), 1398 (m), 1317 (s), 1247 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 6.9 Hz, 2H), 7.41 – 7.32 (m, 3H), 5.61 − 5.54 (m, 1H), 4.92 – 4.84 (m, 2H), 4.24 – 4.16 (m, 1H), 3.98 (dd, J = 12.6, 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 131.9, 129.1, 128.4, 121.6, 93.9, 88.4, 85.0, 79.7, 71.4, 59.0; HRMS (ESI, m/z): calcd for $C_{13}H_{11}Cl_3NO_2^+$ [M + H^+], 317.9850, found 317.9845.

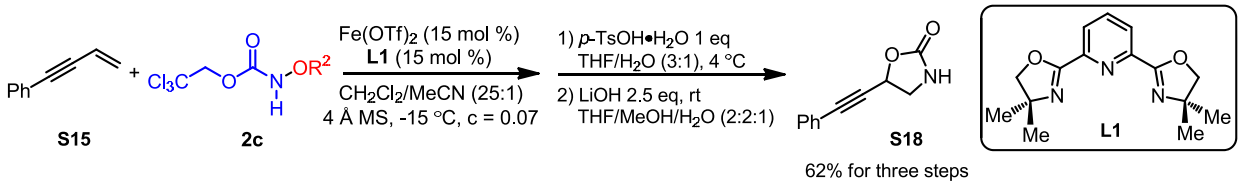


S17

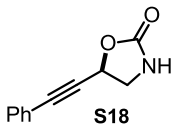
R^2 : 2,4-Cl_2-benzoyl

4-Phenyl-1-(((2,2,2-trichloroethoxy)carbonyl)amino)but-3-yn-2-yl 2,4-dichlorobenzoate (**S17**): product **S17** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) as colorless oil (22.4 mg, 11% yield). IR ν_{max} (neat)/cm^{-1}: 3362 (w), 2922 (w), 2228 (w), 1724 (s), 1585 (m), 1520 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.41 – 7.31 (m, 4H), 5.98-5.93 (m, 1H), 5.40 (brs, 1H), 4.82 – 4.70 (m, 2H), 3.95 – 3.86 (m, 1H), 3.84 – 3.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5,

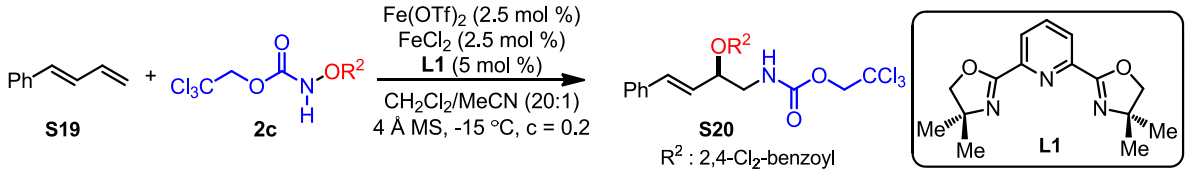
154.6, 138.9, 135.2, 132.9, 132.0, 131.1, 129.2, 128.4, 127.5, 127.2, 121.4, 100.0, 87.4, 82.9, 74.7, 64.8, 44.8; HRMS (ESI, m/z): calcd for $C_{20}H_{14}Cl_6NO_4^-$, [M + Cl^-], 541.9059, found 541.9051.



By following the general hydrolysis procedure, above crude products can also be converted to corresponding oxazolidinone **S18** in good combined yield.



5-(Phenylethynyl)oxazolidin-2-one (**S18**): Compound **S18** was isolated through a silica gel flash column (hexanes/acetone: from 10:1 to 2:1) as colorless oil (46.5 mg, 62% yield). IR ν_{max} (neat)/cm^{-1}: 2324 (m), 1755 (s), 1540 (w), 1489 (s), 1343 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 2H), 7.44 – 7.30 (m, 3H), 6.26 (brs, 1H), 5.49 (t, J = 7.7 Hz, 1H), 3.94 (t, J = 8.6 Hz, 1H), 3.74 (t, J = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 131.9, 129.3, 128.4, 121.3, 88.0, 84.1, 66.5, 47.3; HRMS (ESI, m/z): calcd for $C_{11}H_{10}NO_2^+$ [M + H^+], 188.0706, found 188.0697.

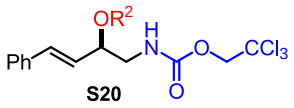


trans-1-Phenyl-1,3-butadiene **S19** was synthesized according to a literature procedure.[15]

More electrophilic $Fe(OTf)_2$ catalyst leads to substrate decomposition during the reaction; therefore, a mixture of $Fe(OTf)_2$ and $FeCl_2$ was applied as the catalyst to achieve both high reactivity and high selectivity.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (3.5 mg, 0.01 mmol), $FeCl_2$ (1.3 mg, 0.01 mmol) and **L1** (5.5 mg, 0.020 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.4 mL) and MeCN (0.1

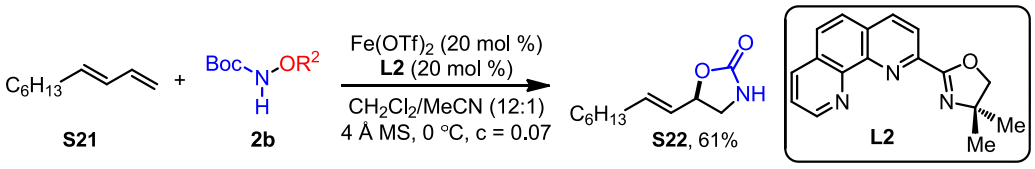
mL) were added via a syringe and the mixture was stirred at room temperature for 20 min and then *trans*-1-Phenyl-1,3-butadiene **S19** (56.2 μL mg, 0.40 mmol) was added to it. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2c** (167.6 mg, 0.44 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (1.5 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then the solution in vial **A** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S20

R^2 : 2,4-Cl_2-benzoyl

(*E*)-4-Phenyl-1-(((2,2,2-trichloroethoxy)carbonyl)amino)but-3-en-2-yl 2,4-dichlorobenzoate (**S20**): compound **S20** was isolated through a silica gel flash column (hexanes/EtOAc: from 50:1 to 6:1) as colorless oil (171.8 mg, 84% yield); IR ν_{max} (neat)/cm^{-1}: 3347 (w), 3028 (w), 2952 (w), 1722 (s), 1583 (m), 1517 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 1H), 7.51 (s, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.27 (m, 4H), 6.83 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 15.9, 7.2 Hz, 1H), 5.87 – 5.75 (m, 1H), 5.36 (t, J = 5.9 Hz, 1H), 4.79 – 4.69 (m, 2H), 3.80 – 3.72 (m, 1H), 3.71 – 3.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 154.8, 138.7, 135.6, 135.1, 134.8, 132.8, 131.1, 128.7, 128.5, 128.0, 127.2, 126.8, 123.3, 95.5, 75.0, 74.6, 44.5; HRMS (ESI, m/z): calcd for $C_{20}H_{16}Cl_6NO_4^-$, [M + Cl^-], 543.9216, found 543.9213.

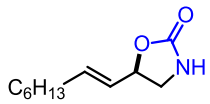


S21 **2b** **S22**, 61% **L2**

(*E*)-Deca-1,3-diene **S21** was synthesized according to a literature procedure.[16]

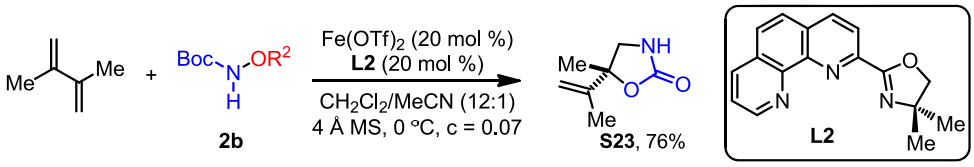
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L2** (22.2 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.5 mL) were added via a

syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2b** (146.9 mg, 0.48 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then (*E*)-deca-1,3-diene **S21** (74.4 μL, 0.4 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S22

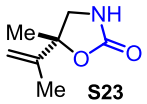
(*E*)-5-(Oct-1-en-1-yl)oxazolidin-2-one (**S22**): product **S22** was isolated through a silica gel flash column (hexanes/EtOAc: from 4 : 1 to 1 : 1) as a white solid (48.2 mg, 61% yield, m.p. 49−50 °C). IR ν_{max} (neat)/cm^{-1}: 3261 (m), 2916 (m), 2850 (m), 1719 (s), 1444 (w), 1373 (m), 1239 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (brs, 1H), 5.93 – 5.80 (m, 1H), 5.56 (dd, *J* = 15.3, 7.8 Hz, 1H), 5.01 (q, *J* = 7.9 Hz, 1H), 3.71 (t, *J* = 8.5 Hz, 1H), 3.33 (t, *J* = 8.1 Hz, 1H), 2.09 (q, *J* = 7.0 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.35 – 1.22 (m, 6H), 0.89 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 137.4, 126.1, 77.9, 46.5, 32.1, 31.6, 28.8, 28.6, 22.6, 14.1; HRMS (ESI, m/z): calcd for $C_{11}H_{20}NO_2^+$, [M + H^+], 198.1489, found 198.1482.



2,3-Dimethyl-1,3-butadiene is commercially available and it was distilled before usage.

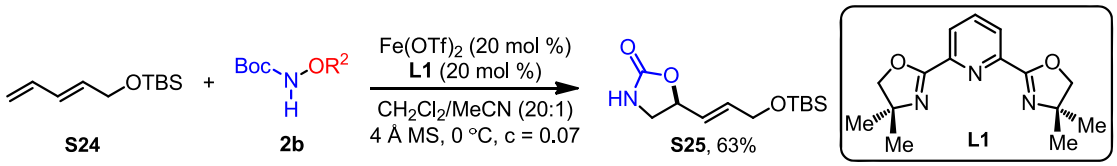
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L2** (22.2 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.5 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg)

and **2b** (122.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then 2,3-dimethyl-1,3-butadiene (94.9 μL, 0.8 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S23

5-Methyl-5-(prop-1-en-2-yl)oxazolidin-2-one (**S23**): compound **S23** was isolated through a silica gel flash column (hexanes/EtOAc: from 4:1 to 1:1) as colorless oil (42.9 mg, 76% yield). IR ν_{max} (neat)/cm^{-1}: 3251 (m), 2977 (w), 1727 (s), 1648 (w), 1436 (m), 1269 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (brs, 1H), 5.09 (s, 1H), 4.92 (s, 1H), 3.54 (d, J = 8.5 Hz, 1H), 3.37 (d, J = 8.5 Hz, 1H), 1.80 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 145.1, 111.2, 84.2, 51.0, 25.3, 18.2; HRMS (ESI, m/z): calcd for $C_7H_{12}NO_2^+$, [M + H^+], 142.0863, found 142.0858.

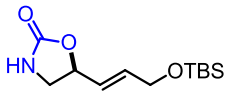


S24 **2b** **S25**, 63% **L1**

Diene **S24** was synthesized according to a literature procedure.[17]

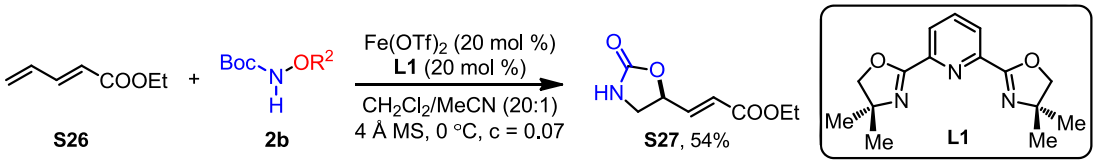
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L1** (21.8 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.5 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2b** (146.9 mg, 0.48 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.8 mL) was added via a syringe. Both solutions were

degassed with brief evacuation and backfilling with N_2 twice. Then diene **S24** (79.4 mg, 0.4 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S25

(*E*)-5-(3-((tert-Butyldimethylsilyl)oxy)prop-1-en-1-yl)oxazolidin-2-one (**S25**): product **S25** was isolated through a silica gel flash column (hexanes/EtOAc: from 4:1 to 1:1) as colorless oil (64.9 mg, 63% yield). IR ν_{max} (neat)/cm^{-1}: 3286 (w), 2927 (m), 2856 (m), 1747 (s), 1472 (w), 1358 (w), 1249 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (brs, 1H), 5.96 (dt, *J* = 15.3, 4.0 Hz, 1H), 5.83 (dd, *J* = 15.3, 6.9 Hz, 1H), 5.10 (q, *J* = 7.6 Hz, 1H), 4.28 – 4.17 (m, 2H), 3.74 (t, *J* = 8.6 Hz, 1H), 3.36 (t, *J* = 8.1 Hz, 1H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 134.8, 125.4, 62.4, 46.4, 25.9, 18.4, -5.30, -5.33; HRMS (ESI, m/z): calcd for $C_{12}H_{23}NNaO_3Si^+$ [M + Na^+], 280.1339, found 280.1329.

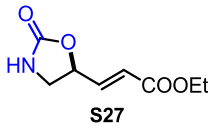


S26 **2b** **S27**, 54%

(*E*)-Ethyl penta-2,4-dienoate **S26** was synthesized according to a literature procedure.[18]

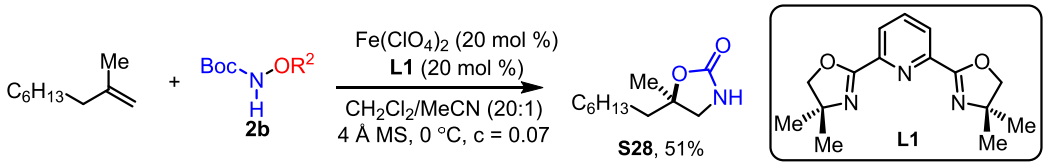
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L1** (21.8 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.5 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2b** (146.9 mg, 0.48 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.2 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then (*E*)-ethyl penta-2,4-dienoate

S26 (50.5 mg, 0.4 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S27

(*E*)-ethyl 3-(2-oxooxazolidin-5-yl)acrylate (**S27**): product **S27** was isolated through a silica gel flash column (hexanes/EtOAc: from 2:1 to 1:1) as colorless oil (40.0 mg, 54% yield). IR ν_{max} (neat)/cm^{-1}: 3281 (w), 2977 (w), 1742 (s), 1714 (s), 1664 (m), 1431 (w), 1368 (m), 1305 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (dd, *J* = 15.7, 5.2 Hz, 1H), 6.31 (brs, 1H), 6.18 (d, *J* = 15.7 Hz, 1H), 5.23 (dd, *J* = 14.0, 6.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.85 (t, *J* = 8.9 Hz, 1H), 3.42 (t, *J* = 7.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 159.3, 141.9, 123.5, 74.5, 60.9, 45.5, 14.2; HRMS (ESI, m/z): calcd for $C_8H_{12}NO_4^+$ [M + H^+], 186.0761, found 186.0753;

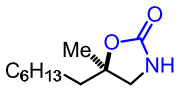


2-Methyl-1-nonene is commercially available and it was distilled before usage.

For this particular substrate, other iron catalysts lead to a large amount of allylic amination product, presumably through addition and the subsequent elimination. We determined that $Fe(ClO_4)_2$ is uniquely effective for the desired reaction.

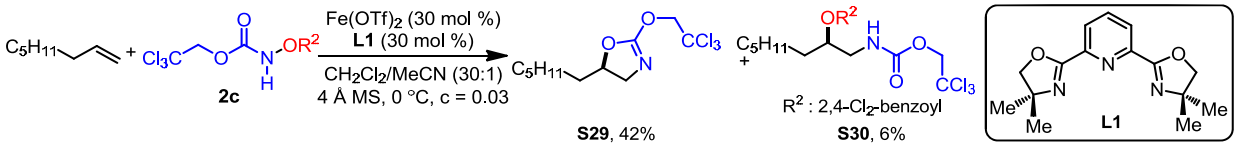
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(ClO_4)_2$ (20.4 mg, 0.08 mmol), **L1** (21.8 mg, 0.08 mmol) and activated 4Å molecular sieves (40 mg). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.5 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added

activated 4Å molecular sieves (200 mg) and **2b** (146.9 mg, 0.48 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.2 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then 2-methylnon-1-ene (75.3 μL, 0.4 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 12 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S28

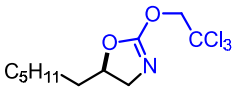
5-Heptyl-5-methyloxazolidin-2-one (**S28**): compound **S28** was isolated through a silica gel flash column (hexanes/EtOAc: from 4:1 to 1:1) as colorless oil (40.7 mg, 51% yield). IR ν_{max} (neat)/cm^{-1}: 3060 (w), 2927 (m), 2856 (w), 1737 (s), 1454 (w), 1378 (w), 1080 (m), 971 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (brd, J = 9.2 Hz, 1H), 3.40 (d, J = 8.4 Hz, 1H), 3.28 (d, J = 8.4 Hz, 1H), 1.73 – 1.65 (m, 2H), 1.45 (s, 3H), 1.43 – 1.20 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 83.3, 51.2, 40.3, 31.7, 29.7, 29.1, 25.5, 23.4, 22.6, 14.1; HRMS (ESI, m/z): calcd for $C_{11}H_{22}NO_2^+$, $[M + H^+]$, 200.1645, found 200.1636.



Octene is commercially available and it was distilled before usage.

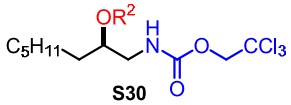
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (42.5 mg, 0.12 mmol) and **L1** (32.8 mg, 0.12 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.6 mL) and MeCN (0.4 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried vial (20mL, vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2c** (152.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three

times and then anhydrous CH_2Cl_2 (10 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then octene (313 μL, 2.0 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature for 24 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S29

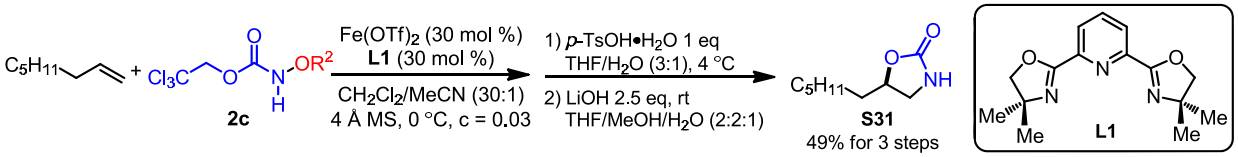
5-Hexyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (**S29**): compound **S29** was isolated through a silica gel flash column (hexanes/EtOAc: from 50:1 to 10:1) as colorless oil (50.8 mg, 42% yield). IR ν_{max} (neat)/cm^{-1}: 3327 (m), 1730 (s), 1702 (s), 1585 (w), 1542 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 – 4.71 (m, 3H), 3.91 (dd, *J* = 12.6, 9.0 Hz, 1H), 3.45 (dd, *J* = 12.6, 7.4 Hz, 1H), 1.78 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.70 – 1.59 (m, 1H), 1.51 – 1.25 (m, 8H), 0.90 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 94.2, 82.7, 79.4, 56.9, 35.2, 31.7, 29.0, 24.8, 22.5, 14.0; HRMS (ESI, m/z): calcd for $C_{11}H_{19}Cl_3NO_2^+$ [M + H^+], 302.0476, found 302.0470.



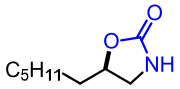
S30

R^2 : 2,4-Cl_2-benzoyl

1-(((2,2,2-Trichloroethoxy)carbonyl)amino)octan-2-yl 2,4-dichlorobenzoate (**S30**): compound **S30** was isolated through a silica gel flash column (hexanes/EtOAc: from 50:1 to 10:1) as colorless oil (11.8 mg, 6% yield); IR ν_{max} (neat)/cm^{-1}:3345, 2922, 2856, 1729, 1669, 1589, 1532; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 5.38 – 5.12 (m, 2H), 4.74 (q, *J* = 12.0 Hz, 2H), 3.69 – 3.57 (m, 1H), 3.57 – 3.46 (m, 1H), 1.82 – 1.65 (m, 2H), 1.45 – 1.19 (m, 8H), 0.89 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 154.7, 138.5, 134.6, 132.5, 131.0, 128.5, 127.2, 74.9, 74.6, 44.3, 31.6, 31.5, 29.7, 29.0, 25.2, 22.5, 14.0; HRMS (ESI, m/z): calcd for $C_{18}H_{22}Cl_5NNaO_4^+$, [M + Na^+], 513.9884, found 513.9873.



By following the typical hydrolysis procedure, the crude products can also be converted to the corresponding oxazolidinone **S31** in decent combined yield.

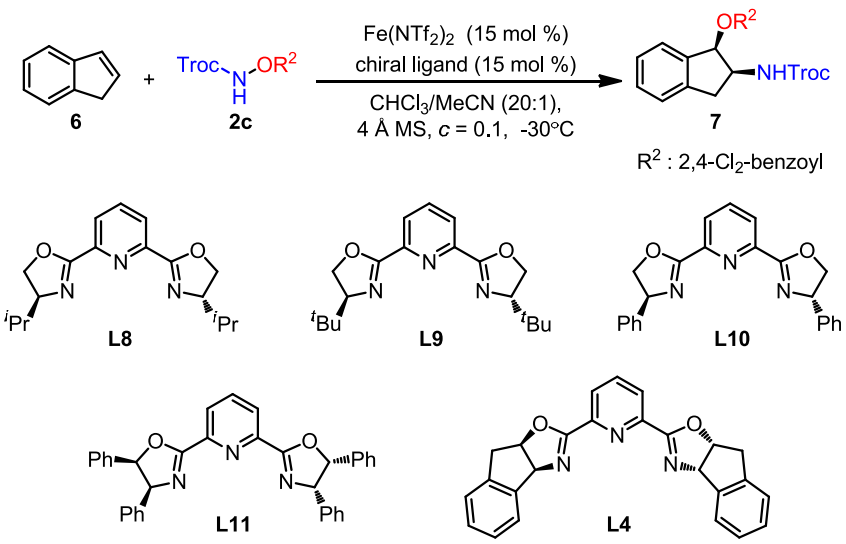


S31

5-Hexyloxazolidin-2-one (**S31**): compound **S31** was isolated through a silica gel flash column (hexanes/acetone: from 10:1 to 2:1) as a white foam (33.5 mg, 49% yield). IR ν_{max} (neat)/cm^{-1}: 2927 (m), 2856 (w), 1745 (s), 1489 (w), 1264 (w), 1239 (m), 1077 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (brs, 1H), 4.73 – 4.56 (m, 1H), 3.68 (dd, J = 11.2, 5.4 Hz, 1H), 3.25 (t, J = 7.8 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.72 – 1.59 (m, 1H), 1.53 – 1.43 (m, 1H), 1.42 – 1.24 (m, 7H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 77.2, 46.0, 34.9, 31.6, 28.9, 24.6, 22.5, 14.0; HRMS (ESI, m/z): calcd for $C_9H_{18}NO_2^+$ [M + H^+], 172.1332, found 172.1324.

D. Procedure for the Iron-Catalyzed Asymmetric Olefin Amino-Oxygenation

a. Discovery of Chiral Ligands for Asymmetric Induction



entry	ligand	isolated yield	ee
1	**L8**	39%	33%
2	**L9**	35%	40%
3	**L10**	42%	56%
4	**L11**	48%	51%
5	**L4**	71%	81%

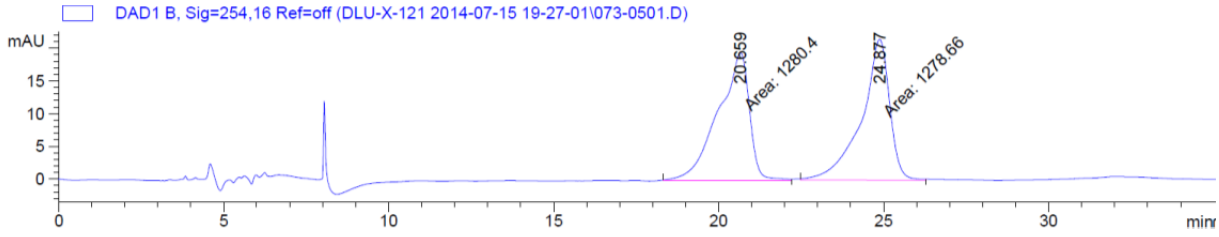
Ligand **L4** was synthesized according to a known procedure.[19]

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(NTf_2)_2$ (36.9 mg, 0.06 mmol) and a chiral ligand (0.06 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous $CHCl_3$ (0.8 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2c** (152.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous $CHCl_3$ (3.0 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then indene **6** (55.9 μL, 0.48 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -30 °C. The reaction was kept stirring at the same temperature for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was

extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product **7** was isolated through a silica gel flash column and analyzed through chiral HPLC columns. The results are listed in the table.

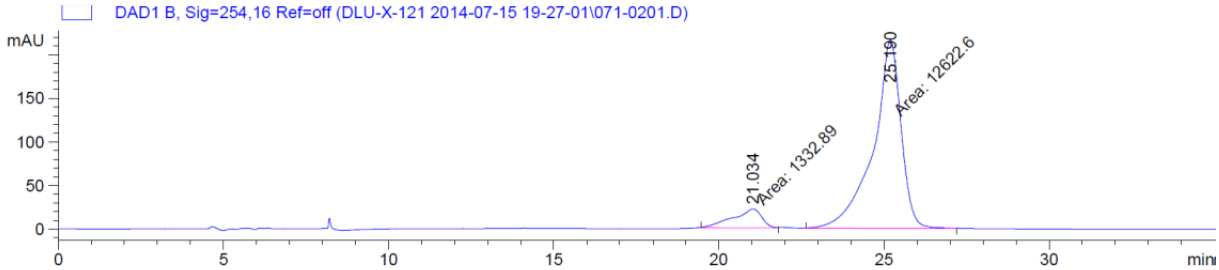
When chiral Ligand **L4** was applied, the product **7** was isolated through a silica gel flash column (hexanes/acetone: from 50:1 to 6:1) as a white solid (141.3 mg, 71% yield). $[\alpha]_D^{20}$ = -60.1 (*c* 1.0, $CHCl_3$). The *ee* was measured by Chiral HPLC analysis (Chiral *S.S.* Whelk, 1.0 mL/min, 254 nm, 5% EtOH in hexanes, t_r (minor) = 20.66 min, t_r (major) = 24.88 min, 81% *ee*).

Racemic sample



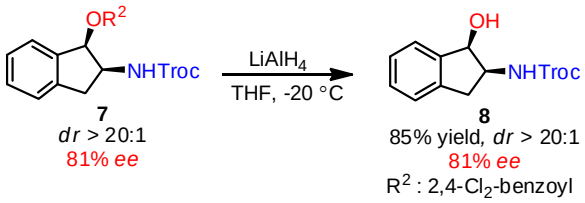
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.659	MM	1.0946	1280.40137	19.49595	50.0340
2	24.877	MM	0.9894	1278.66064	21.53968	49.9660
Totals :				2559.06201	41.03563	

Enantio-enriched sample (81% *ee*)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.034	MM	1.0183	1332.88940	21.81666	9.5510
2	25.190	MM	0.9740	1.26226e4	216.00296	90.4490
Totals :				1.39555e4	237.81962	

b. Derivatization of 7

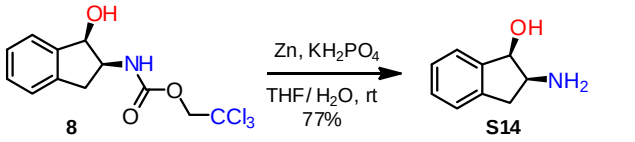


7
dr > 20:1
81% *ee*

8
85% yield, *dr* > 20:1
81% *ee*
R^2 : 2,4-Cl_2-benzoyl

By following the aforementioned $LiAlH_4$ reductive procedure, compound **7** can be selectively converted to 2-amino-1-indanol **8** without erosion of its *dr* and *ee* (85% yield). $[\alpha]_D^{20}$ = +23.2 (*c* 1.0, $CHCl_3$); The *ee* was determined by Chiral HPLC analysis (Chiral *S.S.* Whelk, 1.0 mL/min, 265 nm, 15% EtOH in hexanes, t_r (major) = 12.24 min, t_r (minor) = 16.74 min, 81% *ee*).

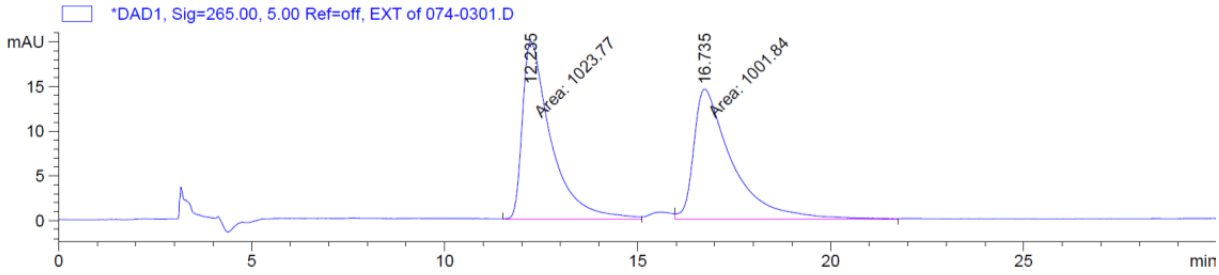
The absolute chemistry was determined by comparison of the rotation data of 2-amino indanol obtained after zinc dust reduction with literature precedent.[20]



8 **S14**

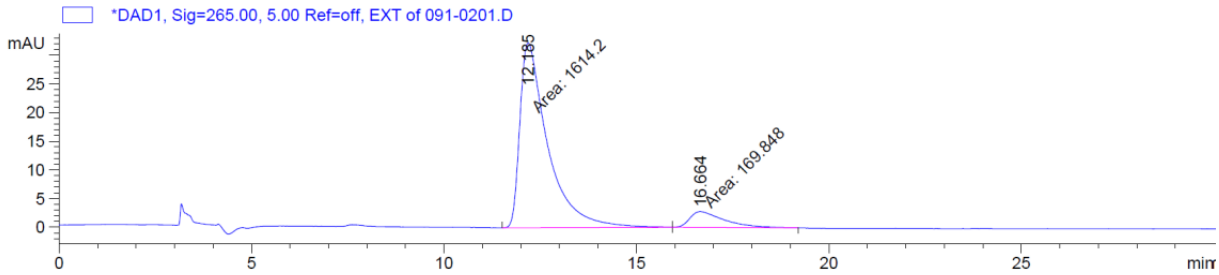
$[\alpha]_D^{20}$ = +40.2 (*c* 1.0, $CHCl_3$)

Racemic sample



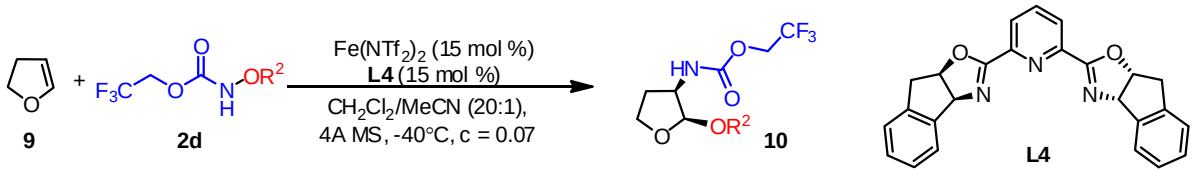
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.235	MF	0.8602	1023.76611	19.83623	50.5412
2	16.735	FM	1.1484	1001.84143	14.53924	49.4588
Totals :				2025.60754	34.37547	

Enantio-enriched sample (81% *ee*)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.185	MM	0.8342	1614.19958	32.24887	90.4796
2	16.664	MM	1.0289	169.84776	2.75140	9.5204
Totals :				1784.04735	35.00026	

c. Asymmetric Amino-Oxygenation of 2,3-Dihydrofuran



R^2 : 2,4-Cl_2-benzoyl

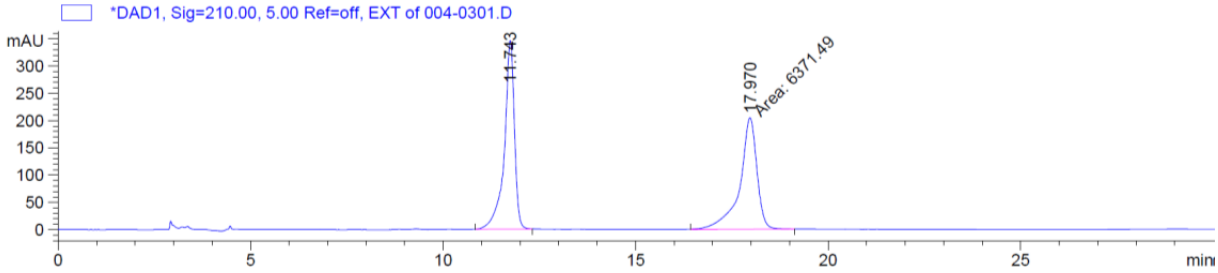
53% yield,
dr > 20:1, 57% ee

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(NTf_2)_2$ (36.9 mg, 0.06 mmol) and **L4** (23.6 mg, 0.06 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2d** (132.8 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (5.0 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then 2,3-dihydrofuran **9** (60.4 μL, 0.80 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -40 °C. The reaction was kept stirring at the same temperature for another 2 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and

stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.

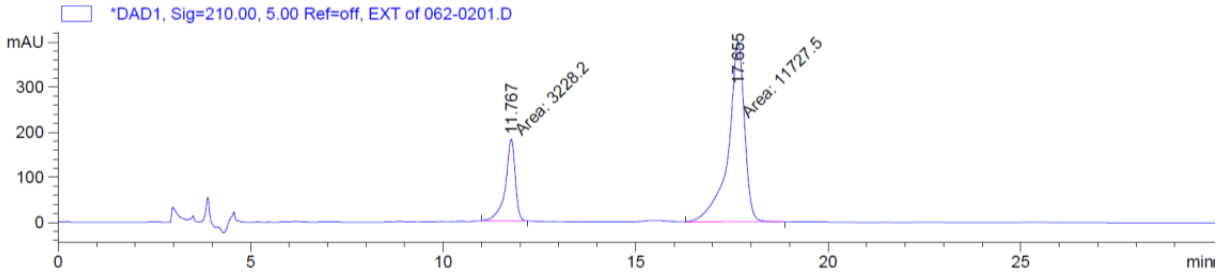
10 was isolated through a silica gel flash column (hexanes/EtOAc: from 20:1 to 4:1) as a white solid (85.2 mg, 53% yield). $[\alpha]_D^{20}$ = -74.0 (*c* 1.0, $CHCl_3$). The *ee* was measured by Chiral HPLC analysis (Chiral *S.S.* Whelk, 1.0 mL/min, 210 nm, 15% EtOH in hexanes, t_r (minor) = 11.74 min, t_r (major) = 17.97 min, 57% *ee*).

Racemic sample



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.743	BB	0.2681	6352.02979	346.15771	49.9235
2	17.970	MM	0.5188	6371.49463	204.66739	50.0765
Totals :				1.27235e4	550.82510	

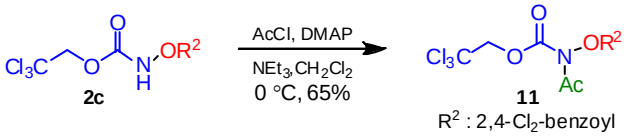
Enantio-enriched sample (57% *ee*)



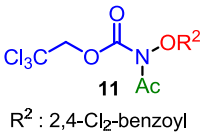
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.767	MM	0.2962	3228.19604	181.66481	21.5851
2	17.655	MM	0.4889	1.17275e4	399.77057	78.4149
Totals :				1.49557e4	581.43538	

E. Mechanistic Studies of the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

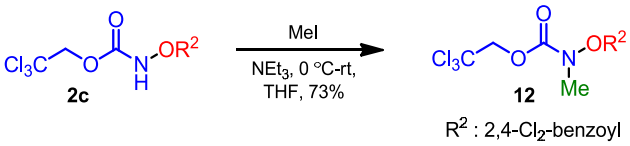
a. Evaluation of *N*-Ac and *N*-Me Protected Acyloxyl Carbamates in the Iron-Catalyzed Olefin Amino-Oxygenation



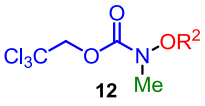
Acyloxyl carbamate **2c** (191 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (3 mL) with DMAP (1.2 mg, 0.01 mmol) and the mixture was cooled to 0 ^oC. To the above solution, acetyl chloride (43 uL, 0.6 mmol, dissolved in 1mL CH_2Cl_2) and TEA (83 µL, 0.6 mmol, dissolved in 1mL CH_2Cl_2) were added drop-wise at the same time. The reaction was kept stirring and monitored by TLC. After **2c** was consumed, the white precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was subsequently purified through a silica gel flash column (Hexanes/EtOAc: from 30:1 to 5:1) to afford **11** as colorless oil (133 mg, 63% yield).



2,2,2-Trichloroethyl acetyl((2,4-dichlorobenzoyl)oxy)carbamate (**11**): IR ν_{max} (neat)/cm^{-1}: 3192, 3056, 2973, 1790 (s), 1765 (s), 1740 (s), 1583, 1375, 1295 (s), 1226 (s), 1125 (s), 1074, 1006, 956; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.56 (s, 1H), 7.39 (d, J = 8.4 Hz, 1H), 4.88 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 161.0, 149.8, 140.3, 136.2, 133.1, 131.4, 127.3, 123.9, 93.6, 76.1, 24.8; HRMS (ESI, m/z): calcd for $C_{12}H_9Cl_5NO_5^+$ [M + H^+], 421.8918, found 421.8899.



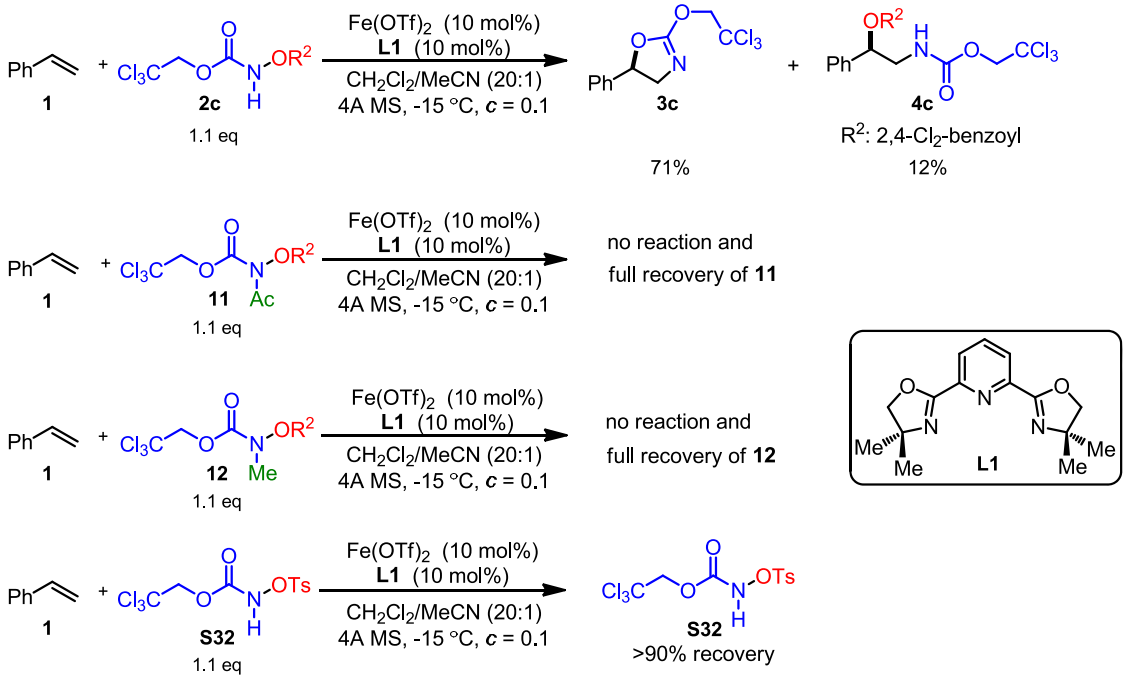
Acyloxyl carbamate **2c** (191 mg, 0.5 mmol) was dissolved in THF (3 mL) with iodomethane (51 µL, 1 mmol) and the mixture was cooled to 0 ^oC. After addition of TEA (70 uL, 0.5 mmol), the reaction was then warmed up to room temperature gradually and kept stirring for another 5 h. The reaction mixture was quenched by 0.5 mL EtOH and concentrated *in vacuo* and the residue was purified through a silica gel flash column (Hexanes/EtOAc: from 30:1 to 7:1) to afford **12** as colorless oil (144 mg, 73% yield).



12

R^2 : 2,4-Cl_2-benzoyl

2,2,2-Trichloroethyl (2,4-dichlorobenzoyl)oxy(methyl)carbamate (**12**): IR ν_{max} (neat)/cm^{-1}: 2982 (w), 1782 (m), 1732 (s), 1583 (m), 1373 (m), 1231 (s), 1160, 1074, 1041, 982; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 7.37 (dd, J = 8.4, 1.7 Hz, 1H), 4.81 (s, 2H), 3.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.7, 139.8, 135.6, 132.7, 131.2, 127.3, 125.1, 94.6, 75.6, 38.0; HRMS (ESI, m/z): calcd for $C_{11}H_9Cl_5NO_4^+$ [M + H^+], 393.8969, found 393.8951.



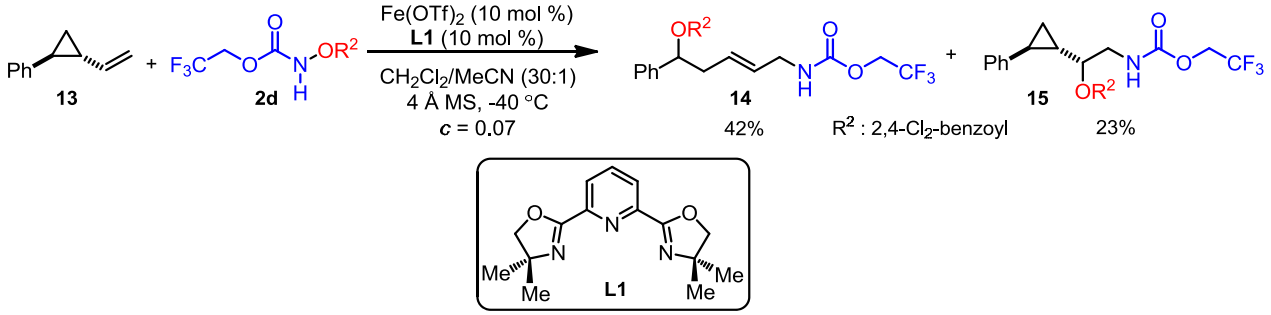
11, **12** and Tosyloxyl carbamate **S32** were evaluated under the optimized reaction condition.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (7.1 mg, 0.02 mmol) and **L1** (5.5 mg, 0.02 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.5 mL) and MeCN (0.1 mL) were added via a syringe and the mixture was stirred at room temperature for 30 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (50 mg) and potential amino-oxygenation reagents (0.22 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (1.4 mL) was added via a syringe. Both vials were degassed with brief evacuation and backfilling with N_2 twice. Then, freshly distilled styrene (23

uL, 0.2 mmol) was added to vial **B** and the catalyst solution in vial **A** was added with a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 30 min.

Both **11** and **12** were fully recovered (>95% recovery) under this condition. **S32** was also recovered with a good mass balance (>90% recovery).

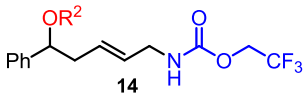
b. Evaluation the Reactivity of a Cyclopropyl-Substituted Olefin



A vinylcyclopropane substrate was evaluated in order to determine whether a radical species is involved in the amino-oxygenation. *trans*-2-Phenyl-1-vinylcyclopropane **13** was synthesized according to a literature procedure.[21]

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (7.1 mg, 0.02 mmol) and **L1** (5.5 mg, 0.02 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.5 mL) and MeCN (0.1 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2d** (66.4 mg, 0.20 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (2.4 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, *trans*-2-phenyl-1-vinylcyclopropane **13** (34.6 mg, 0.24 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -40 °C. The reaction was kept stirring at -40 °C for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were

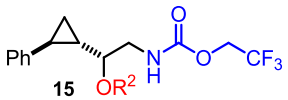
dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Direct amino-oxygenation product **15** and ring opening product **14** were isolated in good combined yield (23% and 42%, respectively).



14

R^2 : 2,4-Cl_2-benzoyl

(*E*)-1-Phenyl-5-(((2,2,2-trifluoroethoxy)carbonyl)amino)pent-3-en-1-yl 2,4-dichlorobenzoate (**14**): product **14** was purified through a flash column (silica gel, hexanes/EtOAc, from 50:1 to 6:1) as colorless oil (40.0 mg, 42% yield). IR ν_{max} (neat)/cm^{-1}: 3352 (w), 2916 (w), 2846, 1722 (s), 1585, 1517, 1376, 1279 (s), 1241(s), 1163(s), 1100 (m), 1047 (m), 969 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.47 – 7.30 (m, 6H), 6.04 (t, *J* = 6.7 Hz, 1H), 5.71 – 5.47 (m, 2H), 4.84 (s, 1H), 4.45 (q, *J* = 8.5 Hz, 2H), 3.76 (t, *J* = 5.5 Hz, 2H), 2.87 – 2.74 (m, 1H), 2.74 – 2.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 139.2, 138.5, 134.9, 132.6, 131.1, 129.3, 128.6, 128.3, 128.0, 127.1, 126.6, 123.1 (q, *J* = 277.5 Hz), 60.9 (q, *J* = 36.6 Hz), 42.9, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.34 (t, *J* = 8.5 Hz); HRMS (ESI, m/z): $C_{21}H_{17}Cl_2F_3NO_4^-$ [M - H^+], 474.0492, found 474.0487.

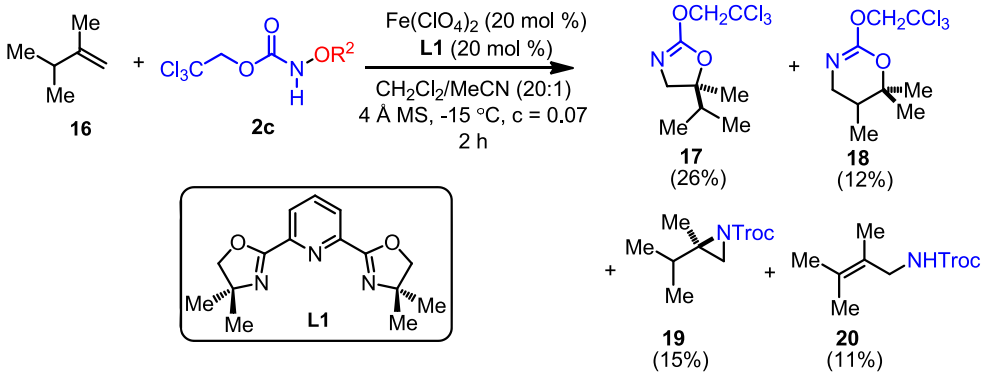


15

R^2 : 2,4-Cl_2-benzoyl

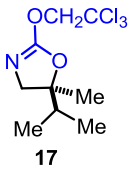
2-Phenylcyclopropyl-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)ethyl 2,4-dichlorobenzoate (**15**): product **15** was purified through a flash column (silica gel, hexanes/EtOAc, from 50:1 to 6:1) as colorless oil (21.8 mg, 23% yield). IR ν_{max} (neat)/cm^{-1}: 2921 (m) , 1727 (s), 1585, 1522, 1375, 1282 (s), 1241, 1168 (s), 1100, 1050; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.21 (t, *J* = 5.5 Hz, 1H), 4.86 (td, *J* = 8.3, 4.2 Hz, 1H), 4.53 – 4.41 (m, 1H), 4.40 – 4.29 (m, 1H), 3.81 – 3.69 (m, 1H), 3.66 – 3.54 (m, 1H), 2.08 – 1.98 (m, 1H), 1.47 – 1.38 (m, 1H), 1.14 – 1.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 154.4, 141.0, 138.6, 134.7, 132.6, 131.1, 128.5, 128.3, 127.2, 126.2, 125.9, 123.0 (q, *J* = 277.4 Hz), 60.9 (q, *J* = 36.6 Hz), 44.7, 29.7, 24.2, 21.4, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.33 (t, *J* = 8.5 Hz); HRMS (ESI, m/z): $C_{21}H_{17}Cl_2F_3NO_4$- [M - H^+], 474.0492, found 474.0496.

c. Evaluation of 16 that is Prone to 1,2-Hydride Shift



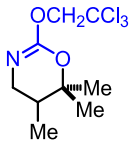
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(ClO_4)_2$ (20.4 mg, 0.08 mmol), **L1** (21.8 mg, 0.08 mmol) and activated 4Å molecular sieves (40 mg). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.5 mL) and MeCN (0.3 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (200 mg) and **2c** (152.4 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (4.2 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then 2,3-dimethyl-1-butene **16** (99 μL, 0.8 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for 1.5 h until it was completed monitored by TLC. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.

Four products were isolated.



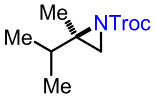
5-*iso*-Propyl-5-methyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (**17**): compound **17** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/EtOAc from 50:1 to 10:1) as colorless oil (28.6 mg, 26% yield). IR ν_{max} (neat)/cm^{-1}: 2967 (w), 2876 (w), 1689 (s),

1449 (w), 1396 (m), 1333 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.77 (m, 2H), 3.68 (d, *J* = 12.7 Hz, 1H), 3.42 (d, *J* = 12.7 Hz, 1H), 2.05 – 1.88 (m, 1H), 1.40 (s, 3H), 0.98 (t, *J* = 5.5 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 94.3, 92.2, 79.1, 60.4, 36.2, 22.6, 16.9, 16.8; HRMS (ESI, m/z): calcd for $C_9H_{15}Cl_3NO_2^+$ [M + H^+], 274.0163, found 274.0154.



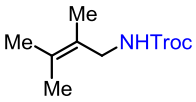
18

5,6,6-Trimethyl-2-(2,2,2-trichloroethoxy)-5,6-dihydro-4H-1,3-oxazine (**18**): compound **18** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/EtOAc from 50:1 to 10:1) as colorless oil (13.2 mg, 12% yield). IR ν_{max} (neat)/cm^{-1}: 2977 (w), 1686 (s), 1456 (w), 1370 (m), 1279 (s), 1199 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 – 4.65 (m, 2H), 3.38 (dd, *J* = 15.7, 5.3 Hz, 1H), 3.06 (dd, *J* = 15.7, 10.2 Hz, 1H), 1.90 – 1.77 (m, 1H), 1.42 (s, 3H), 1.25 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 95.2, 82.1, 76.5, 47.8, 35.6, 27.1, 20.5, 13.4; HRMS (ESI, m/z): calcd for $C_9H_{15}Cl_3NO_2^+$ [M + H^+], 274.0163, found 274.0154.



19

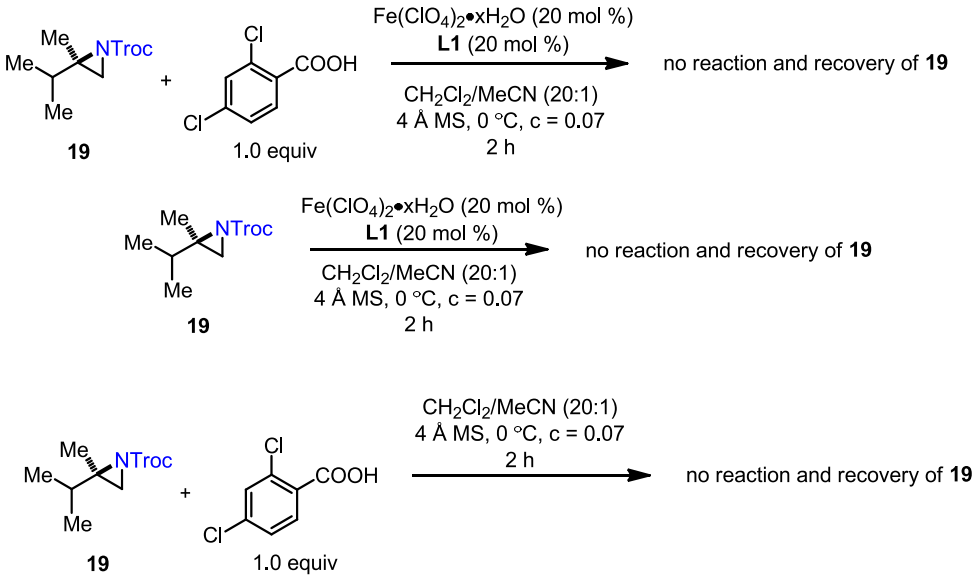
2,2,2-Trichloroethyl 2-isopropyl-2-methylaziridine-1-carboxylate (**19**): compound **19** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/EtOAc from 50:1 to 10:1) as colorless oil (16.5 mg, 15% yield). IR ν_{max} (neat)/cm^{-1}: 2922 (w), 1727 (s), 1378 (m), 1305 (m), 1226 (s), 1135 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (q, *J* = 11.9 Hz, 2H), 2.23 (d, *J* = 3.7 Hz, 2H), 1.56 – 1.45 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 95.1, 75.5, 48.9, 38.1, 34.7, 18.5, 18.2, 15.8; HRMS (ESI, m/z): calcd for $C_9H_{15}Cl_3NO_2^+$ [M + H^+], 274.0163, found 274.0155.



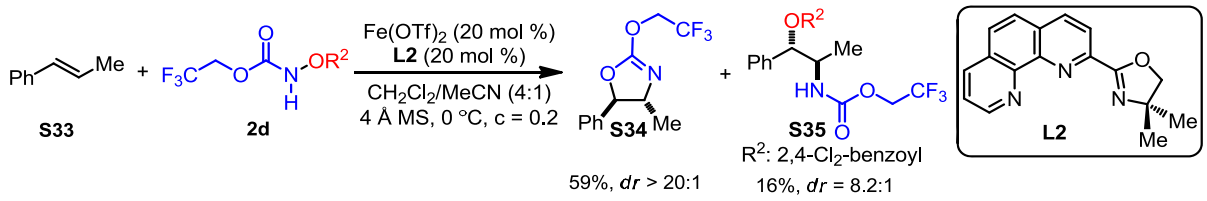
20

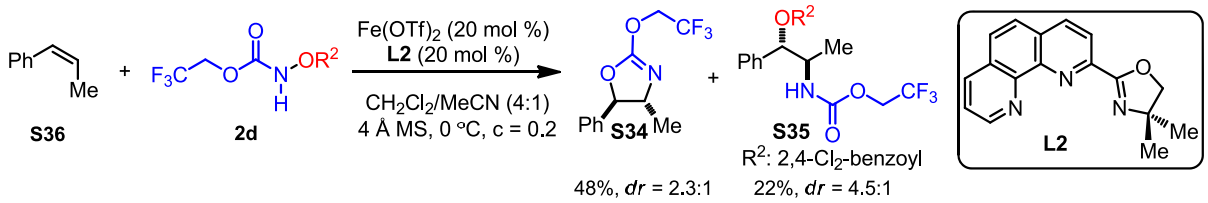
2,2,2-Trichloroethyl (2,3-dimethylbut-2-en-1-yl)carbamate (**20**): compound **20** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/EtOAc from 50:1 to 10:1) as colorless oil (12.1 mg, 11% yield). IR ν_{max} (neat)/cm^{-1}: 3332 (w), 2916 (w), 1714 (s), 1520 (m), 1489 (w), 1234 (s), 1135 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (brs, 1H), 4.78 (s, 2H), 3.87 (d, J = 5.4 Hz, 2H), 1.76 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 129.8, 123.7, 95.7, 74.5, 44.0, 20.8, 20.2, 16.9; HRMS (ESI, m/z): calcd for $C_9H_{15}Cl_3NO_2^+$ [M + H^+], 274.0163, found 274.0154.

In order to distinguish whether or not the aziridine **19** is the intermediate *en route* to compounds **17**, **18**, or **20**, we subjected the aziridine **19** to the reaction condition and two other relevant conditions and did not observe its conversion to **17**, **18**, or **20**.



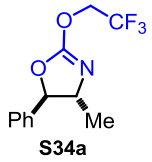
d. Iron-Catalyzed Amino-Oxygenation of Isomeric β-Methyl Styrenes





Both *trans* and *cis* *β*-methylstyrene are commercially available and they were distilled before usage.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (28.3 mg, 0.08 mmol) and **L2** (22.2 mg, 0.08 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (0.7 mL) and MeCN (0.5 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2d** (132.8 mg, 0.40 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (0.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, *trans*- (**S33**) or *cis*-β-methyl styrene (**S36**) (94.6 mg, 0.8 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at 0 °C. The reaction was kept stirring at the same temperature until it was completed (another 1.5 h for *trans* and 2.5 h for *cis*). The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.

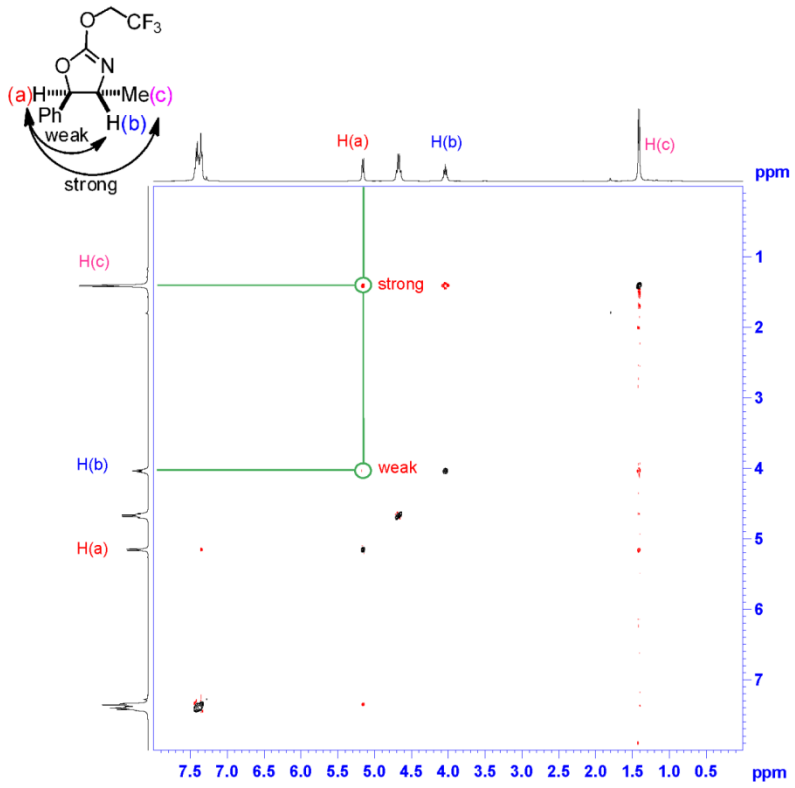


S34a

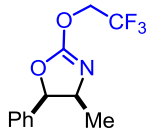
***anti*-4-Methyl-5-phenyl-2-(2,2,2-trifluoroethoxy)-4,5-dihydrooxazole** (**S34a**): compound **S34a** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) from the reaction of *trans*-*β*-methyl styrene as colorless oil (61.2 mg, 59% yield); IR ν_{max} (neat)/cm^{-1}: 2967 (w), 1761 (s), 1421 (m), 1345 (m), 1264 (s), 1166 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 5H), 5.16 (d, J = 7.5 Hz, 1H), 4.67 (q, J = 8.0 Hz, 2H), 4.04 (p, J = 6.7 Hz, 1H), 1.41 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 138.8, 128.9, 126.7, 125.6, 122.5 (q, J = 277.6 Hz), 90.5, 67.7, 66.2 (q, J = 37.1 Hz), 21.6; ^{19}F NMR (377

MHz, $CDCl_3$) δ -74.26 (t, J = 8.2 Hz); HRMS (ESI, m/z): calcd for $C_{12}H_{13}F_3NO_2^+$ [M + H^+], 260.0893, found 260.0882.

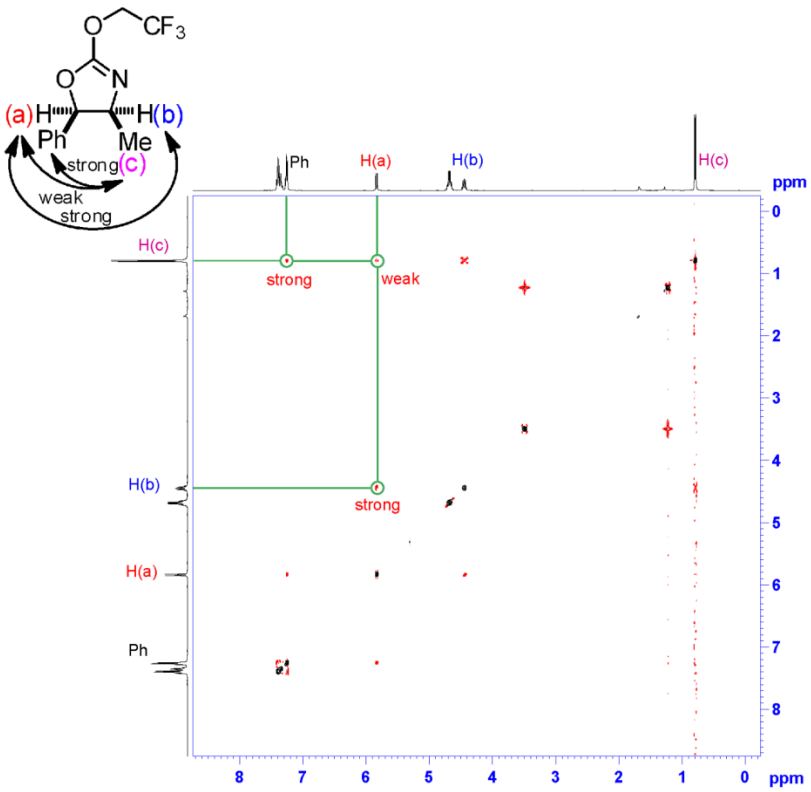
The relative stereochemistry of **S34a** and **S34b** was determined through *NOE* analysis for both diastereomers.



For the major (*anti*) diastereomer **S34a**: H(a) demonstrates a strong *NOE* with H(c), while it has a very weak *NOE* with H(b).

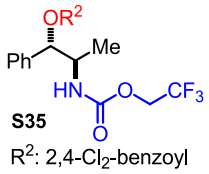


S34b



***syn*-4-Methyl-5-phenyl-2-(2,2,2-trifluoroethoxy)-4,5-dihydrooxazole (S34b)**: compound **S34b** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/EtOAc: 50:1 to 5:1) from the reaction of *cis*-*β*-methyl styrene as colorless oil (15.1 mg, 14% yield); IR ν_{max} (neat)/cm^{-1}: 2968 (w), 1761 (s), 1421 (m), 1343 (m), 1264 (s), 1167 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 3H), 7.31 – 7.19 (m, 2H), 5.84 (d, J = 9.1 Hz, 1H), 4.76 – 4.59 (m, 2H), 4.45 (dq, J = 13.9, 6.9 Hz, 1H), 0.79 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 135.7, 128.4, 128.2, 125.8, 122.5 (d, J = 277.3 Hz), 86.3, 66.2 (q, J = 37.1 Hz), 62.7, 18.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.25 (t, J = 8.2 Hz; HRMS (ESI, m/z): calcd for $C_{12}H_{13}F_3NO_2^+$ [M + Na^+], 260.0893, found 260.0887;

For the minor (*syn*) diastereomer **S34b**: H(a) has a strong *NOE* with H(b), while the effect between it and H(c) is relatively weak. In addition, strong *NOE* is also observed between H(c) and protons in the aromatic region.



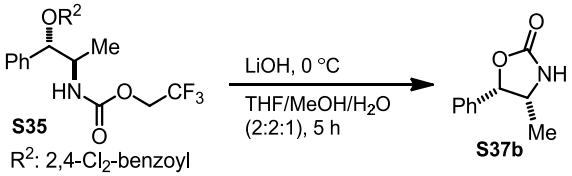
S35

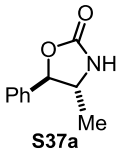
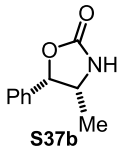
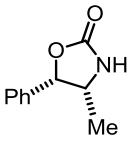
R^2: 2,4-Cl_2-benzoyl

***anti*-1-Phenyl-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)propyl 2,4-dichlorobenzoate** (**S35**): compound **S35** was isolated through a silica gel flash column (hexanes (buffered with 1% TEA)/acetone: from 50:1 to 10:1) from the reaction of *trans*-*β*-methyl styrene as colorless oil (major diastereomer, 32.0 mg, 16% yield); IR ν_{max} (neat)/cm^{-1}: 3352 (w), 2977 (w), 1719 (s), 1585 (m), 1520 (m), 1279 (m), 1163 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.44 – 7.29 (m, 6H), 6.13 (d, J = 3.3 Hz, 1H), 5.12 (d, J = 9.0 Hz, 1H), 4.57 – 4.39 (m, 2H), 4.39 – 4.24 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 153.8, 138.8, 136.0, 134.9, 133.1, 131.2, 128.6, 128.5, 127.8, 127.2, 126.6, 79.0, 50.9, 15.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.25 (t, J = 8.5 Hz); HRMS (ESI, m/z): calcd for $C_{19}H_{16}Cl_2F_3NNaO_4^+$ [M + H^+], 472.0301, found 472.0281.

Determination of the Relative Stereochemistry of S35

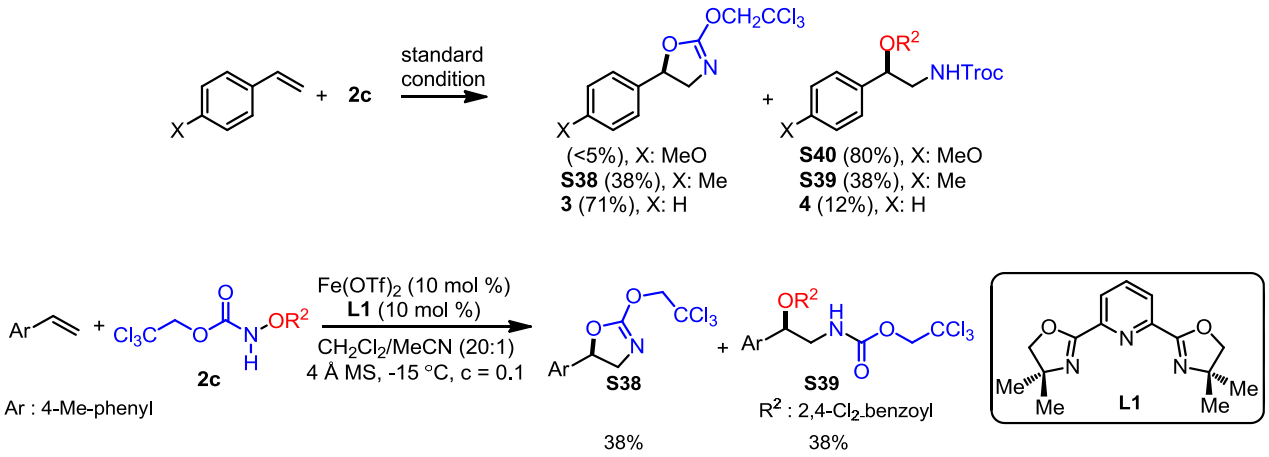
The relative stereochemistry of **S35** was determined by comparison of the ^{1}H NMR data of its derivative with known compounds **S37a** and **S37b**.[22,23] The oxazolidinone derived from **S35** fits **S37b** through ^{1}H NMR analysis; therefore, the relative stereochemistry of **S35** was determined to be *anti*.



	 **S37a** (Literature Data)[22]	 **S37b** (Literature Data)[23]	 (hydrolysis product obtained from **S35**)

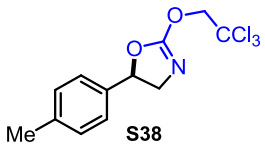
^{1}H NMR (400 MHz, $CDCl_3$):	δ 7.5-7.3 (m, 5H), 6.41 (br s, 1H), 5.04 (d, J = 7.3 Hz, 1H), 3.84 (p, J = 4 × 6.3 Hz, 1H), 1.39 (d, J = 6.2 Hz, 3H)	δ 7.35 (m, 5H), 6.40 (bs, 1H), 5.71 (d, J = 8.0, 1H), 4.21 (m, 1H), 0.81 (d, J = 6.5, 3H).	δ 7.43 – 7.27 (m, 5H), 5.72 (d, J = 7.9 Hz, 1H), 5.50 (br s, 1H), 4.20 (p, J = 6.7 Hz, 1H), 0.81 (d, J = 6.5 Hz, 1H).

e. Evaluation of the Electronic Effect in the Styrene Amino-oxygenation



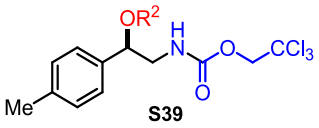
4-Methyl styrene was commercially available and it was distilled before usage.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (14.2 mg, 0.04 mmol) and **L1** (10.9 mg, 0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min. To another flame dried 3-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2c** (167.6 mg, 0.44 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (2.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then, 4-methyl styrene (52.7 µL, 0.40 mmol) was added to vial **B** and the catalyst solution (vial **A)** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S38

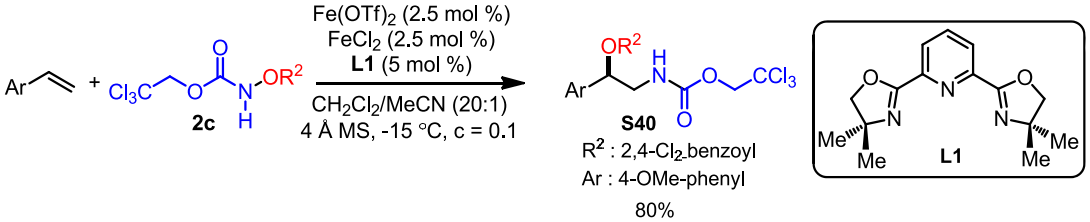
5-(*p*-Tolyl)-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (S**38**): compound S**38** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/acetone from 50:1 to 10:1) as colorless oil (46.9 mg, 38% yield). IR ν_{max} (neat)/cm^{-1}: 2951 (w), 2921 (m), 1667 (s), 1396 (s), 1328 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 4H), 5.71 (t, *J* = 8.6 Hz, 1H), 5.01 – 4.83 (m, 2H), 4.24 (dd, *J* = 12.4, 10.0 Hz, 1H), 3.81 (dd, *J* = 12.9, 7.8 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 138.7, 136.4, 129.5, 125.8, 94.2, 83.3, 79.5, 59.6, 21.2; HRMS (ESI, m/z): calcd for $C_{12}H_{13}Cl_3NO_2^+$ [M + H$^+$], 308.0006, found 307.9999.



S39

R^2 : 2,4-Cl$_2$-benzoyl

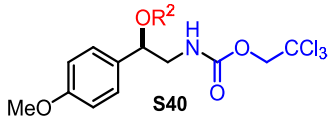
1-(*p*-Tolyl)-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)ethyl 2,4-dichlorobenzoate (S**39**): compound S**39** was purified through a flash column (silica gel, hexanes(buffered with 1% TEA)/acetone from 50:1 to 10:1) as colorless oil (75.9 mg, 38% yield). IR ν_{max} (neat)/cm^{-1}:3352 (w), 2947 (w), 2921 (w), 1719 (s), 1953 (m), 1515 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.09 (dd, *J* = 7.4, 4.7 Hz, 1H), 5.31 (t, *J* = 4.7 Hz, 1H), 4.78 – 4.69 (m, 2H), 3.86 – 3.66 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 154.6, 138.7, 138.7, 134.9, 133.8, 132.9, 131.1, 129.6, 128.0, 127.2, 126.6, 95.5, 76.0, 74.6, 46.0, 21.2; HRMS (ESI, m/z): calcd for $C_{19}H_{16}Cl_5NNaO_4^+$ [M + Na$^+$], 519.9414, found 519.9405.



4-Methoxyl styrene is commercially available and it was distilled before usage.

To a flame-dried sealable 2-dram vial (vial **A**) equipped with a stir bar were added $Fe(OTf)_2$ (3.5 mg, 0.01 mmol), $FeCl_2$ (1.3 mg, 0.01 mmol) and **L1** (5.5 mg, 0.02 mmol). After the vial was

evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) and MeCN (0.2 mL) were added via a syringe and the mixture was stirred at room temperature for 20 min and then 4-methoxyl styrene (53.9 μL, 0.40 mmol) was added to it. To another flame dried 2-dram vial (vial **B**) equipped with a stir bar were added activated 4Å molecular sieves (100 mg) and **2c** (167.6 mg, 0.44 mmol). The vial was also was evacuated and backfilled with N_2 for three times and then anhydrous CH_2Cl_2 (2.8 mL) was added via a syringe. Both solutions were degassed with brief evacuation and backfilling with N_2 twice. Then the solution in vial **A** was added by a syringe pump over 30 min to vial **B** at -15 °C. The reaction was kept stirring at the same temperature for another 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (2 mL) and stirred vigorously for additional 10 min. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 mL × 2) and EtOAc (2 mL× 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*.



S40

R^2 : 2,4-Cl_2-benzoyl

1-(4-Methoxyphenyl)-2-(((2,2,2-trifluoroethoxy)carbonyl)amino)ethyl 2,4-dichlorobenzoate (**S40**): compound **S40** was isolated by flash column (silica gel, hexanes : EtOAc = 30:1 to 5:1) as colorless oil (165.0 mg, 80% yield). IR ν_{max} (neat)/cm^{-1}:3362 (w), 2952 (w), 1724 (s), 1583 (m), 1512 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 0.8 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.08 (t, *J* = 6.1 Hz, 1H), 5.35 (t, *J* = 5.6 Hz, 1H), 4.78 – 4.68 (m, 2H), 3.82 (s, 3H), 3.75 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 159.9, 154.6, 138.7, 134.9, 132.9, 131.1, 128.8, 128.2, 127.2, 114.2, 95.5, 75.8, 74.6, 55.3, 45.9; HRMS (ESI, m/z): calcd for $C_{19}H_{16}Cl_5NNaO_5^+$ [M + Na^+], 535.9363, found 535.9350.

F. References

(1) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862.

(2) Behr, J.-B.; Chevrier, C.; Defoin, A.; Tarnus, C.; Streith, J. *Tetrahedron* **2003**, *59*, 543.

(3) Luo, S.-X.; Tiwow, V.; Maeder, M.; Lawrance, G. A. *J. Coord. Chem.* **2010**, *63*, 2400.

(4) Zhang, M.; Gao, R.; Hao, X.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 3867.

(5) Jiang, H.-F.; Ye, J.-W.; Qi, C.-R.; Huang, L.-B. *Tetrahedron Lett.* **2010**, *51*, 928.

(6) He, T.; Gao, W.-C.; Wang, W.-K.; Zhang, C. *Adv. Synth. Catal.* **2014**, *356*, 1113.

(7) Murakami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2009**, *74*, 1415.

(8) Endeshaw, M. M.; Bayer, A.; Hansen, L. K.; Gautun, O. R. *Eur. J. Org. Chem.* **2006**, *2006*, 5249.

(9) Gómez-Sánchez, E.; Soriano, E.; Marco-Contelles, J. *J. Org. Chem.* **2007**, *72*, 8656.

(10) Denmark, S. E.; Kobayashi, T.; Regens, C. S. *Tetrahedron* **2010**, *66*, 4745.

(11) Rouf, A.; Gupta, P.; Aga, M. A.; Kumar, B.; Parshad, R.; Taneja, S. C. *Tetrahedron: Asymmetry* **2011**, *22*, 2134.

(12) Mitrochkine, A.; Gil, G.; Réglier, M. *Tetrahedron: Asymmetry* **1995**, *6*, 1535.

(13) Goto, R.; Okura, K.; Sakazaki, H.; Sugawara, T.; Matsuoka, S.; Inoue, M. *Tetrahedron* **2011**, *67*, 6659.

(14) Punner, F.; Hilt, G. *Chem. Comm.* **2012**, *48*, 3617.

(15) Wei, X.-J.; Yang, D.-T.; Wang, L.; Song, T.; Wu, L.-Z.; Liu, Q. *Org. Lett.* **2013**, *15*, 6054.

(16) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

(17) Pullin, R. D. C.; Sellars, J. D.; Steel, P. G. *Org. Biomol. Chem.* **2007**, *5*, 3201.

(18) Barrett, A. G. M.; Hamprecht, D.; Ohkubo, M. *J. Org. Chem.* **1997**, *62*, 9376.

(19) Gutierrez, E. G.; Wong, C. J.; Sahin, A. H.; Franz, A. K. *Org. Lett.* **2011**, *13*, 5754.

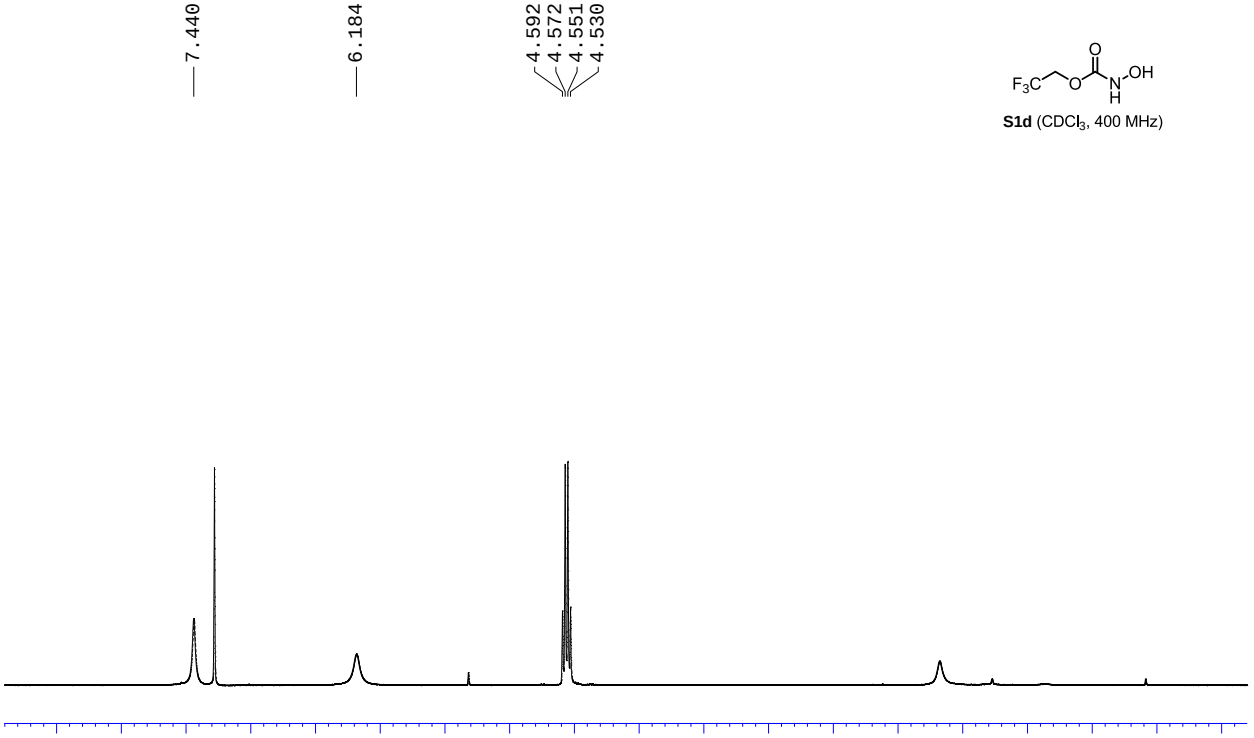
(20) Corey, E. J.; Roper, T. D.; Ishihara, K.; Sarakinos, G. *Tetrahedron Lett.* **1993**, *34*, 8399.

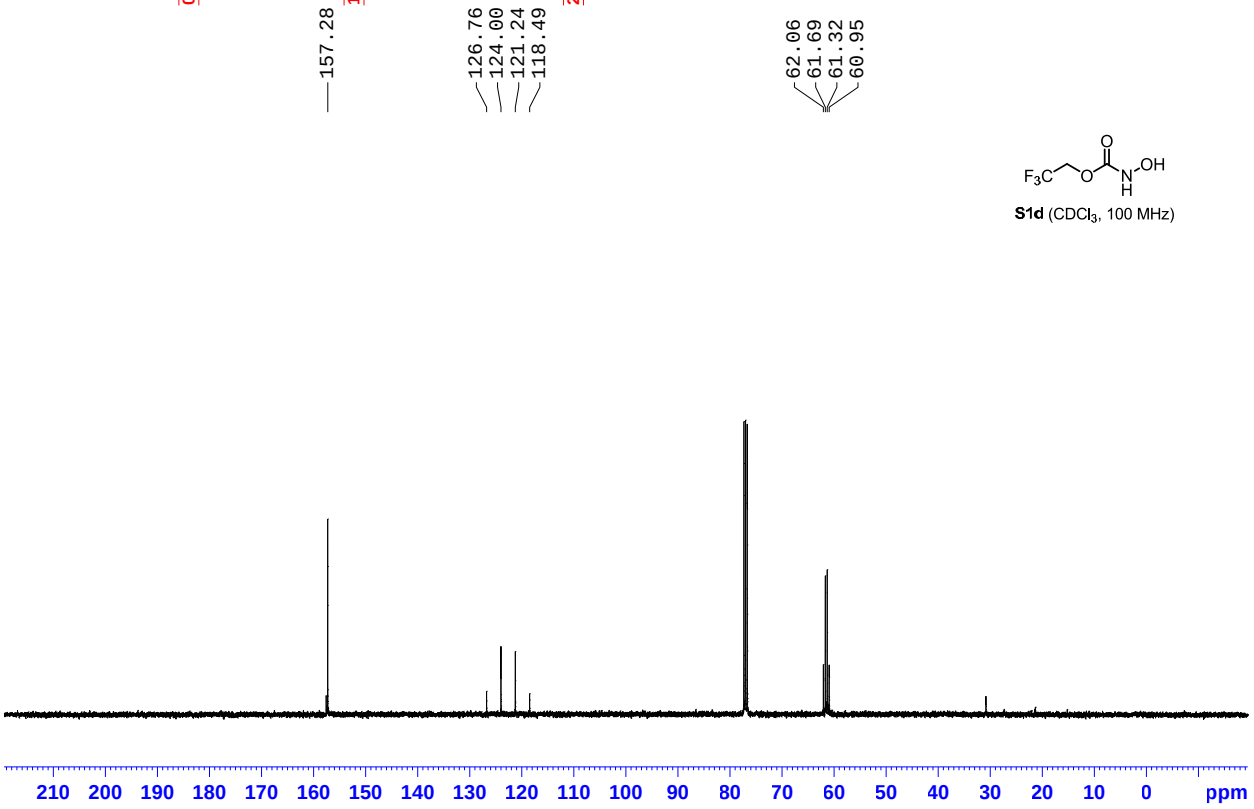
(21) Fu, H.; Look, G. C.; Zhang, W.; Jacobsen, E. N.; Wong, C. H. *J. Org. Chem.* **1991**, *56*, 6497.

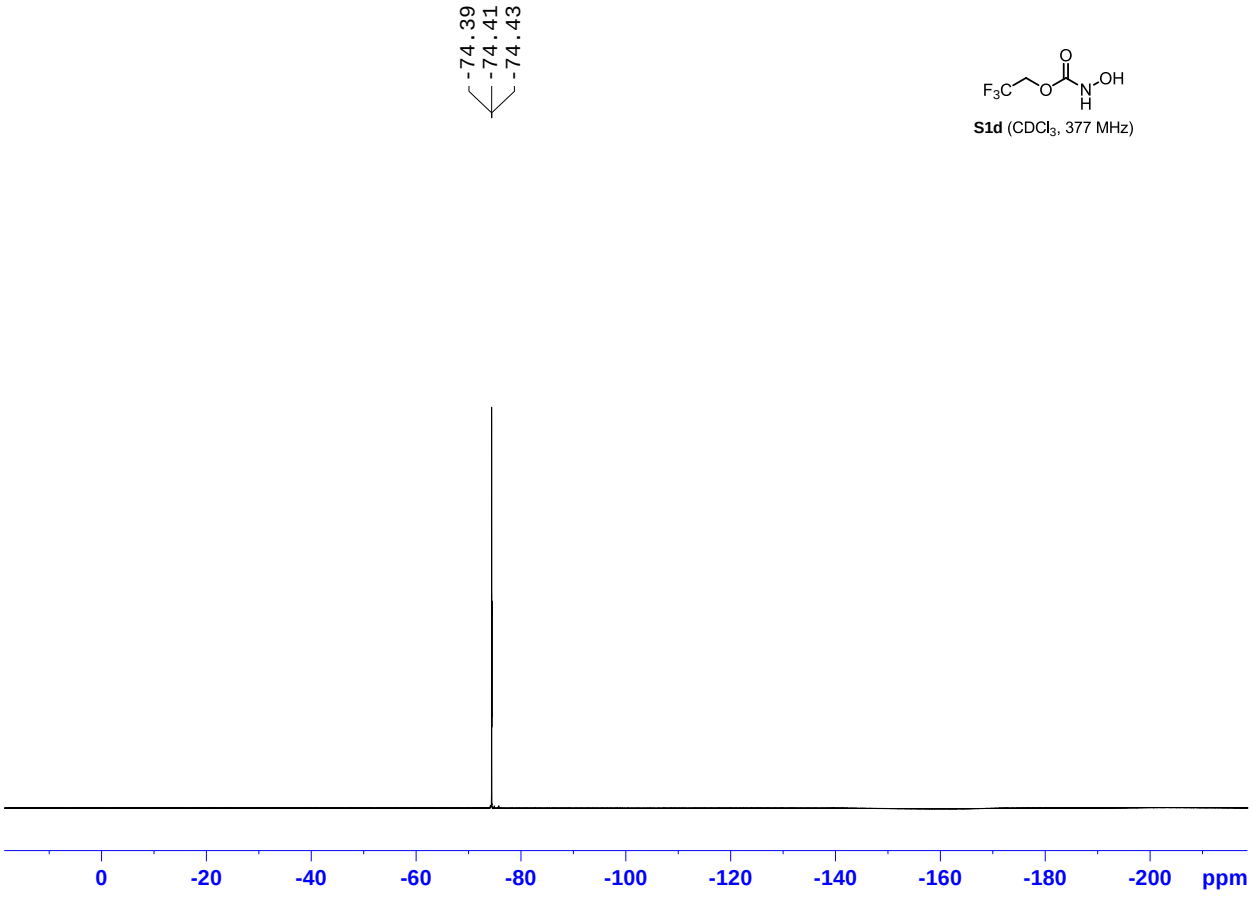
(22) Johannes, M.; Altmann, K.-H. *Org. Lett.* **2012**, *14*, 3752.

(23) Paz, J.; Pérez-Balado, C.; Iglesias, B.; Muñoz, L. *J. Org. Chem.* **2010**, *75*, 3037.

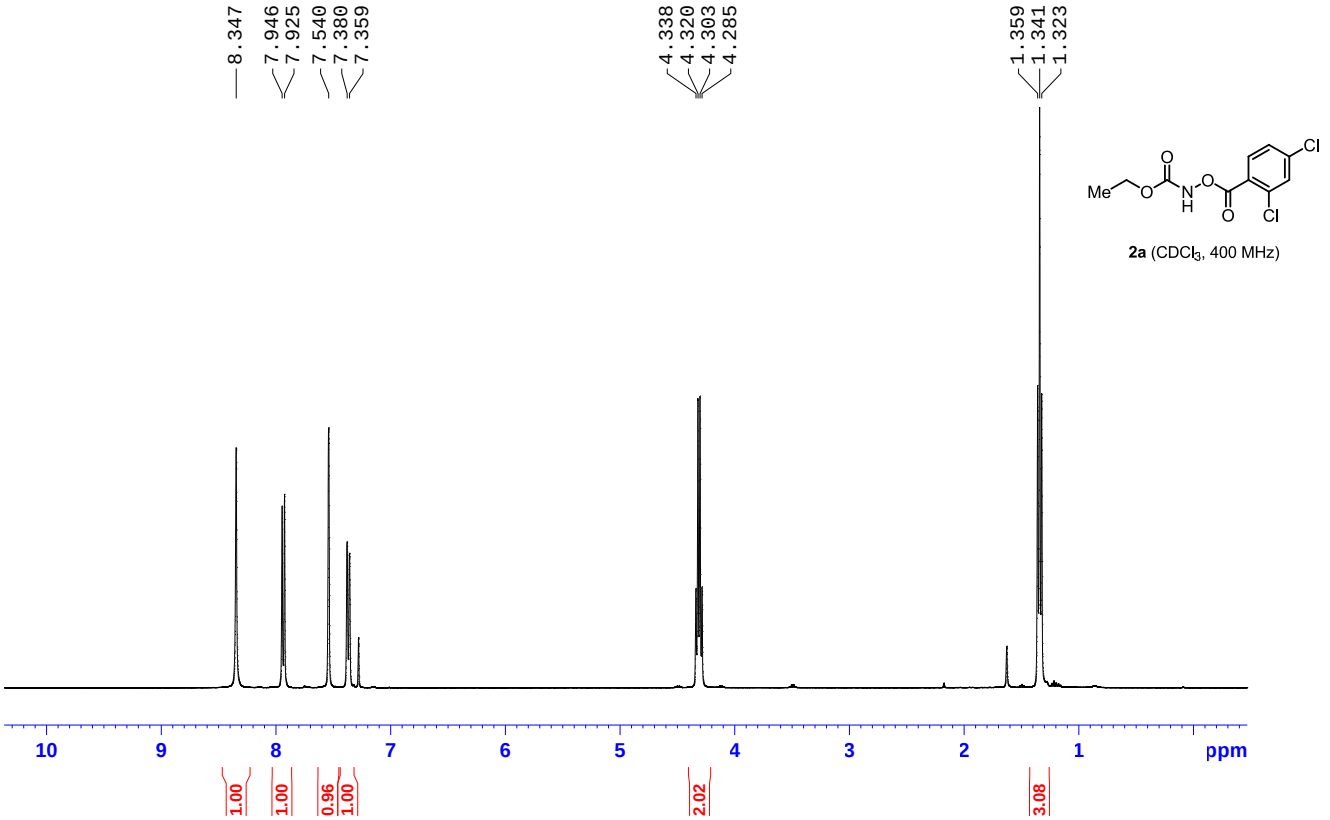
G. NMR Spectra

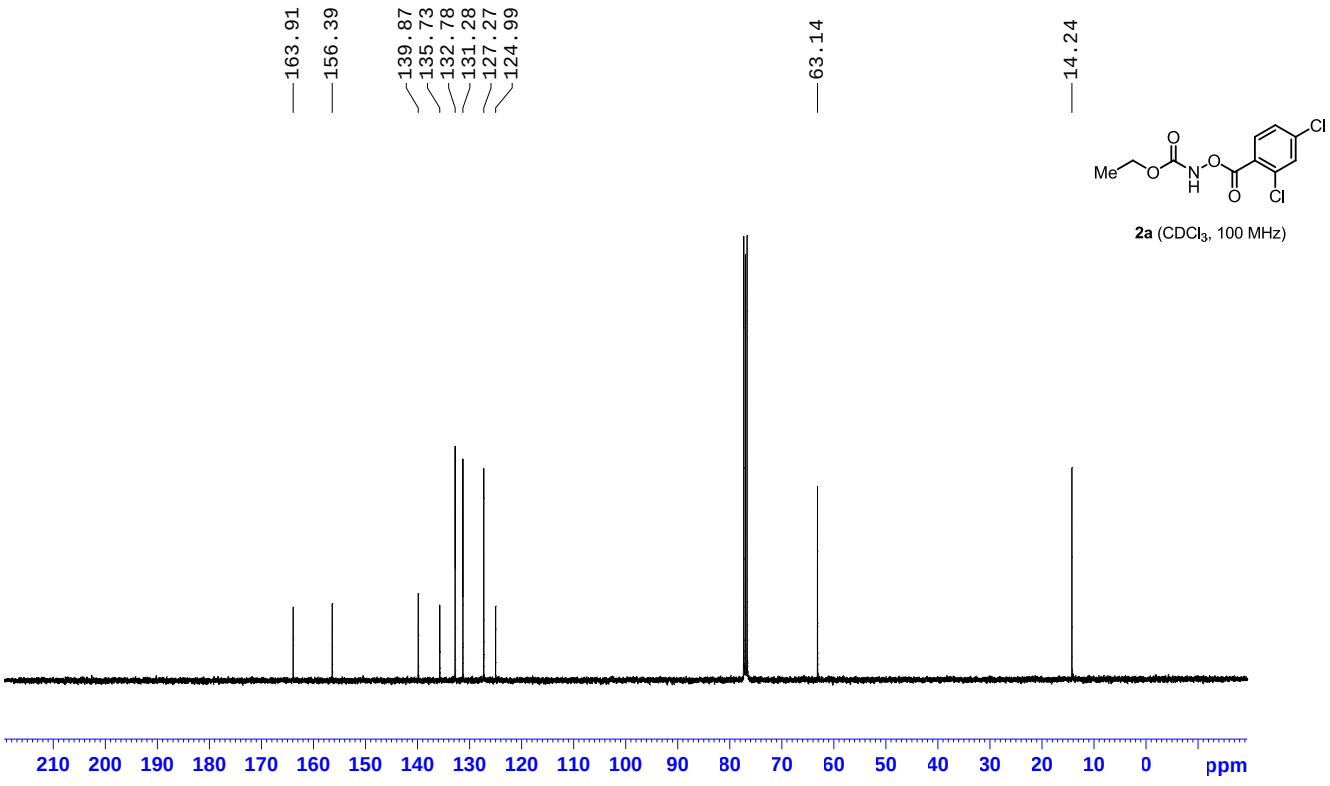


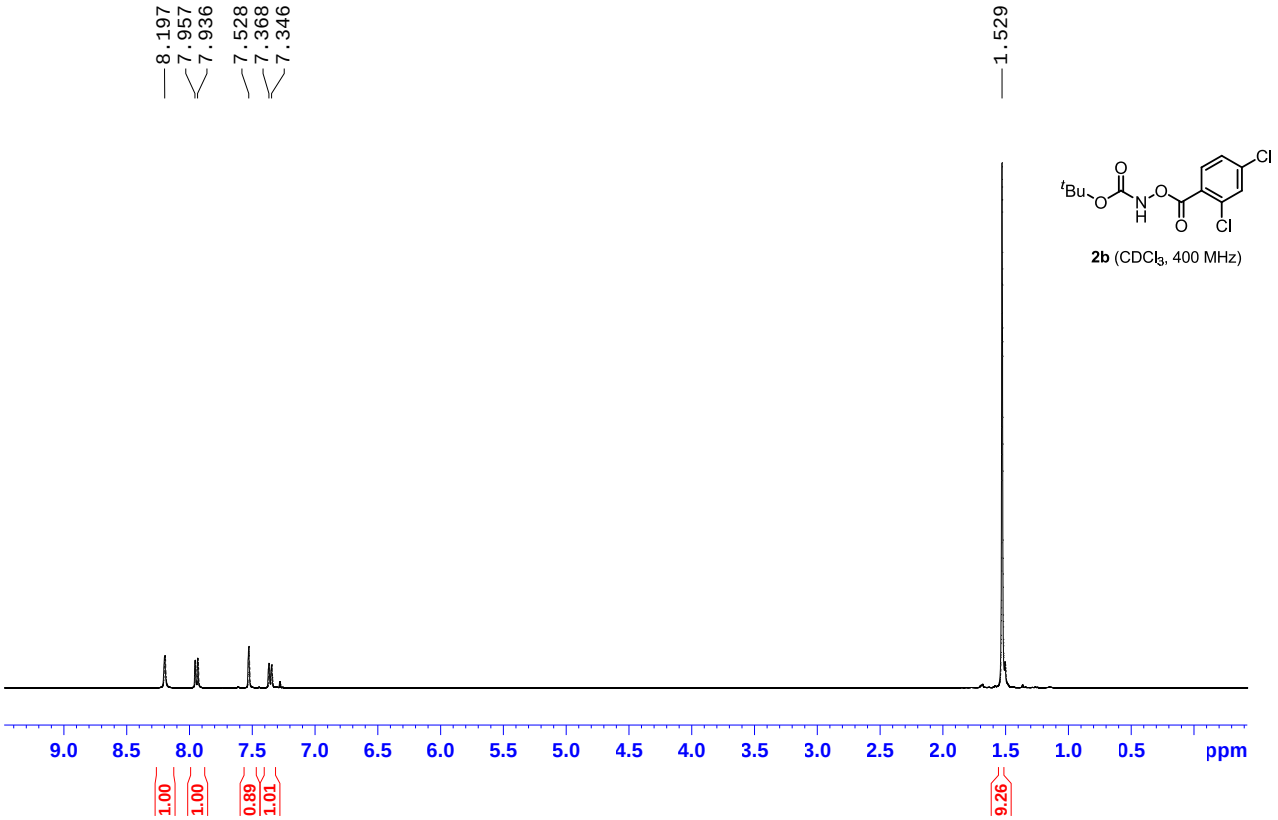


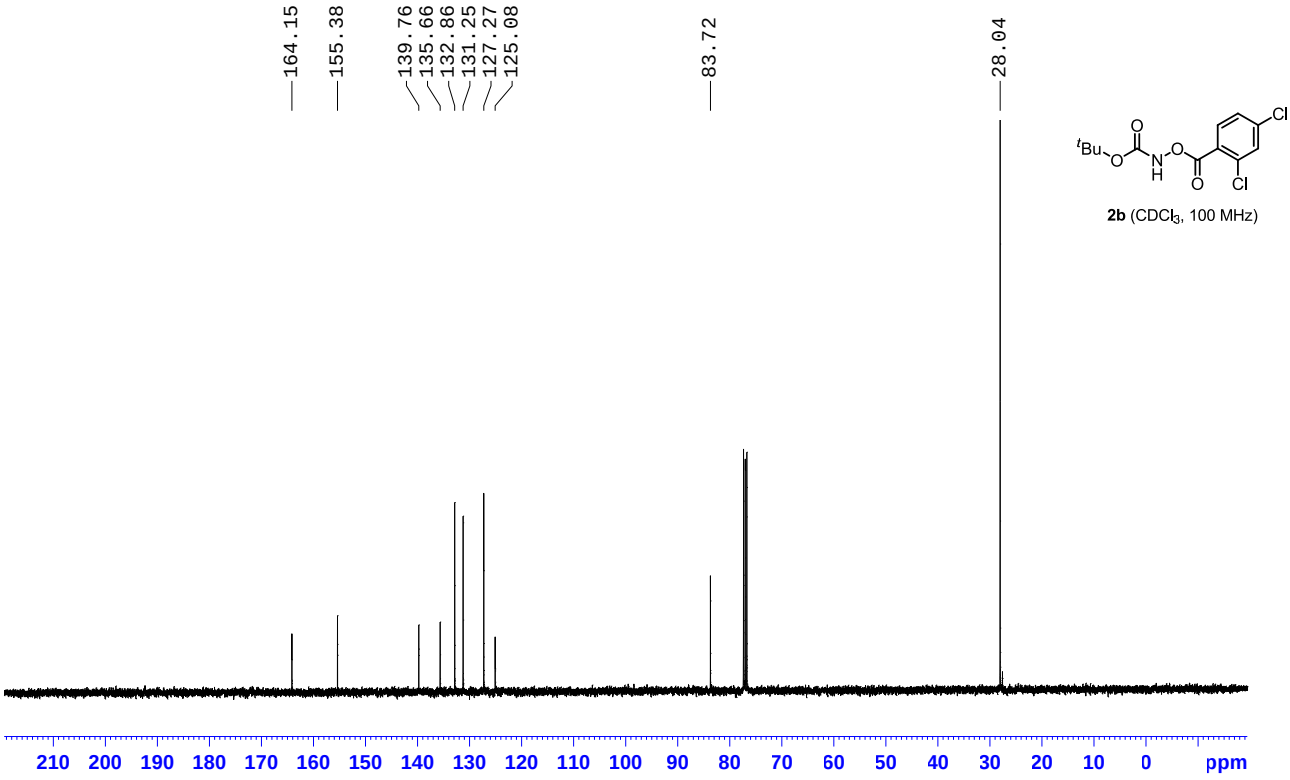


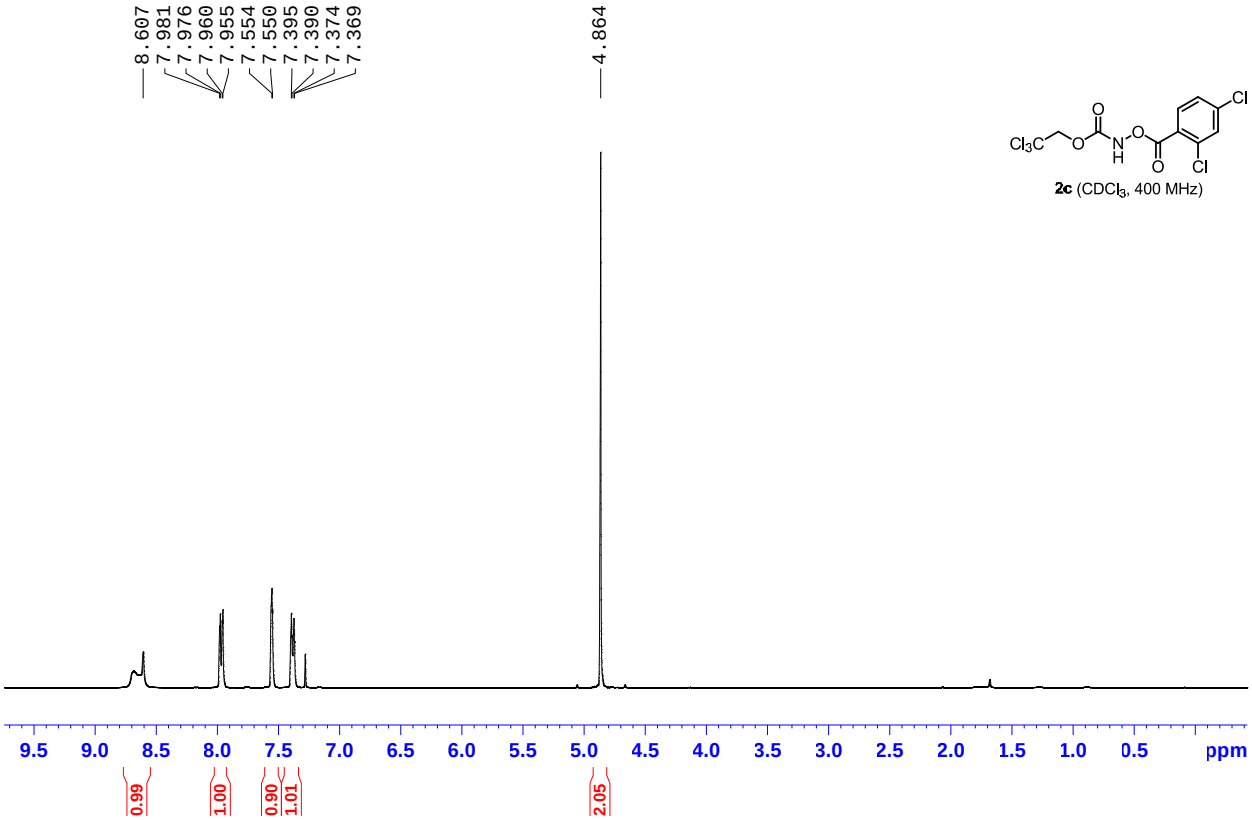
S1d ($CDCl_3$, 377 MHz)


8.347
7.946
7.925
7.540
7.380
7.359
4.338
4.320
4.303
4.285
1.359
1.341
1.323
Me
O
O
N
H
O
O
Cl
Cl
2a (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
0.96
1.00
2.02
3.08

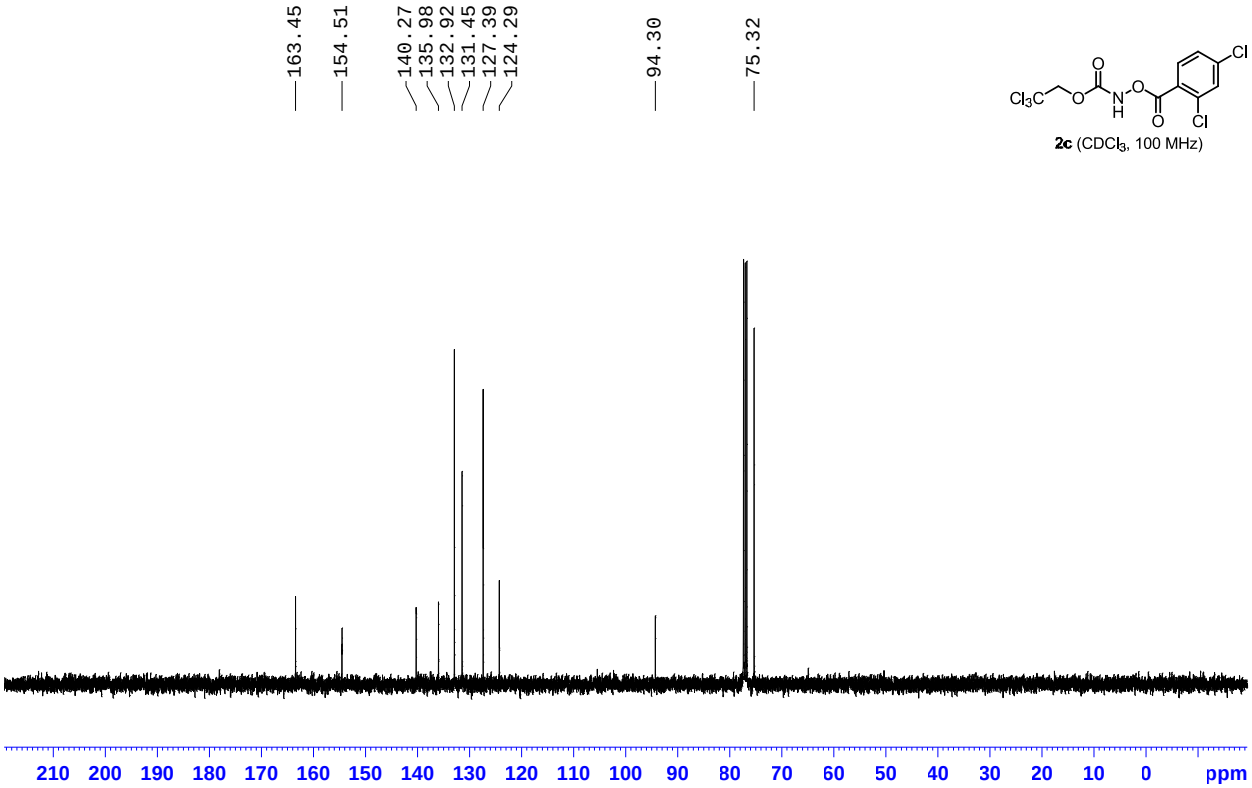

163.91
156.39
139.87
135.73
132.78
131.28
127.27
124.99
63.14
14.24
Me
O
O
N
H
O
O
Cl
Cl
2a (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.197
7.957
7.936
7.528
7.368
7.346
1.529
2b (CDCl3, 400 MHz)
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 ppm
1.00
1.00
0.89
1.01
9.26

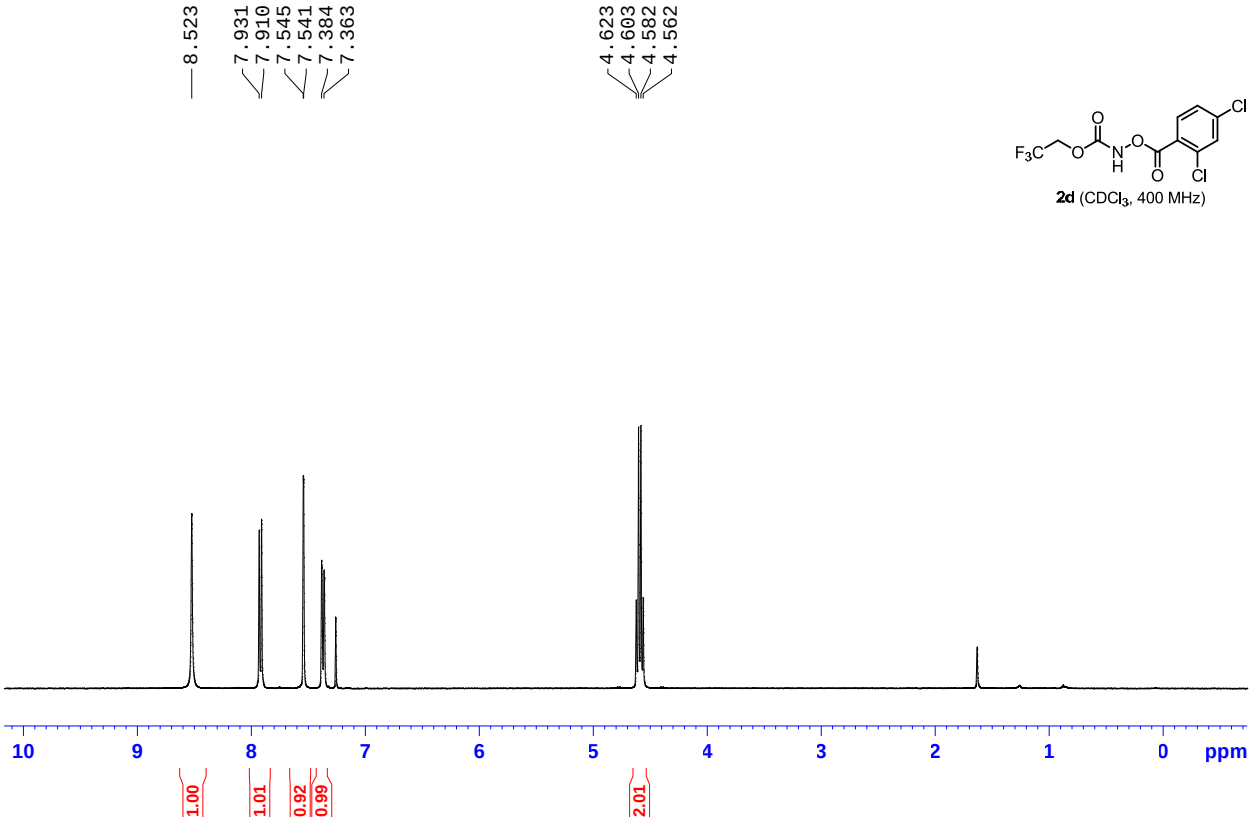

164.15
155.38
139.76
135.66
132.86
131.25
127.27
125.08
83.72
28.04
2b (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

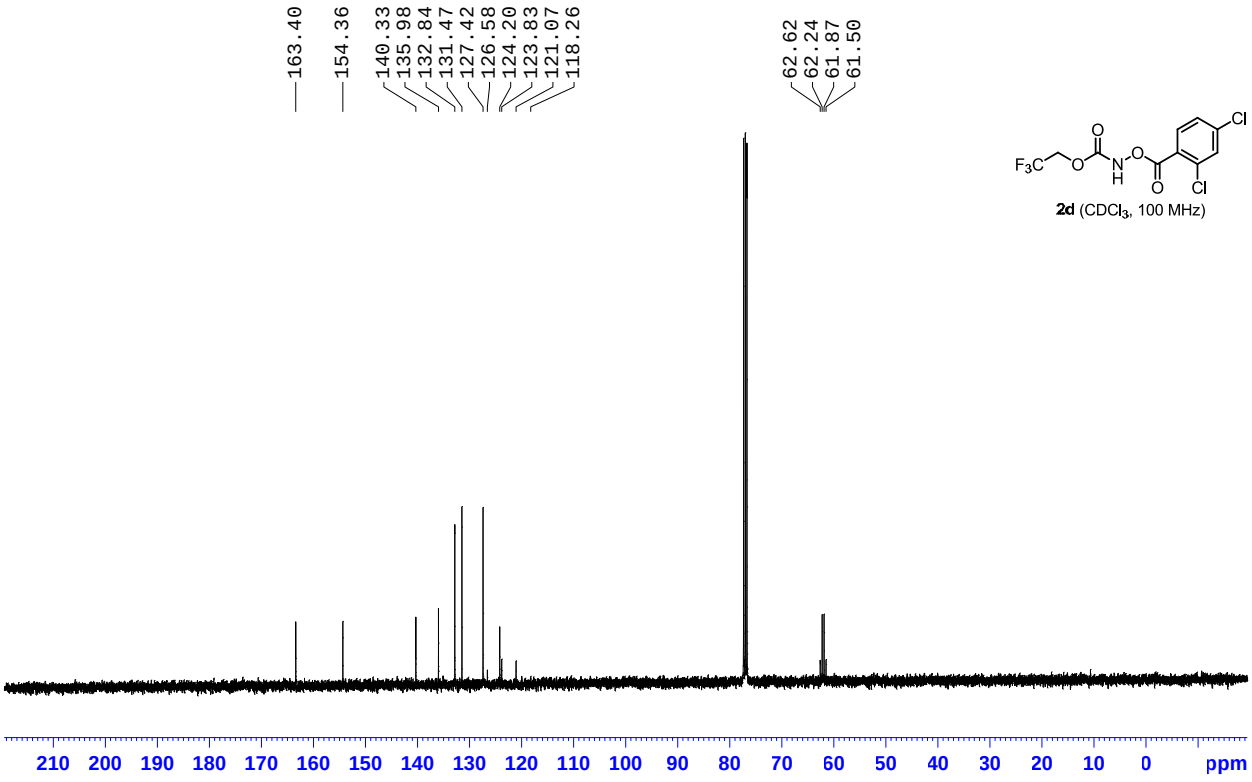


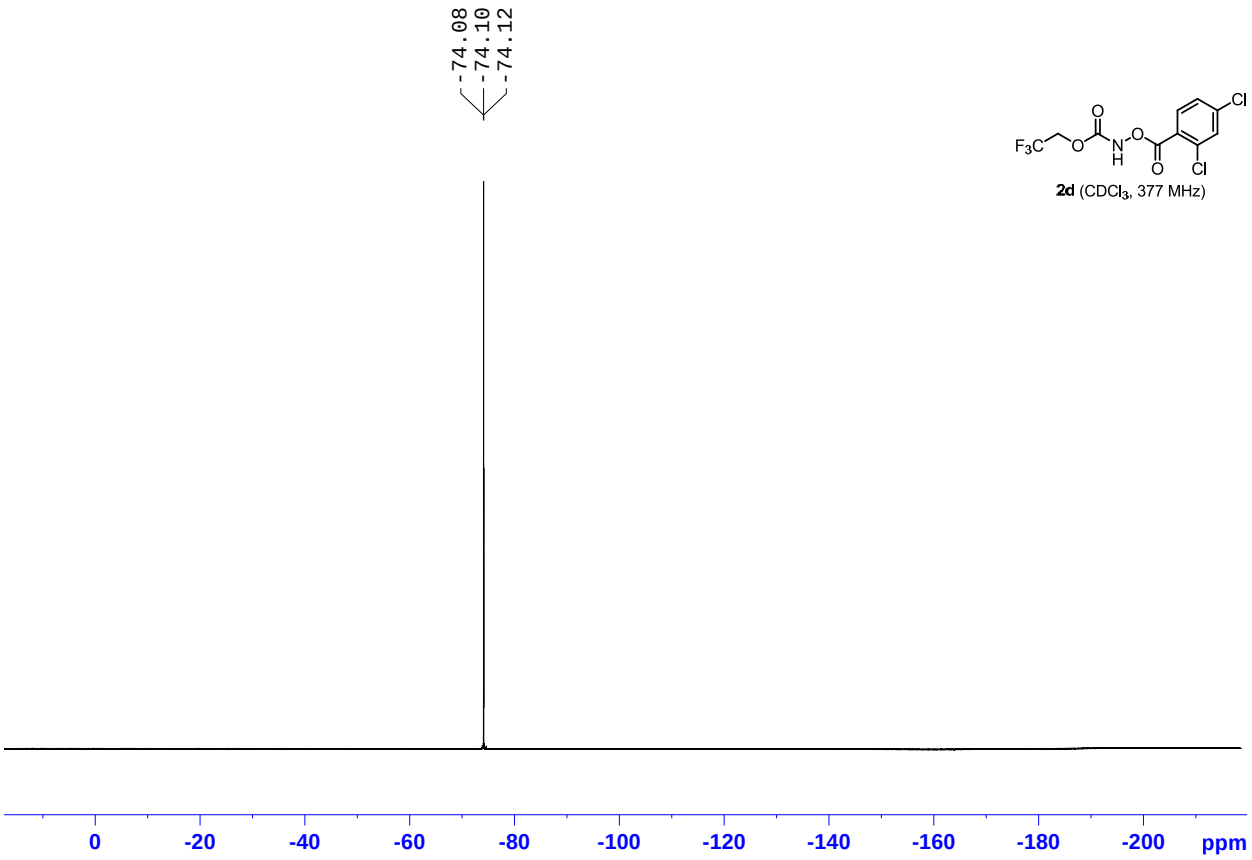
2c ($CDCl_3$, 400 MHz)

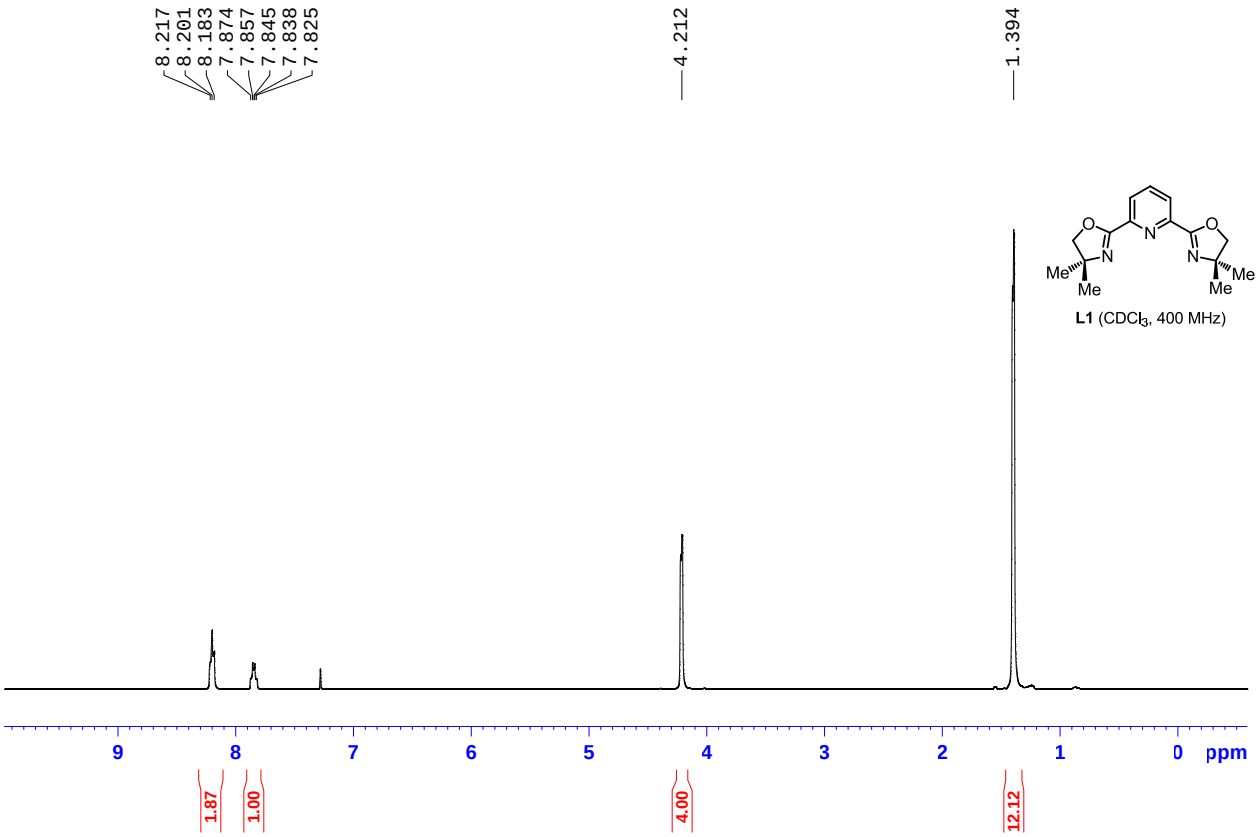


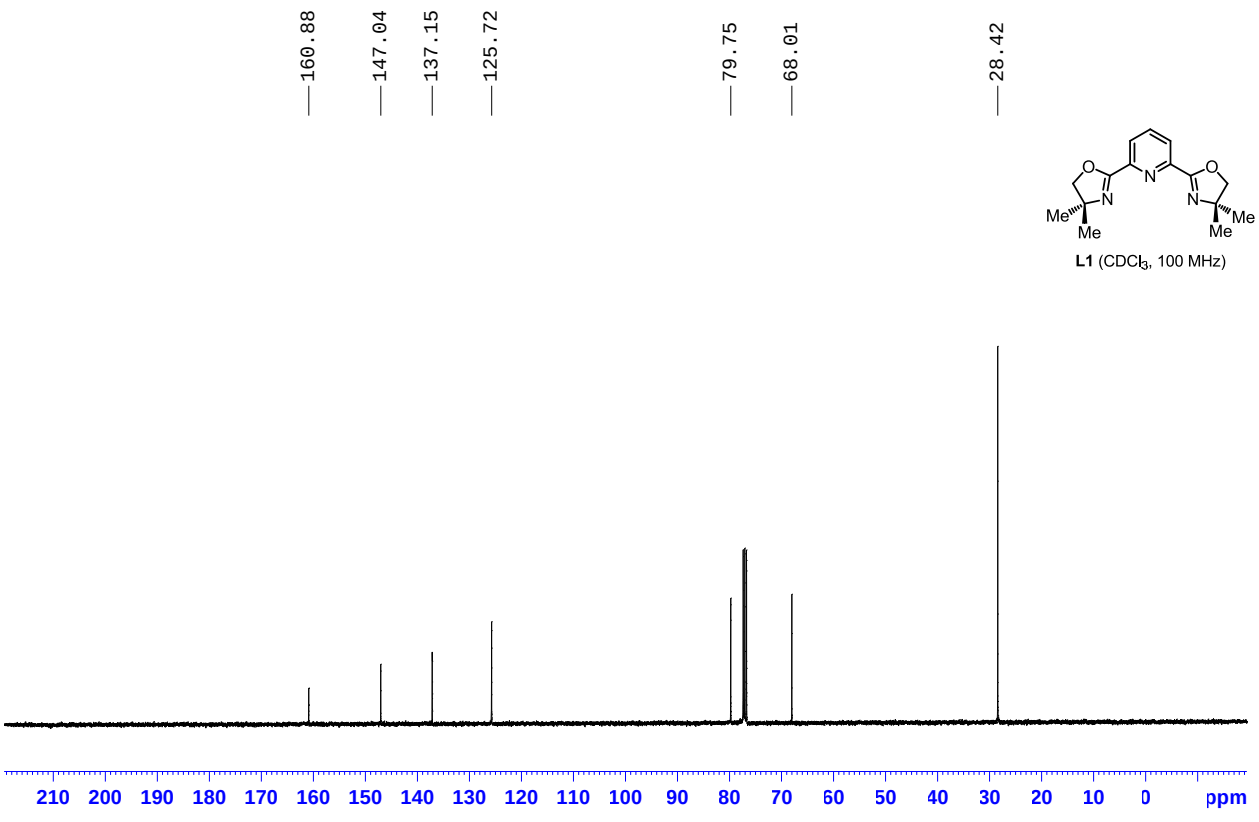
2c ($CDCl_3$, 100 MHz)

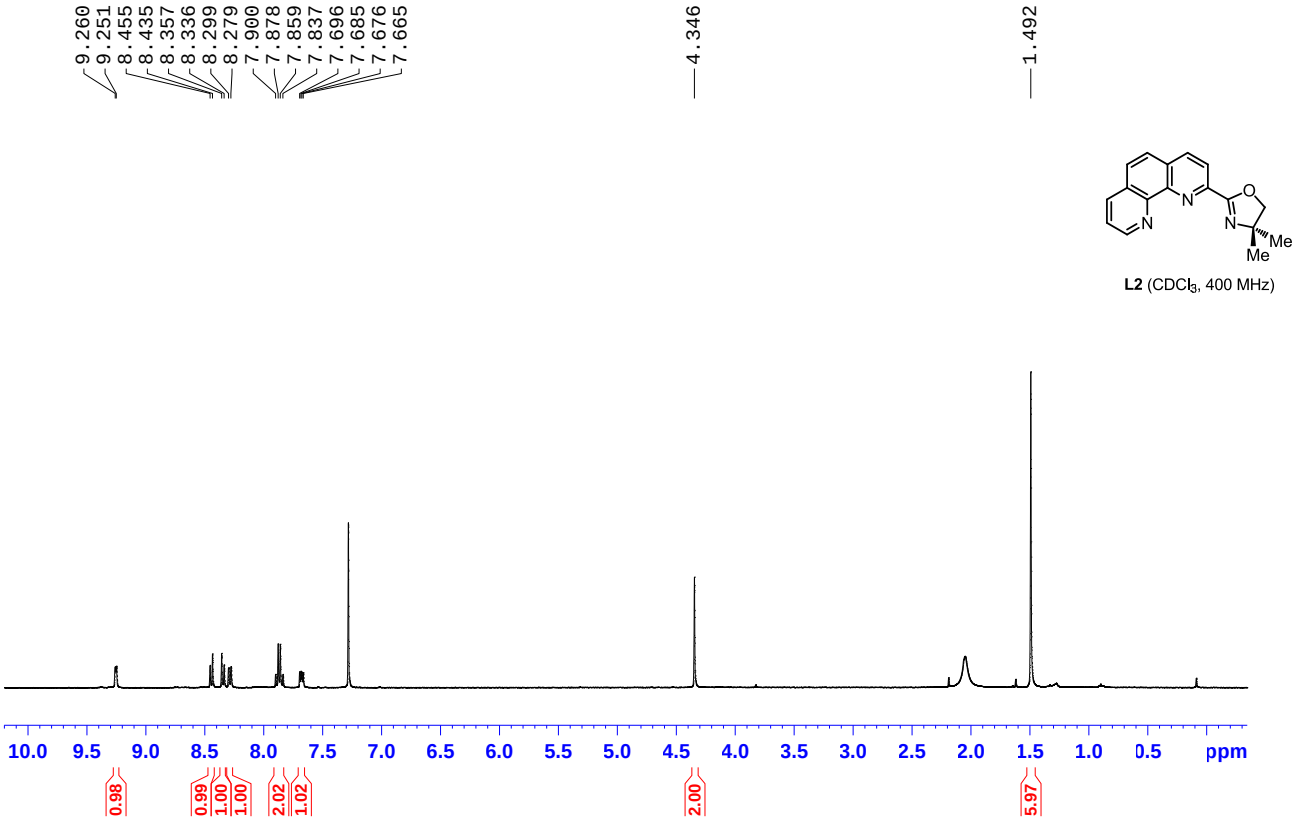

8.523
7.931
7.910
7.545
7.541
7.384
7.363
4.623
4.603
4.582
4.562
2d (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
0.92
0.99
2.01


163.40
154.36
140.33
135.98
132.84
131.47
127.42
126.58
124.20
123.83
121.07
118.26
62.62
62.24
61.87
61.50
2d (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

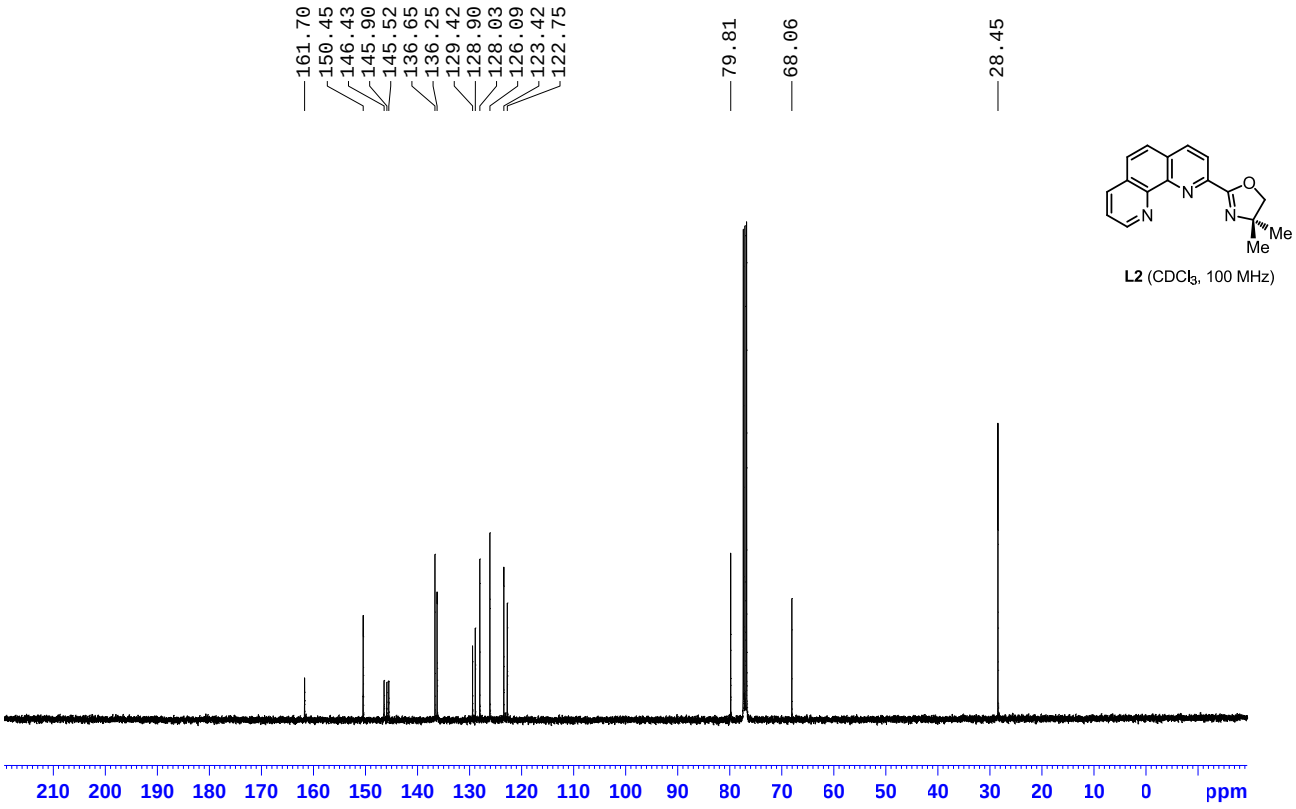

-74.08
-74.10
-74.12
F3C
O
O
N
H
O
O
Cl
Cl
2d (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


8.217
8.201
8.183
7.874
7.857
7.845
7.838
7.825
4.212
1.394
Me
Me
Me
Me
L1 (CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.87
1.00
4.00
12.12

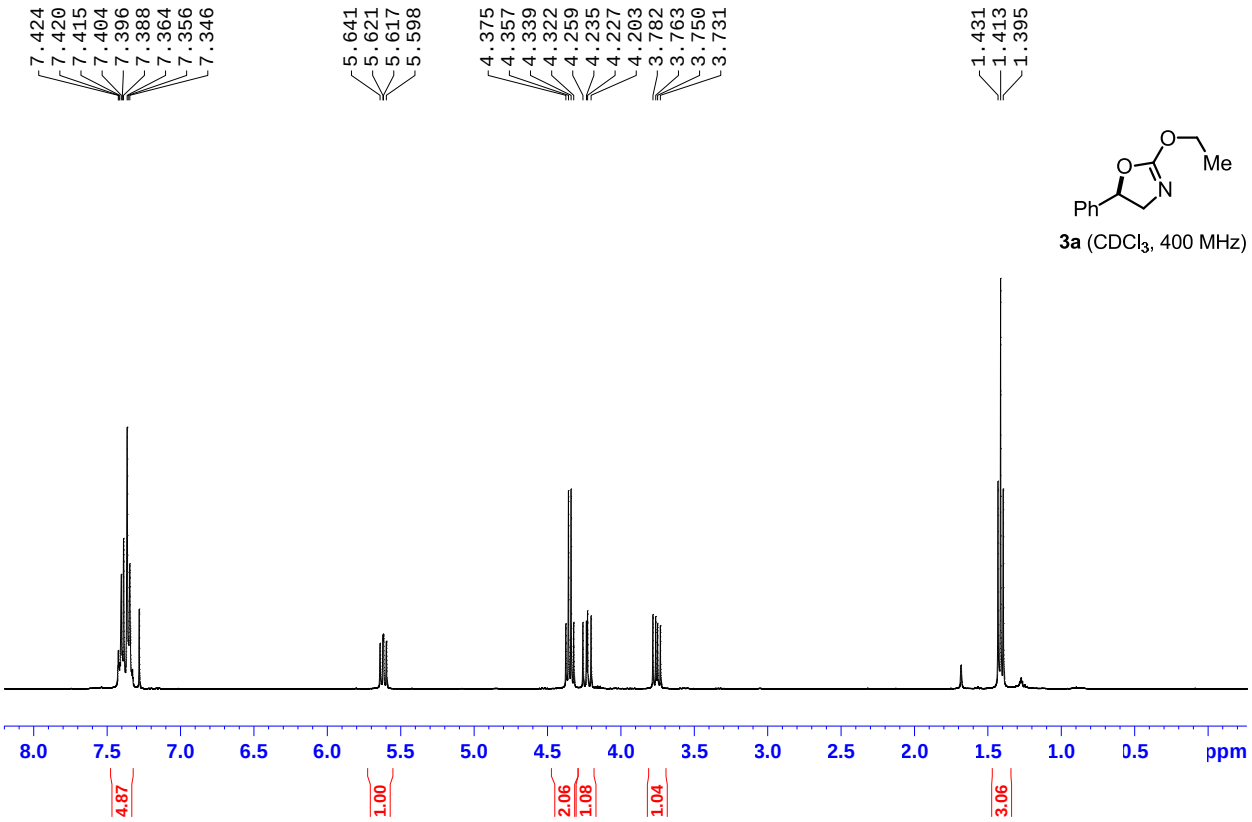

160.88
147.04
137.15
125.72
79.75
68.01
28.42
Me
Me
Me
Me
L1 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



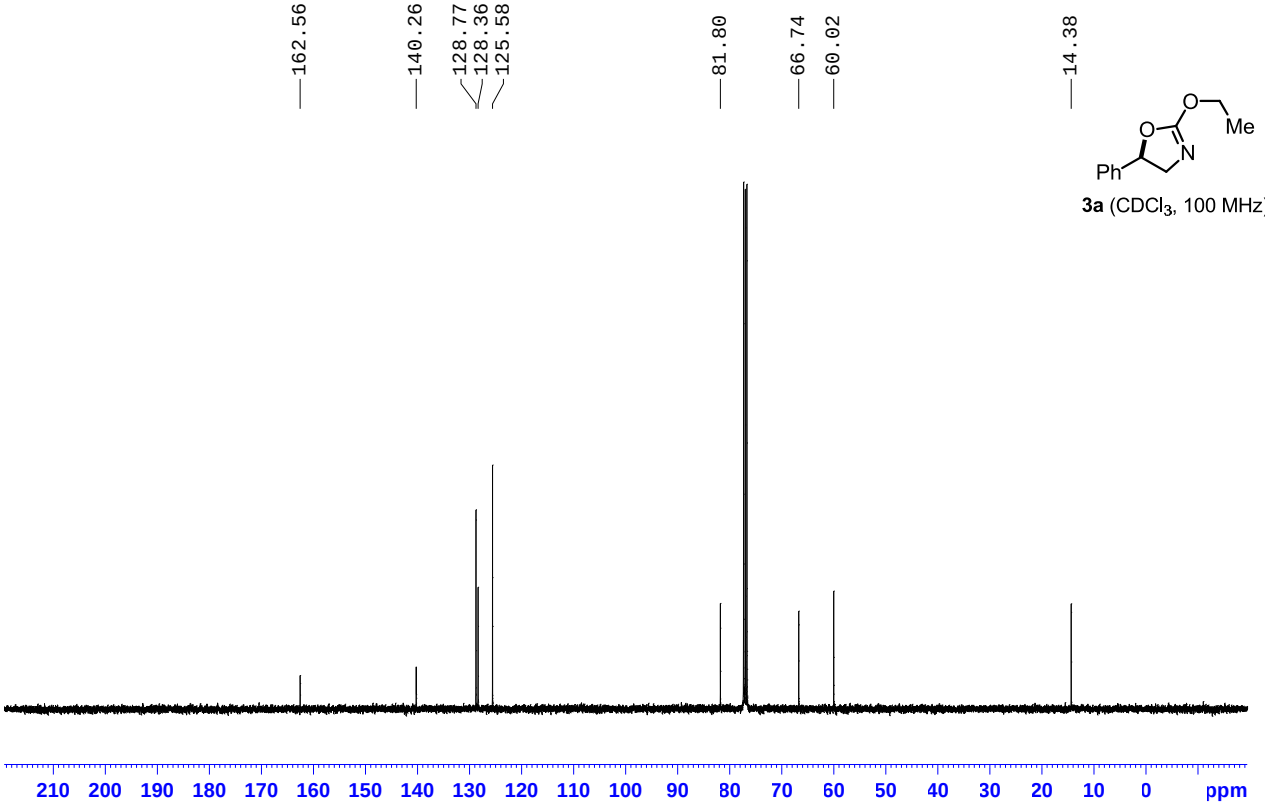
L2 ($CDCl_3$, 400 MHz)



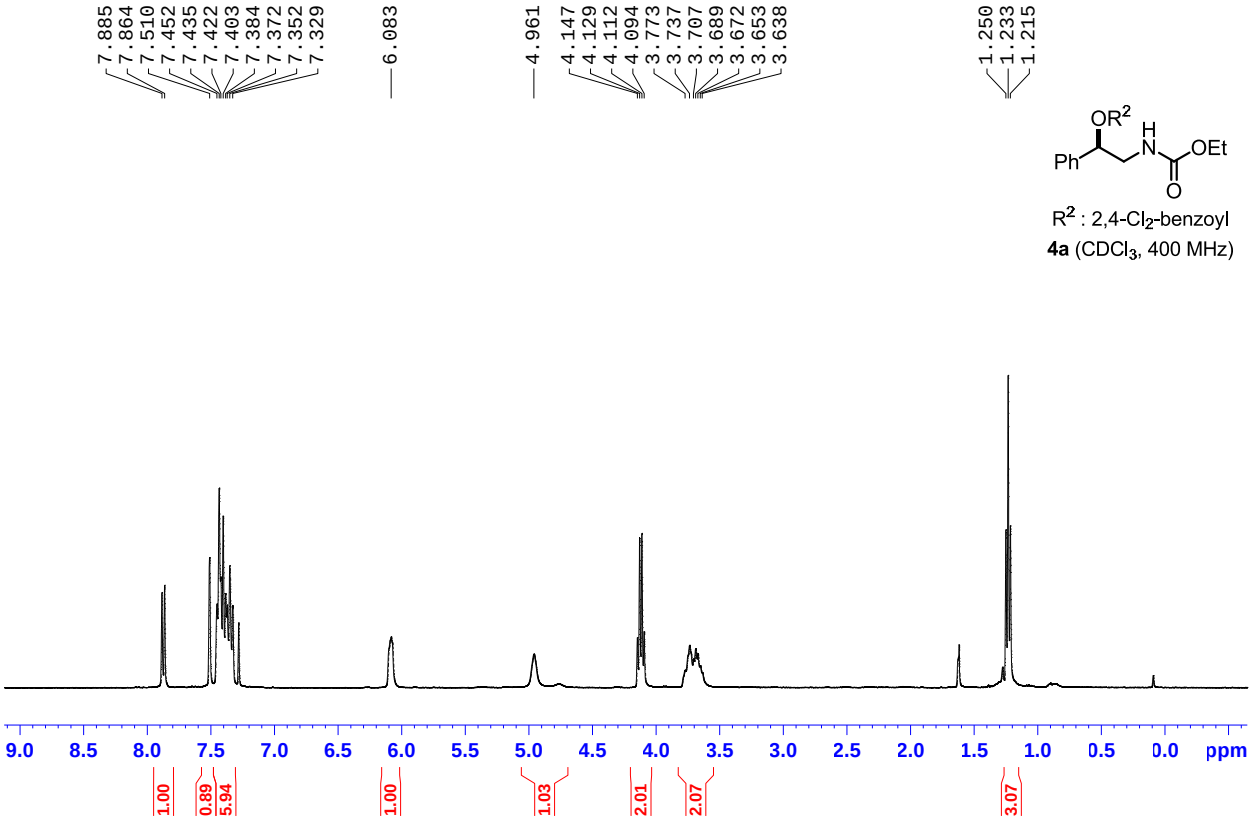
L2 ($CDCl_3$, 100 MHz)

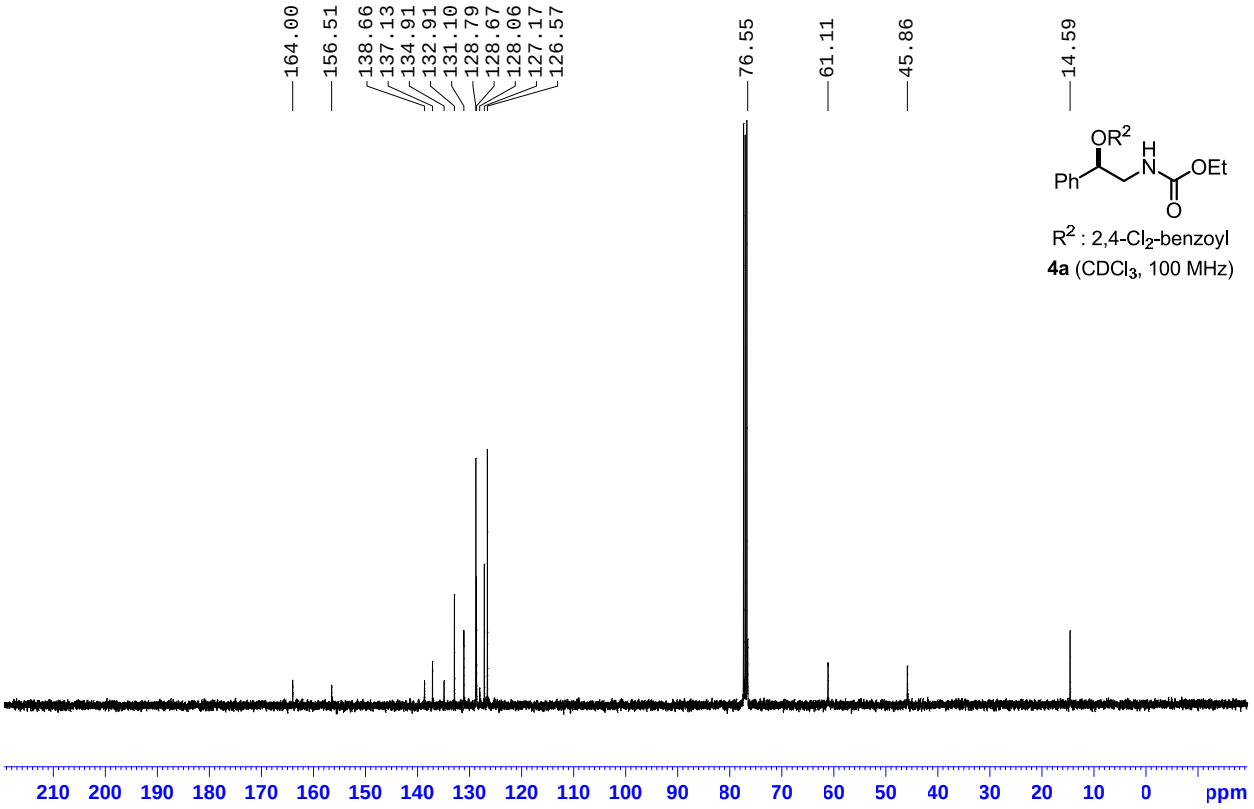


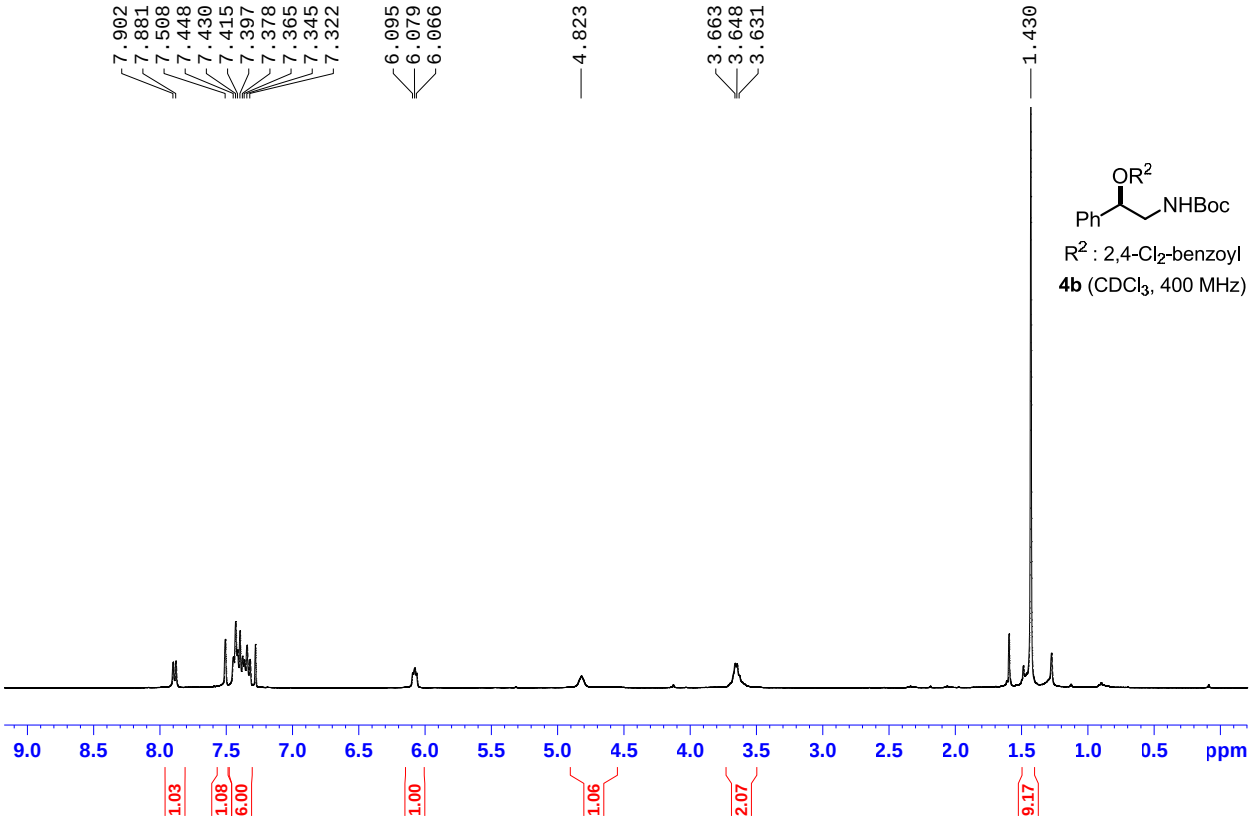
3a ($CDCl_3$, 400 MHz)

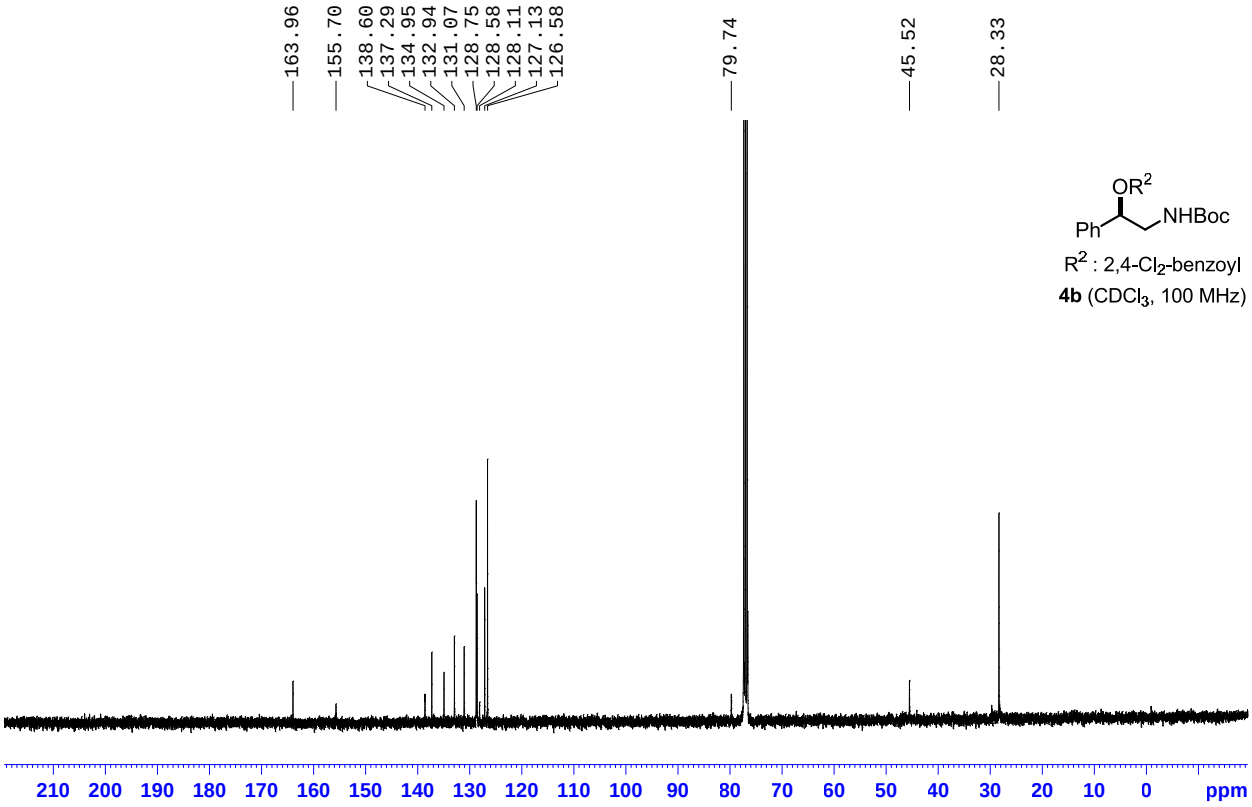


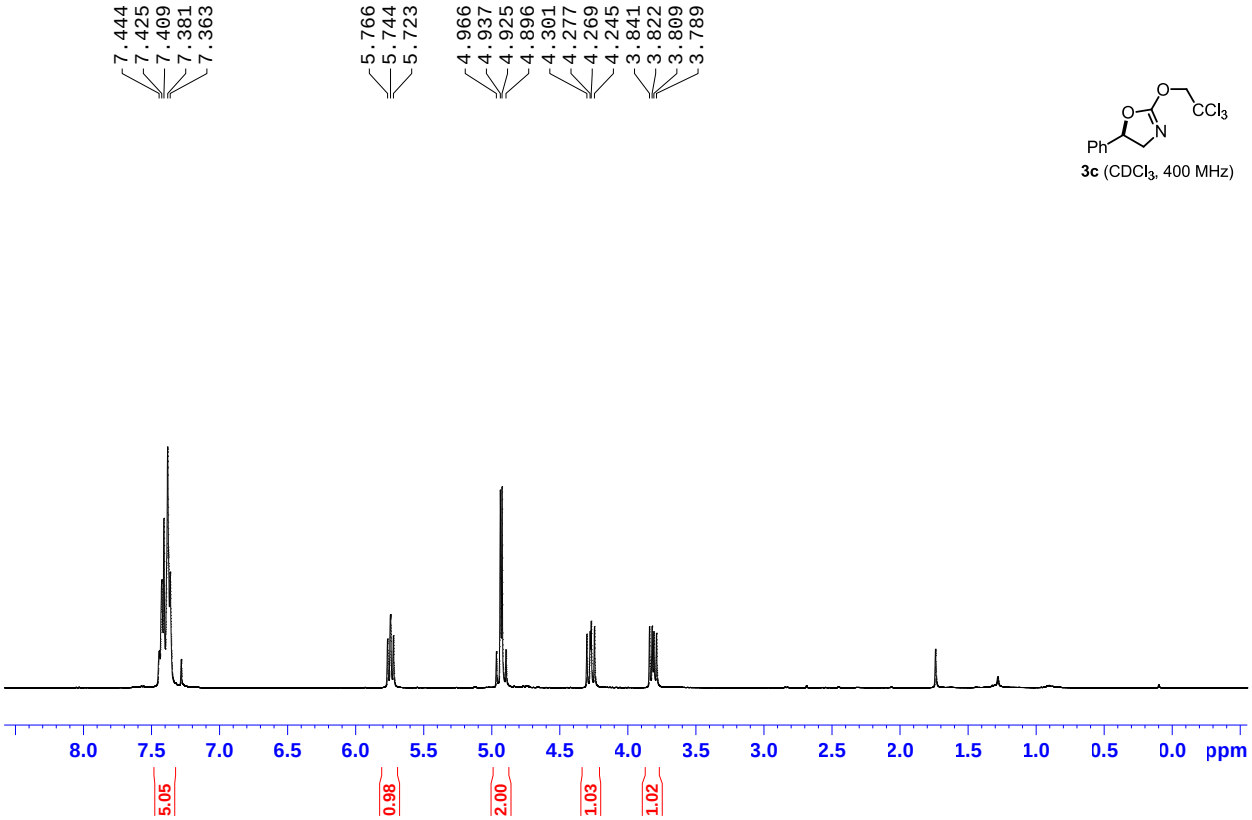
3a ($CDCl_3$, 100 MHz)

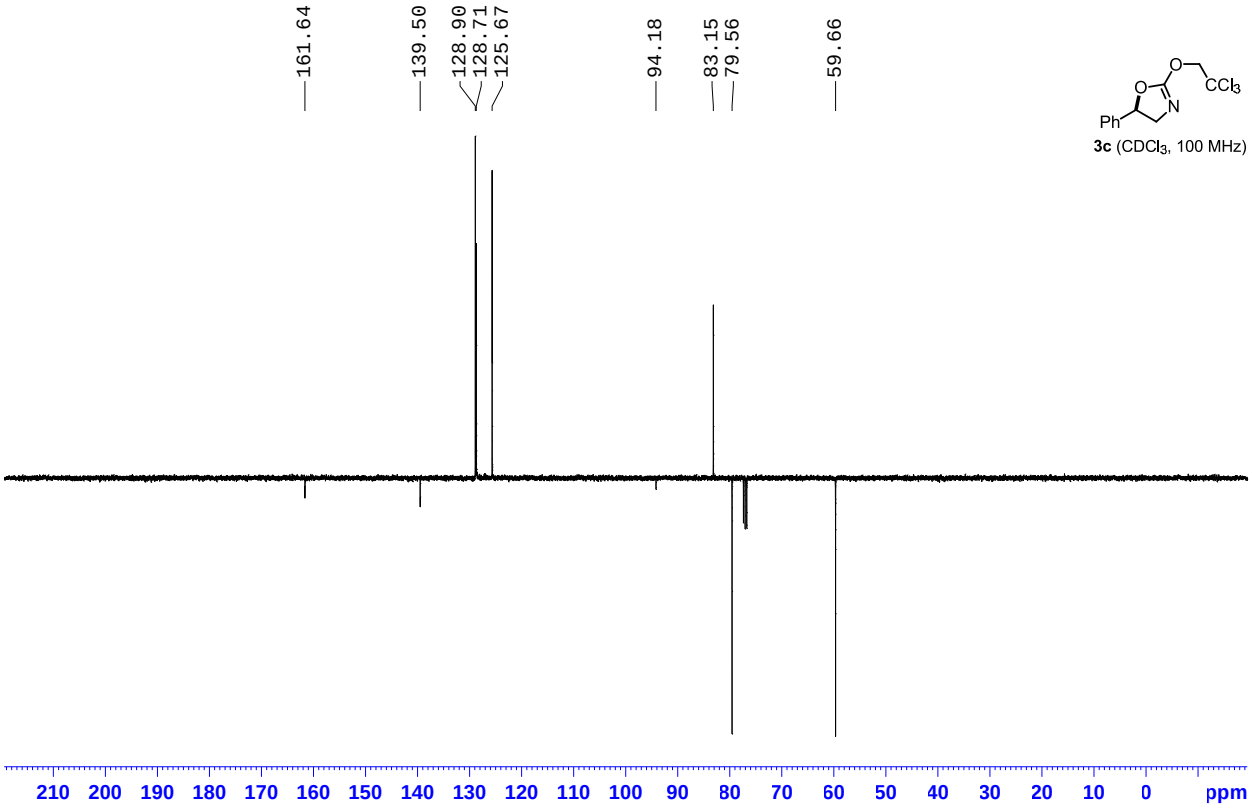

7.885
7.864
7.510
7.452
7.435
7.422
7.403
7.384
7.372
7.352
7.329
6.083
4.961
4.147
4.129
4.112
4.094
3.773
3.737
3.707
3.689
3.672
3.653
3.638
1.250
1.233
1.215
OR2
H
N
Ph
OEt
O
R2 : 2,4-Cl2-benzoyl
4a (CDCl3, 400 MHz)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.89
5.94
1.00
1.03
2.01
2.07
3.07

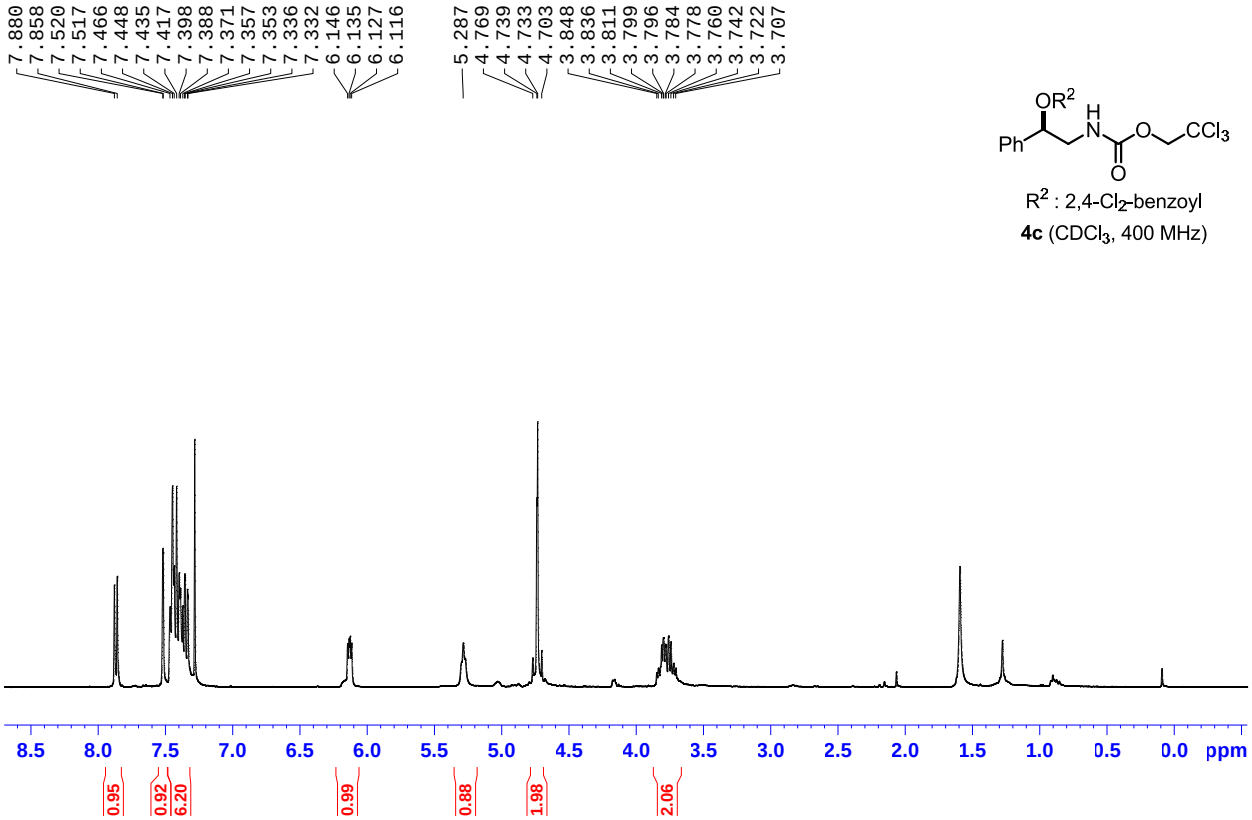

164.00
156.51
138.66
137.13
134.91
132.91
131.10
128.79
128.67
128.06
127.17
126.57
76.55
61.11
45.86
14.59
OR2
H
N
Ph
OEt
O
R2 : 2,4-Cl2-benzoyl
4a (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

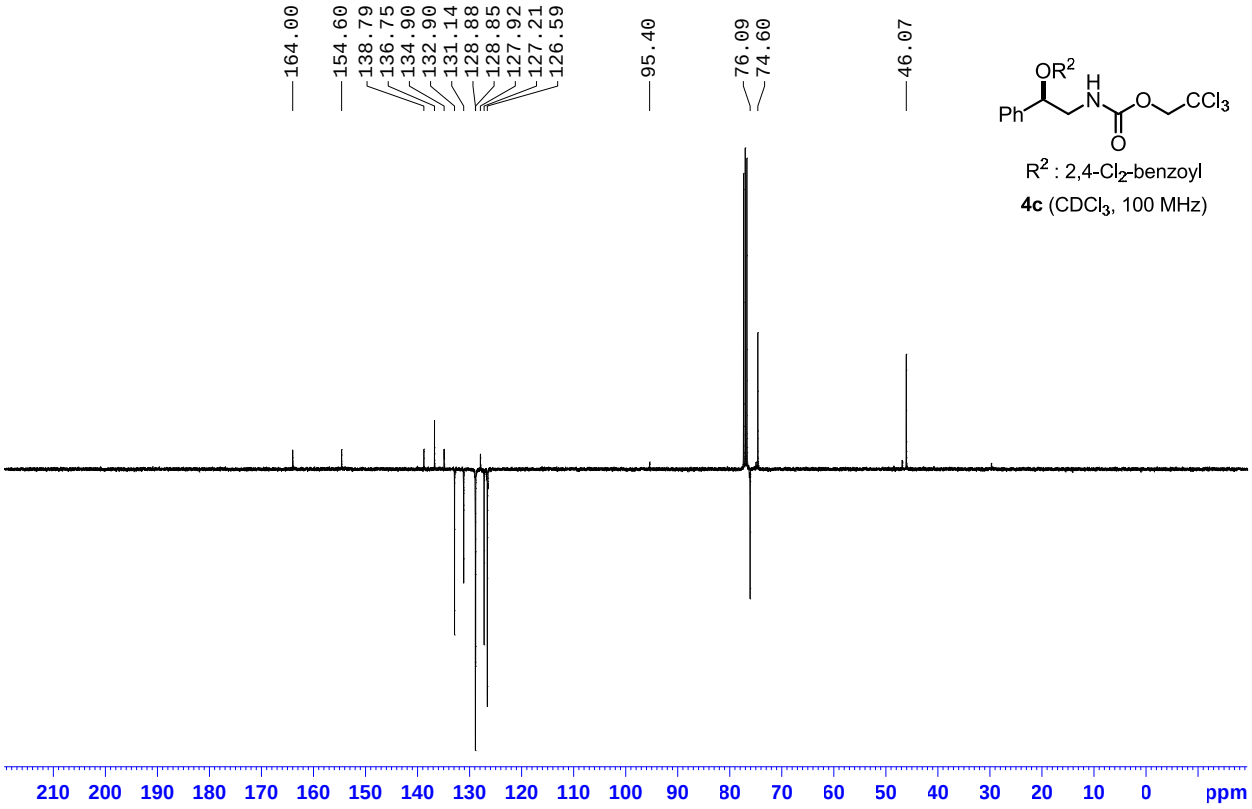

7.902
7.881
7.508
7.448
7.430
7.415
7.397
7.378
7.365
7.345
7.322
6.095
6.079
6.066
4.823
3.663
3.648
3.631
1.430
OR2
Ph
NHBoc
R2 : 2,4-Cl2-benzoyl
4b (CDCl3, 400 MHz)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
1.08
6.00
1.00
1.06
2.07
9.17

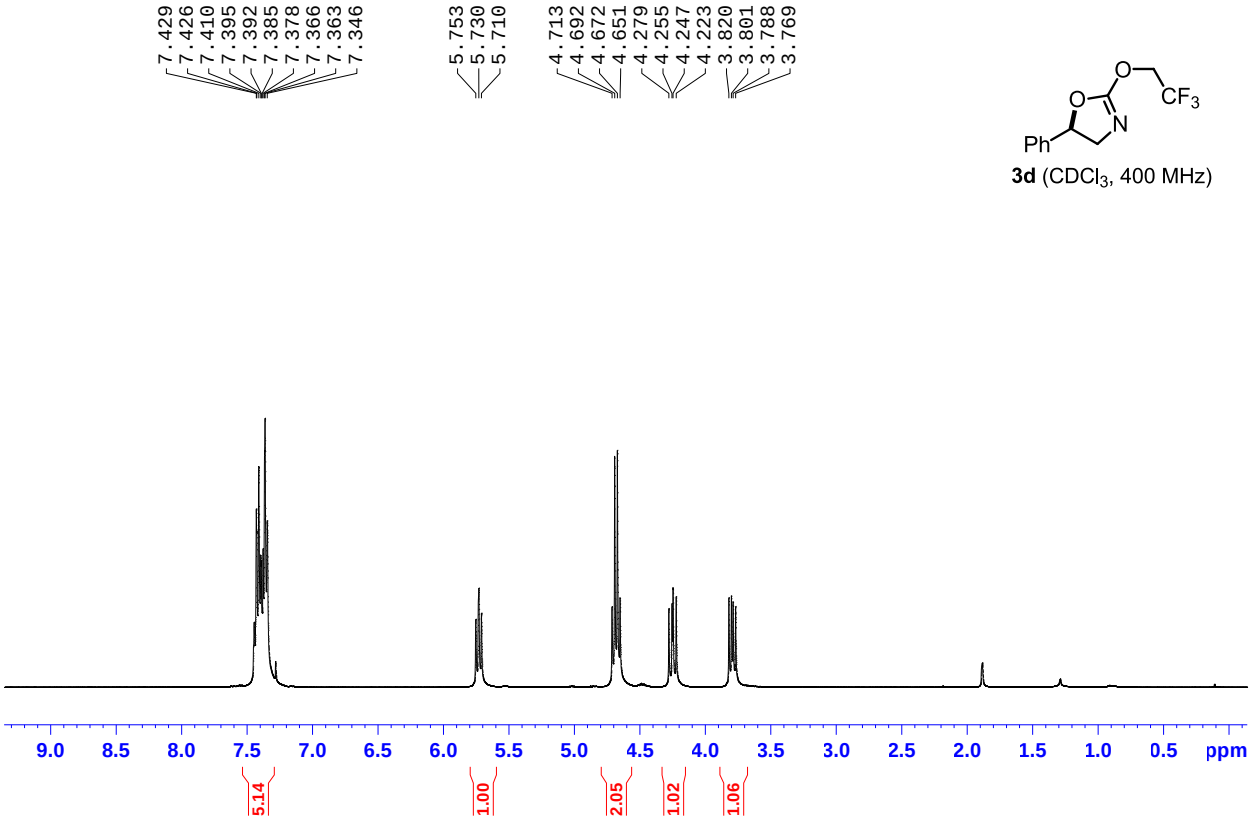

163.96
155.70
138.60
137.29
134.95
132.94
131.07
128.75
128.58
128.11
127.13
126.58
79.74
45.52
28.33
OR2
Ph
NHBoc
R2 : 2,4-Cl2-benzoyl
4b (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

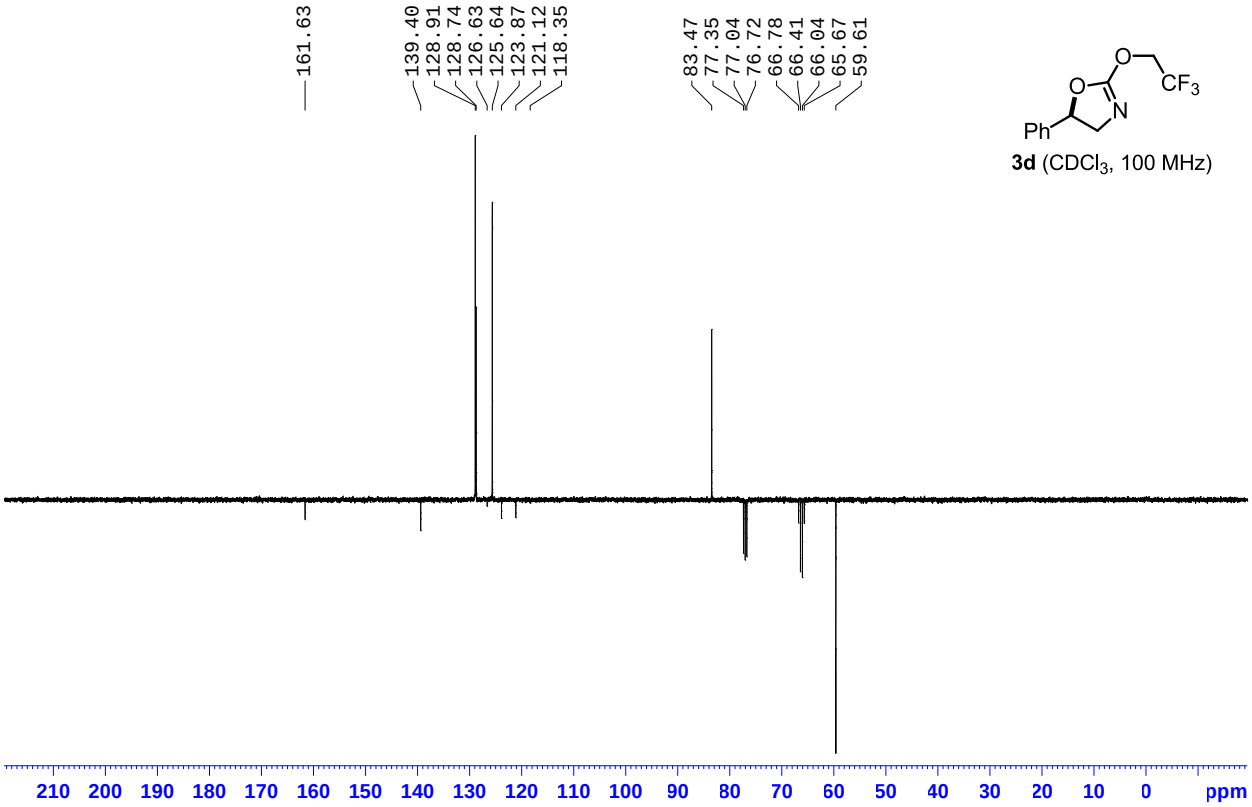

7.444
7.425
7.409
7.381
7.363
5.766
5.744
5.723
4.966
4.937
4.925
4.896
4.301
4.277
4.269
4.245
3.841
3.822
3.809
3.789
O
O
N
CCl3
Ph
3c (CDCl3, 400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.05
0.98
2.00
1.03
1.02

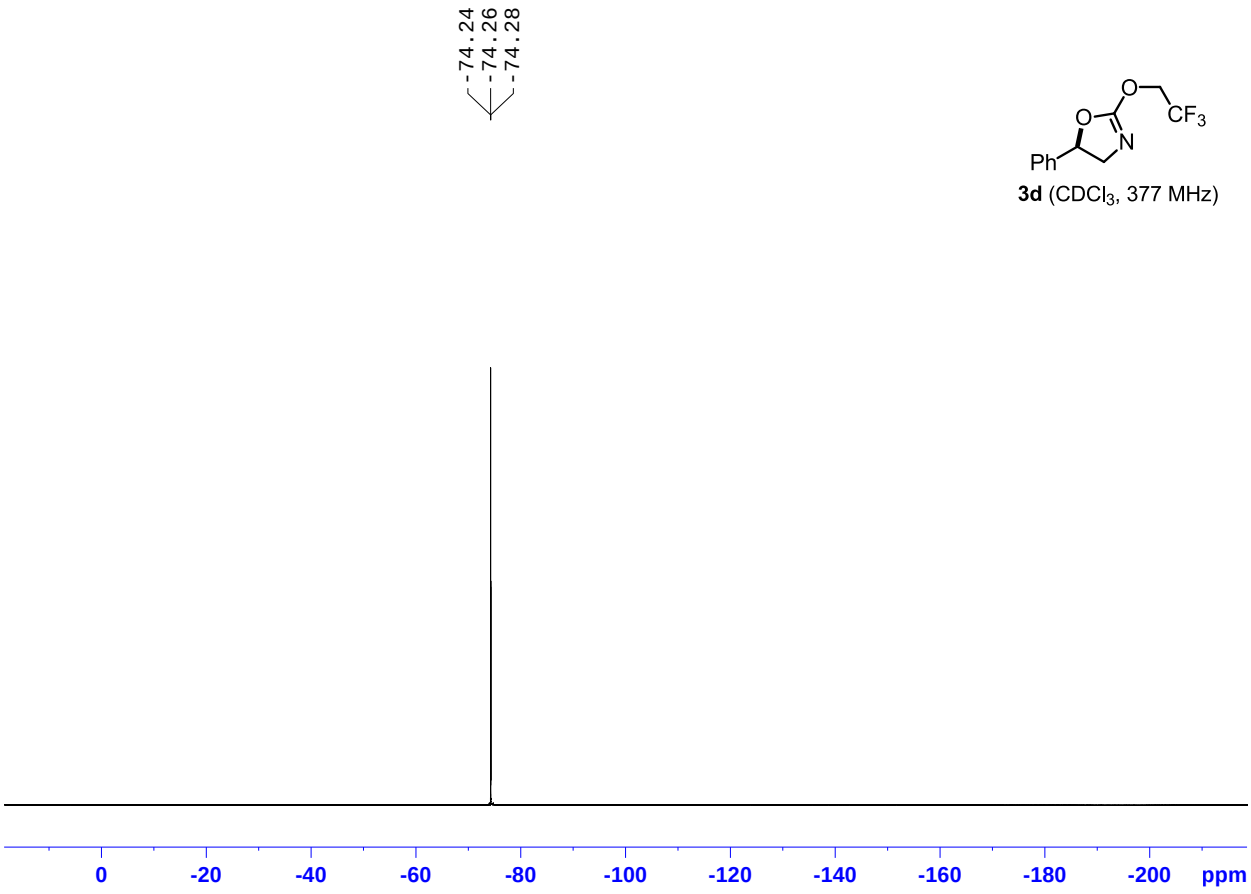

161.64
139.50
128.90
128.71
125.67
94.18
83.15
79.56
59.66
O
O
N
CCl3
Ph
3c (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.880
7.858
7.520
7.517
7.466
7.448
7.435
7.417
7.398
7.388
7.371
7.357
7.353
7.336
7.332
6.146
6.135
6.127
6.116
5.287
4.769
4.739
4.733
4.703
3.848
3.836
3.811
3.799
3.796
3.784
3.778
3.760
3.742
3.722
3.707
OR2
H
N
O
Ph
O
CCl3
O
R2 : 2,4-Cl2-benzoyl
4c (CDCl3, 400 MHz)
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
ppm
0.95
0.92
6.20
0.99
0.88
1.98
2.06

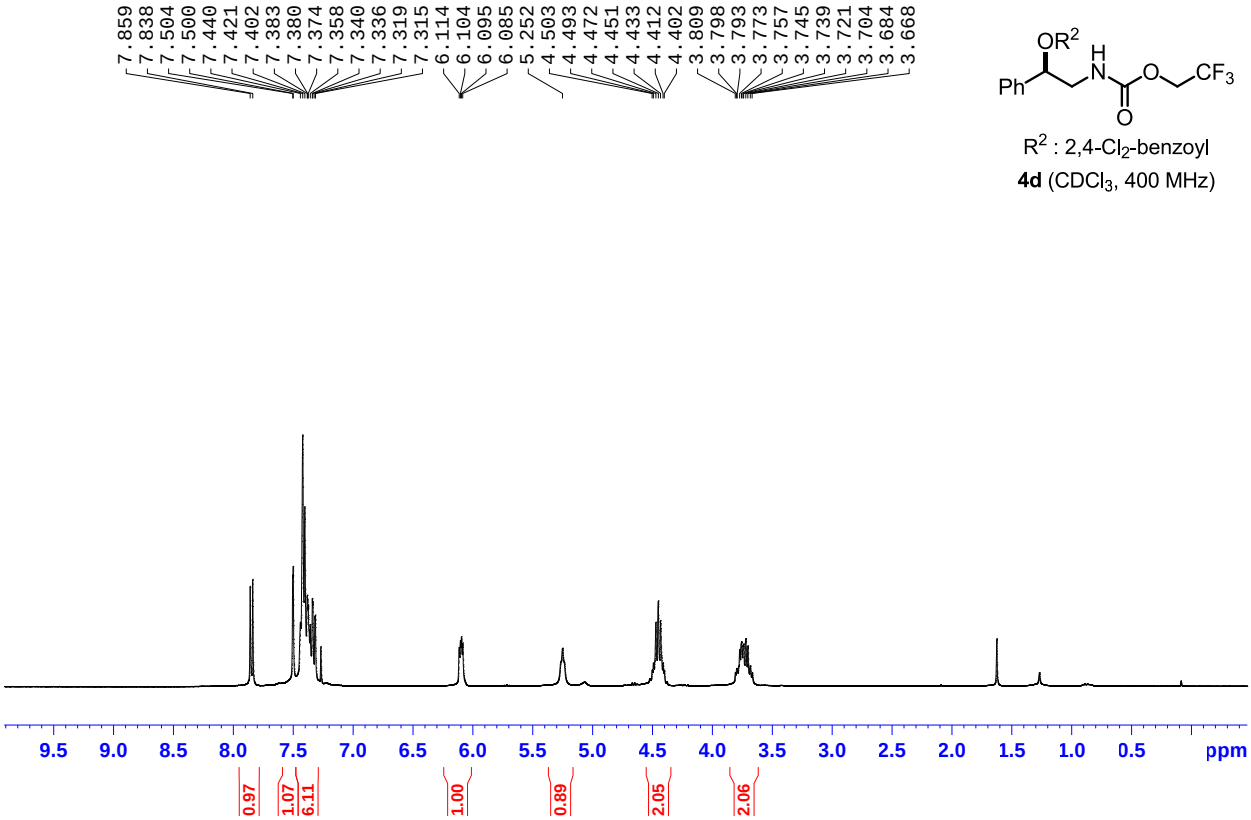

164.00
154.60
138.79
136.75
134.90
132.90
131.14
128.88
128.85
127.92
127.21
126.59
95.40
76.09
74.60
46.07
OR2
H
N
O
Ph
O
CCl3
O
R2 : 2,4-Cl2-benzoyl
4c (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

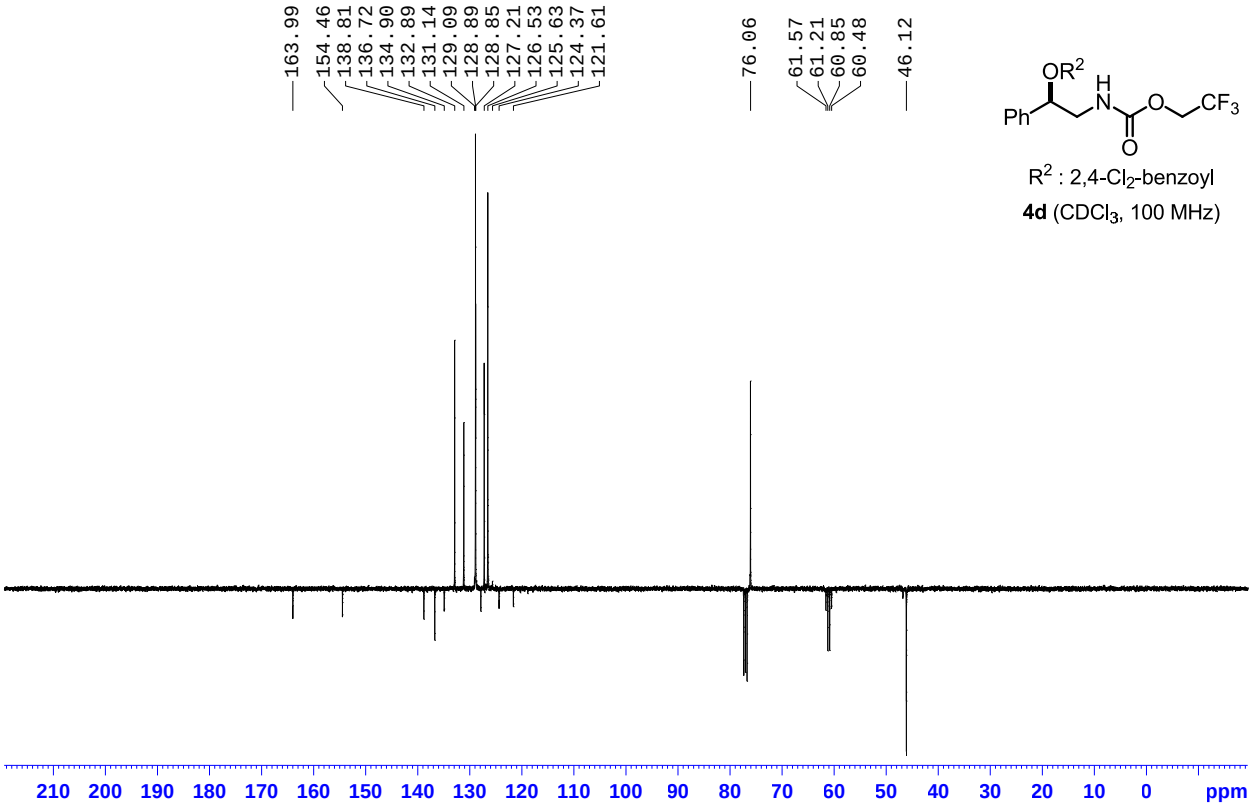

7.429
7.426
7.410
7.395
7.392
7.385
7.378
7.366
7.363
7.346
5.753
5.730
5.710
4.713
4.692
4.672
4.651
4.279
4.255
4.247
4.223
3.820
3.801
3.788
3.769
O
CF3
O
N
Ph
3d (CDCl3, 400 MHz)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.14
1.00
2.05
1.02
1.06

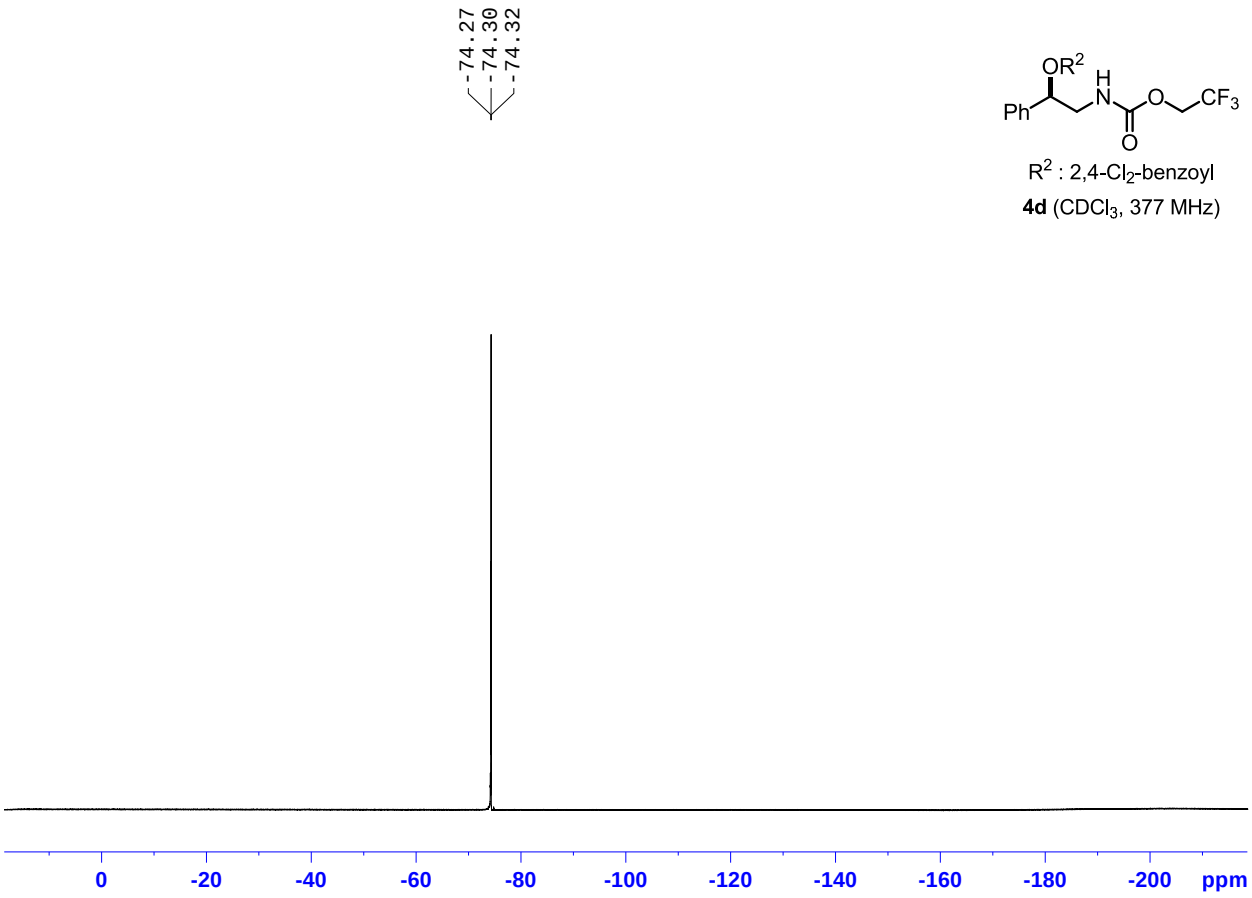

161.63
139.40
128.91
128.74
126.63
125.64
123.87
121.12
118.35
83.47
77.35
77.04
76.72
66.78
66.41
66.04
65.67
59.61
O
CF3
O
N
Ph
3d (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

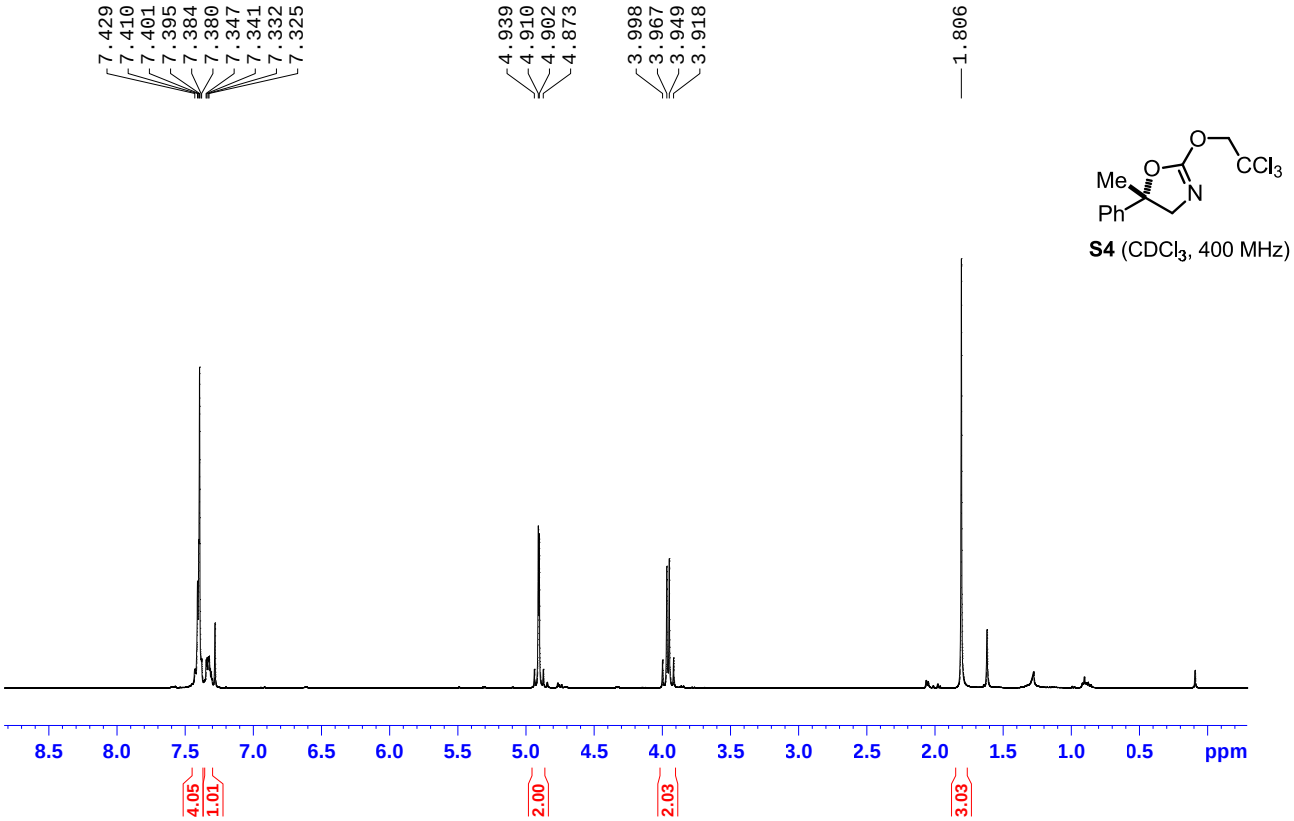


3d ($CDCl_3$, 377 MHz)

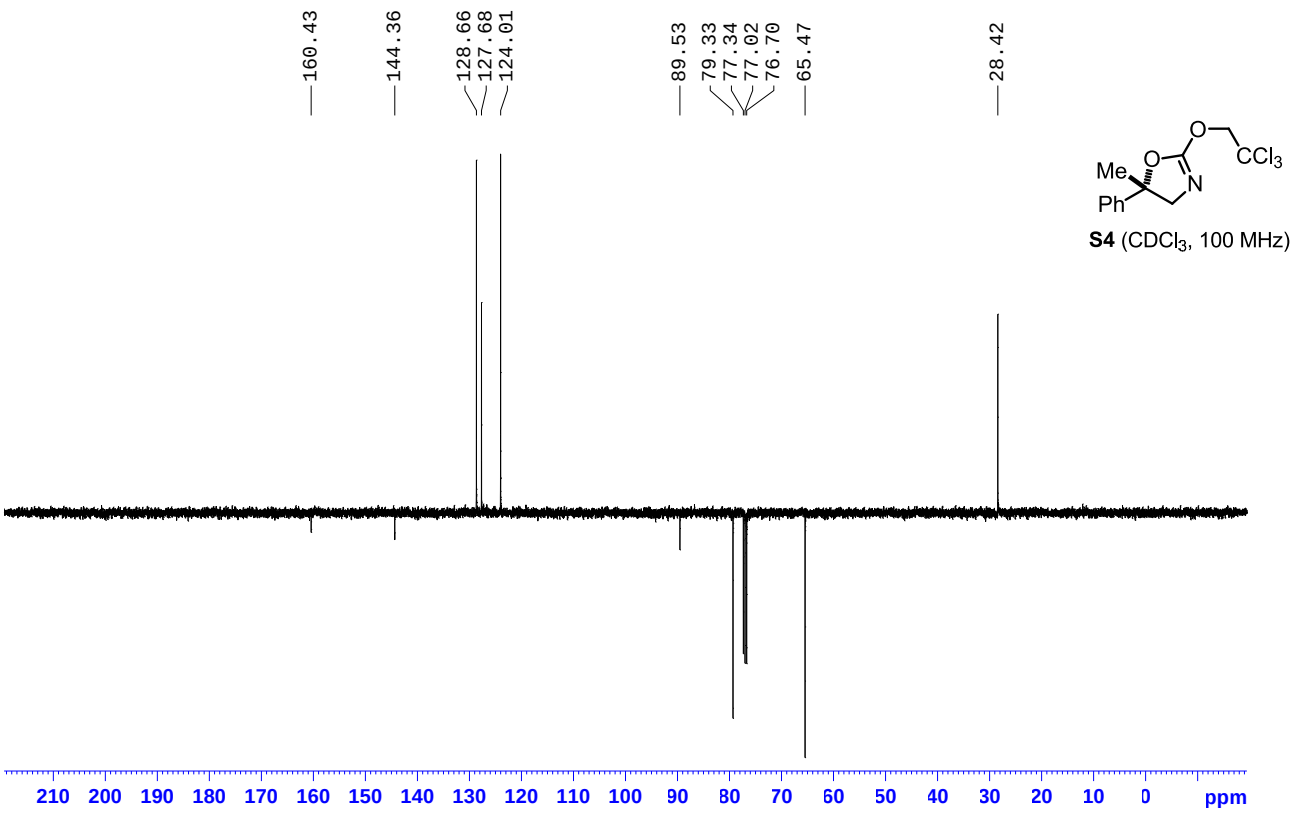

7.859
7.838
7.504
7.500
7.440
7.421
7.402
7.383
7.380
7.374
7.358
7.340
7.336
7.319
7.315
6.114
6.104
6.095
6.085
5.252
4.503
4.493
4.472
4.451
4.433
4.412
4.402
3.809
3.798
3.793
3.773
3.757
3.745
3.739
3.721
3.704
3.684
3.668
OR2
H
N
Ph
O
O
CF3
R2 : 2,4-Cl2-benzoyl
4d (CDCl3, 400 MHz)
9.5 9.0 8.5 8.0 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 ppm
0.97
1.07
6.11
1.00
0.89
2.05
2.06


163.99
154.46
138.81
136.72
134.90
132.89
131.14
129.09
128.89
128.85
127.21
126.53
125.63
124.37
121.61
76.06
61.57
61.21
60.85
60.48
46.12
OR2
H
N
Ph
O
O
CF3
R2 : 2,4-Cl2-benzoyl
4d (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

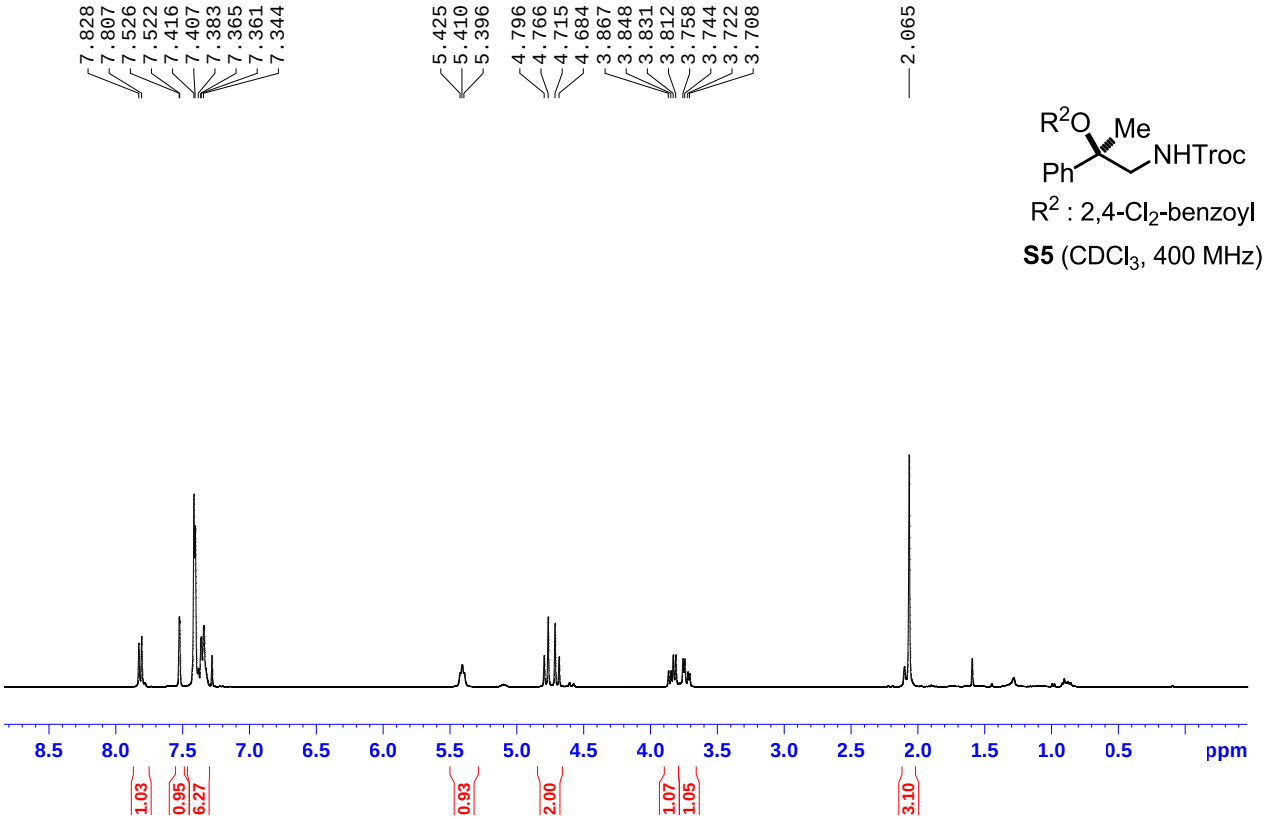

-74.27
-74.30
-74.32
OR2
H
N
Ph
O
O
CF3
R2 : 2,4-Cl2-benzoyl
4d (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



S4 ($CDCl_3$, 400 MHz)

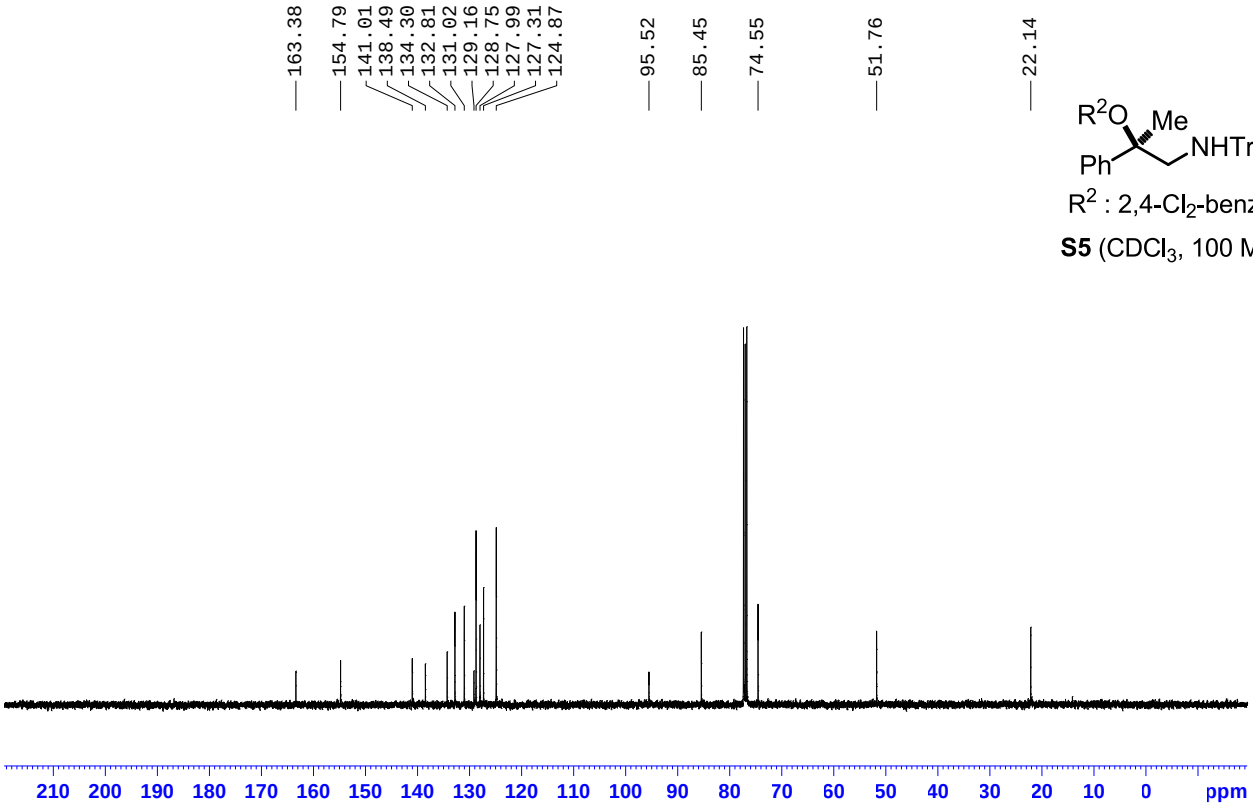


S4 ($CDCl_3$, 100 MHz)



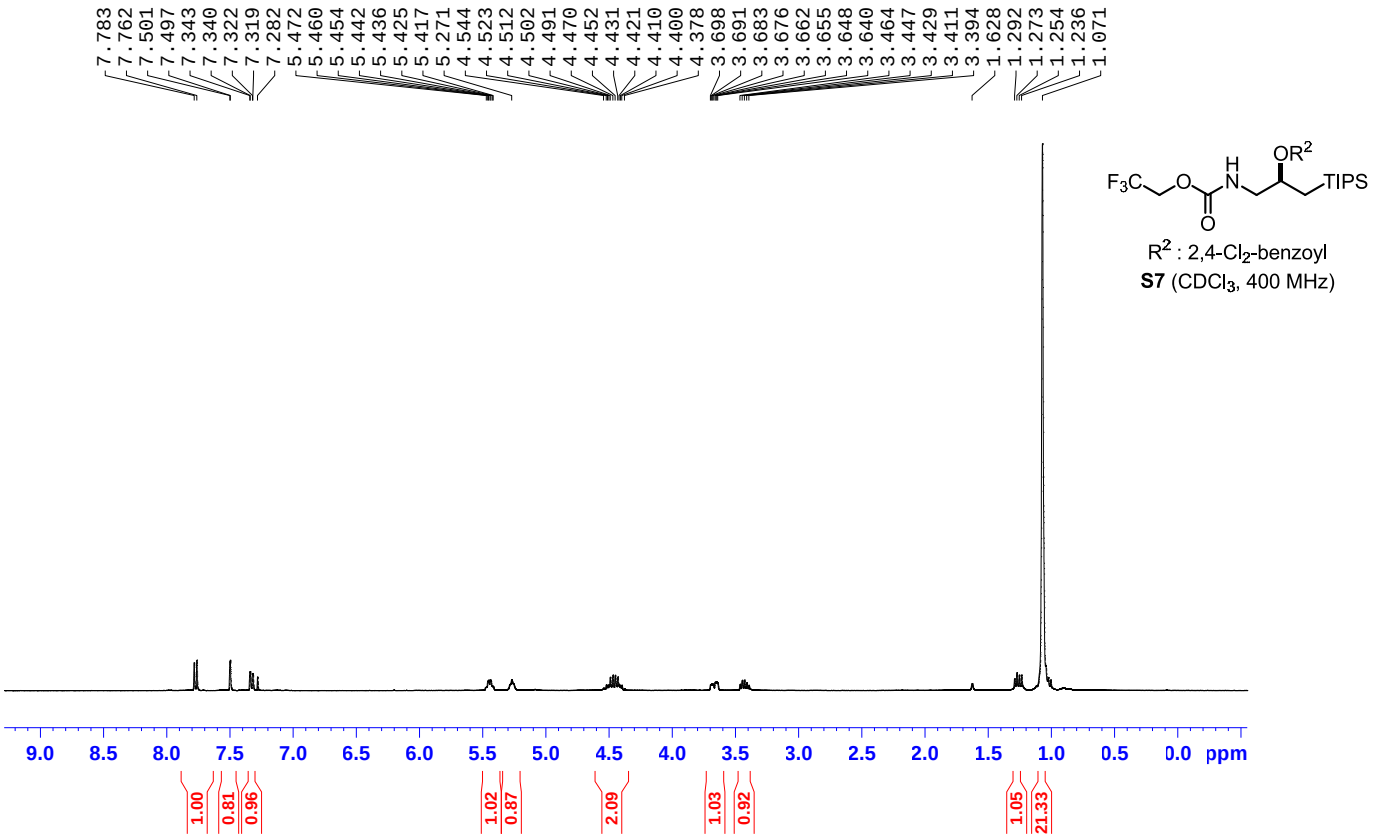
R^2 : 2,4-Cl_2-benzoyl

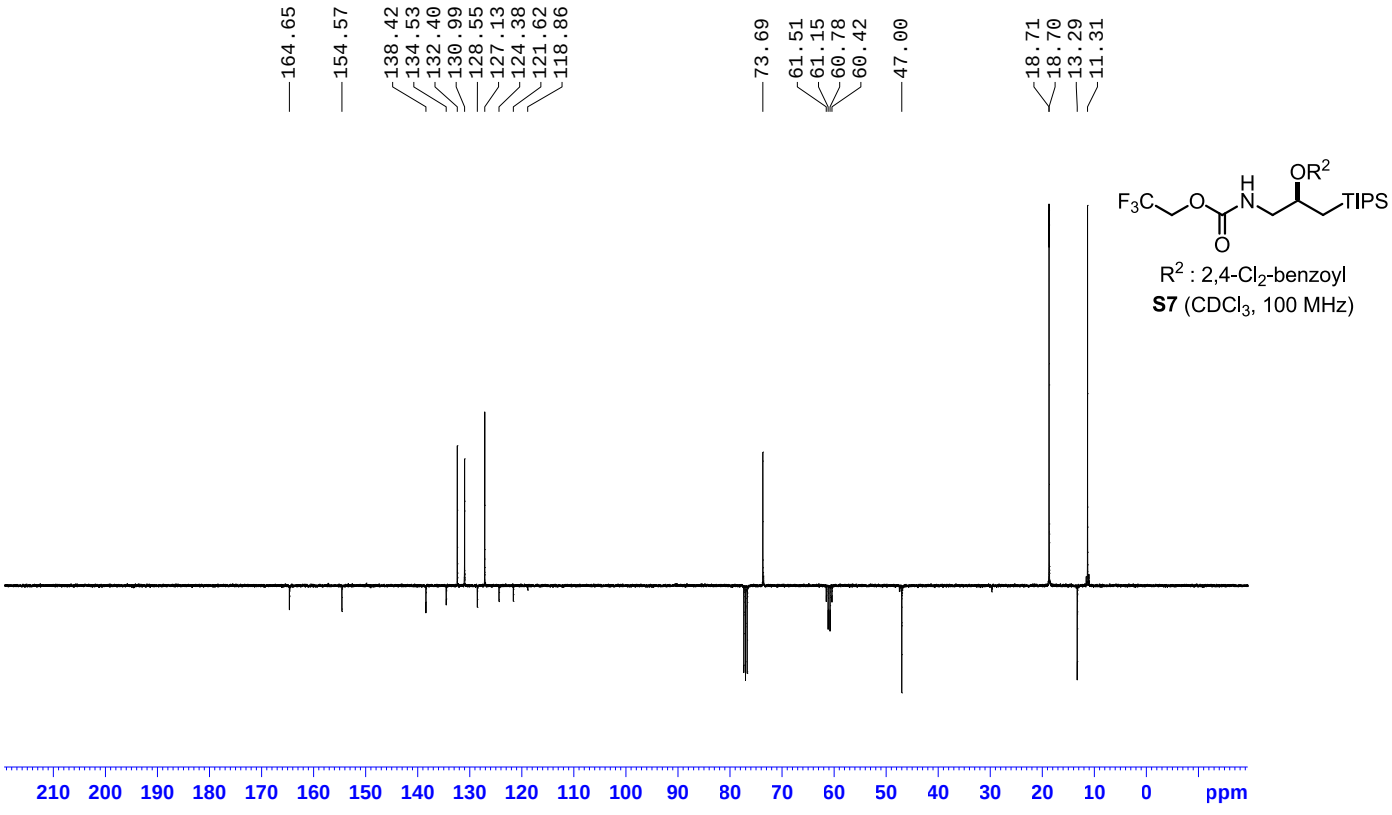
S5 ($CDCl_3$, 400 MHz)

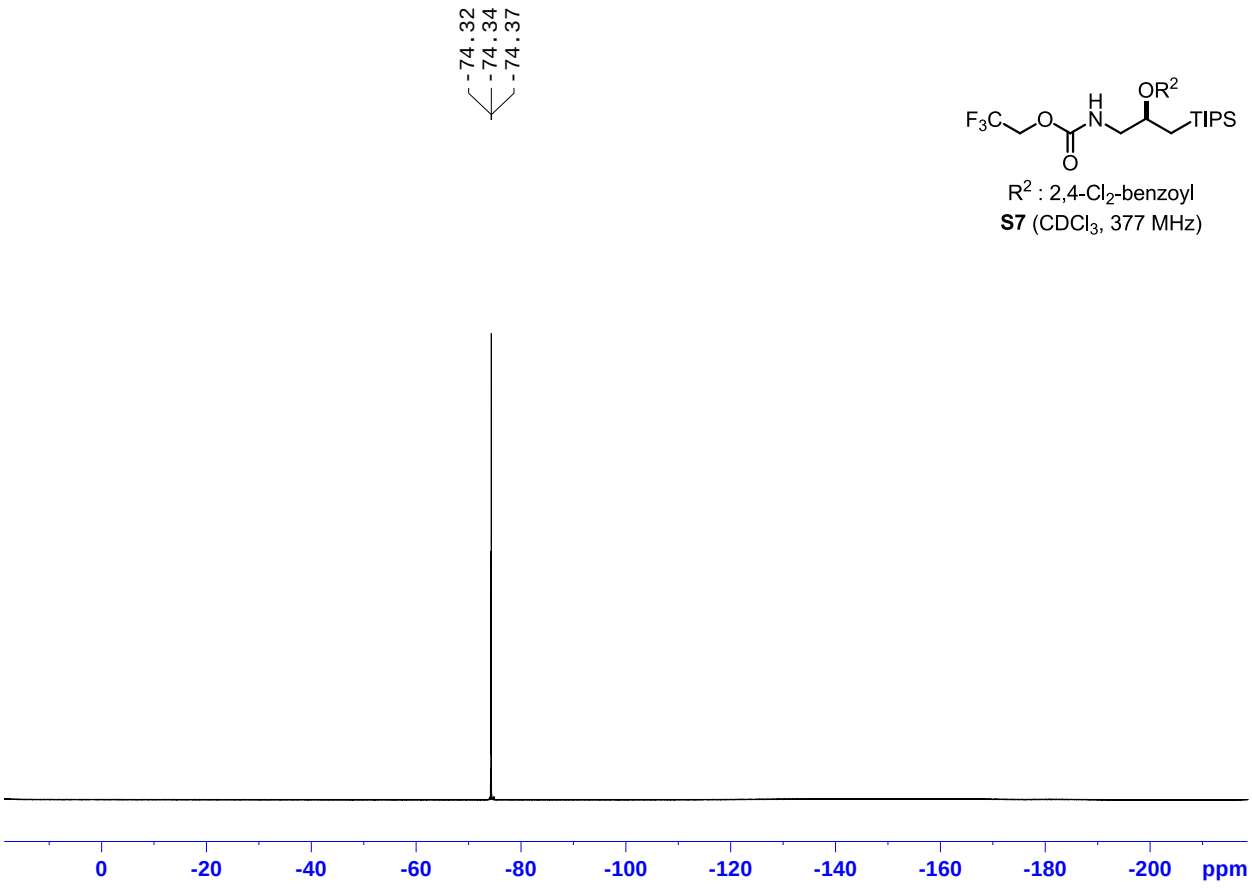


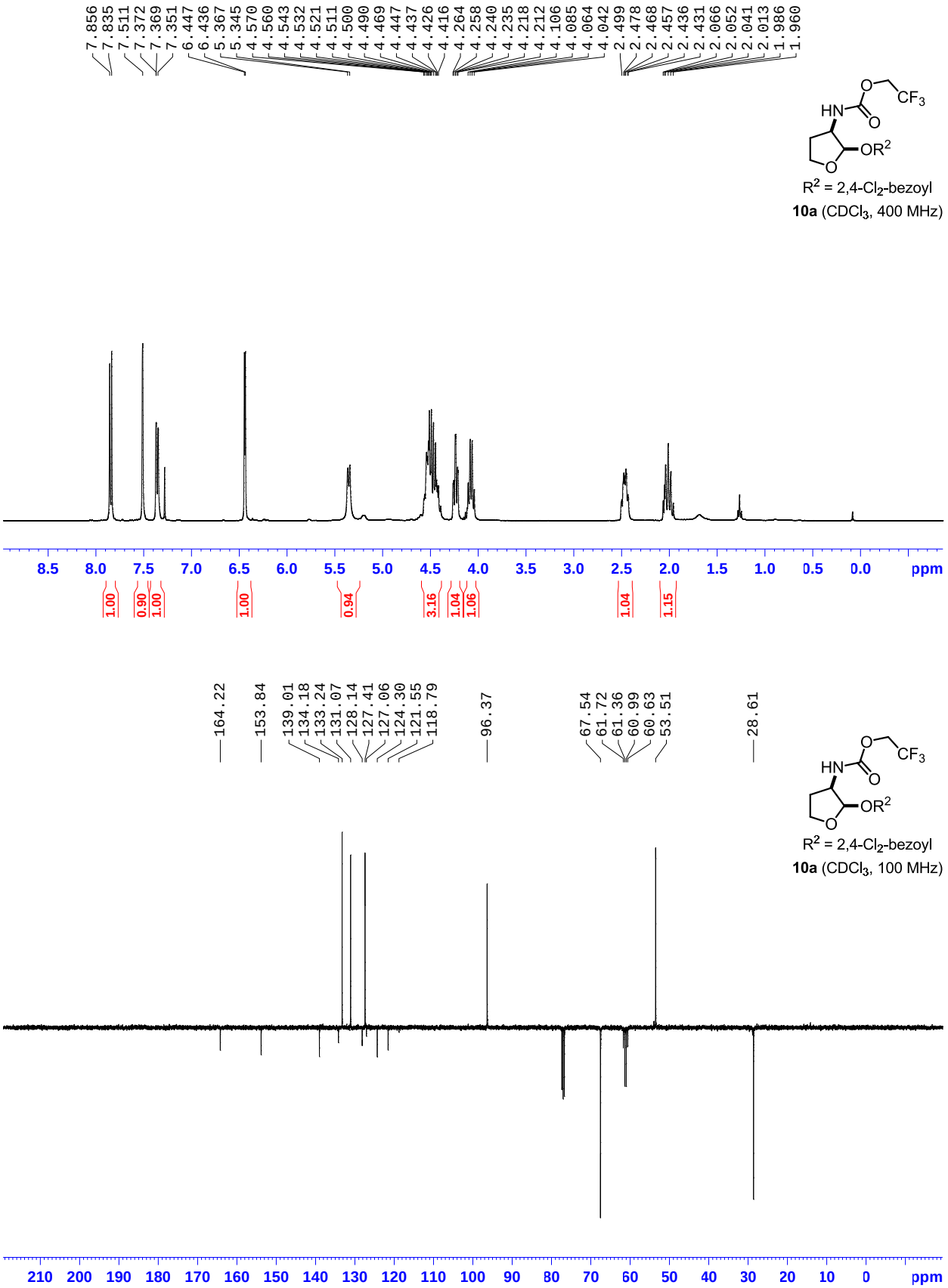
R^2 : 2,4-Cl_2-benzoyl

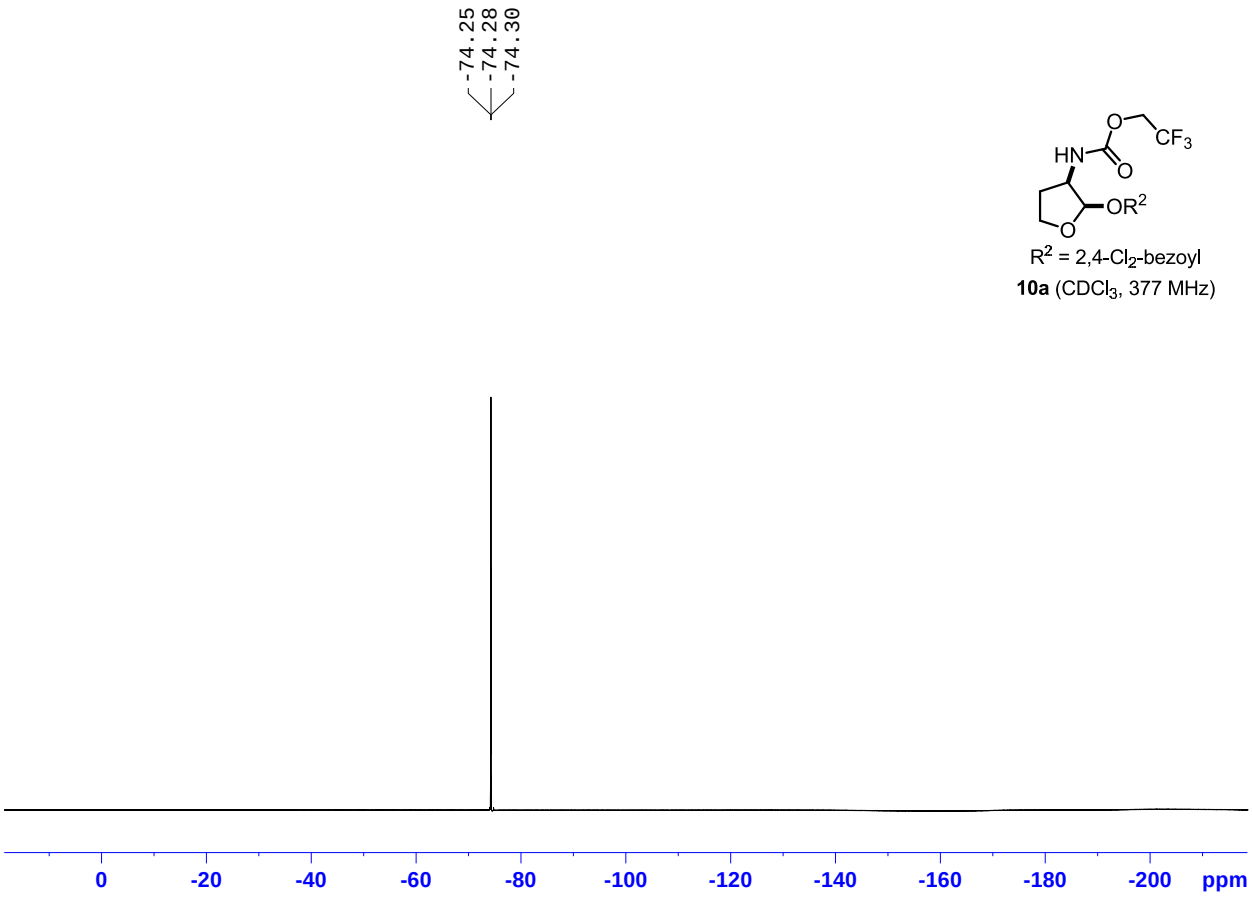
S5 ($CDCl_3$, 100 MHz)


7.783
7.762
7.501
7.497
7.343
7.340
7.322
7.319
7.282
5.472
5.460
5.454
5.442
5.436
5.425
5.417
5.271
4.544
4.523
4.512
4.502
4.491
4.470
4.452
4.431
4.421
4.410
4.400
4.378
3.698
3.691
3.683
3.676
3.662
3.655
3.648
3.640
3.464
3.447
3.429
3.411
3.394
1.628
1.292
1.273
1.254
1.236
1.071
F3C
O
H
N
OR2
TIPS
O
R2 : 2,4-Cl2-benzoyl
S7 (CDCl3, 400 MHz)
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
ppm
1.00
0.81
0.96
1.02
0.87
2.09
1.03
0.92
1.05
21.33


164.65
154.57
138.42
134.53
132.40
130.99
128.55
127.13
124.38
121.62
118.86
73.69
61.51
61.15
60.78
60.42
47.00
18.71
18.70
13.29
11.31
F3C
O
H
N
OR2
TIPS
O
R2 : 2,4-Cl2-benzoyl
S7 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

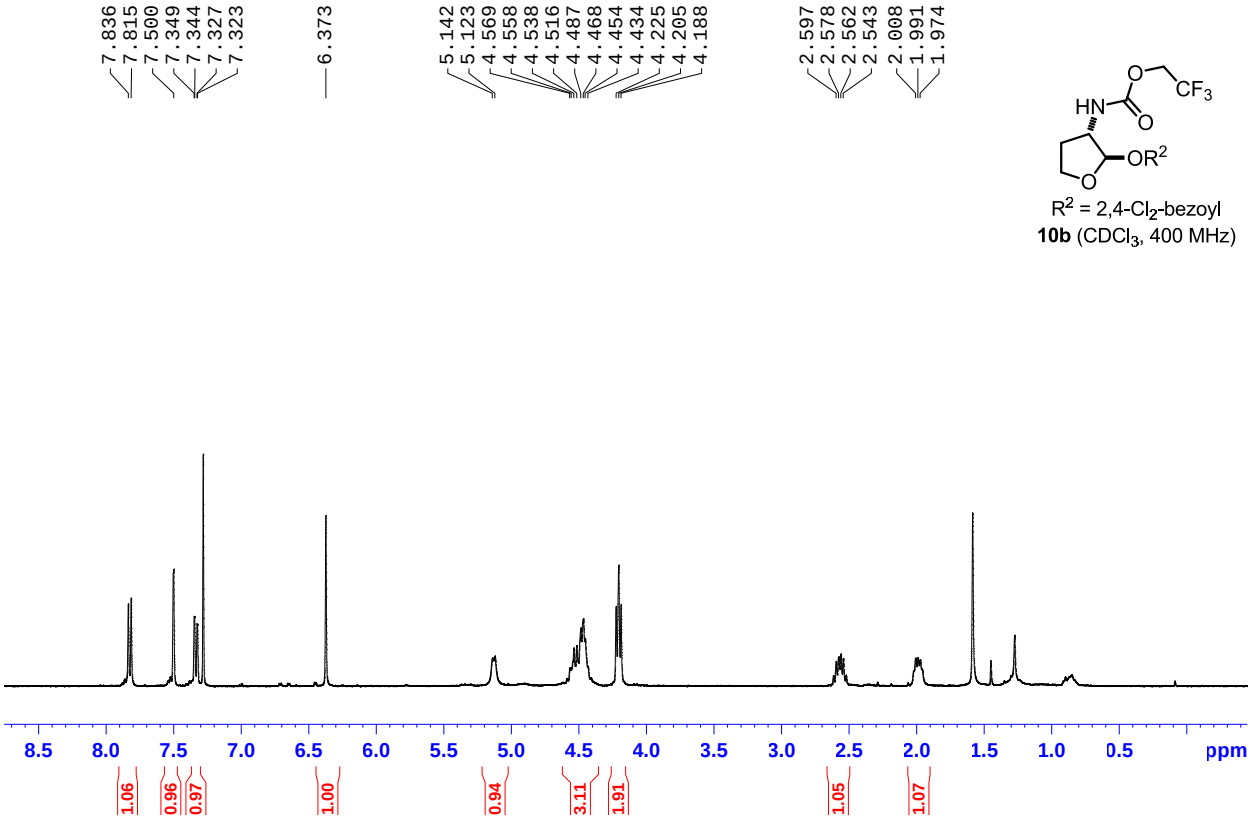

-74.32
-74.34
-74.37
F3C
O
H
N
OR2
TIPS
O
R2 : 2,4-Cl2-benzoyl
S7 (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

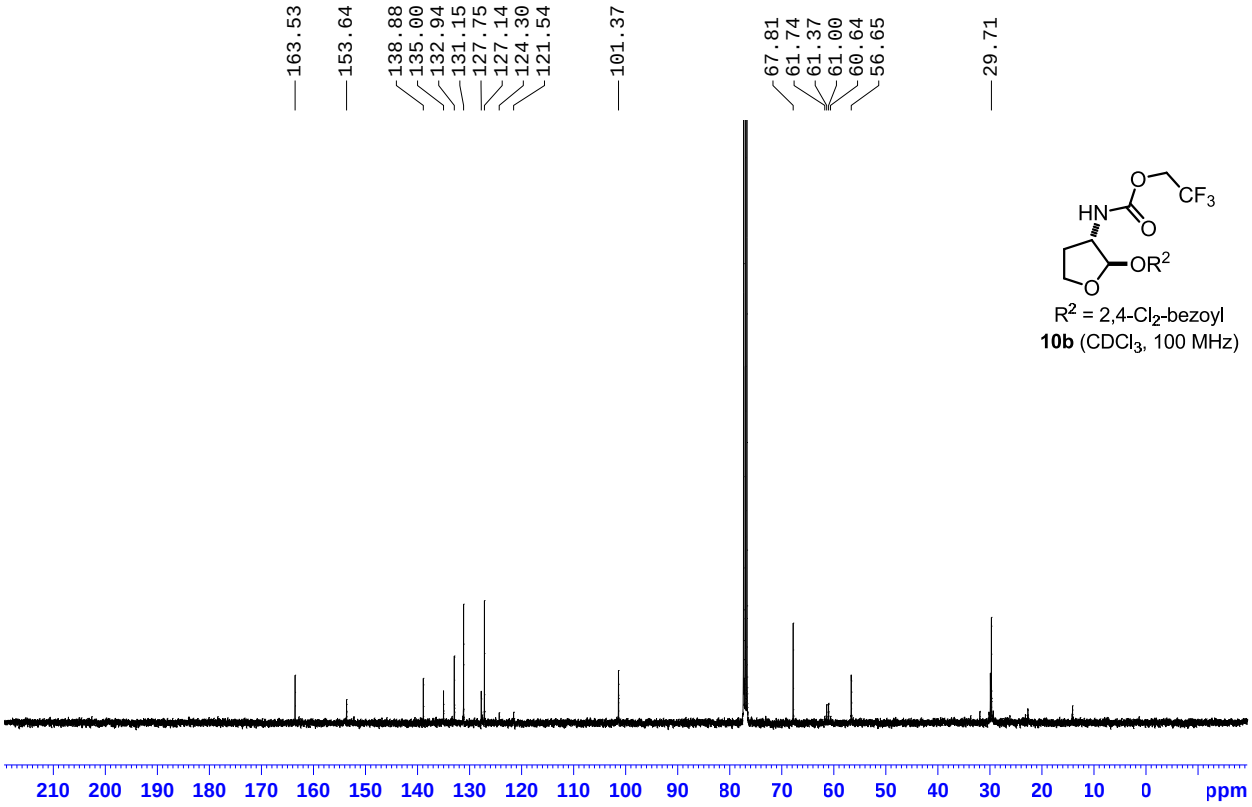

7.856
7.835
7.511
7.372
7.369
7.351
6.447
6.436
5.367
5.345
4.570
4.560
4.543
4.532
4.521
4.511
4.500
4.490
4.469
4.447
4.437
4.426
4.416
4.264
4.258
4.240
4.235
4.218
4.212
4.106
4.085
4.064
4.042
2.499
2.478
2.468
2.457
2.436
2.431
2.066
2.052
2.041
2.013
1.986
1.960
HN
O
CF3
OR2
R2 = 2,4-Cl2-bezoyl
10a (CDCl3, 400 MHz)
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 ppm
1.00
0.90
1.00
1.00
0.94
3.16
1.04
1.06
1.04
1.15
164.22
153.84
139.01
134.18
133.24
131.07
128.14
127.41
127.06
124.30
121.55
118.79
96.37
67.54
61.72
61.36
60.99
60.63
53.51
28.61
R2 = 2,4-Cl2-bezoyl
10a (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

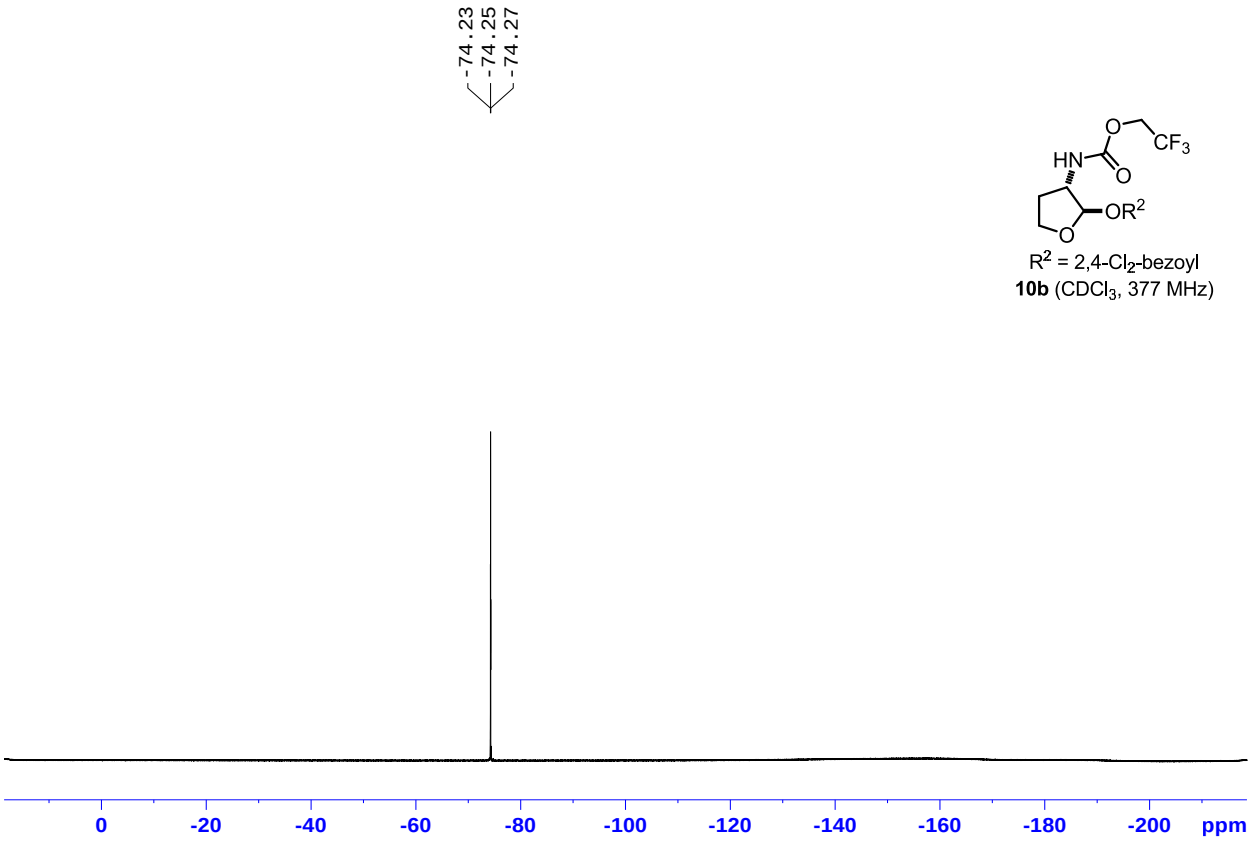


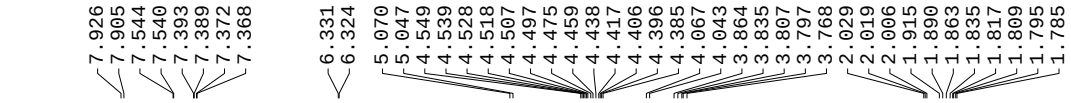
R^2 = 2,4-Cl_2-bezoyl

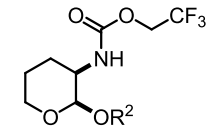
10a ($CDCl_3$, 377 MHz)


7.836
7.815
7.500
7.349
7.344
7.327
7.323
6.373
5.142
5.123
4.569
4.558
4.538
4.516
4.487
4.468
4.454
4.434
4.225
4.205
4.188
2.597
2.578
2.562
2.543
2.008
1.991
1.974
HN
O
CF3
OR2
R2 = 2,4-Cl2-bezoyl
10b (CDCl3, 400 MHz)
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 ppm
1.06
0.96
0.97
1.00
0.94
3.11
1.91
1.05
1.07


163.53
153.64
138.88
135.00
132.94
131.15
127.75
127.14
124.30
121.54
101.37
67.81
61.74
61.37
61.00
60.64
56.65
29.71
HN
O
CF3
OR2
R2 = 2,4-Cl2-bezoyl
10b (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

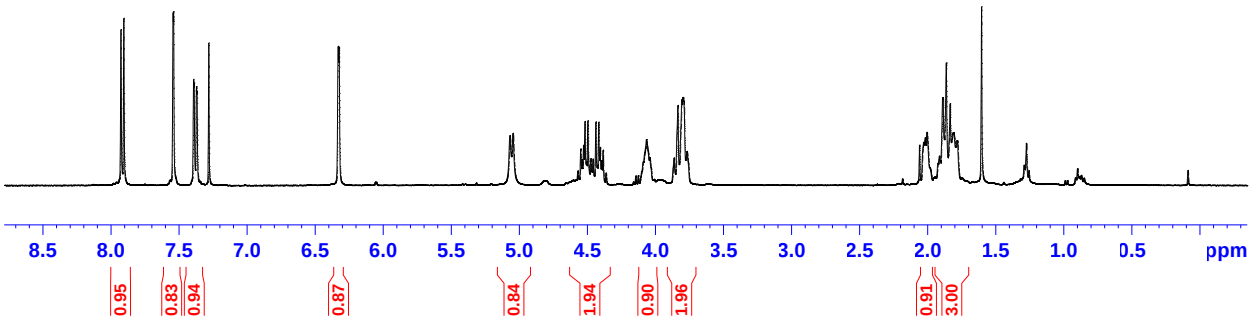

-74.23
-74.25
-74.27
O
CF3
HN
O
OR2
O
R2 = 2,4-Cl2-bezoyl
10b (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

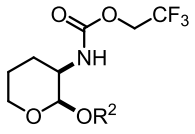




R^2 = 2,4-Cl_2-bezoyl

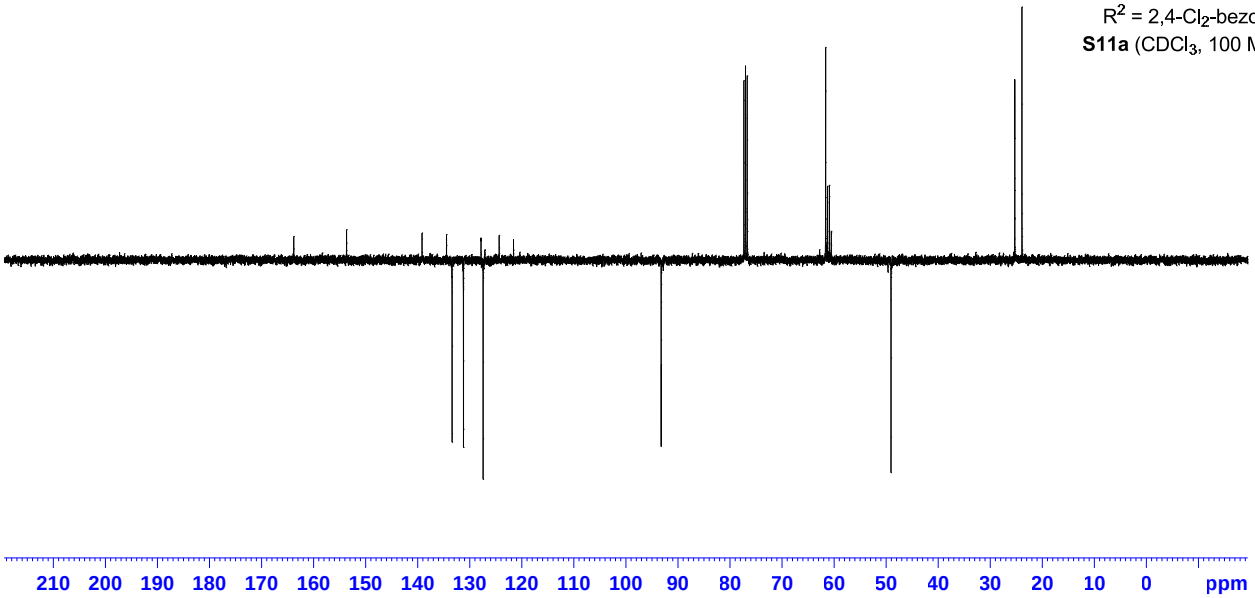
S11a ($CDCl_3$, 400 MHz)

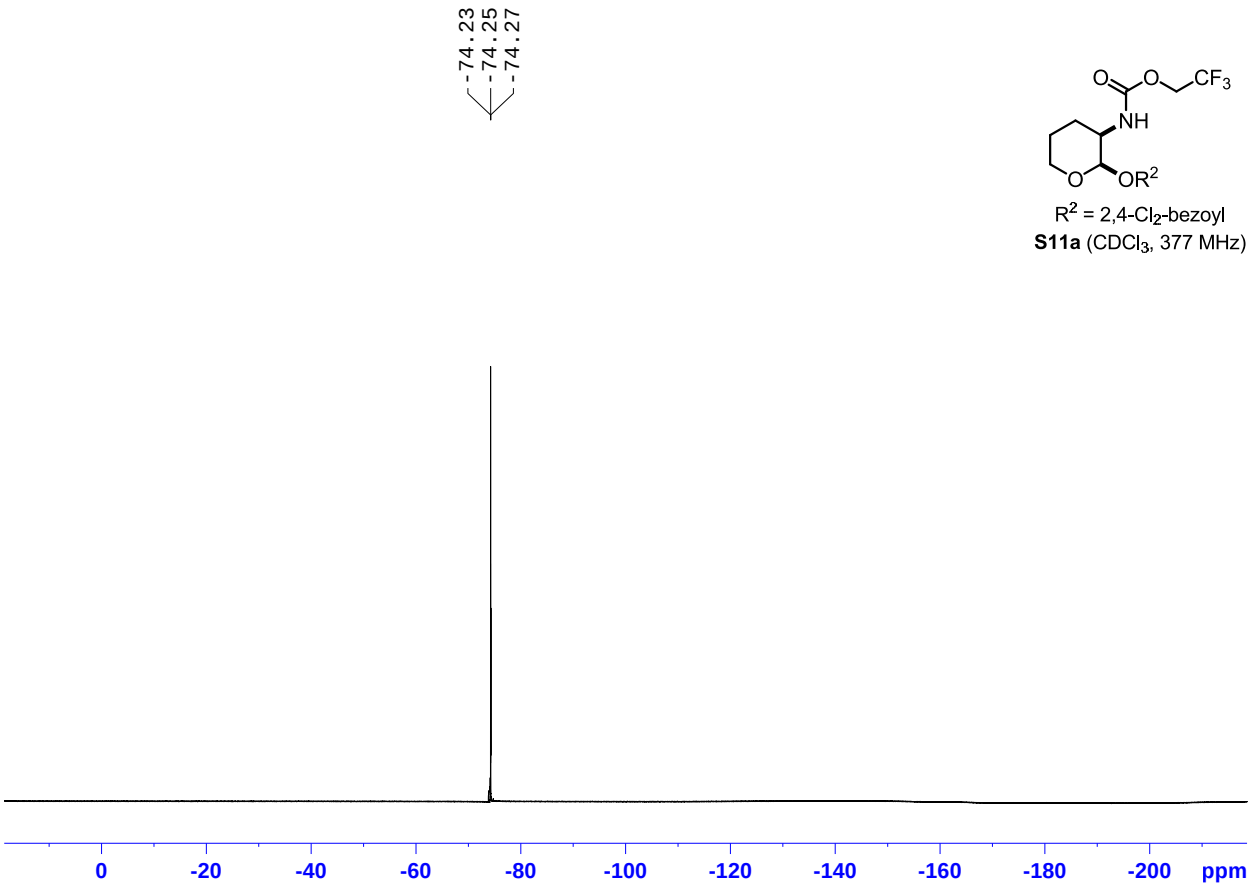




R^2 = 2,4-Cl_2-bezoyl

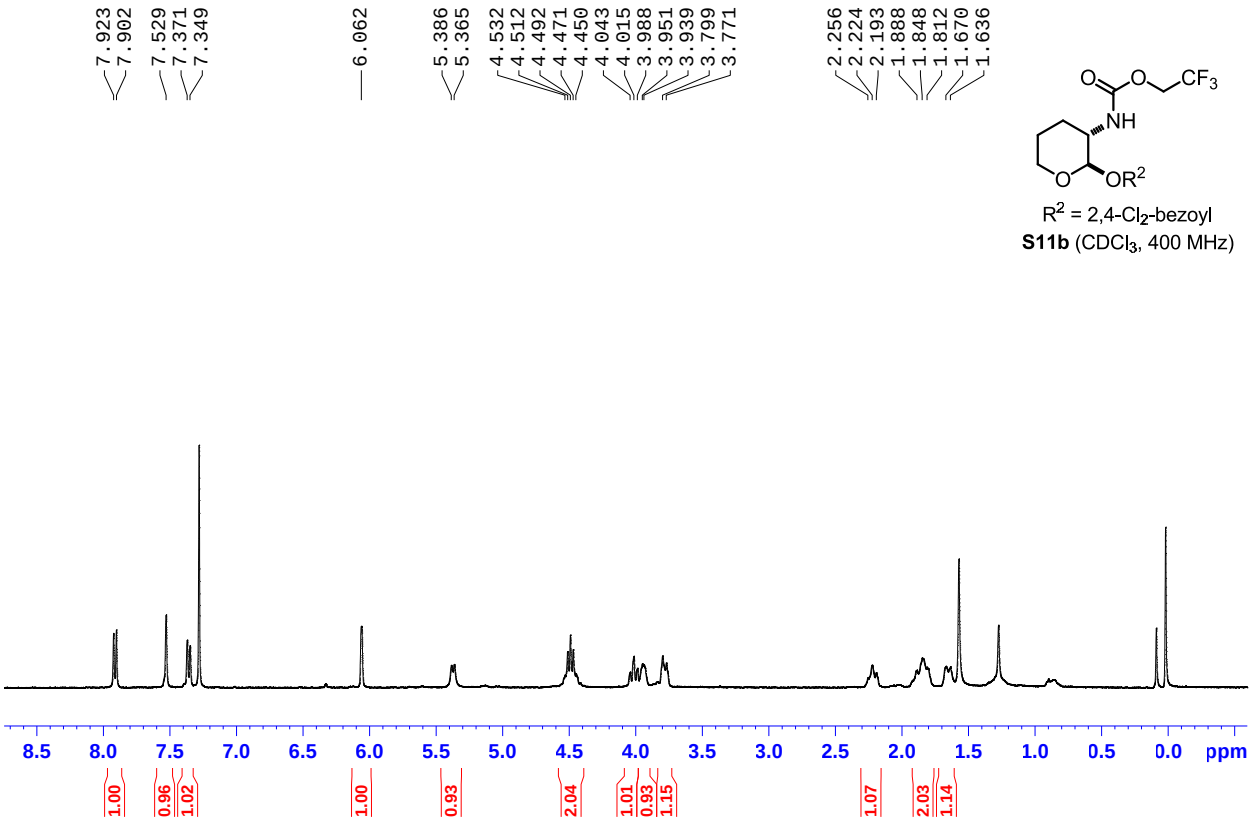
S11a ($CDCl_3$, 100 MHz)

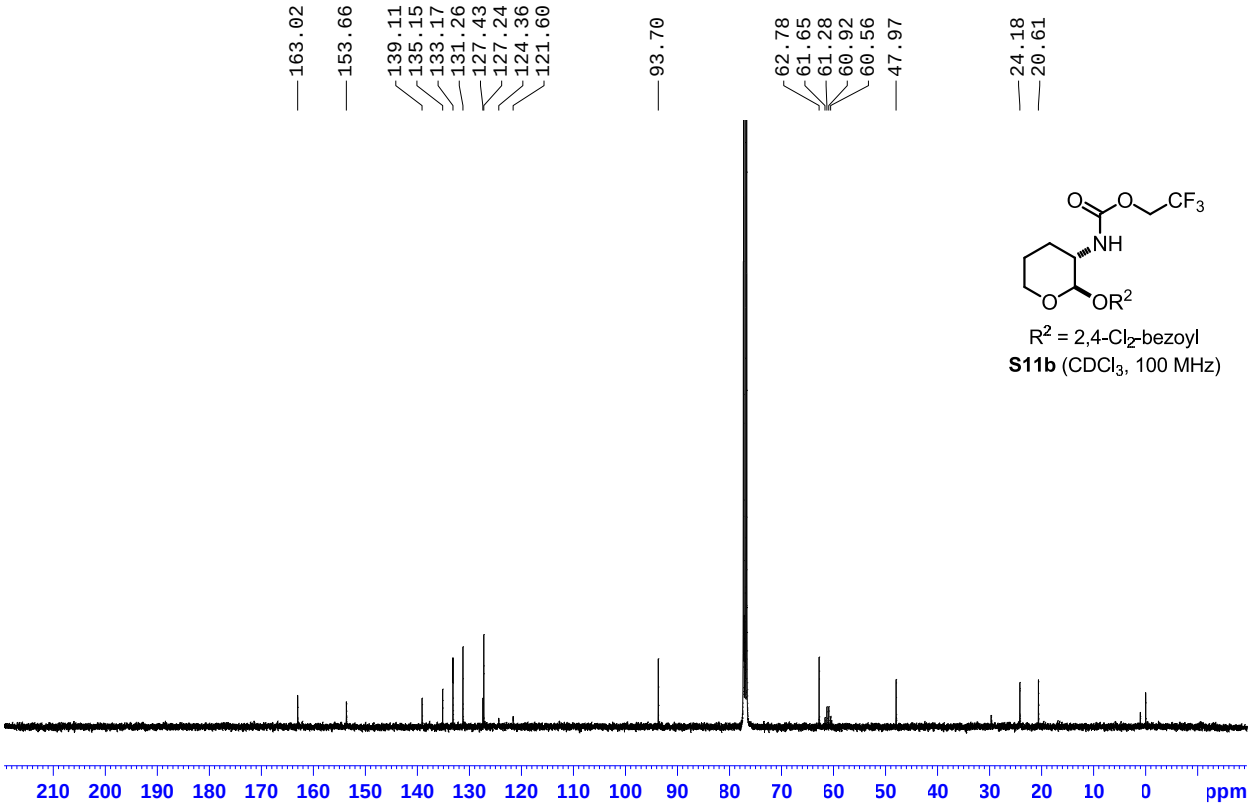


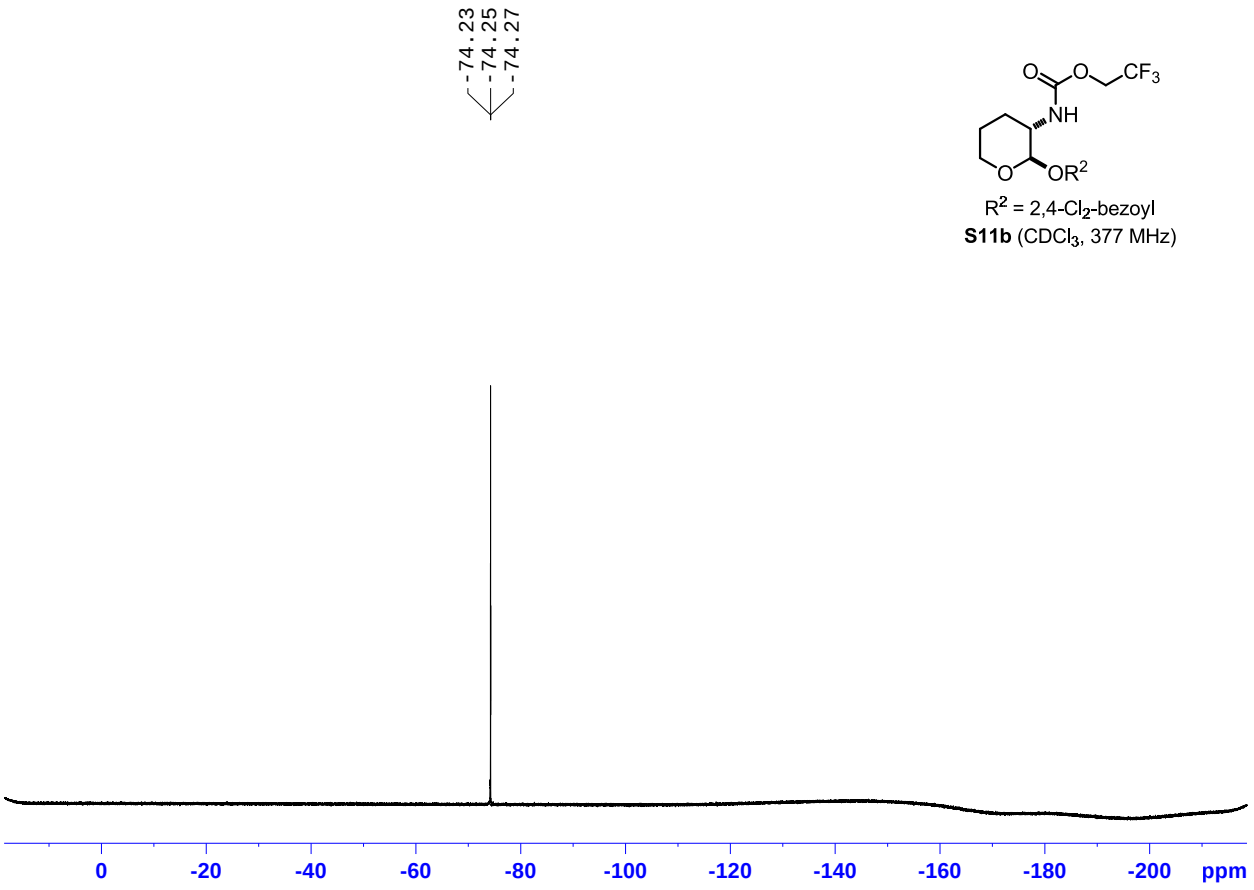


R^2 = 2,4-Cl_2-bezoyl

S11a ($CDCl_3$, 377 MHz)

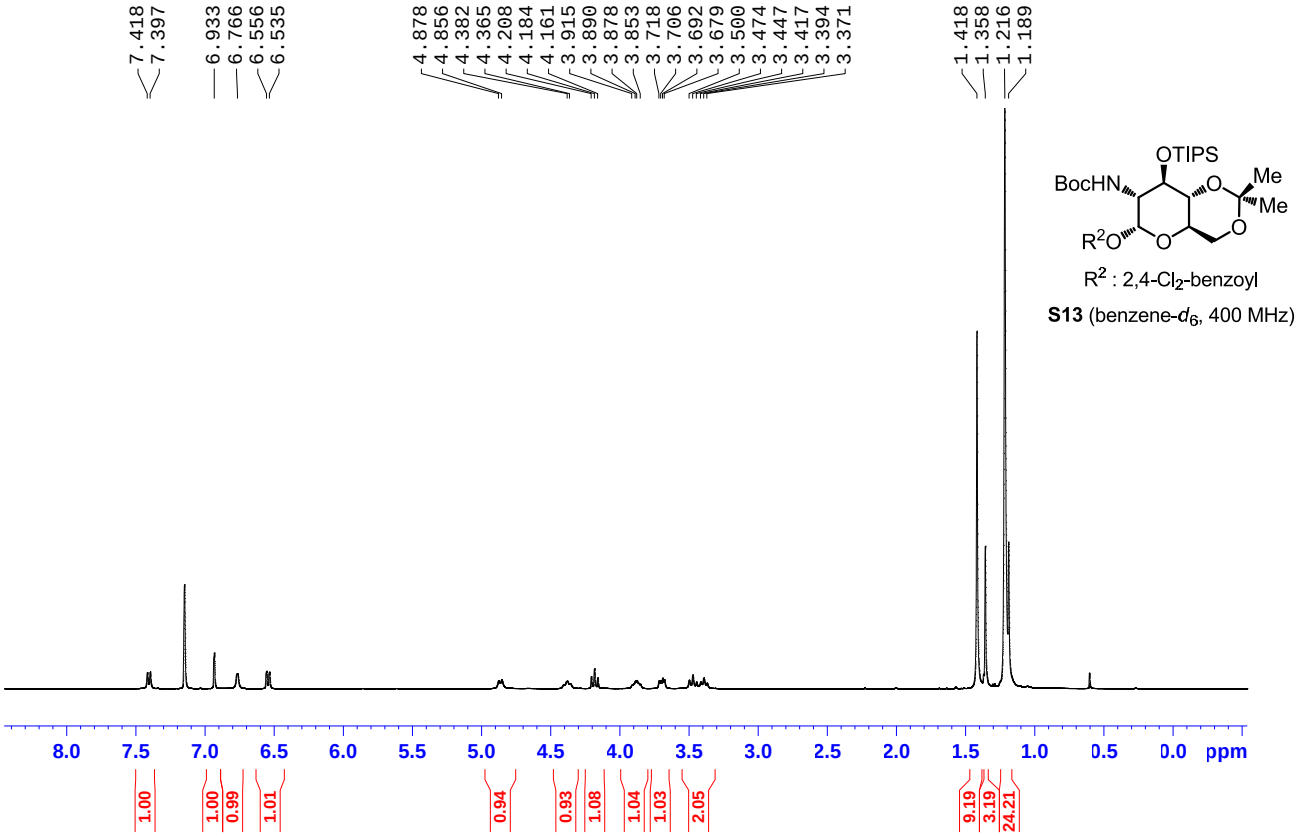

7.923
7.902
7.529
7.371
7.349
6.062
5.386
5.365
4.532
4.512
4.492
4.471
4.450
4.043
4.015
3.988
3.951
3.939
3.799
3.771
2.256
2.224
2.193
1.888
1.848
1.812
1.670
1.636
O
O
CF3
NH
O
OR2
R2 = 2,4-Cl2-bezoyl
S11b (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.96
1.02
1.00
0.93
2.04
1.01
0.93
1.15
1.07
2.03
1.14

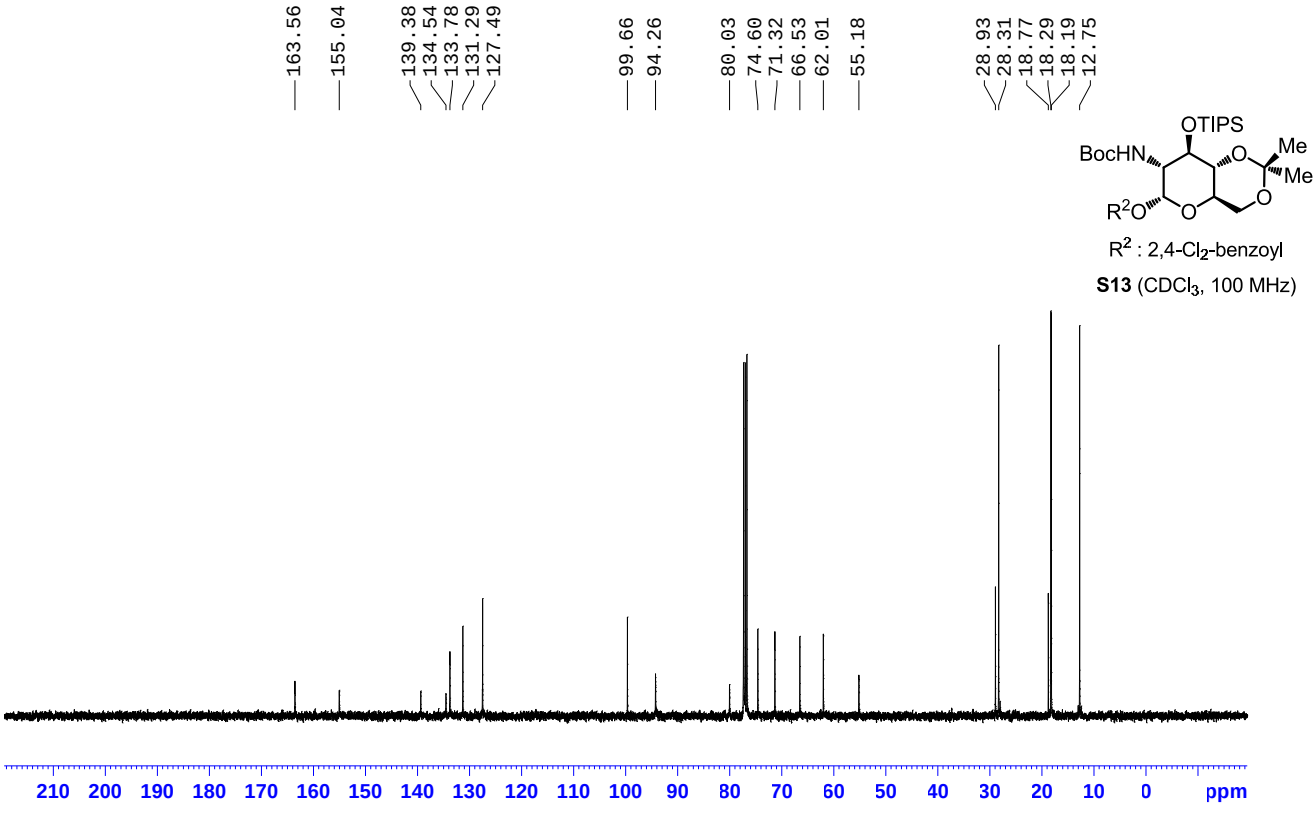

163.02
153.66
139.11
135.15
133.17
131.26
127.43
127.24
124.36
121.60
93.70
62.78
61.65
61.28
60.92
60.56
47.97
24.18
20.61
O
O
CF3
NH
O
OR2
R2 = 2,4-Cl2-bezoyl
S11b (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

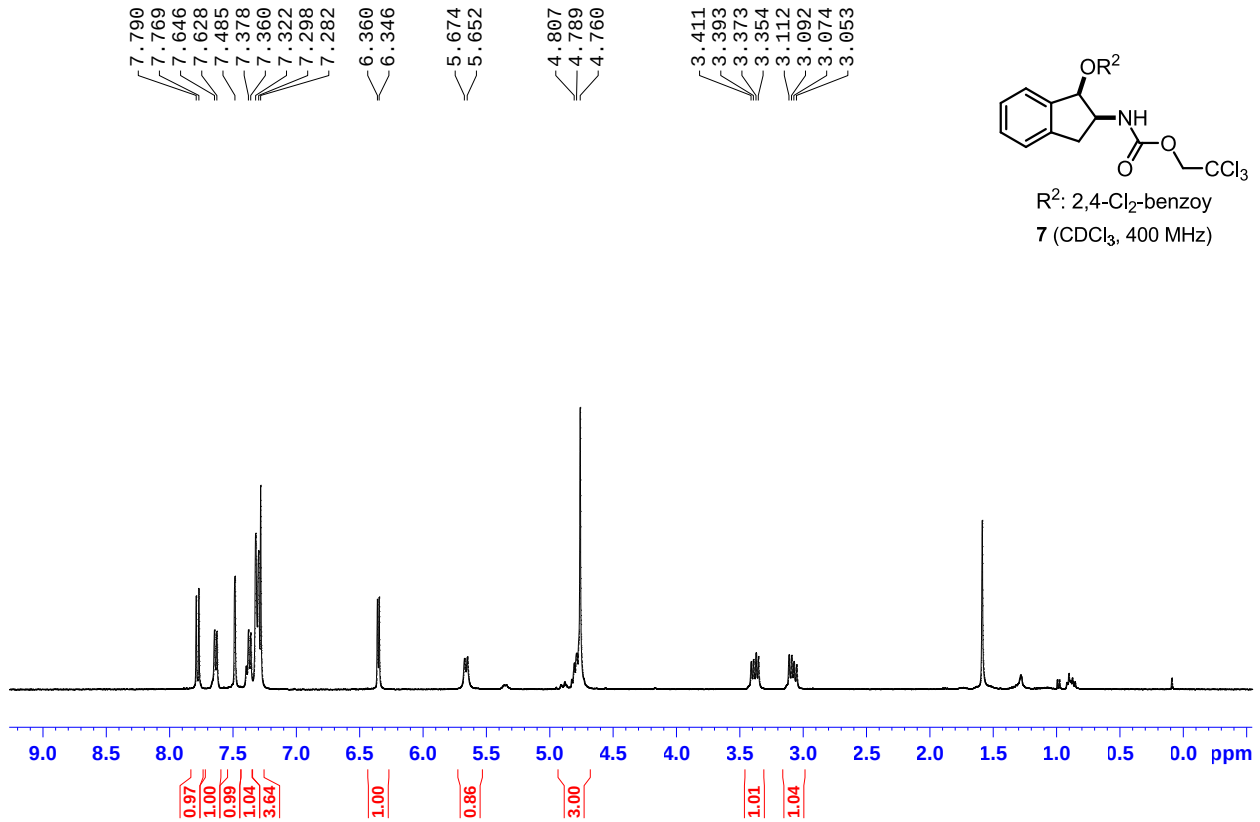


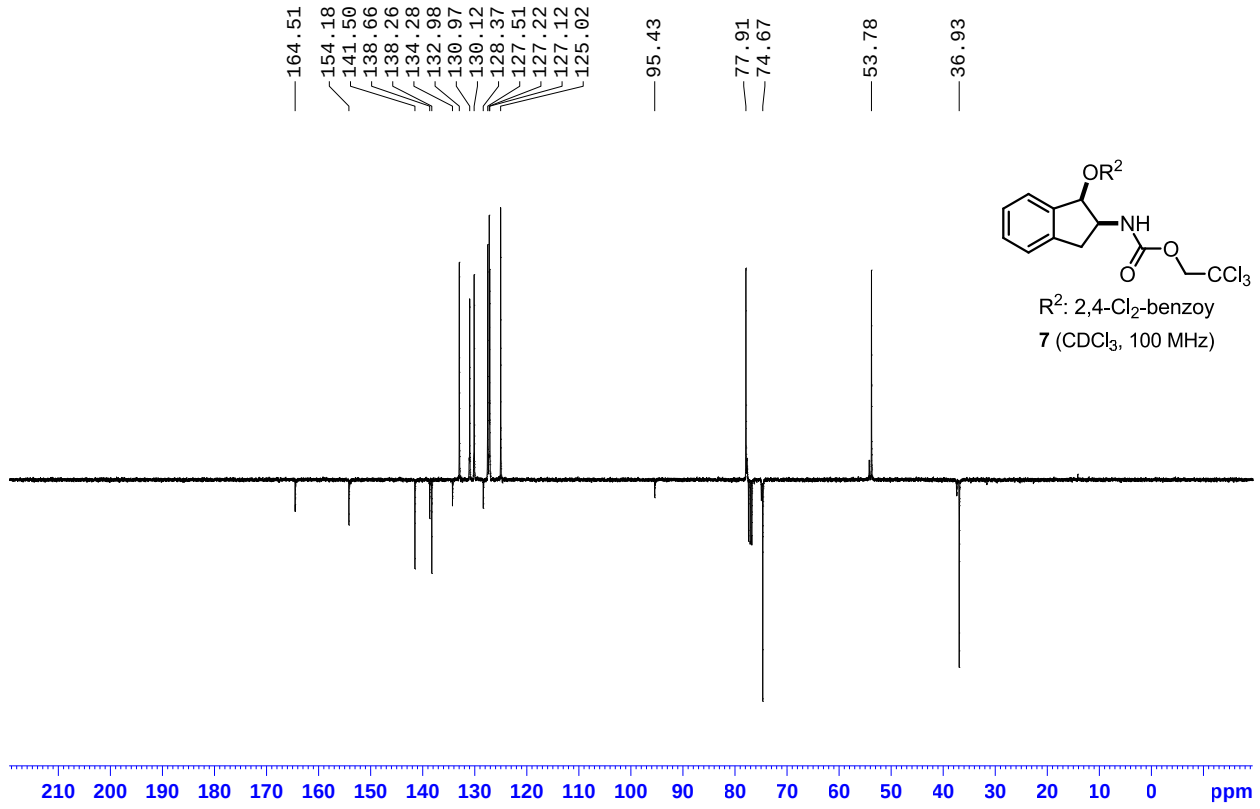
R^2 = 2,4-Cl_2-bezoyl

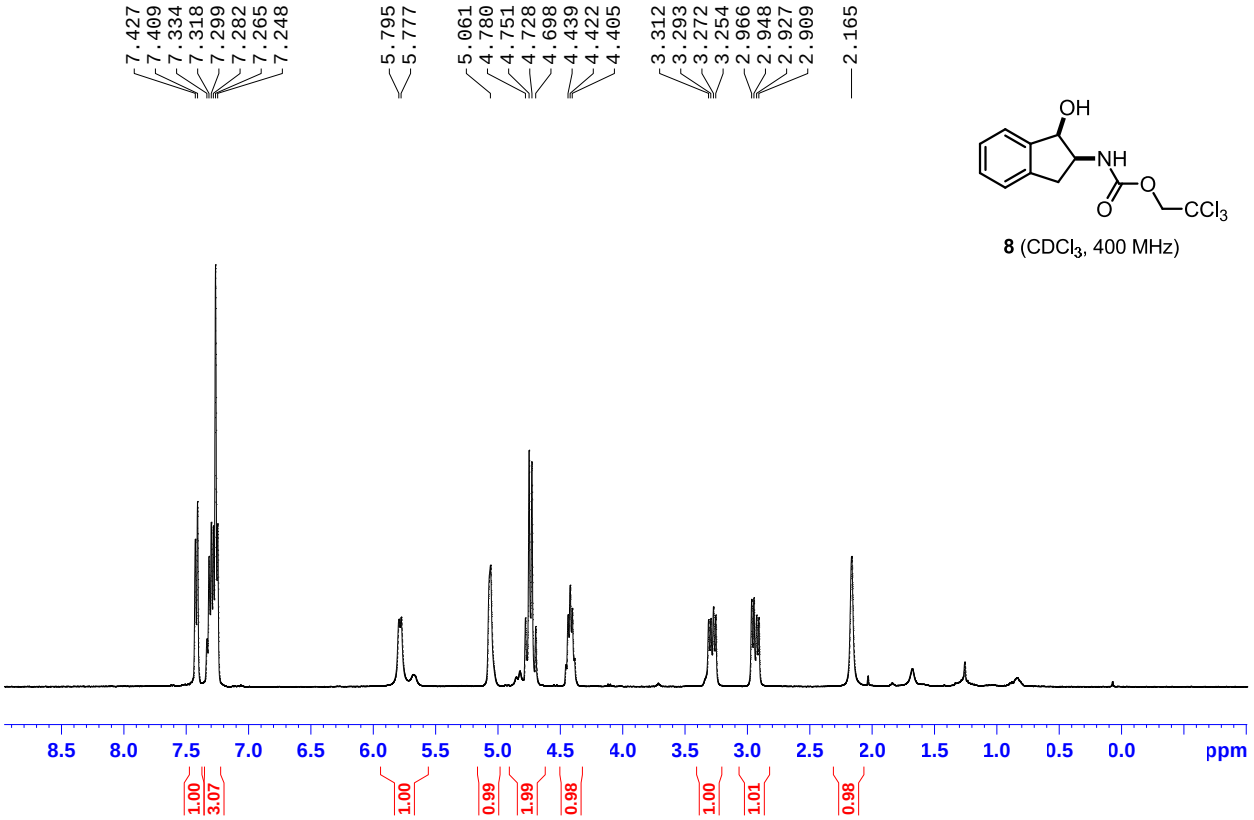
S11b ($CDCl_3$, 377 MHz)

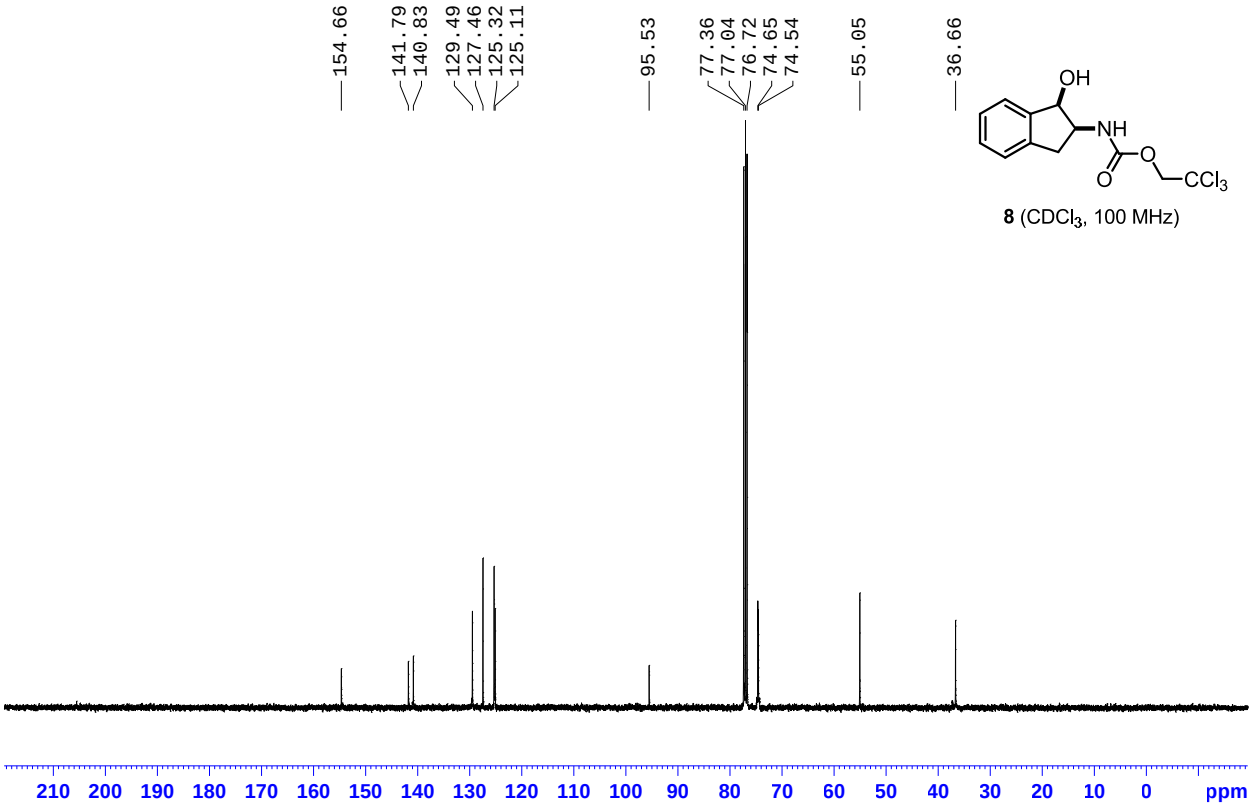

7.418
7.397
6.933
6.766
6.556
6.535
4.878
4.856
4.382
4.365
4.208
4.184
4.161
3.915
3.890
3.878
3.853
3.718
3.706
3.692
3.679
3.500
3.474
3.447
3.417
3.394
3.371
1.418
1.358
1.216
1.189
OTIPS
BocHN
Me
Me
R2O
O
R2 : 2,4-Cl2-benzoyl
S13 (benzene-d6, 400 MHz)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
0.99
1.01
0.94
0.93
1.08
1.04
1.03
2.05
9.19
3.19
24.21

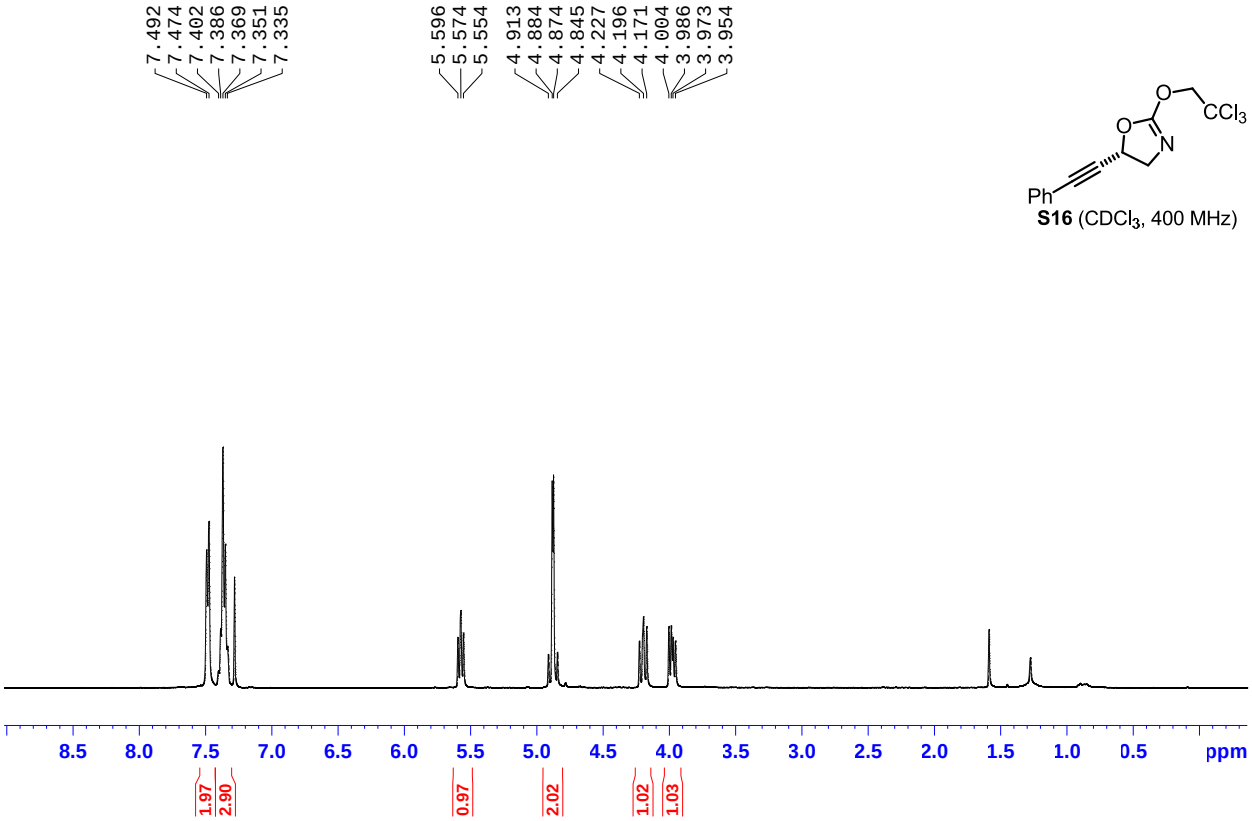

163.56
155.04
139.38
134.54
133.78
131.29
127.49
99.66
94.26
80.03
74.60
71.32
66.53
62.01
55.18
28.93
28.31
18.77
18.29
18.19
12.75
OTIPS
BocHN
Me
Me
R2O
O
R2 : 2,4-Cl2-benzoyl
S13 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

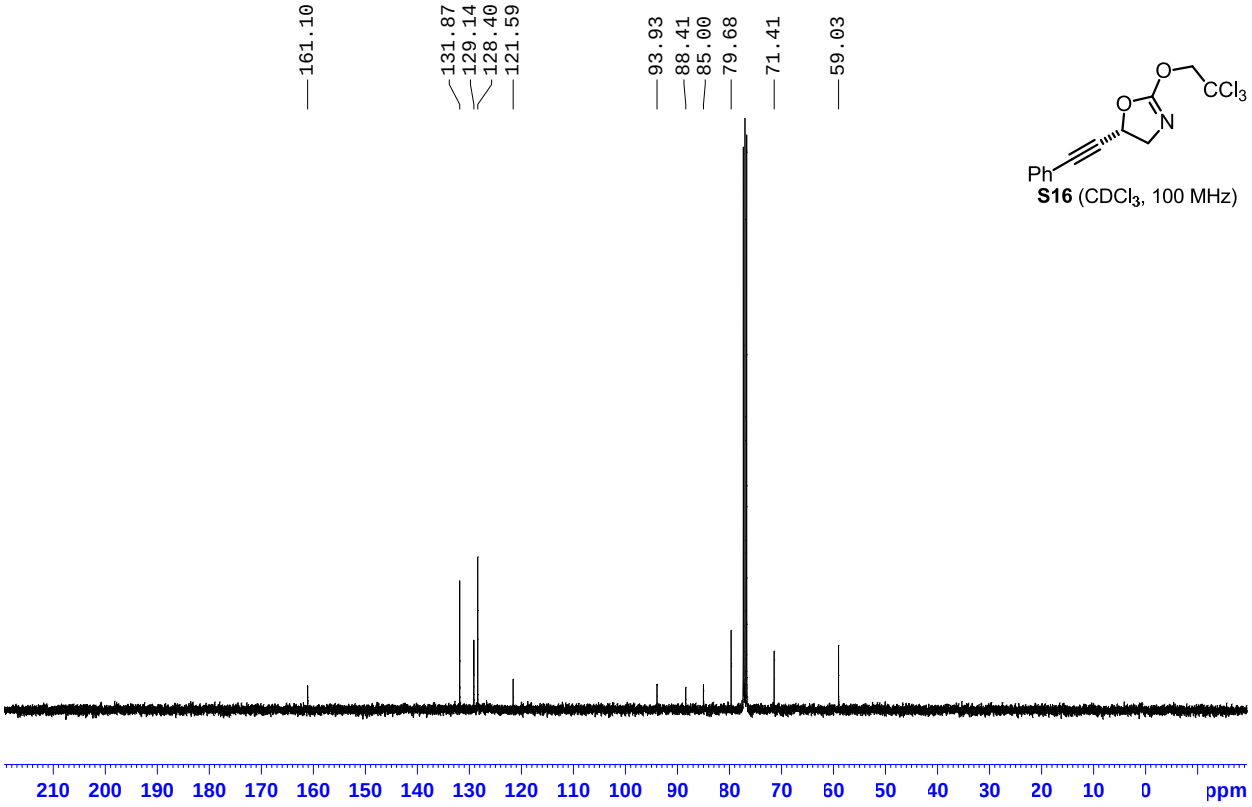

7.790
7.769
7.646
7.628
7.485
7.378
7.360
7.322
7.298
7.282
6.360
6.346
5.674
5.652
4.807
4.789
4.760
3.411
3.393
3.373
3.354
3.112
3.092
3.074
3.053
OR2
NH
O
O
CCl3
R2: 2,4-Cl2-benzoy
7 (CDCl3, 400 MHz)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
1.00
0.99
1.04
3.64
1.00
0.86
3.00
1.01
1.04

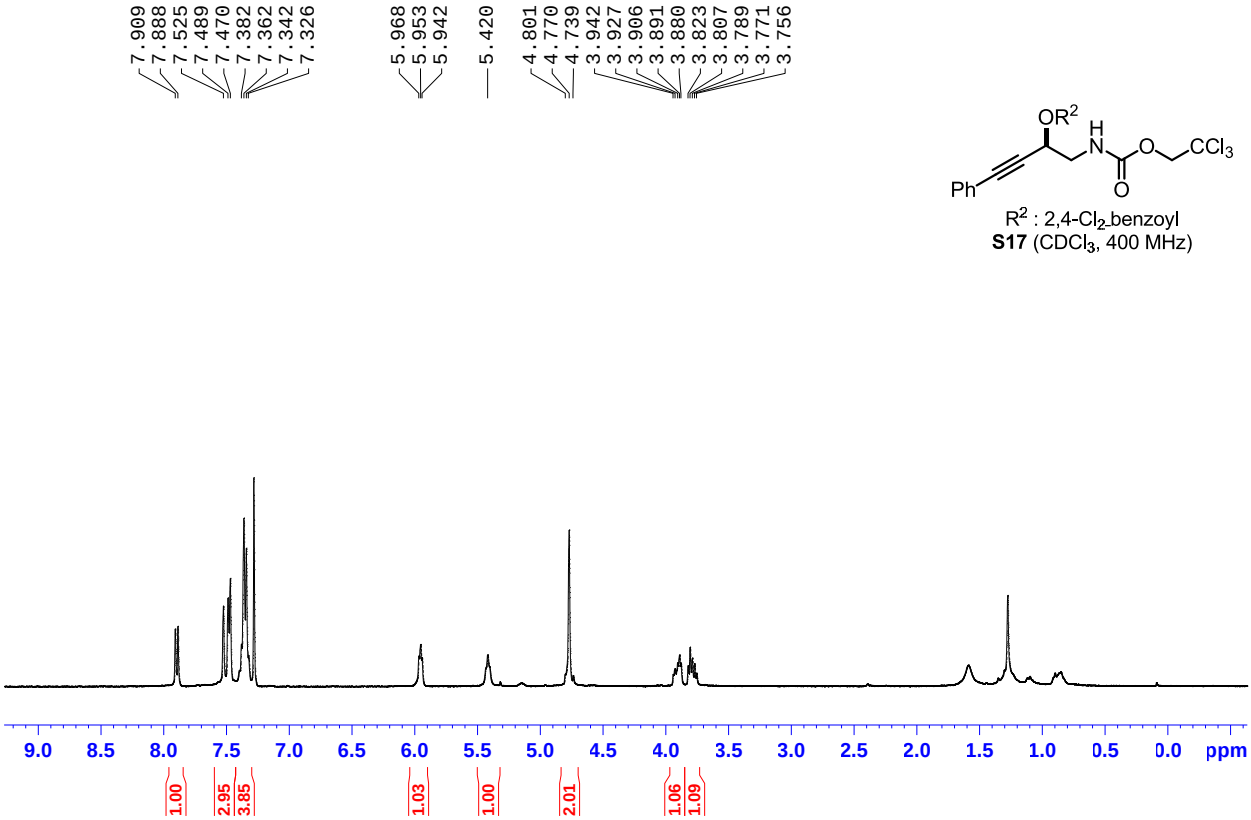

164.51
154.18
141.50
138.66
138.26
134.28
132.98
130.97
130.12
128.37
127.51
127.22
127.12
125.02
95.43
77.91
74.67
53.78
36.93
OR2
NH
O
O
CCl3
R2: 2,4-Cl2-benzoy
7 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

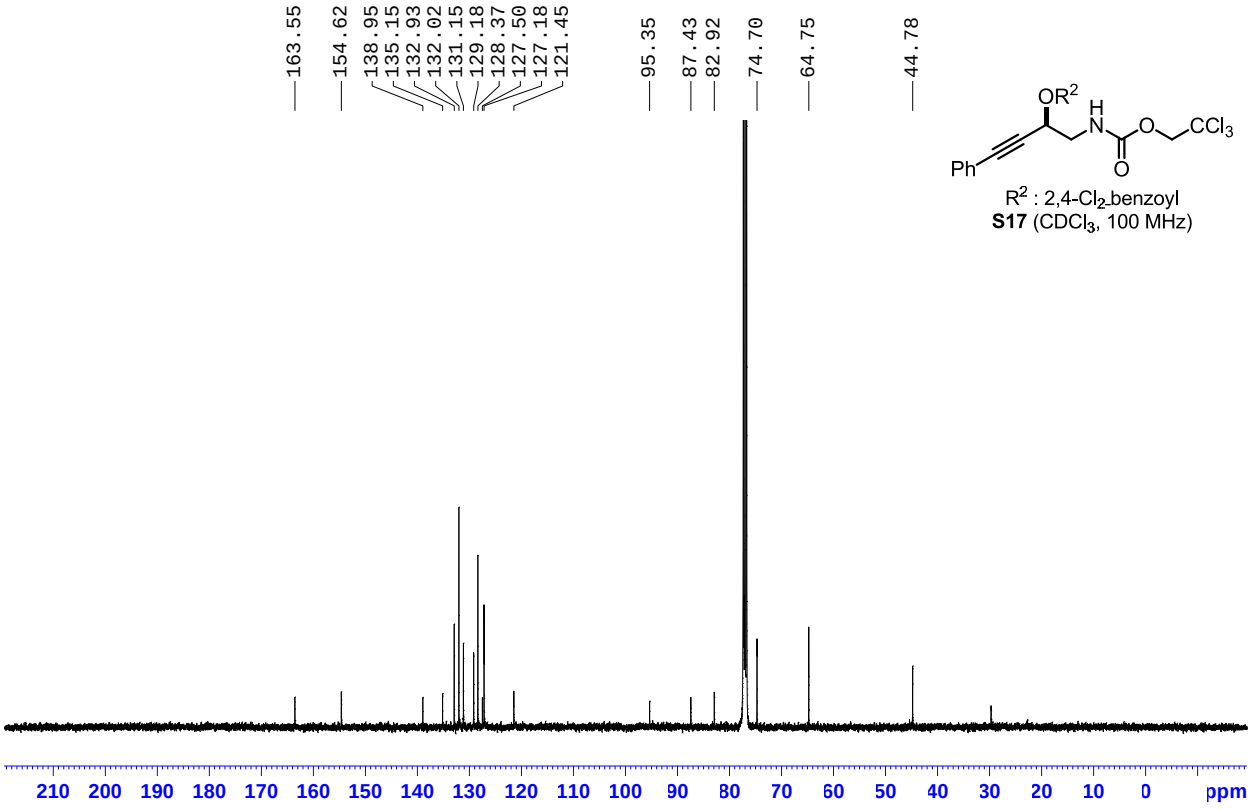

7.427
7.409
7.334
7.318
7.299
7.282
7.265
7.248
5.795
5.777
5.061
4.780
4.751
4.728
4.698
4.439
4.422
4.405
3.312
3.293
3.272
3.254
2.966
2.948
2.927
2.909
2.165
OH
NH
O
O
CCl3
8 (CDCl3, 400 MHz)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
3.07
1.00
0.99
1.99
0.98
1.00
1.01
0.98

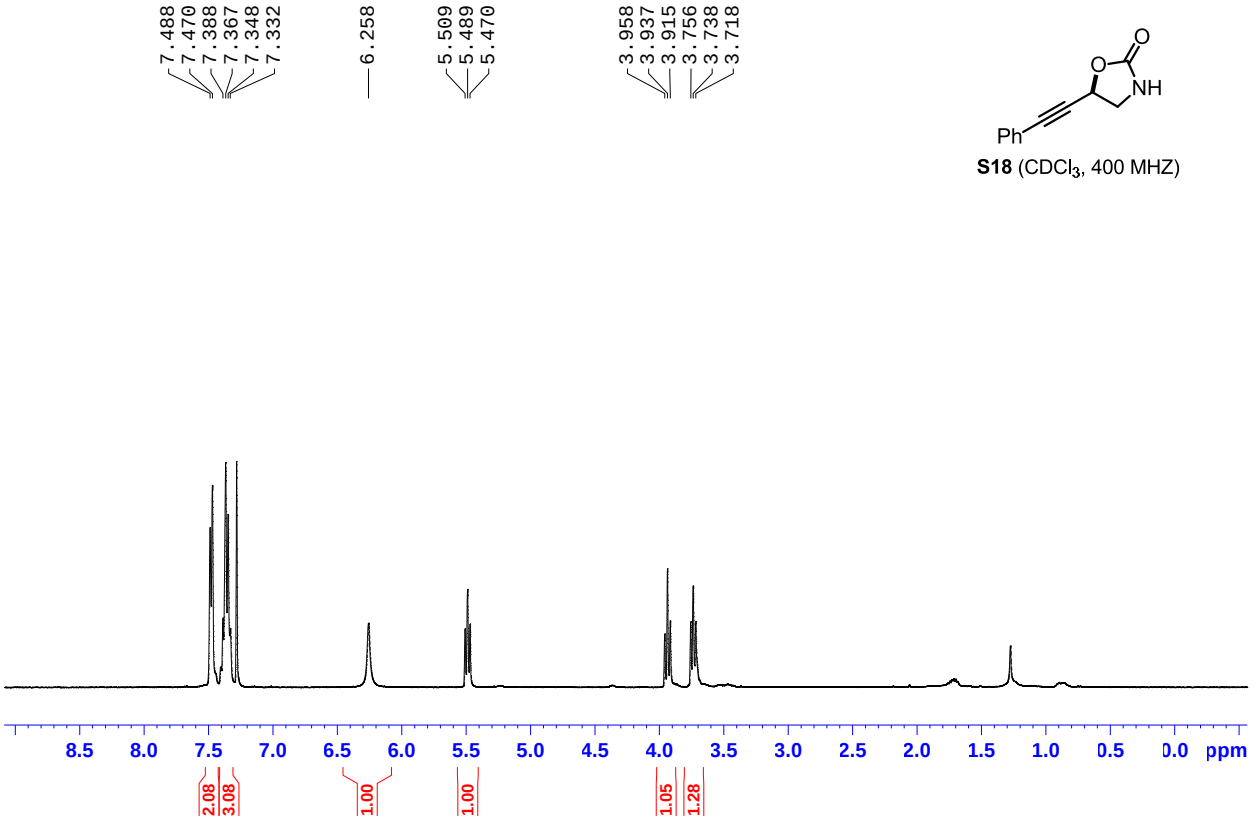

154.66
141.79
140.83
129.49
127.46
125.32
125.11
95.53
77.36
77.04
76.72
74.65
74.54
55.05
36.66
OH
NH
O
O
CCl3
8 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.492
7.474
7.402
7.386
7.369
7.351
7.335
5.596
5.574
5.554
4.913
4.884
4.874
4.845
4.227
4.196
4.171
4.004
3.986
3.973
3.954
O
CCl3
O
N
Ph
S16 (CDCl3, 400 MHz)
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
ppm
1.97
2.90
0.97
2.02
1.02
1.03

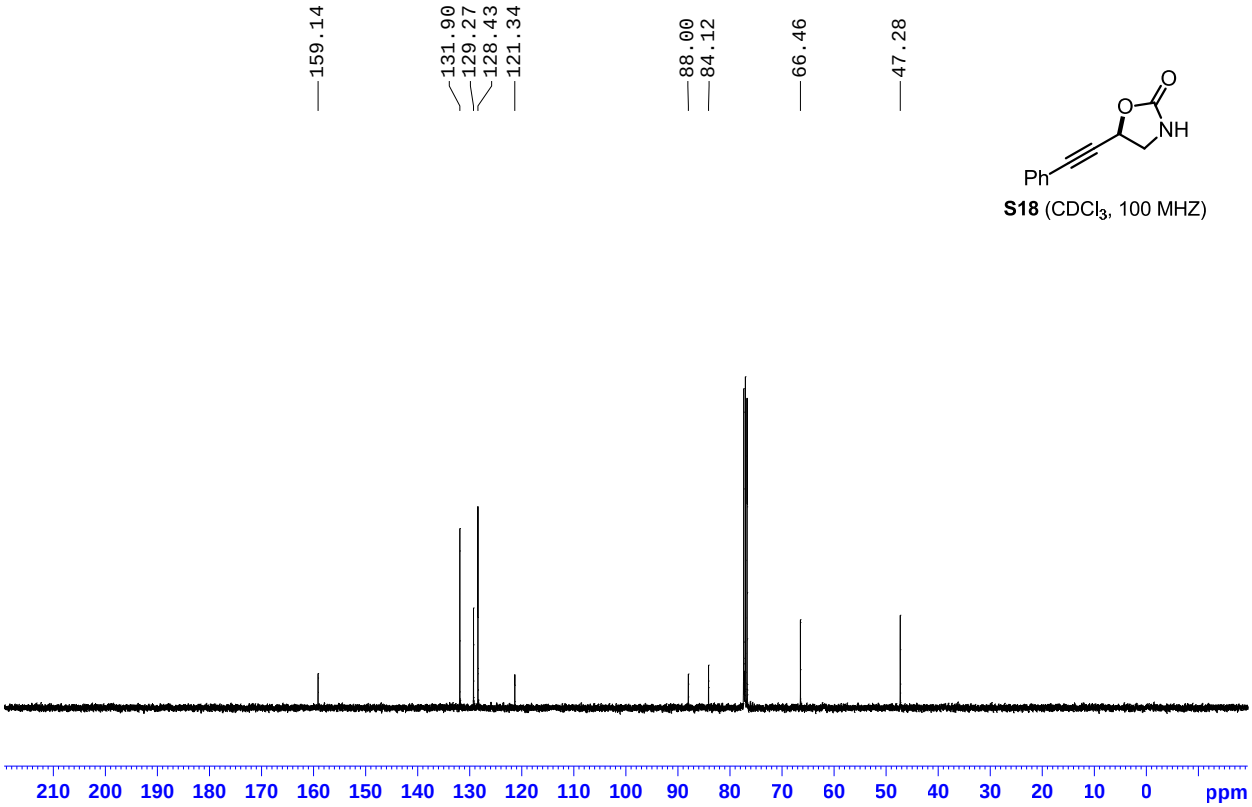

161.10
131.87
129.14
128.40
121.59
93.93
88.41
85.00
79.68
71.41
59.03
O
CCl3
O
N
Ph
S16 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.909
7.888
7.525
7.489
7.470
7.382
7.362
7.342
7.326
5.968
5.953
5.942
5.420
4.801
4.770
4.739
3.942
3.927
3.906
3.891
3.880
3.823
3.807
3.789
3.771
3.756
OR2
H
N
O
CCl3
Ph
O
R2 : 2,4-Cl2-benzoyl
S17 (CDCl3, 400 MHz)
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
ppm
1.00
2.95
3.85
1.03
1.00
2.01
1.06
1.09

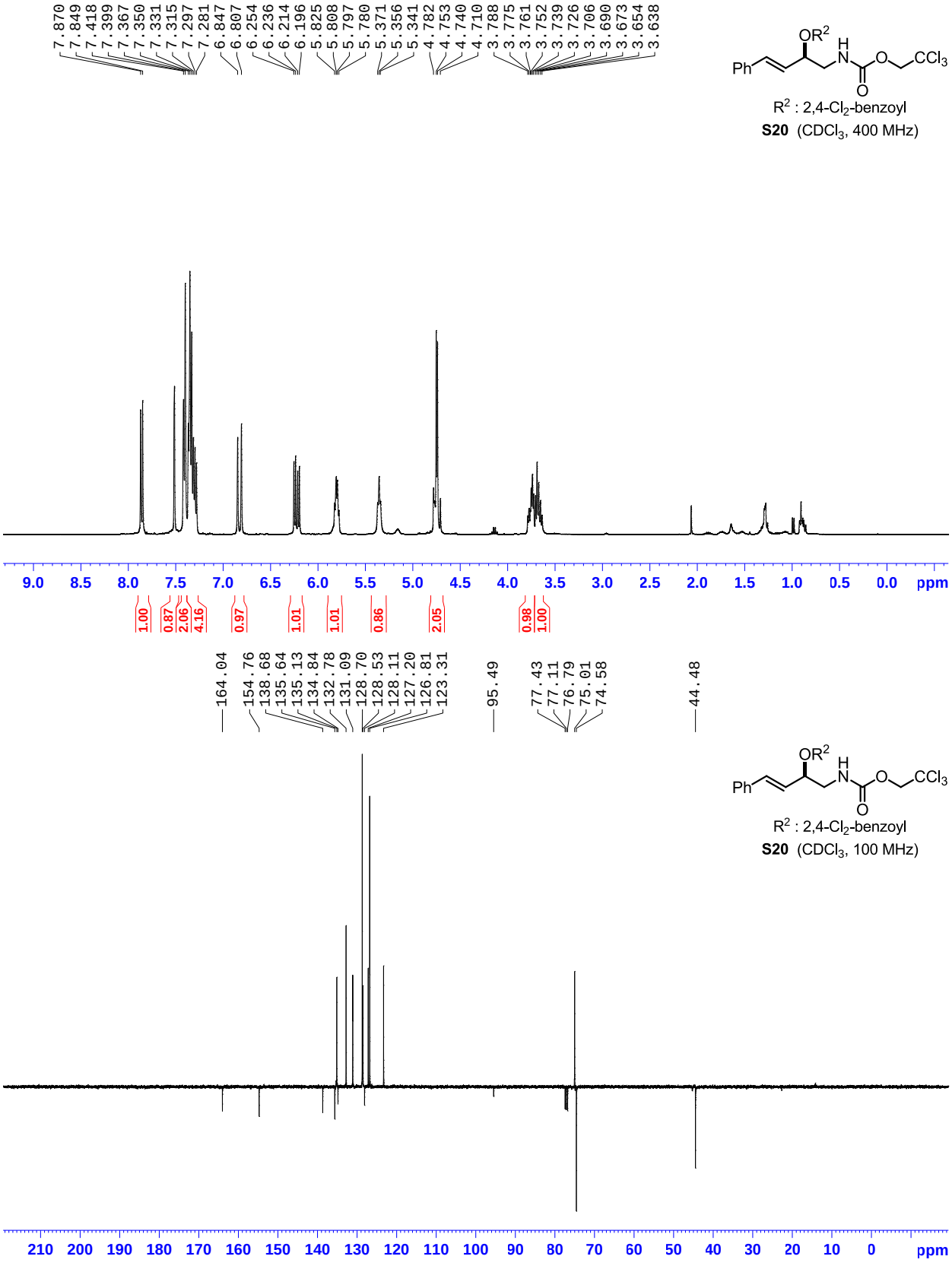

163.55
154.62
138.95
135.15
132.93
132.02
131.15
129.18
128.37
127.50
127.18
121.45
95.35
87.43
82.92
74.70
64.75
44.78
OR2
H
N
O
CCl3
Ph
O
R2 : 2,4-Cl2-benzoyl
S17 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

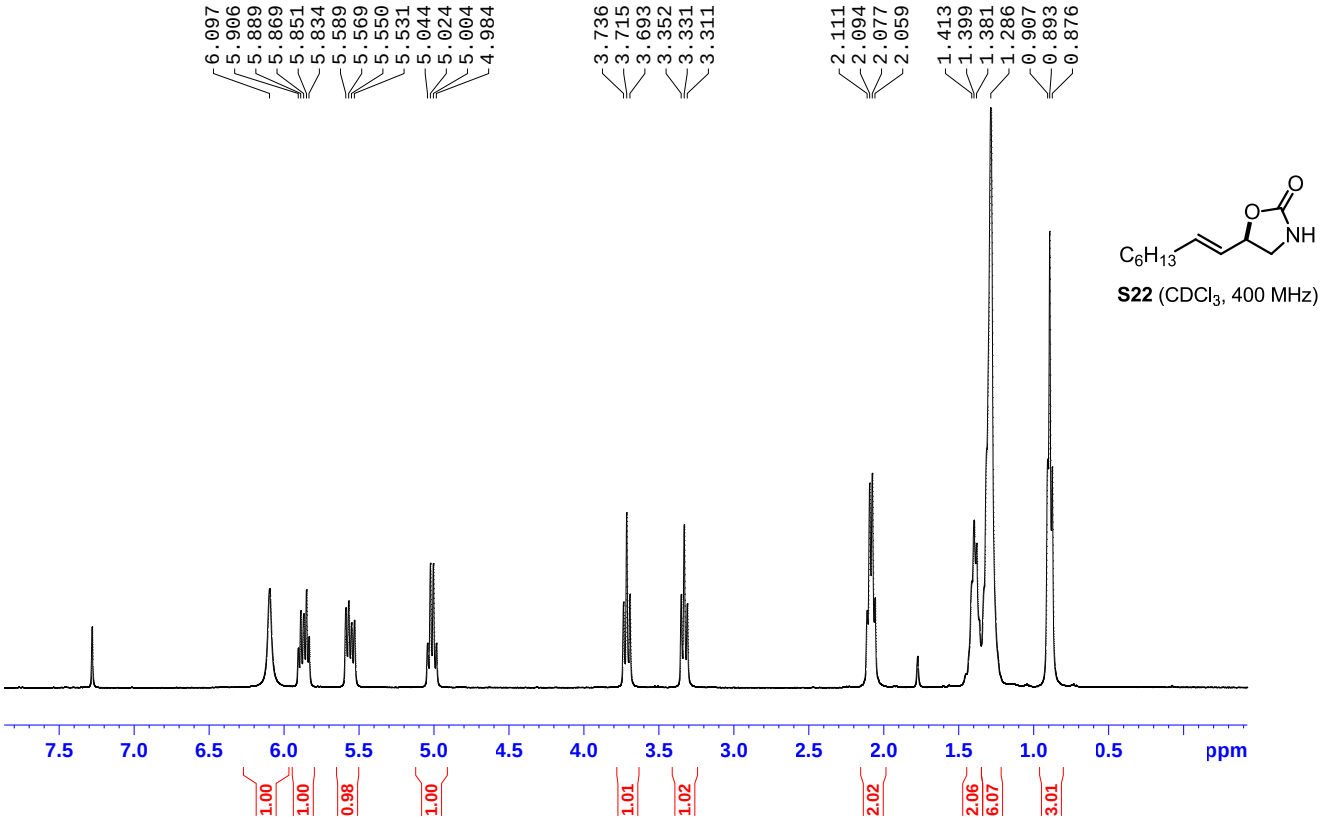


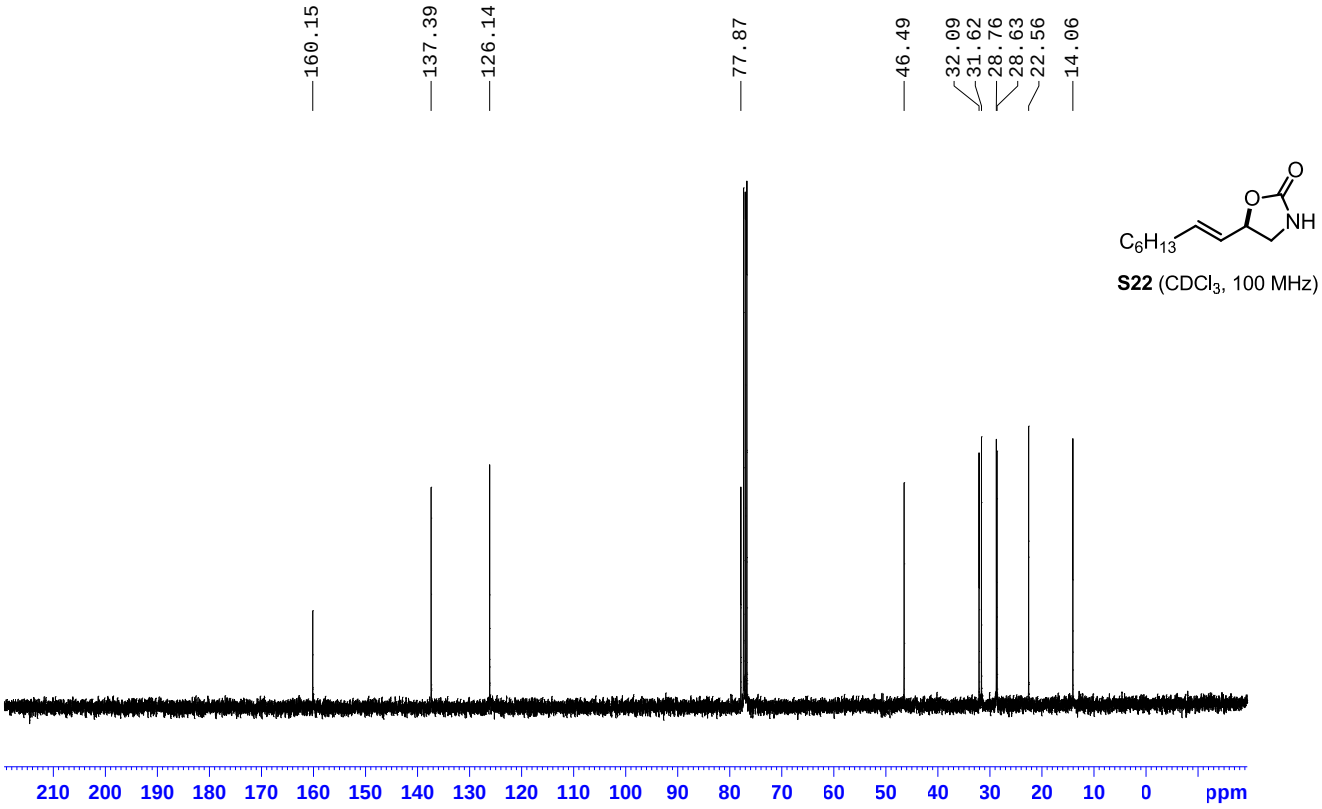
S18 ($CDCl_3$, 400 MHZ)

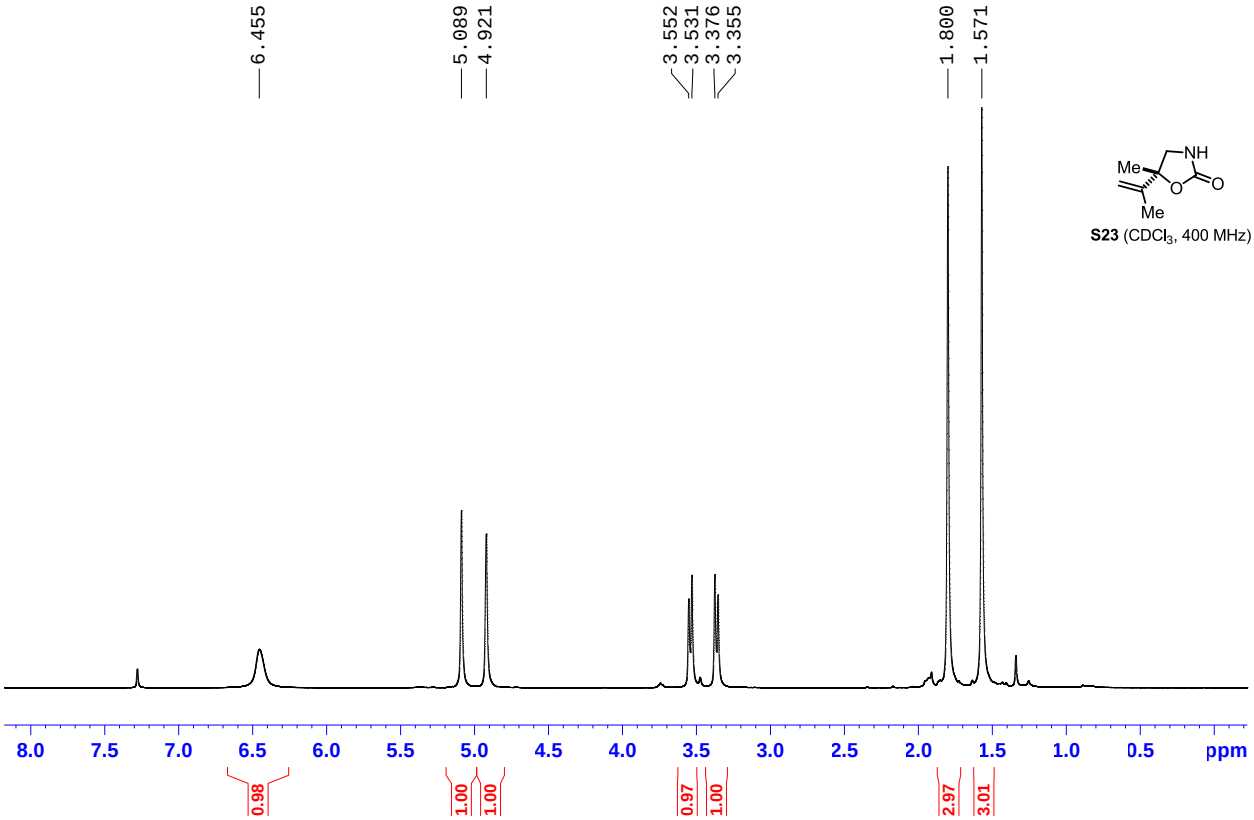


S18 ($CDCl_3$, 100 MHZ)

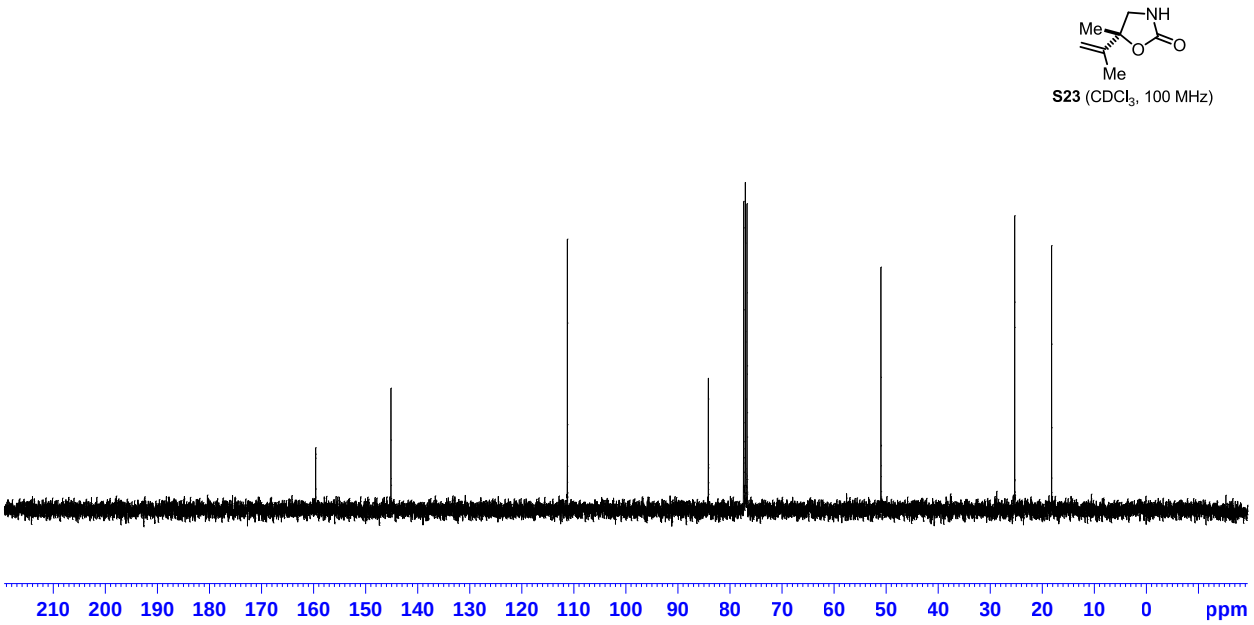

7.870
7.849
7.418
7.399
7.367
7.350
7.331
7.315
7.297
7.281
6.847
6.807
6.254
6.236
6.214
6.196
5.825
5.808
5.797
5.780
5.371
5.356
5.341
4.782
4.753
4.740
4.710
3.788
3.775
3.761
3.752
3.739
3.726
3.706
3.690
3.673
3.654
3.638
OR2
H
N
O
O
CCl3
Ph
R2 : 2,4-Cl2-benzoyl
S20 (CDCl3, 400 MHz)
9.0 8.5 8.0 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 ppm
1.00
0.87
2.06
4.16
0.97
1.01
1.01
0.86
2.05
0.98
1.00
164.04
154.76
138.68
135.64
135.13
134.84
132.78
131.09
128.70
128.53
128.11
127.20
126.81
123.31
95.49
77.43
77.11
76.79
75.01
74.58
44.48
OR2
H
N
O
O
CCl3
Ph
R2 : 2,4-Cl2-benzoyl
S20 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6.097
5.906
5.889
5.869
5.851
5.834
5.589
5.569
5.550
5.531
5.044
5.024
5.004
4.984
3.736
3.715
3.693
3.352
3.331
3.311
2.111
2.094
2.077
2.059
1.413
1.399
1.381
1.286
0.907
0.893
0.876
O
O
NH
C6H13
S22 (CDCl3, 400 MHz)
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
ppm
1.00
1.00
0.98
1.00
1.01
1.02
2.02
2.06
6.07
3.01

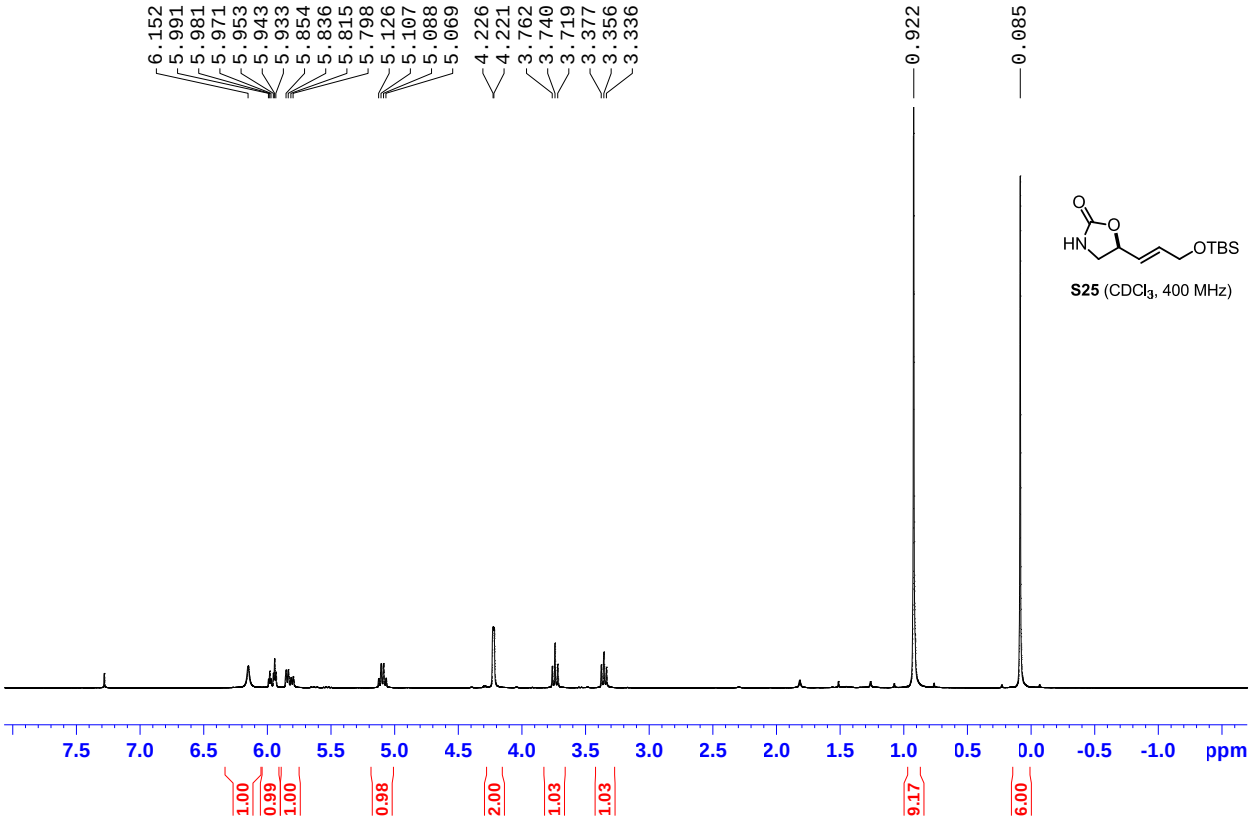

160.15
137.39
126.14
77.87
46.49
32.09
31.62
28.76
28.63
22.56
14.06
O
O
NH
C6H13
S22 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

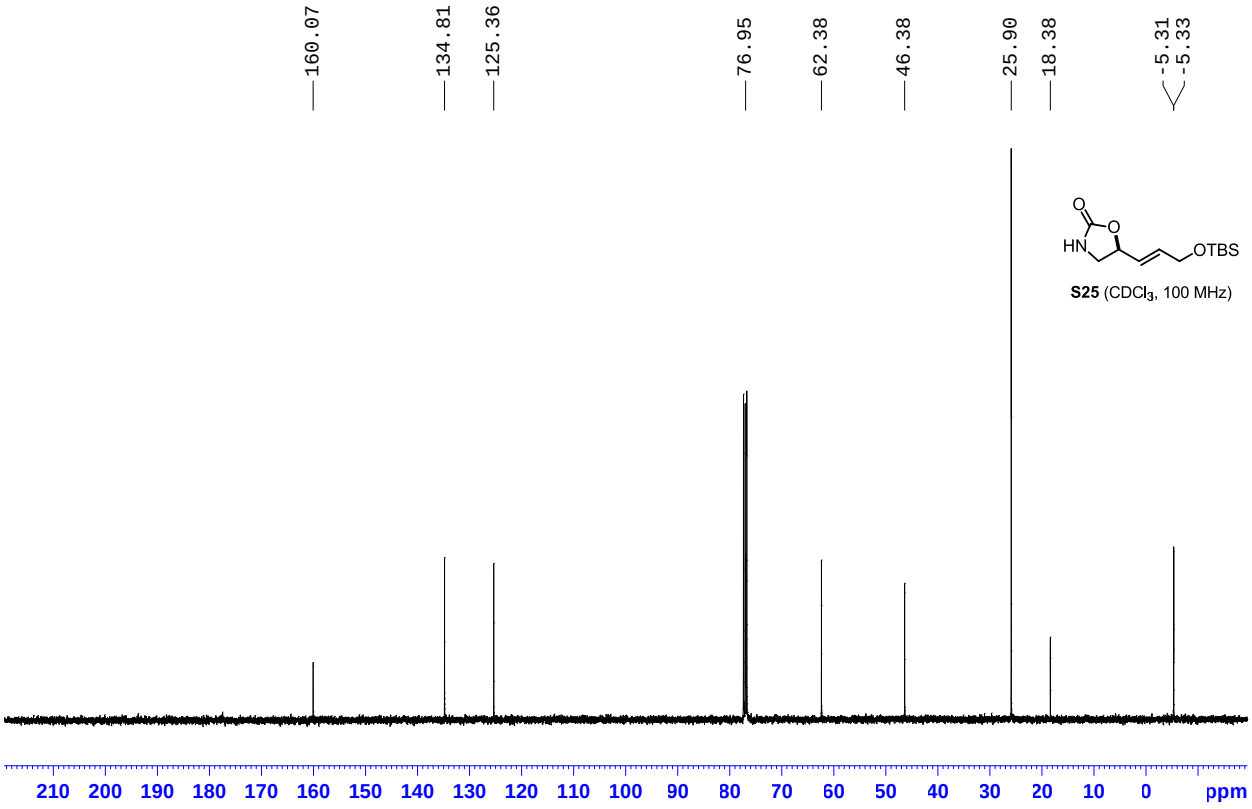


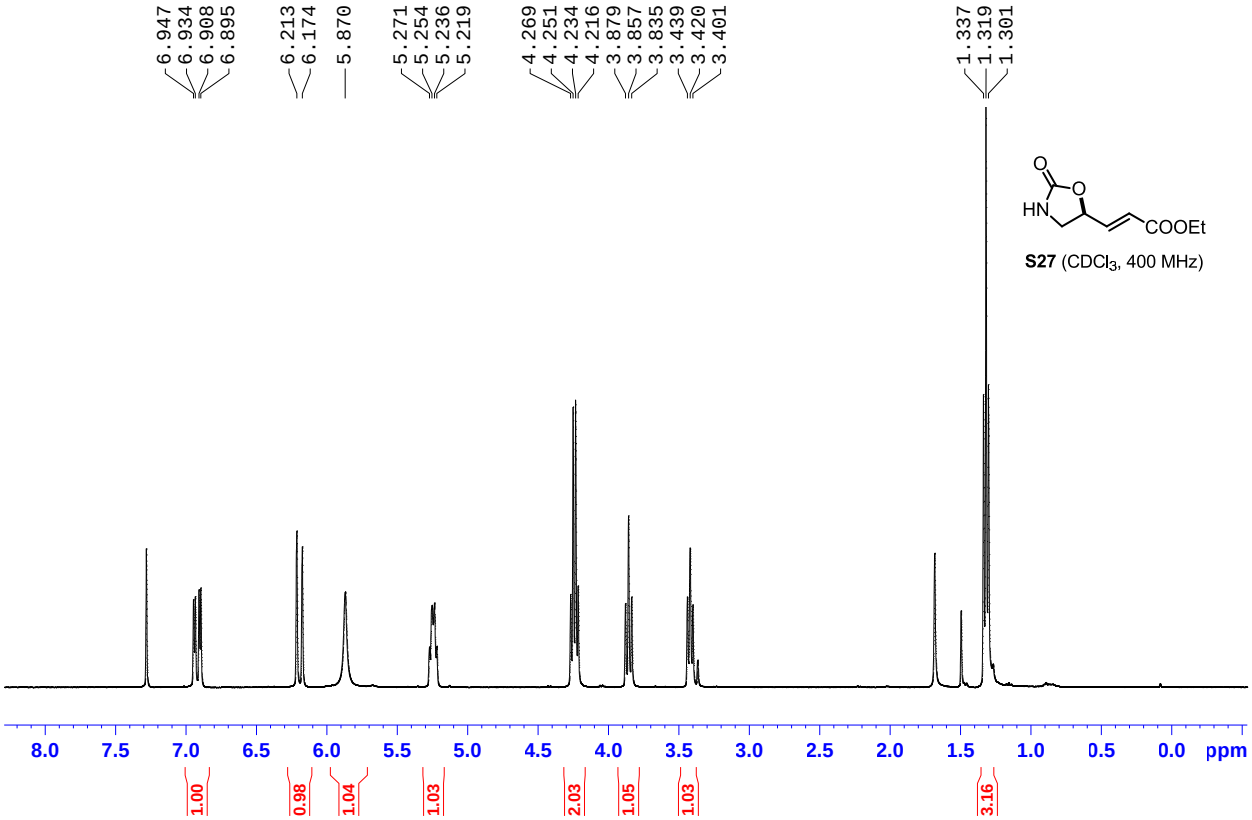
S23 ($CDCl_3$, 400 MHz)

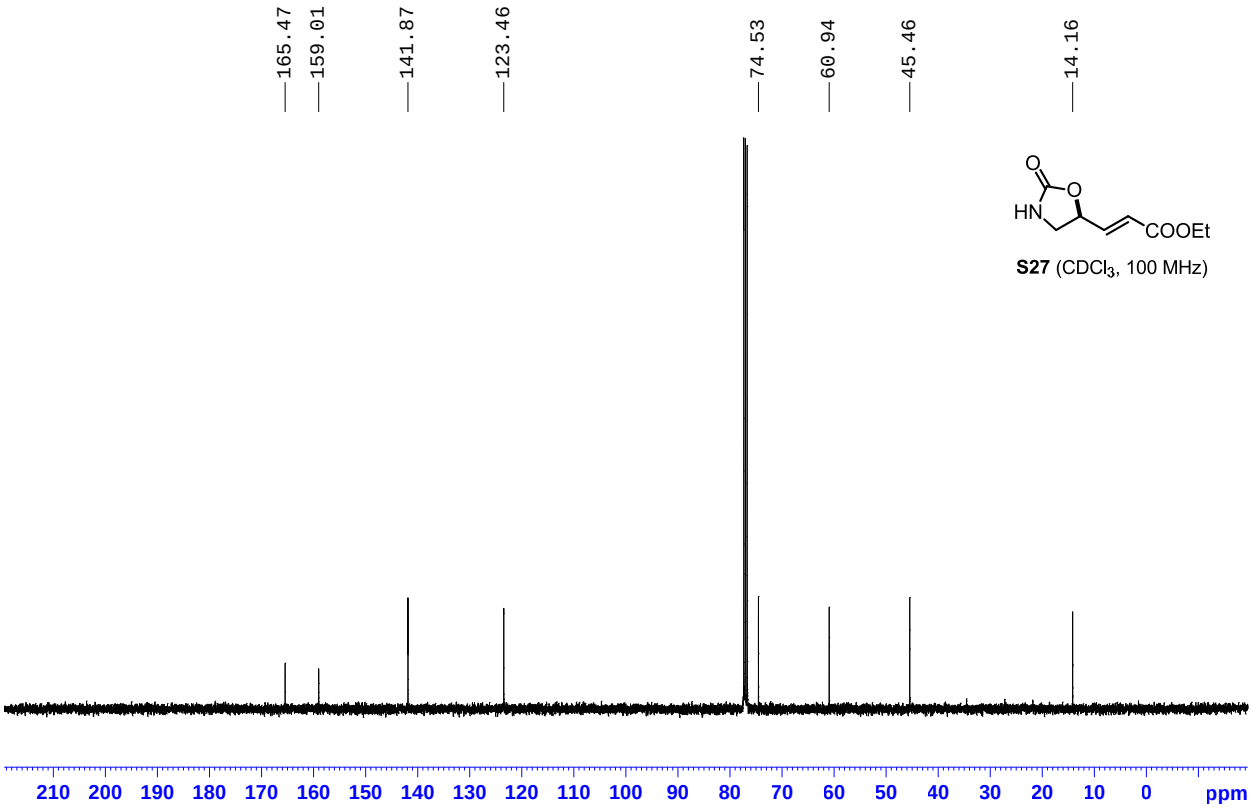


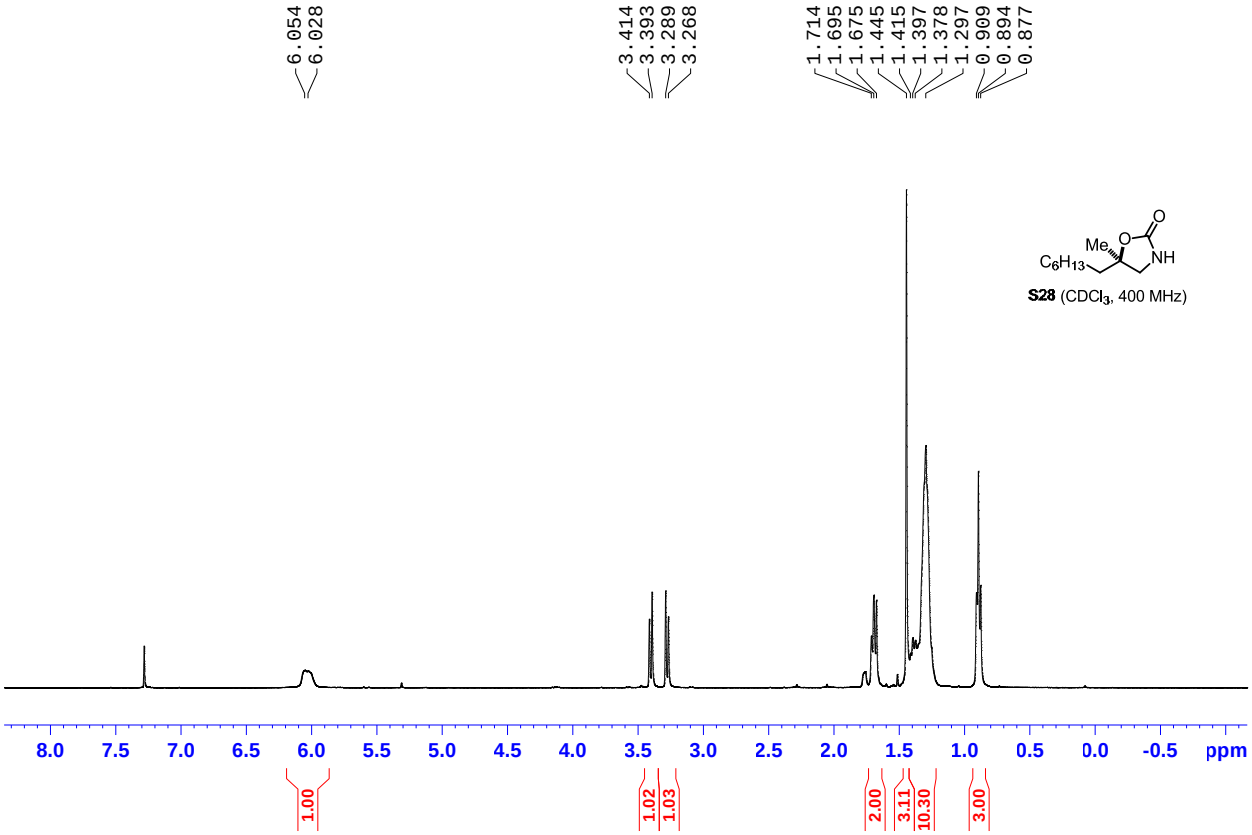
S23 ($CDCl_3$, 100 MHz)

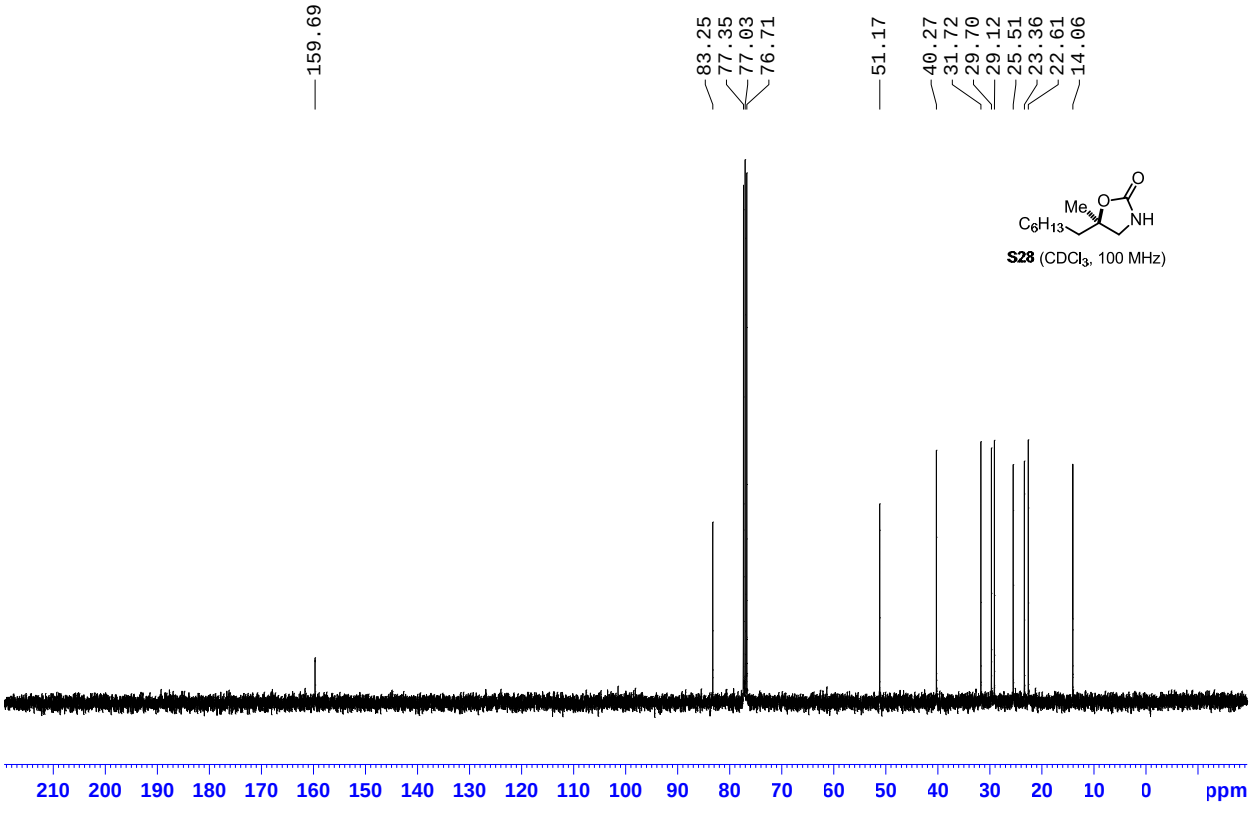

6.152
5.991
5.981
5.971
5.953
5.943
5.933
5.854
5.836
5.815
5.798
5.126
5.107
5.088
5.069
4.226
4.221
3.762
3.740
3.719
3.377
3.356
3.336
0.922
0.085
HN
O
OTBS
S25 (CDCl3, 400 MHz)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm
1.00
0.99
1.00
0.98
2.00
1.03
1.03
9.17
6.00

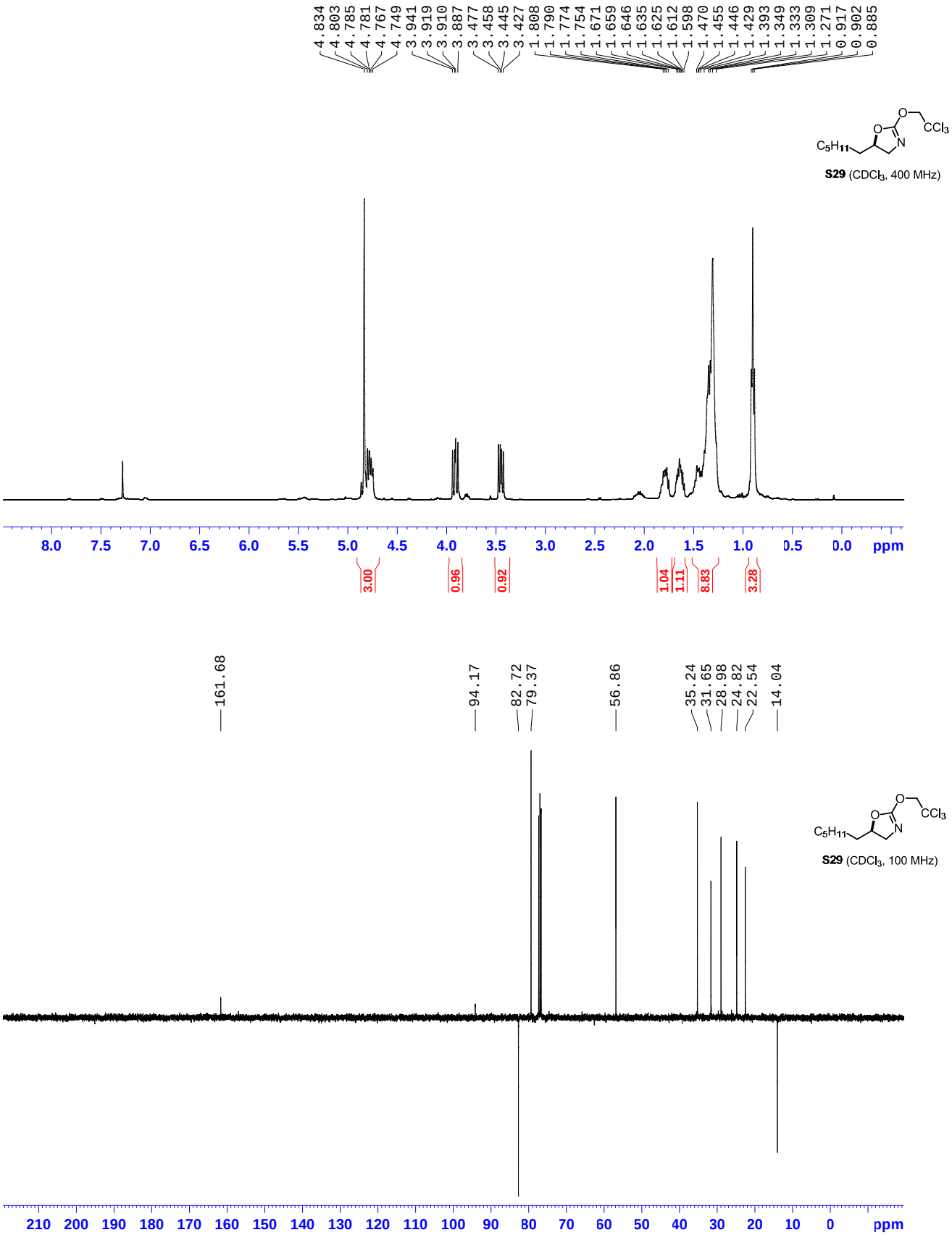

160.07
134.81
125.36
76.95
62.38
46.38
25.90
18.38
-5.31
-5.33
HN
O
OTBS
S25 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

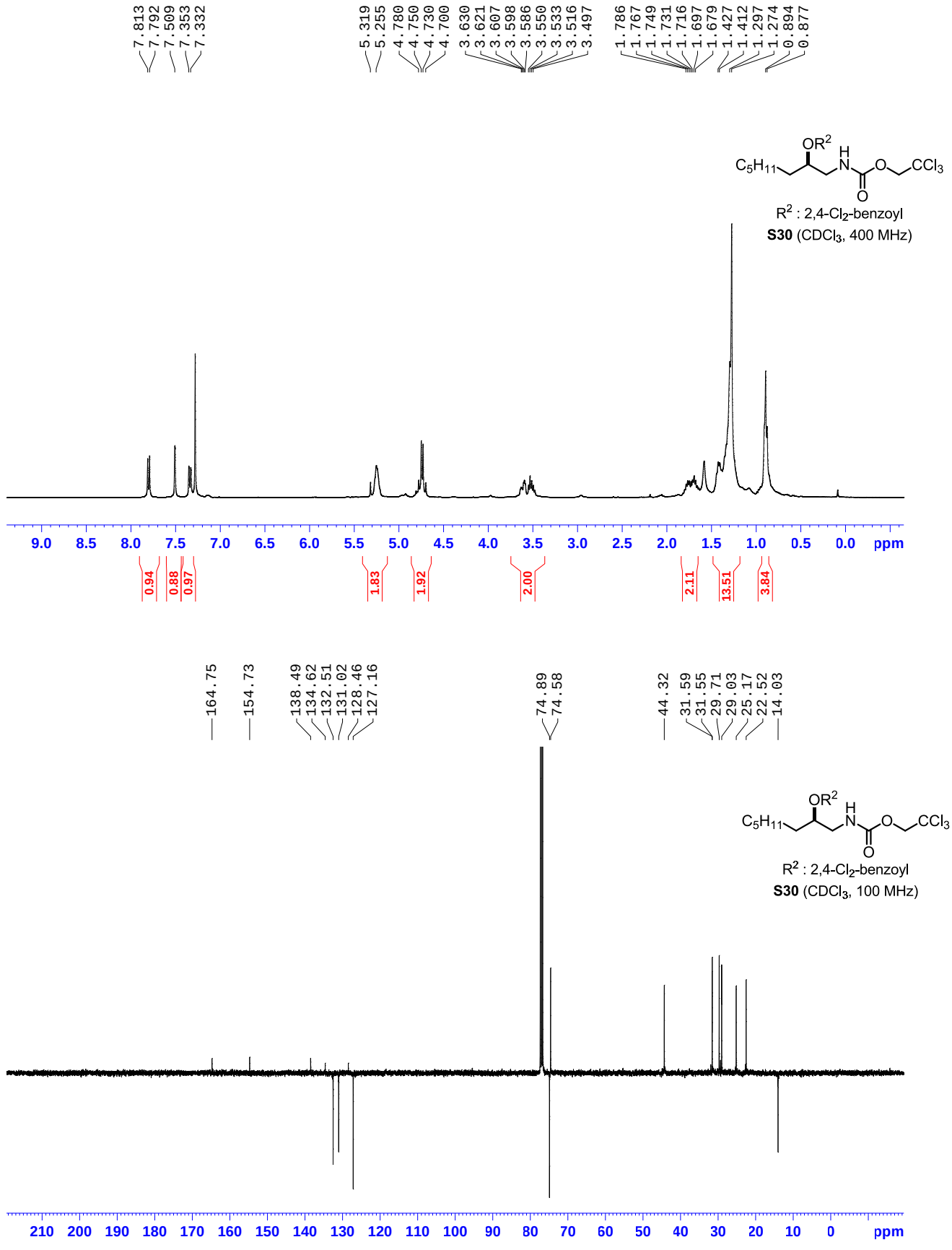

6.947
6.934
6.908
6.895
6.213
6.174
5.870
5.271
5.254
5.236
5.219
4.269
4.251
4.234
4.216
3.879
3.857
3.835
3.439
3.420
3.401
1.337
1.319
1.301
HN
O
O
COOEt
S27 (CDCl3, 400 MHz)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
1.04
1.03
2.03
1.05
1.03
3.16

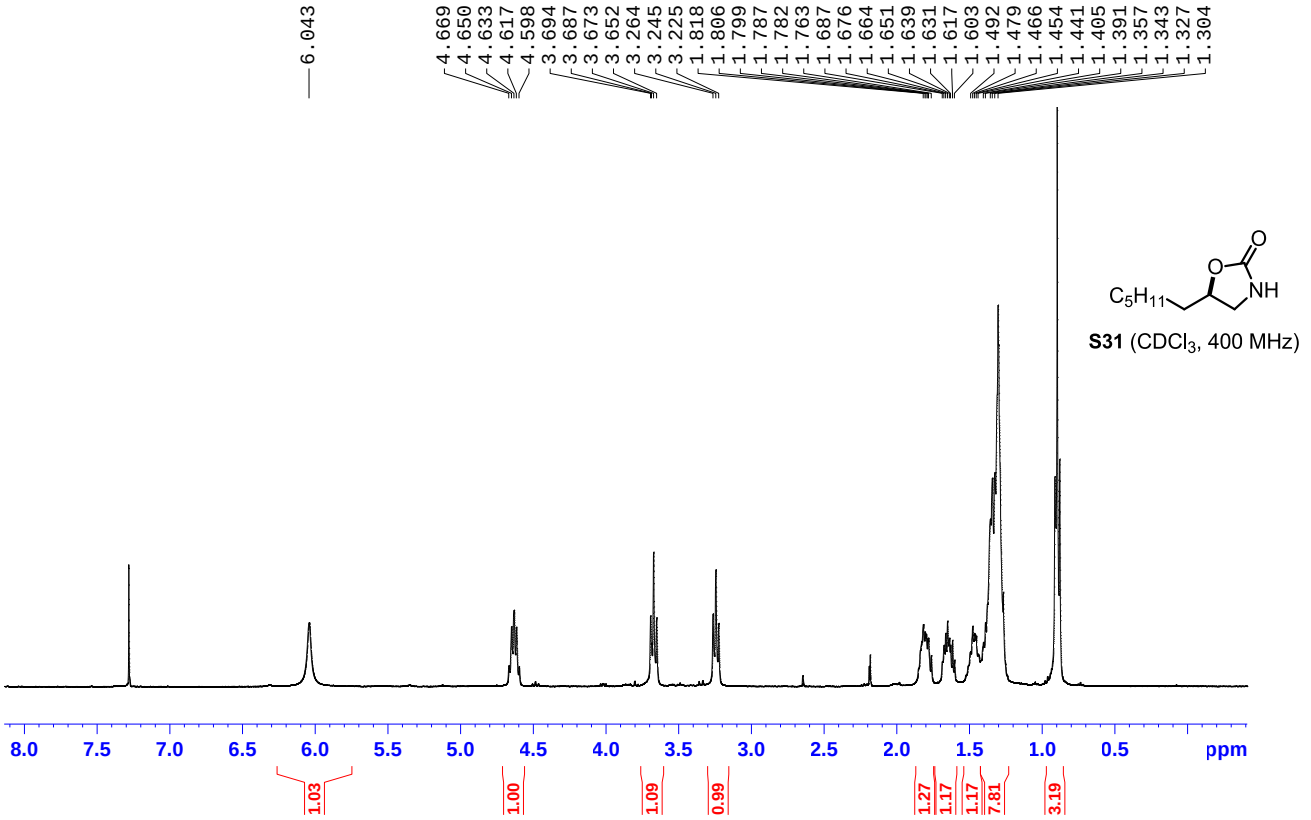

165.47
159.01
141.87
123.46
74.53
60.94
45.46
14.16
HN
O
O
COOEt
S27 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6.054
6.028
3.414
3.393
3.289
3.268
1.714
1.695
1.675
1.445
1.415
1.397
1.378
1.297
0.909
0.894
0.877
Me
C6H13
O
NH
S28 (CDCl3, 400 MHz)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
1.02
1.03
2.00
3.11
10.30
3.00

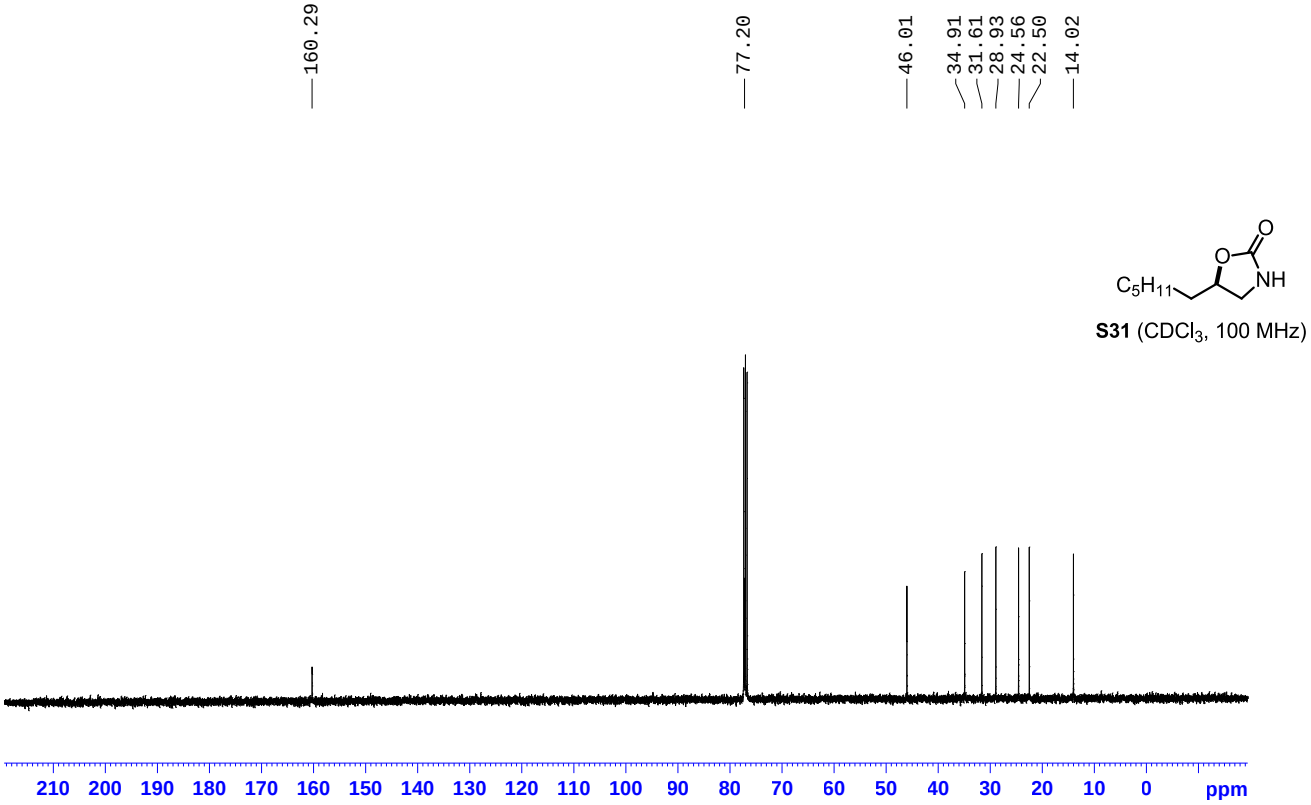

159.69
83.25
77.35
77.03
76.71
51.17
40.27
31.72
29.70
29.12
25.51
23.36
22.61
14.06
Me
C6H13
O
NH
S28 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


4.834
4.803
4.785
4.781
4.767
4.749
3.941
3.919
3.910
3.887
3.477
3.458
3.445
3.427
1.808
1.790
1.774
1.754
1.671
1.659
1.646
1.635
1.625
1.612
1.598
1.470
1.455
1.446
1.429
1.393
1.349
1.333
1.309
1.271
0.917
0.902
0.885
O
CCl3
O
N
C5H11
S29 (CDCl3, 400 MHz)
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
ppm
3.00
0.96
0.92
1.04
1.11
8.83
3.28
161.68
94.17
82.72
79.37
56.86
35.24
31.65
28.98
24.82
22.54
14.04
O
CCl3
O
N
C5H11
S29 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

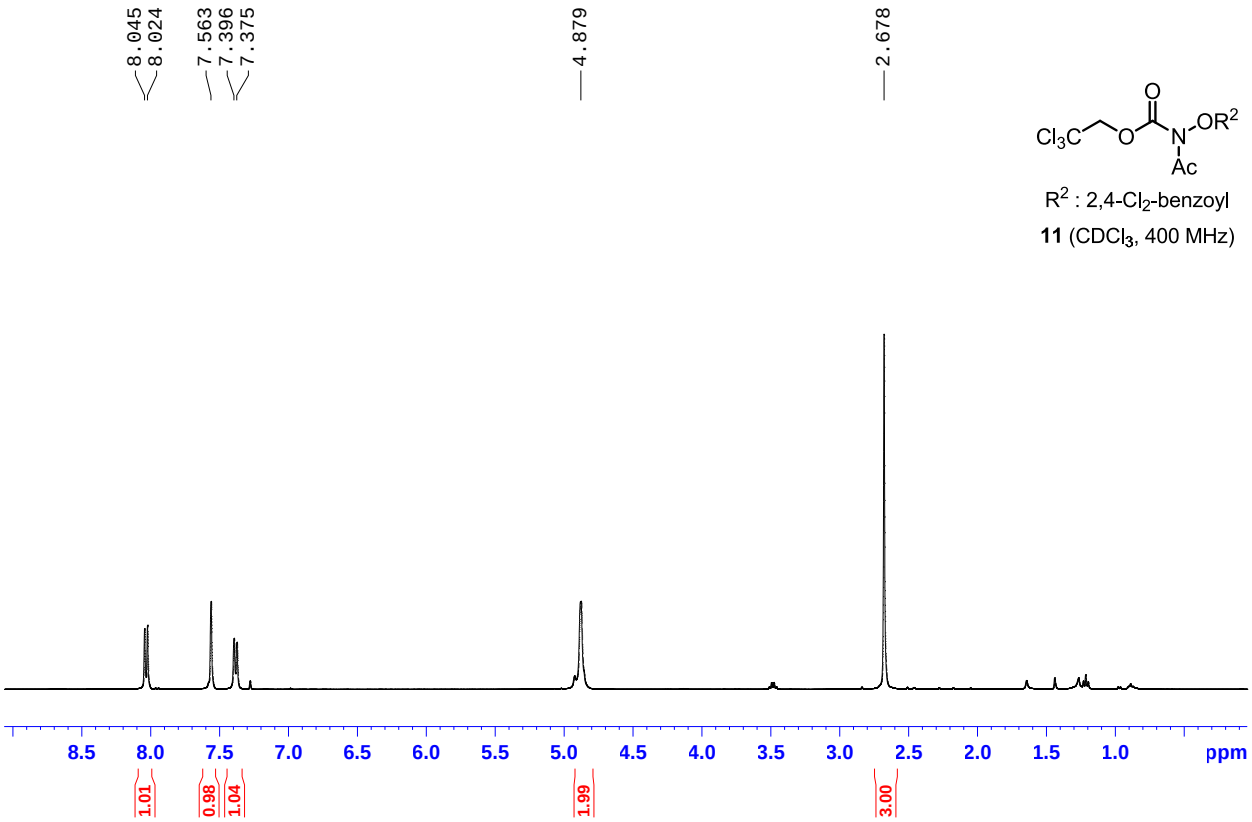

7.813
7.792
7.509
7.353
7.332
5.319
5.255
4.780
4.750
4.730
4.700
3.630
3.621
3.607
3.598
3.586
3.550
3.533
3.516
3.497
1.786
1.767
1.749
1.731
1.716
1.697
1.679
1.427
1.412
1.297
1.274
0.894
0.877
OR2
H
N
O
C5H11
CCl3
O
R2 : 2,4-Cl2-benzoyl
S30 (CDCl3, 400 MHz)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.94
0.88
0.97
1.83
1.92
2.00
2.11
13.51
3.84
164.75
154.73
138.49
134.62
132.51
131.02
128.46
127.16
74.89
74.58
44.32
31.59
31.55
29.71
29.03
25.17
22.52
14.03
OR2
H
N
O
C5H11
CCl3
O
R2 : 2,4-Cl2-benzoyl
S30 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

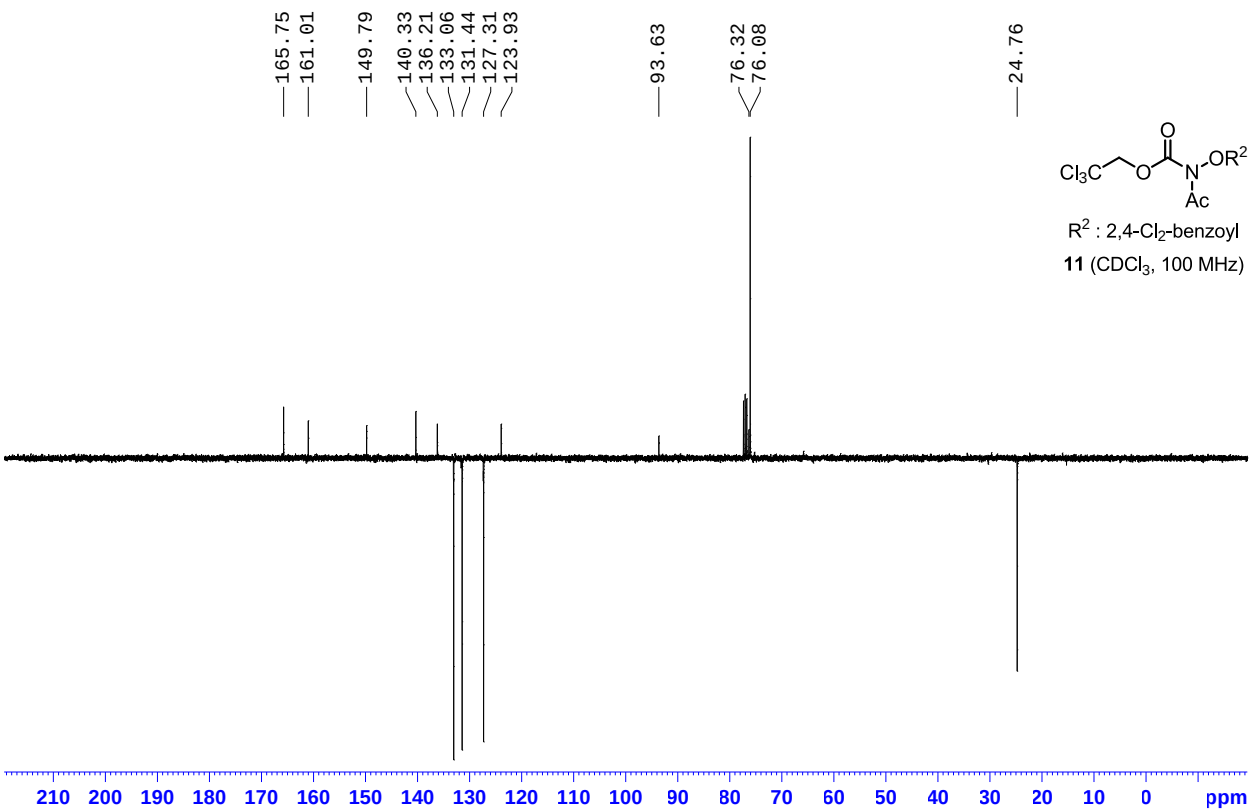


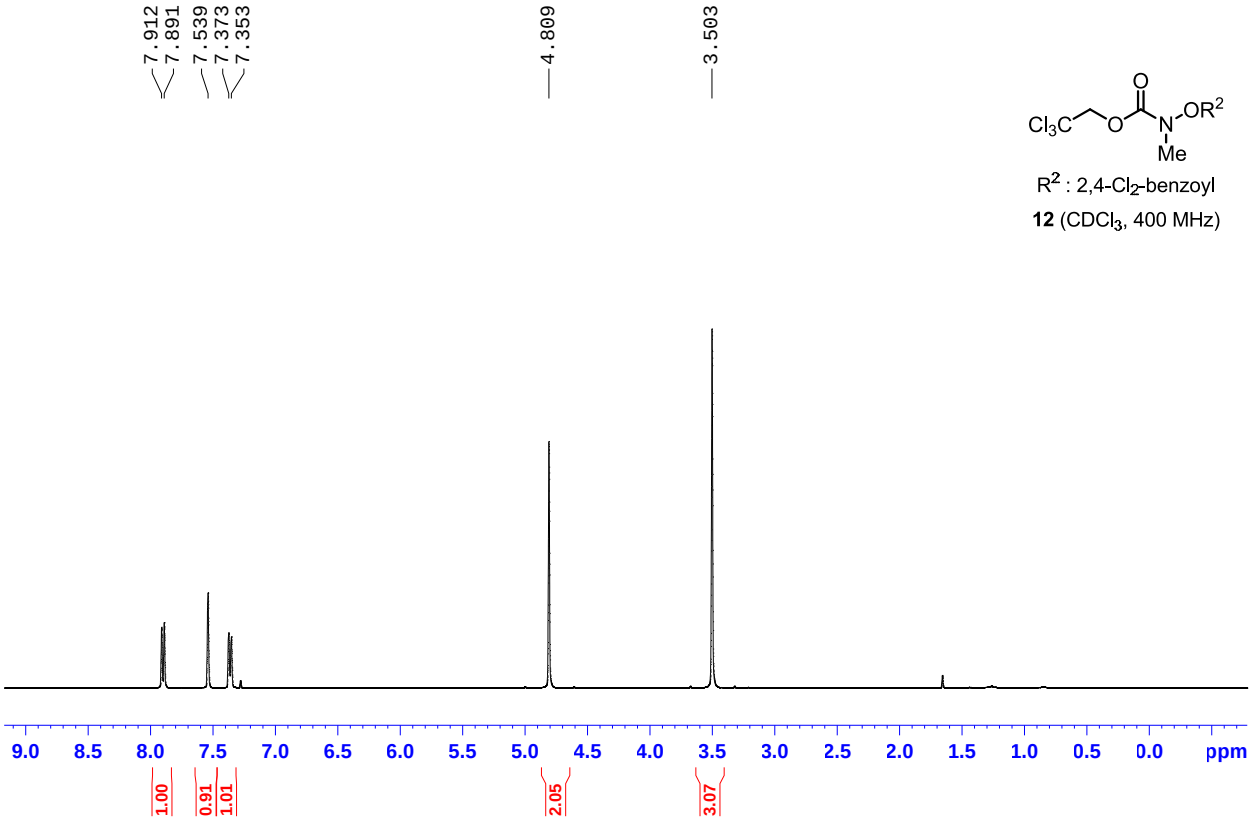
S31 ($CDCl_3$, 400 MHz)

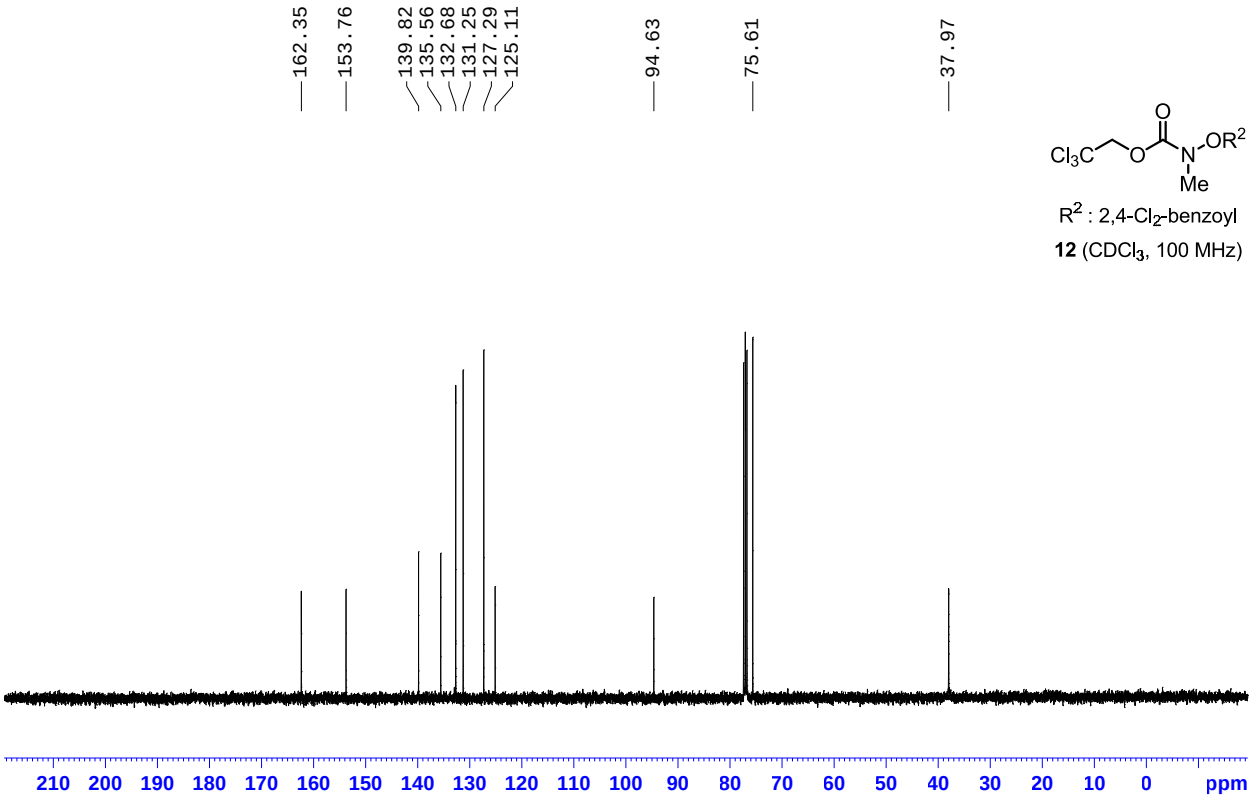


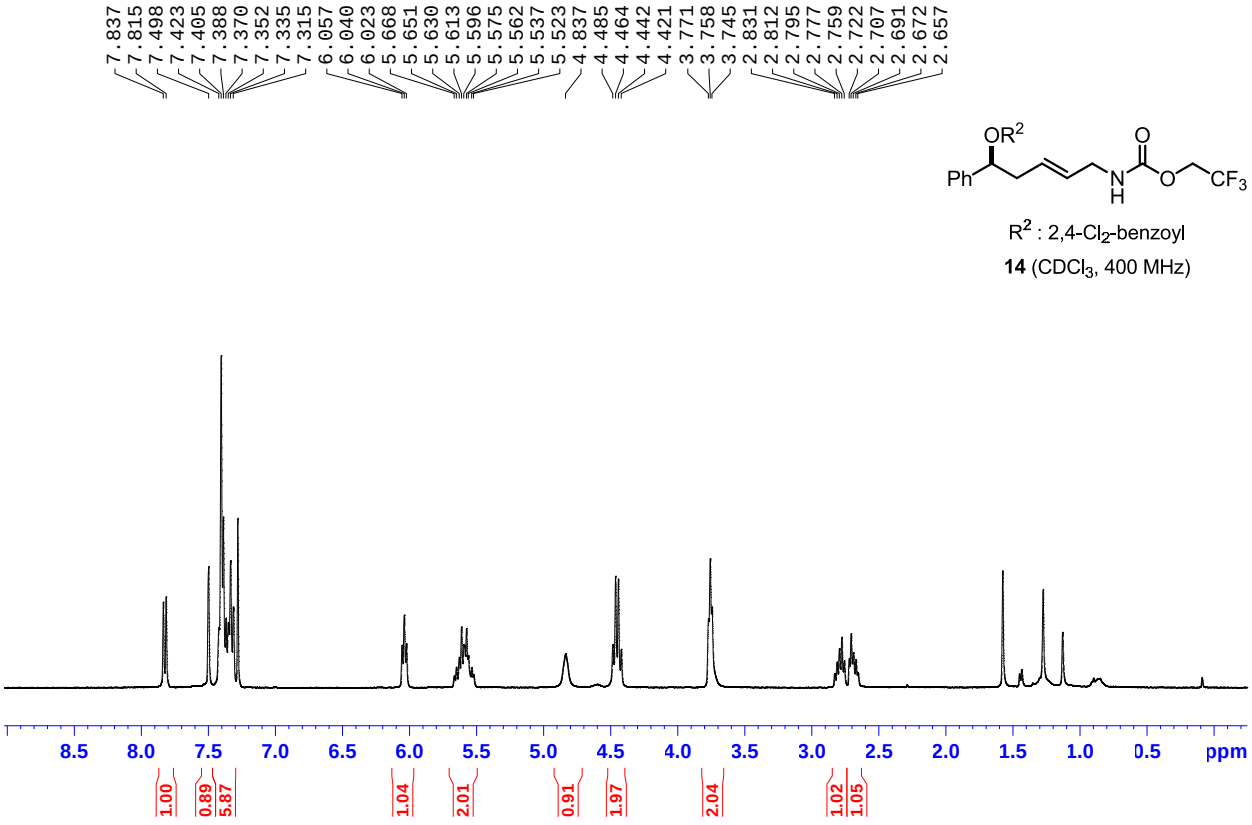
S31 ($CDCl_3$, 100 MHz)

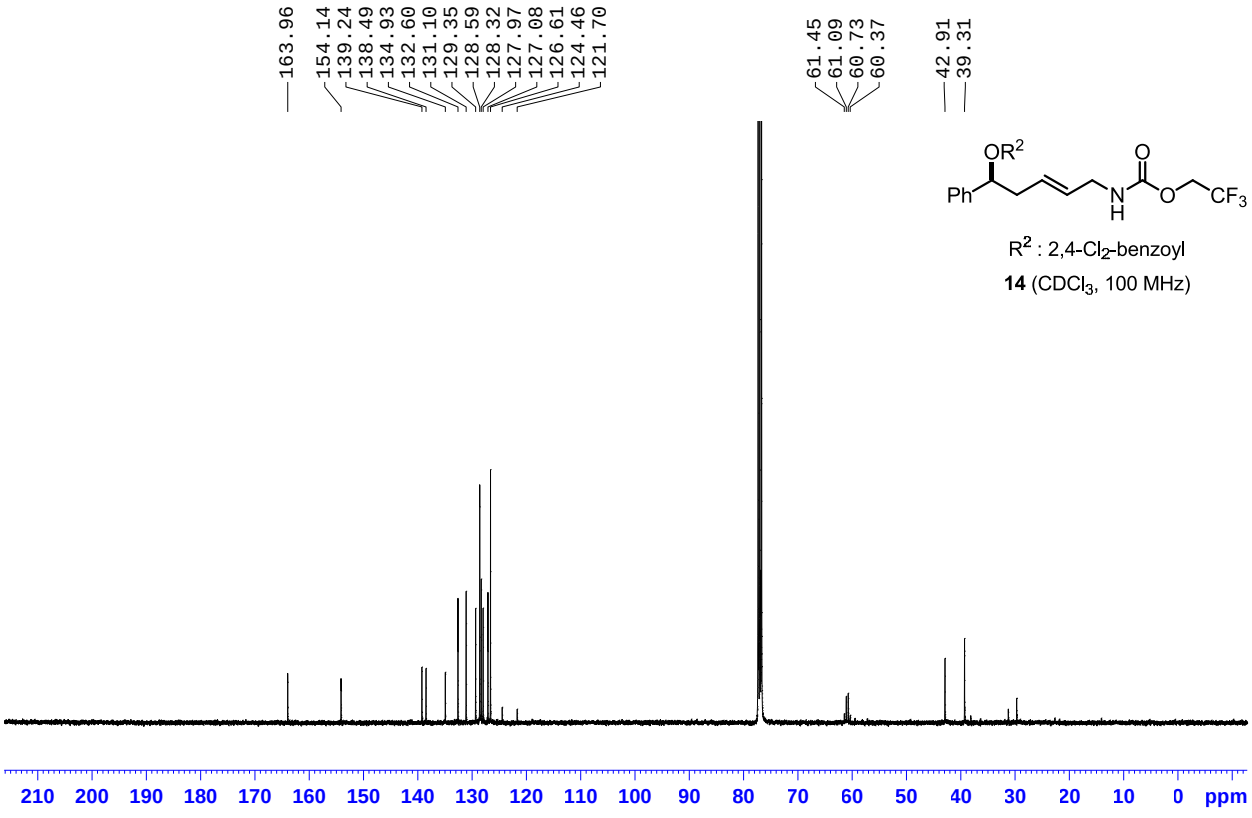

8.045
8.024
7.563
7.396
7.375
4.879
2.678
Cl3C
O
O
N
OR2
Ac
R2 : 2,4-Cl2-benzoyl
11 (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.01
0.98
1.04
1.99
3.00

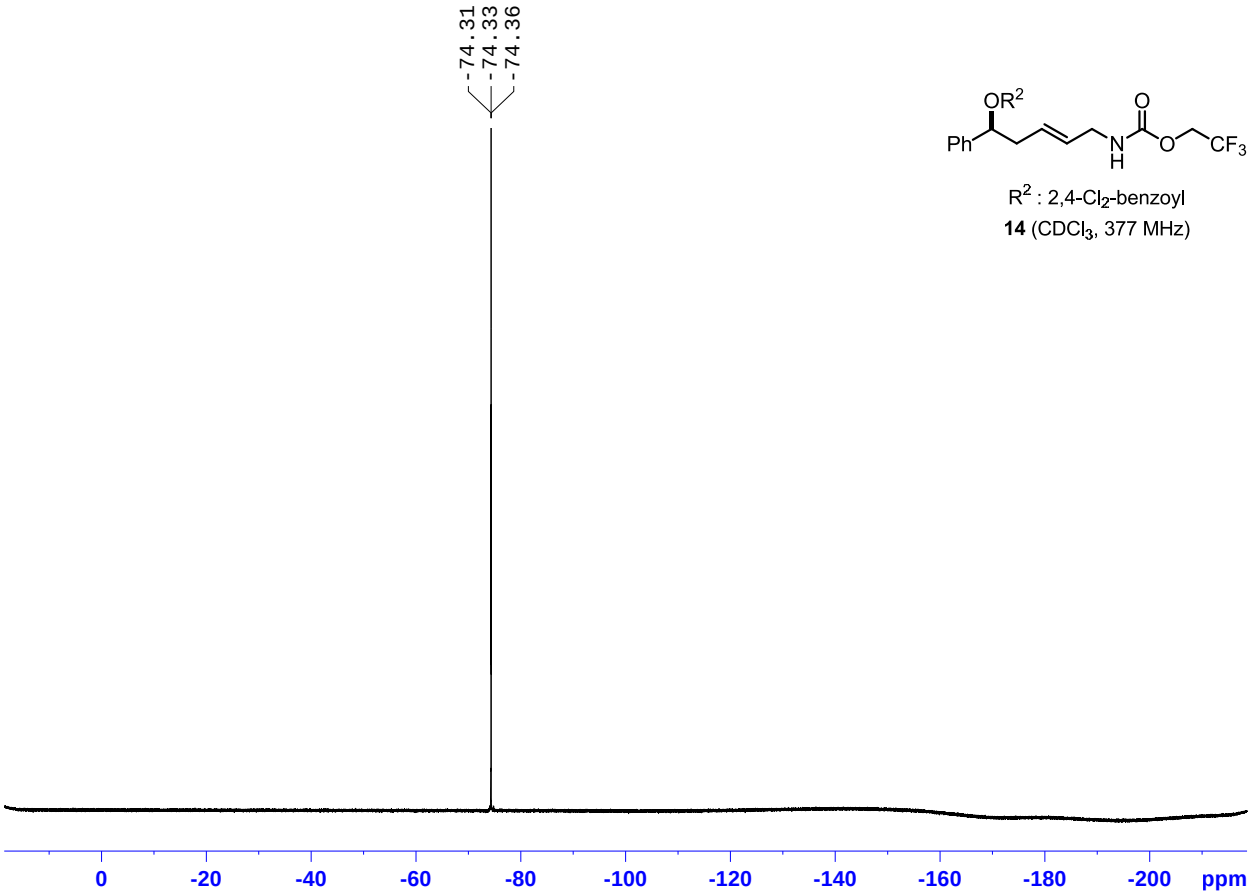

165.75
161.01
149.79
140.33
136.21
133.06
131.44
127.31
123.93
93.63
76.32
76.08
24.76
Cl3C
O
O
N
OR2
Ac
R2 : 2,4-Cl2-benzoyl
11 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

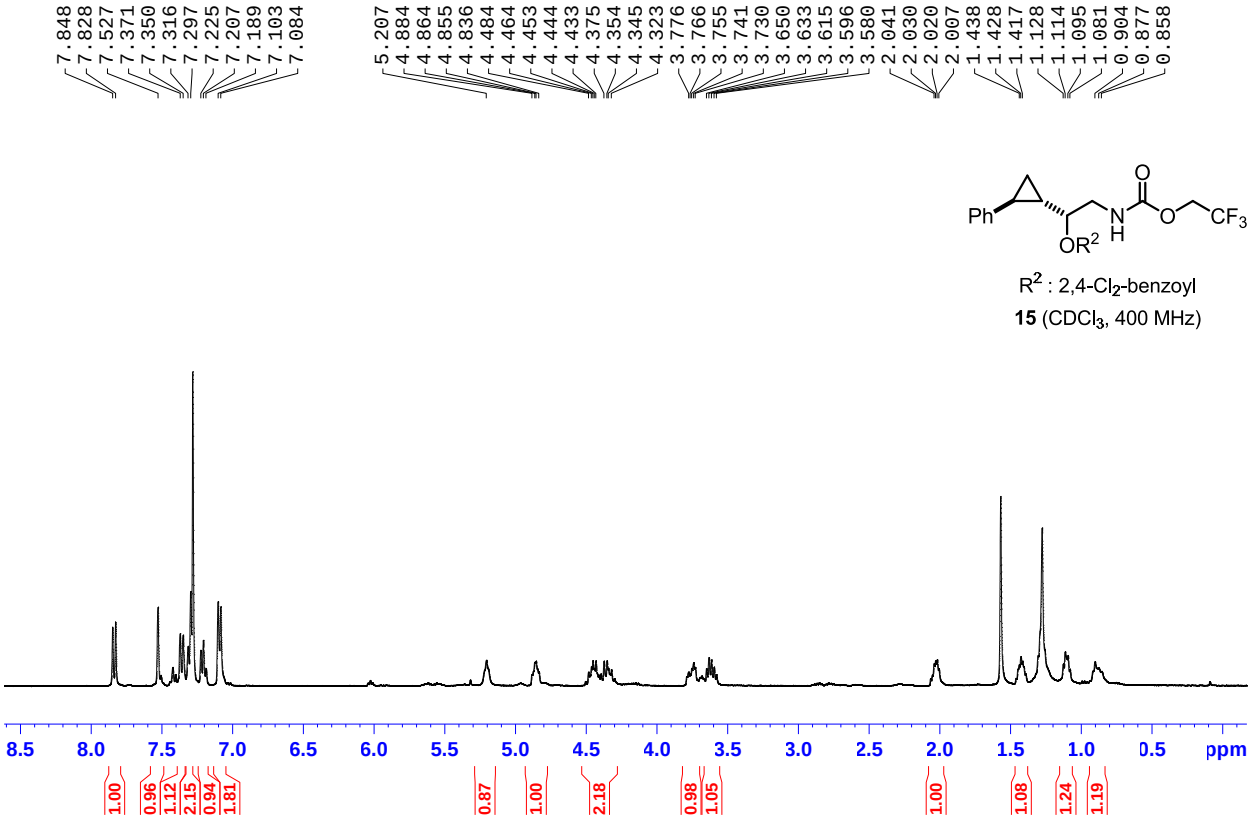

7.912
7.891
7.539
7.373
7.353
4.809
3.503
Cl3C
O
O
N
OR2
Me
R2 : 2,4-Cl2-benzoyl
12 (CDCl3, 400 MHz)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.91
1.01
2.05
3.07

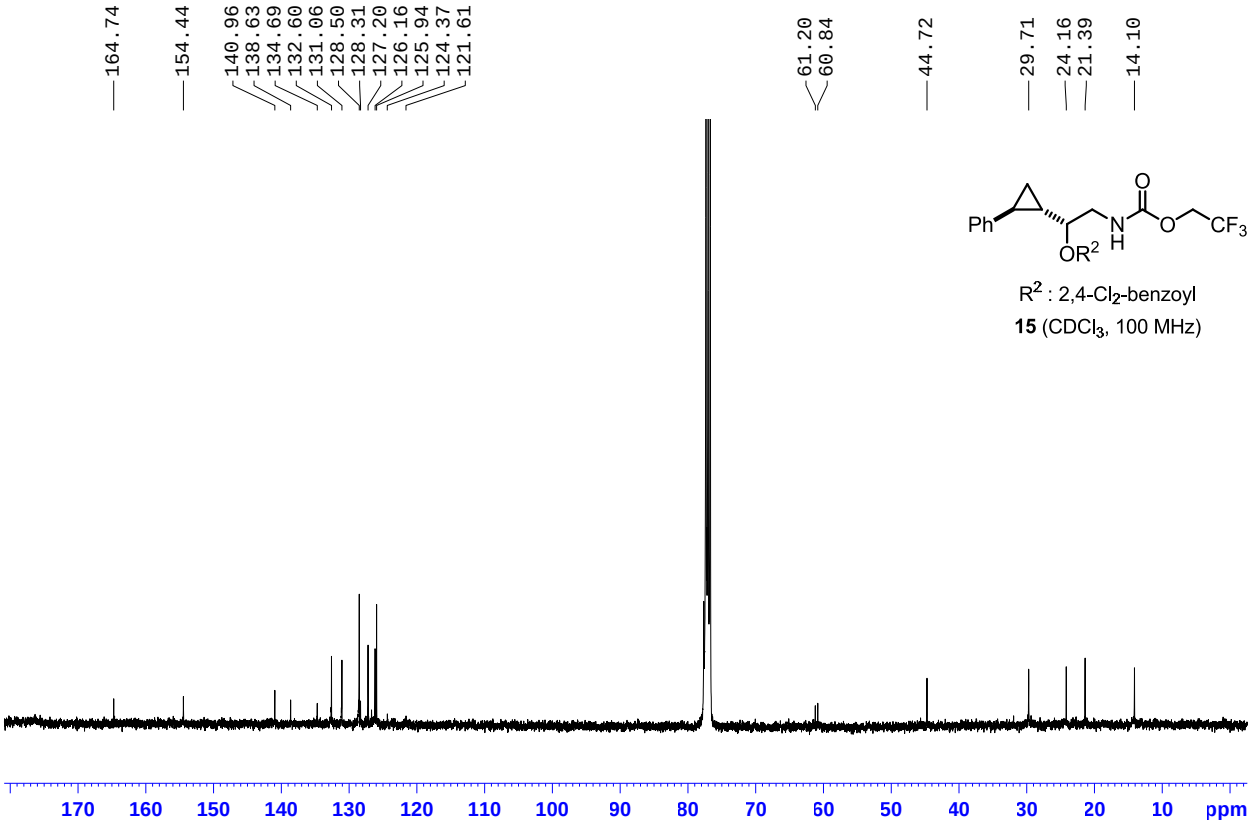

162.35
153.76
139.82
135.56
132.68
131.25
127.29
125.11
94.63
75.61
37.97
Cl3C
O
O
N
OR2
Me
R2 : 2,4-Cl2-benzoyl
12 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

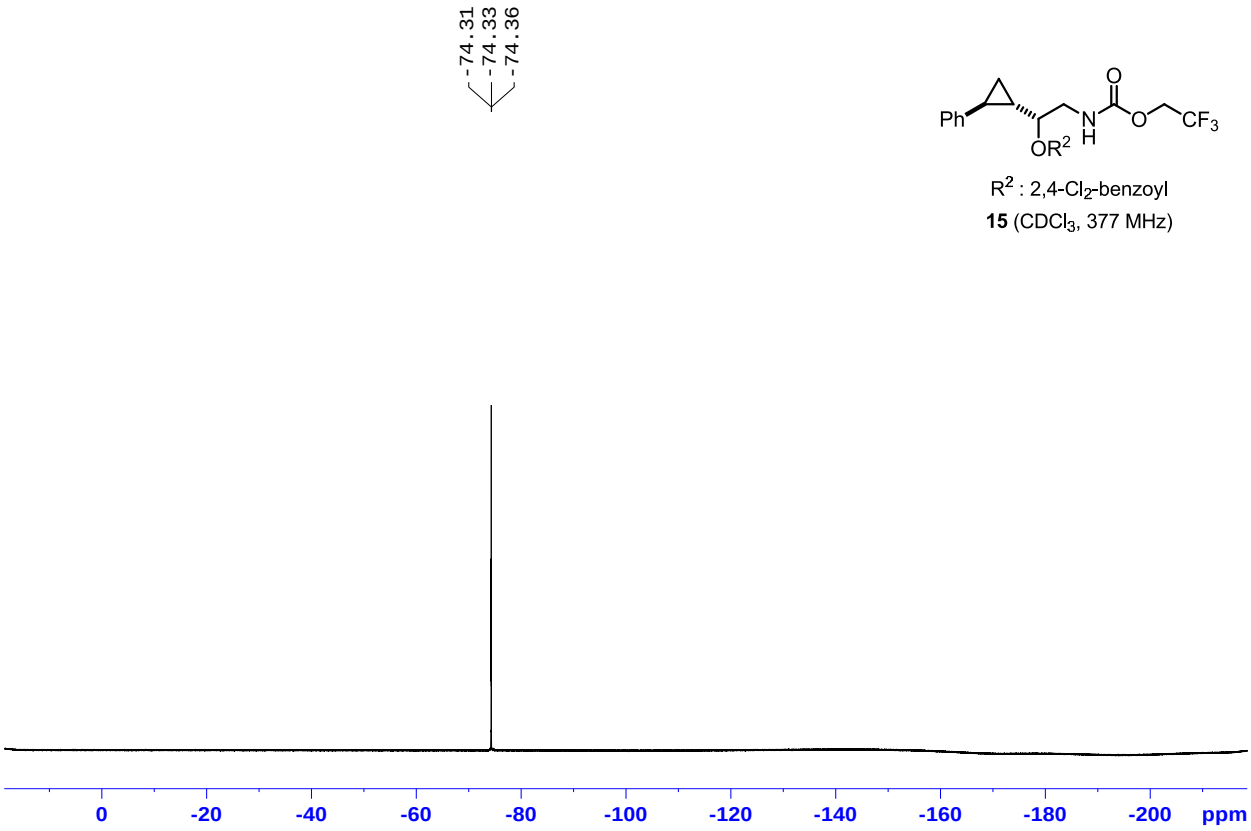

7.837
7.815
7.498
7.423
7.405
7.388
7.370
7.352
7.335
7.315
6.057
6.040
6.023
5.668
5.651
5.630
5.613
5.596
5.575
5.562
5.537
5.523
4.837
4.485
4.464
4.442
4.421
3.771
3.758
3.745
2.831
2.812
2.795
2.777
2.759
2.722
2.707
2.691
2.672
2.657
OR2
O
Ph
N
H
O
CF3
R2 : 2,4-Cl2-benzoyl
14 (CDCl3, 400 MHz)
8.5
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
ppm
1.00
0.89
5.87
1.04
2.01
0.91
1.97
2.04
1.02
1.05

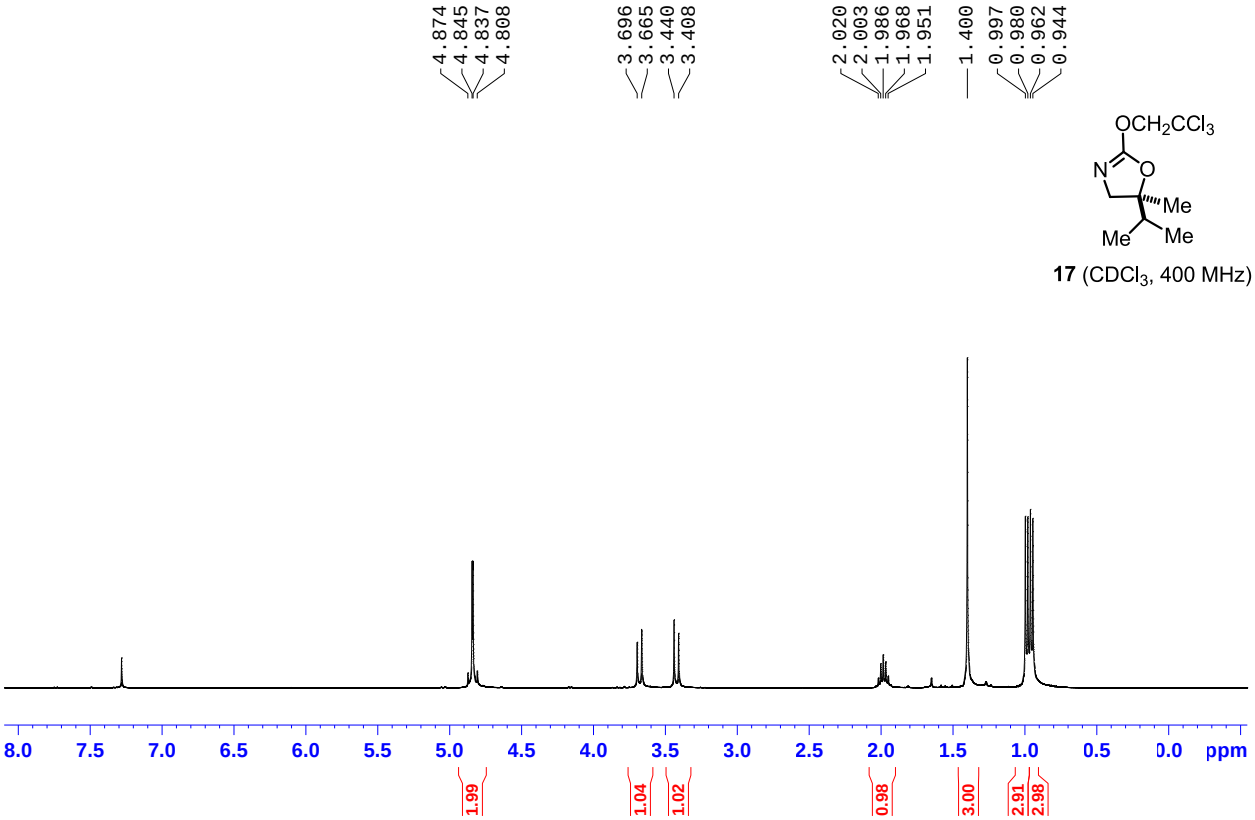

163.96
154.14
139.24
138.49
134.93
132.60
131.10
129.35
128.59
128.32
127.97
127.08
126.61
124.46
121.70
61.45
61.09
60.73
60.37
42.91
39.31
OR2
O
Ph
N
H
O
CF3
R2 : 2,4-Cl2-benzoyl
14 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-74.31
-74.33
-74.36
OR2
O
Ph
N
H
O
CF3
R2 : 2,4-Cl2-benzoyl
14 (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

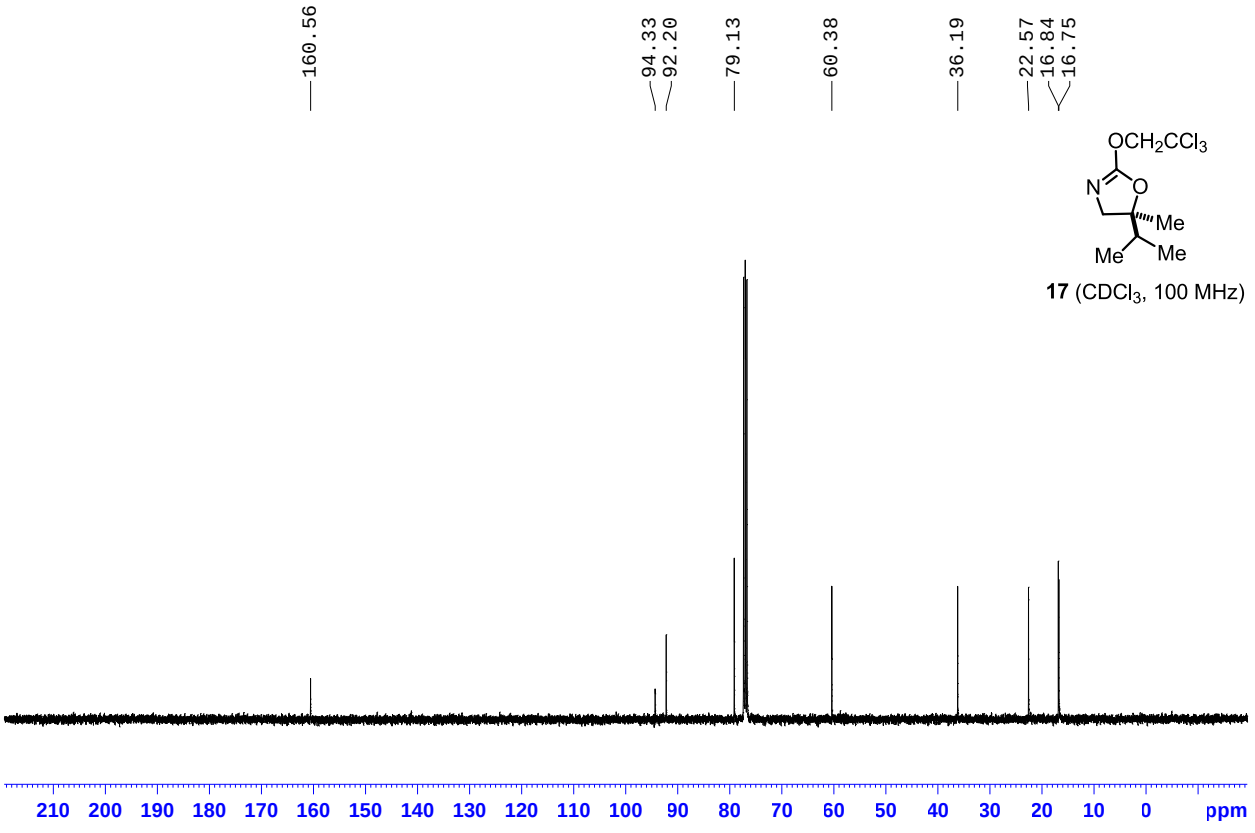

7.848
7.828
7.527
7.371
7.350
7.316
7.297
7.225
7.207
7.189
7.103
7.084
5.207
4.884
4.864
4.855
4.836
4.484
4.464
4.453
4.444
4.433
4.375
4.354
4.345
4.323
3.776
3.766
3.755
3.741
3.730
3.650
3.633
3.615
3.596
3.580
2.041
2.030
2.020
2.007
1.438
1.428
1.417
1.128
1.114
1.095
1.081
0.904
0.877
0.858
Ph
OR2
N
H
O
O
CF3
R2 : 2,4-Cl2-benzoyl
15 (CDCl3, 400 MHz)
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
ppm
1.00
0.96
1.12
2.15
0.94
1.81
0.87
1.00
2.18
0.98
1.05
1.00
1.08
1.24
1.19


164.74
154.44
140.96
138.63
134.69
132.60
131.06
128.50
128.31
127.20
126.16
125.94
124.37
121.61
61.20
60.84
44.72
29.71
24.16
21.39
14.10
Ph
OR2
N
H
O
O
CF3
R2 : 2,4-Cl2-benzoyl
15 (CDCl3, 100 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

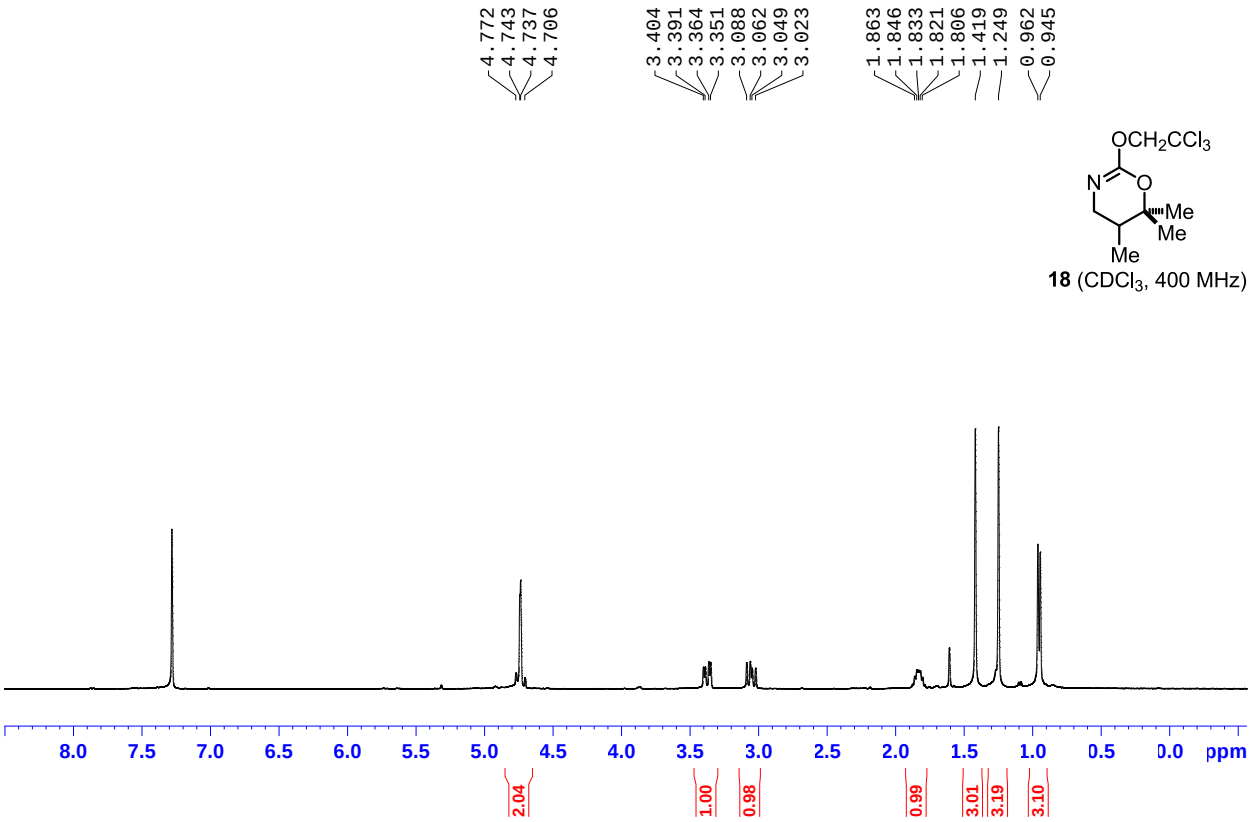

-74.31
-74.33
-74.36
Ph
OR2
N
H
O
O
CF3
R2 : 2,4-Cl2-benzoyl
15 (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm



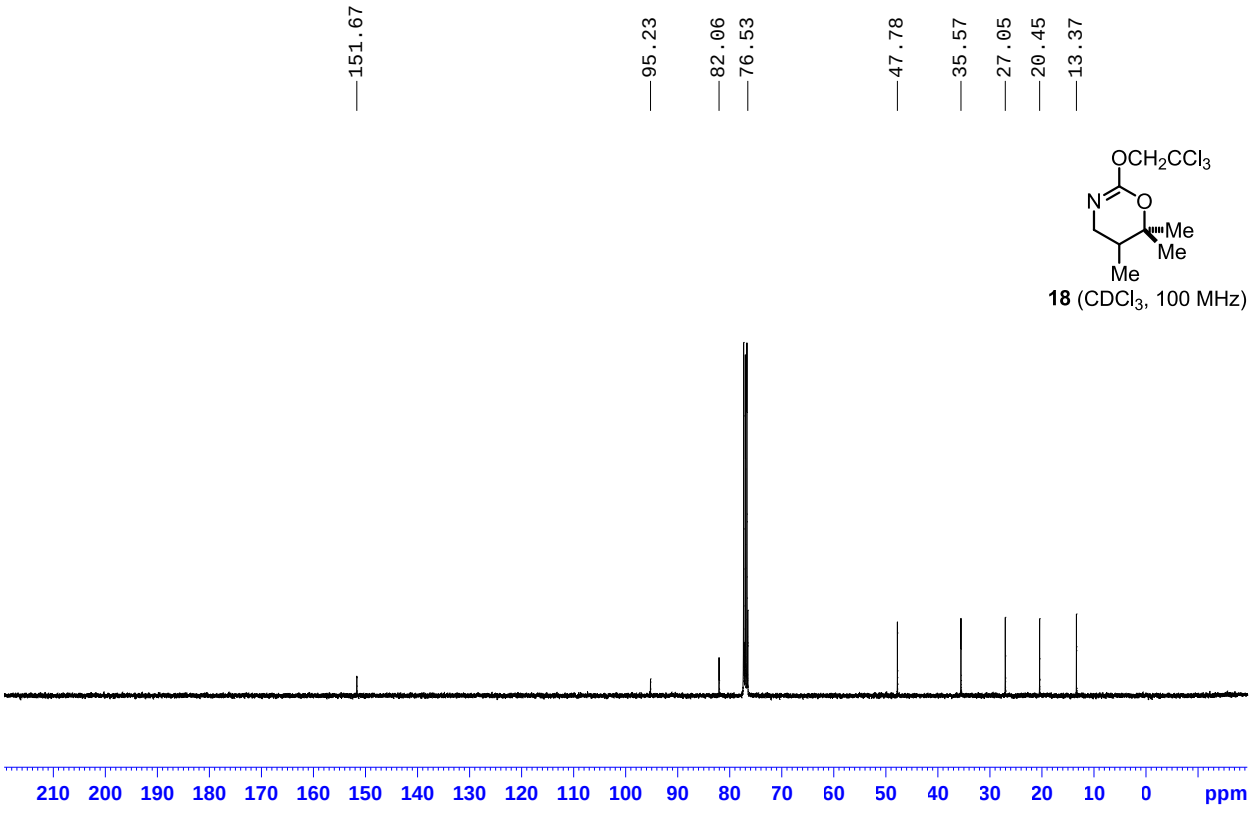
17 ($CDCl_3$, 400 MHz)



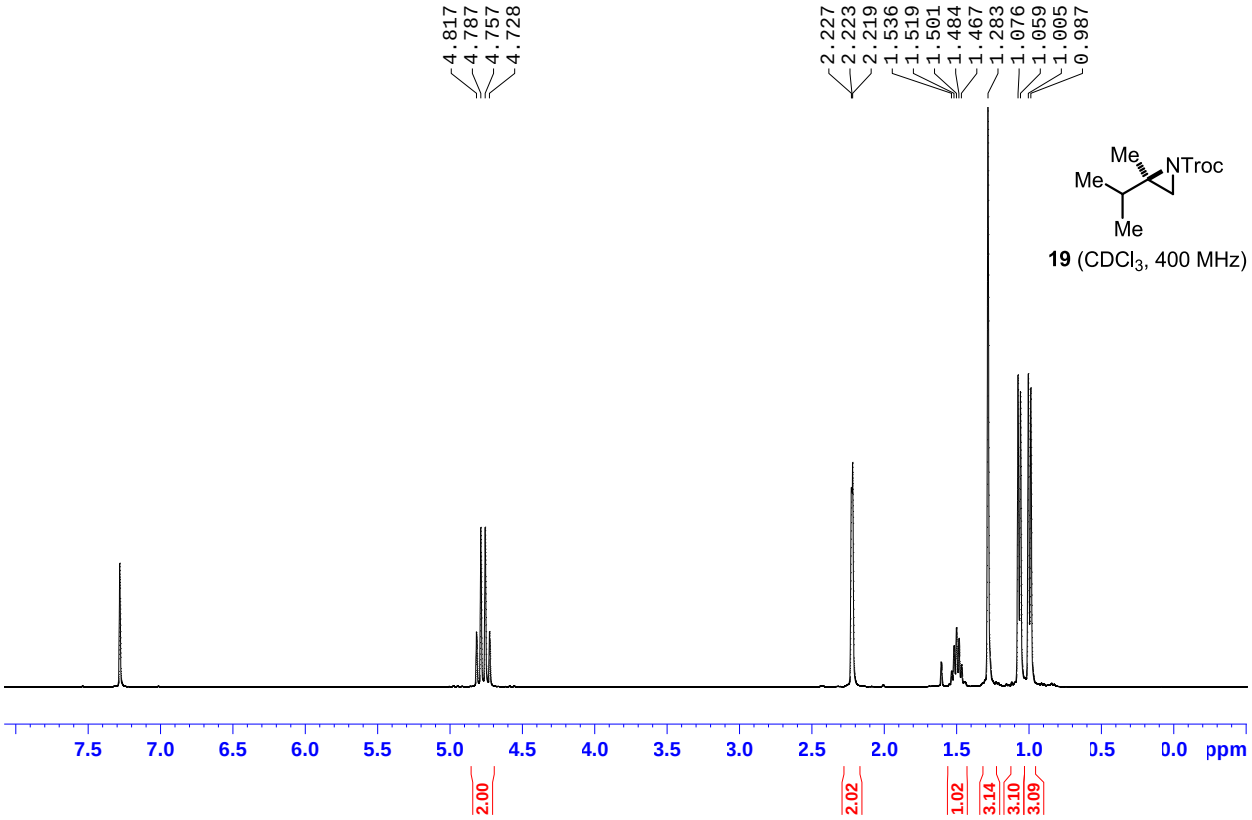
17 ($CDCl_3$, 100 MHz)

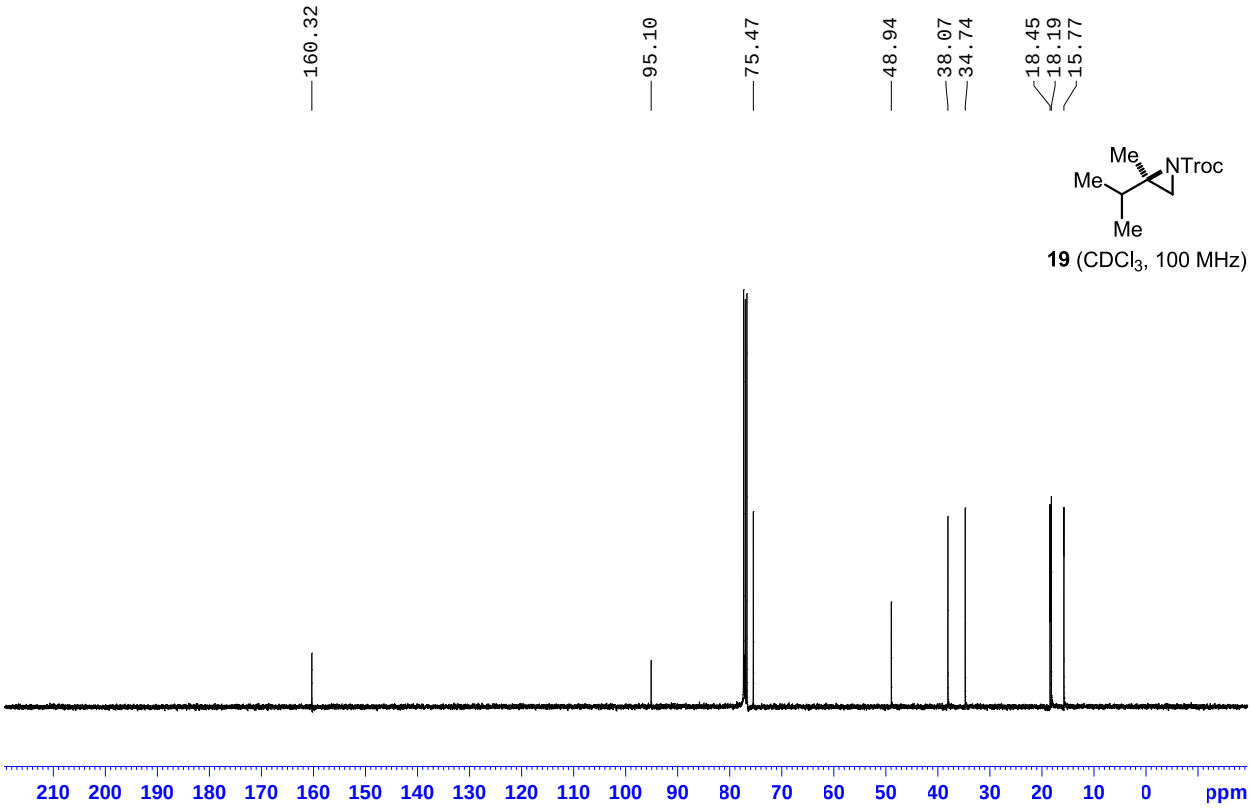


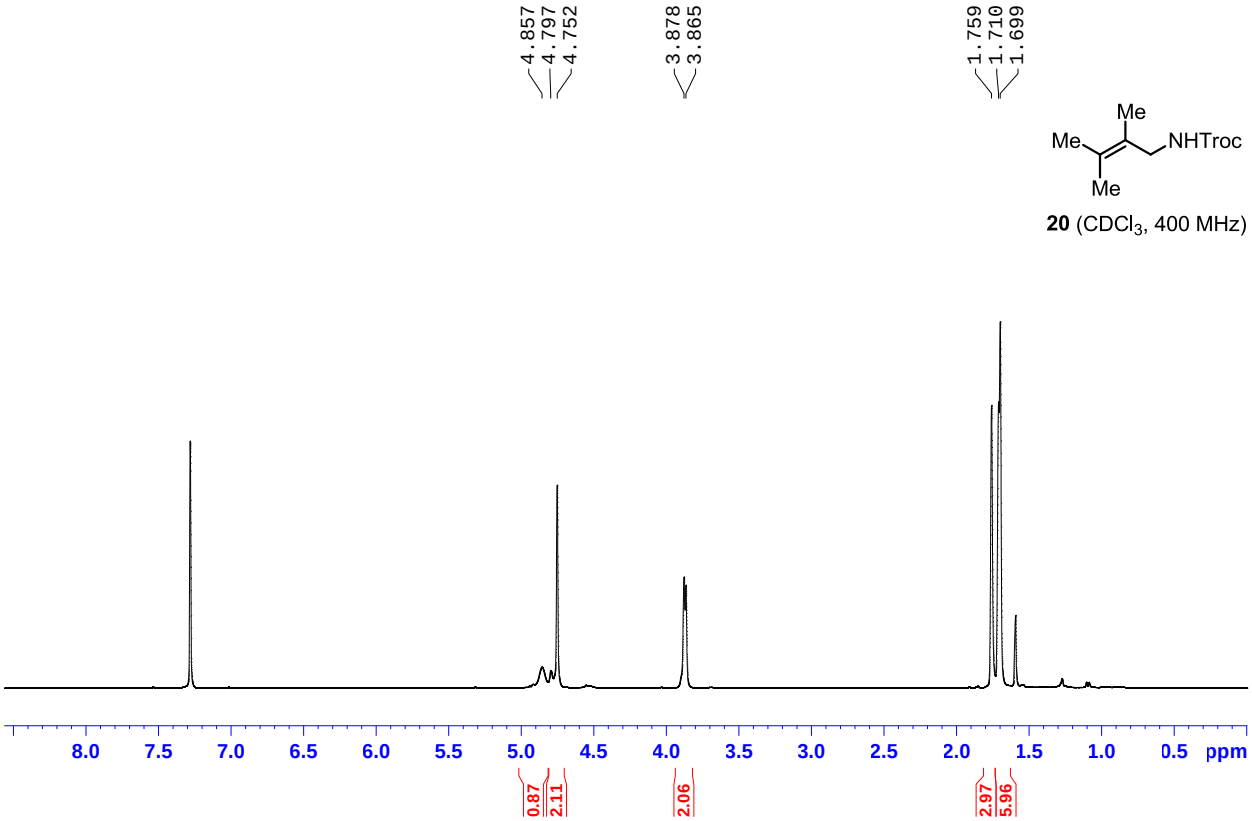
18 ($CDCl_3$, 400 MHz)



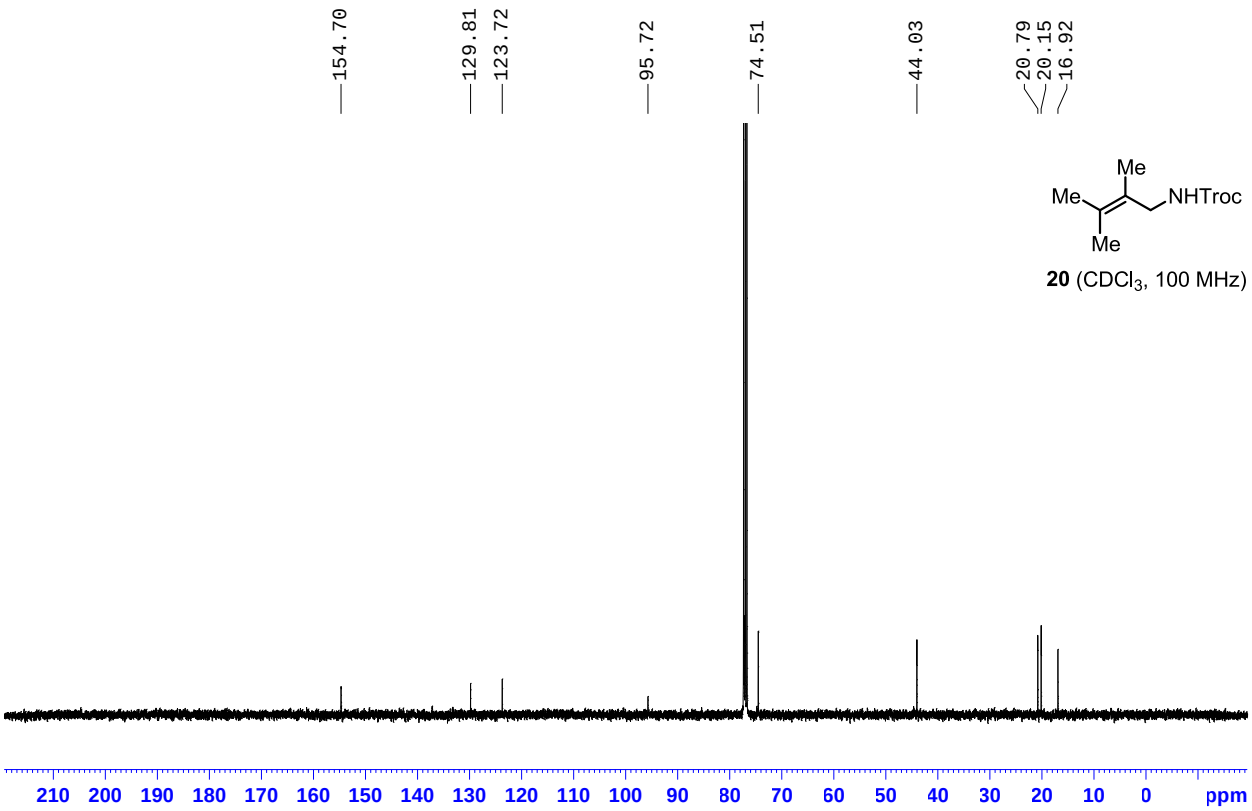
18 ($CDCl_3$, 100 MHz)


4.817
4.787
4.757
4.728
2.227
2.223
2.219
1.536
1.519
1.501
1.484
1.467
1.283
1.076
1.059
1.005
0.987
Me
NTroc
Me
Me
19 (CDCl3, 400 MHz)
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 ppm
2.00
2.02
1.02
3.14
3.10
3.09

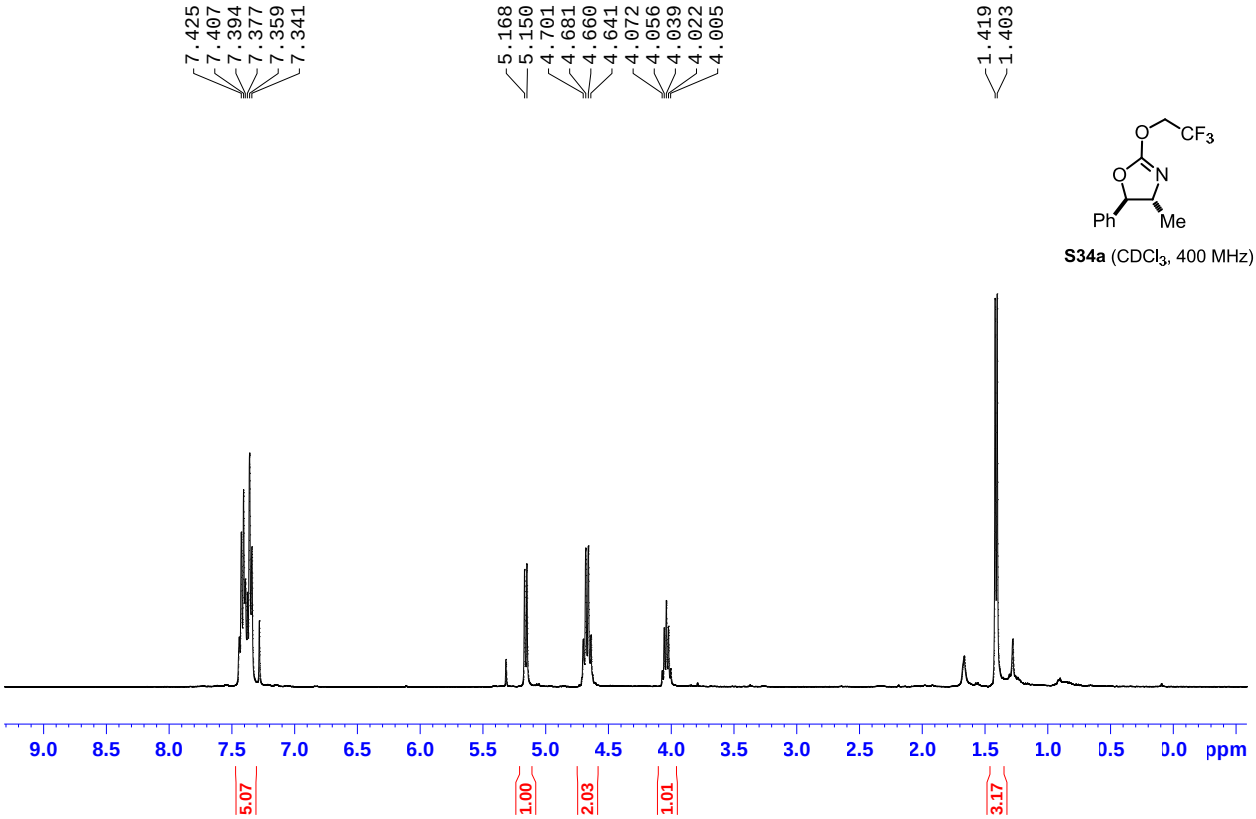

160.32
95.10
75.47
48.94
38.07
34.74
18.45
18.19
15.77
Me
NTroc
Me
Me
19 (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



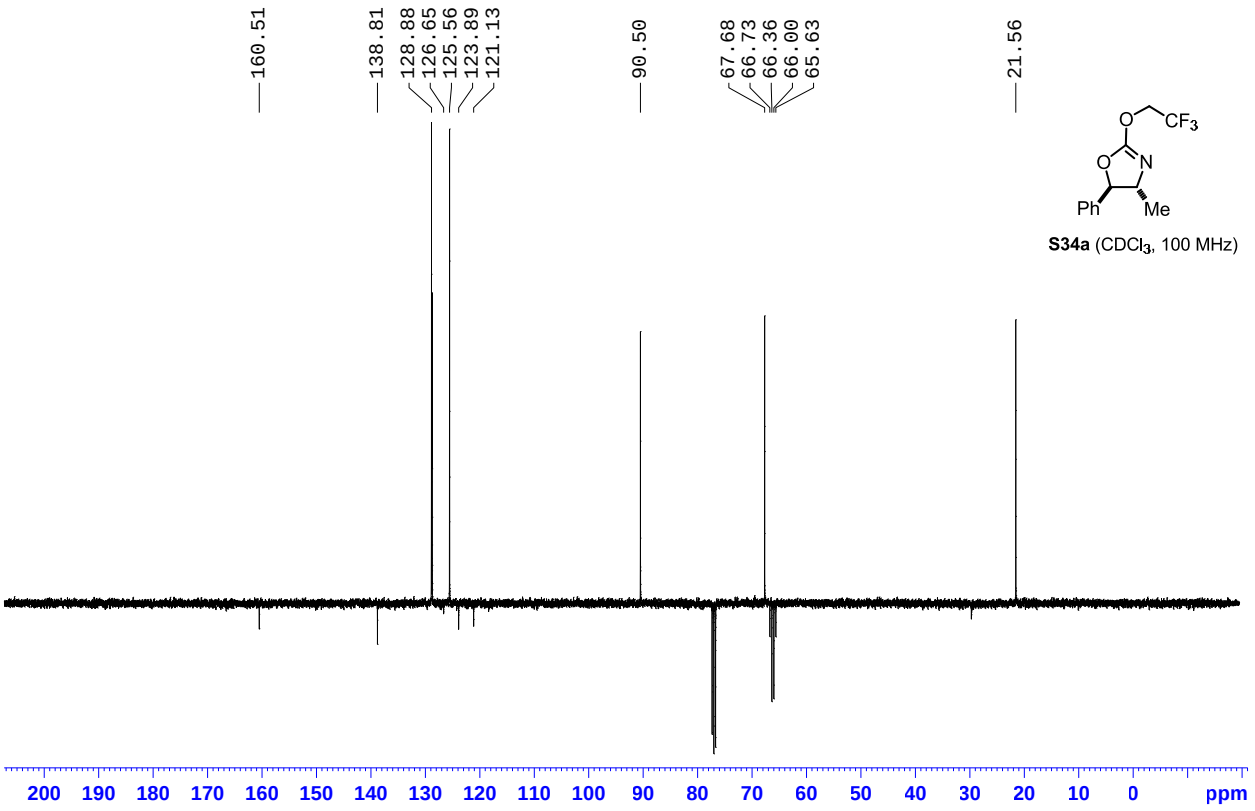
20 ($CDCl_3$, 400 MHz)



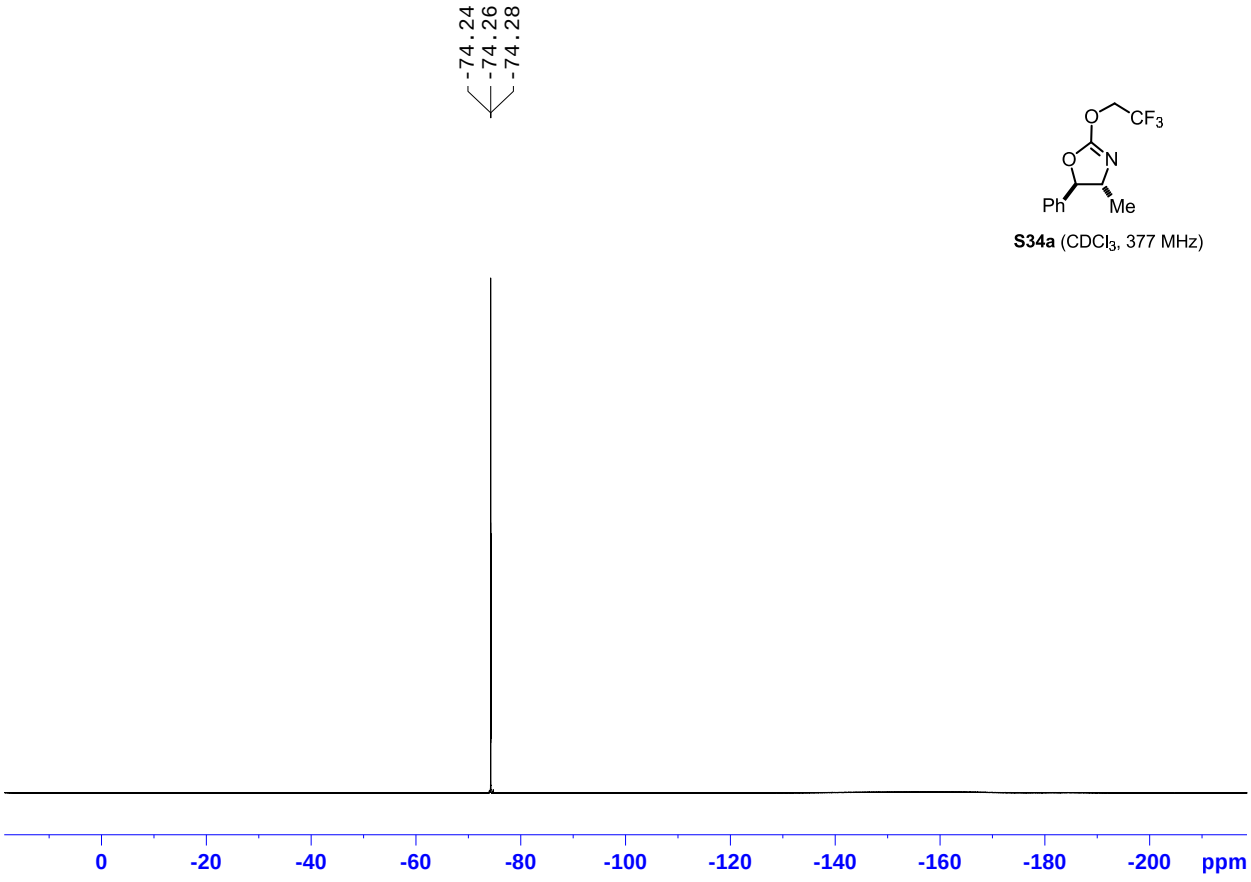
20 ($CDCl_3$, 100 MHz)



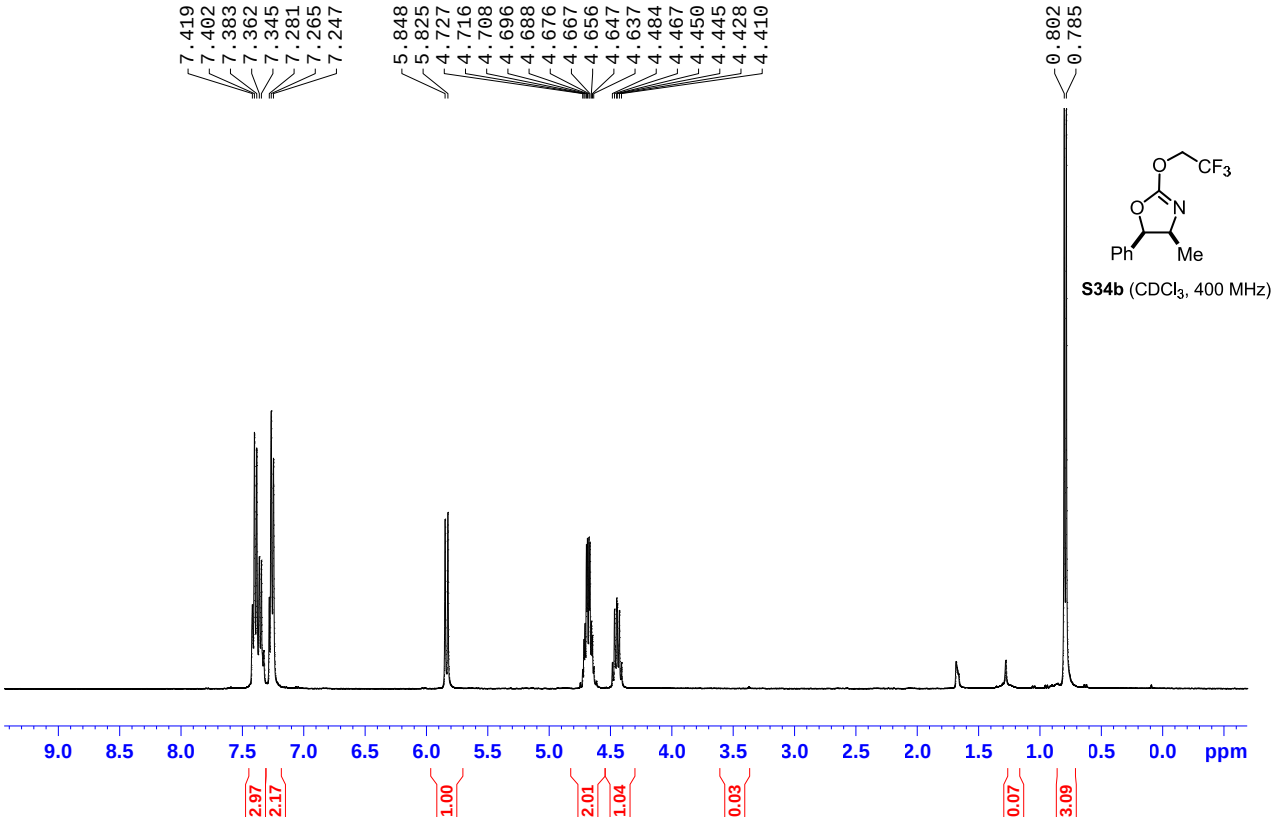
S34a ($CDCl_3$, 400 MHz)



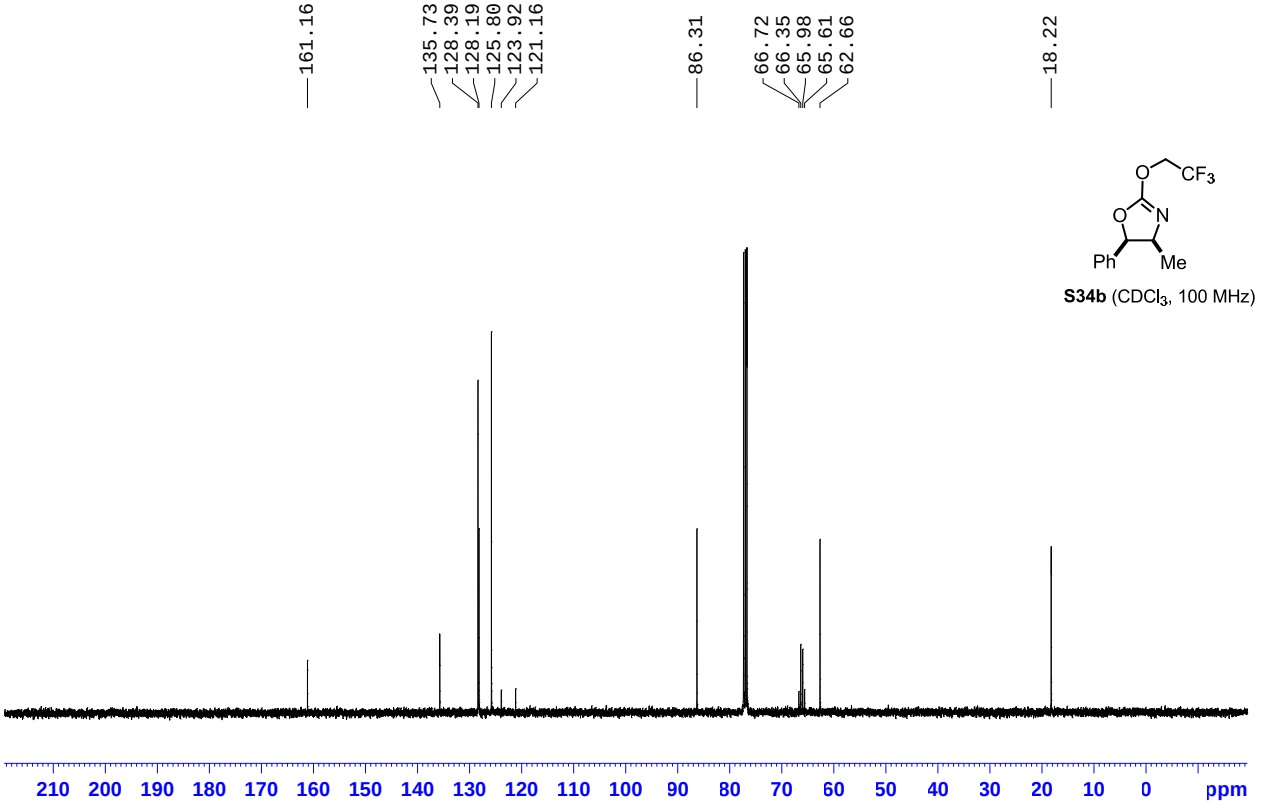
S34a ($CDCl_3$, 100 MHz)



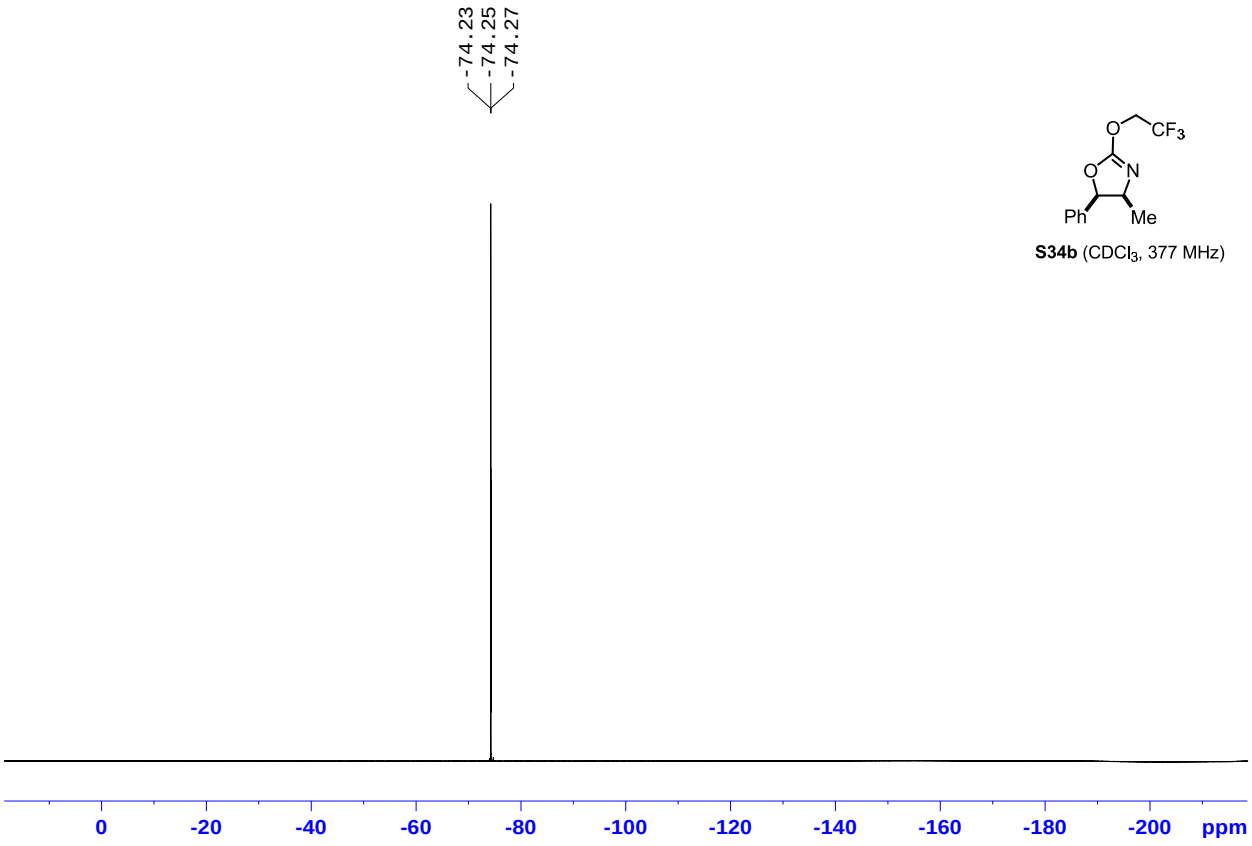
S34a ($CDCl_3$, 377 MHz)



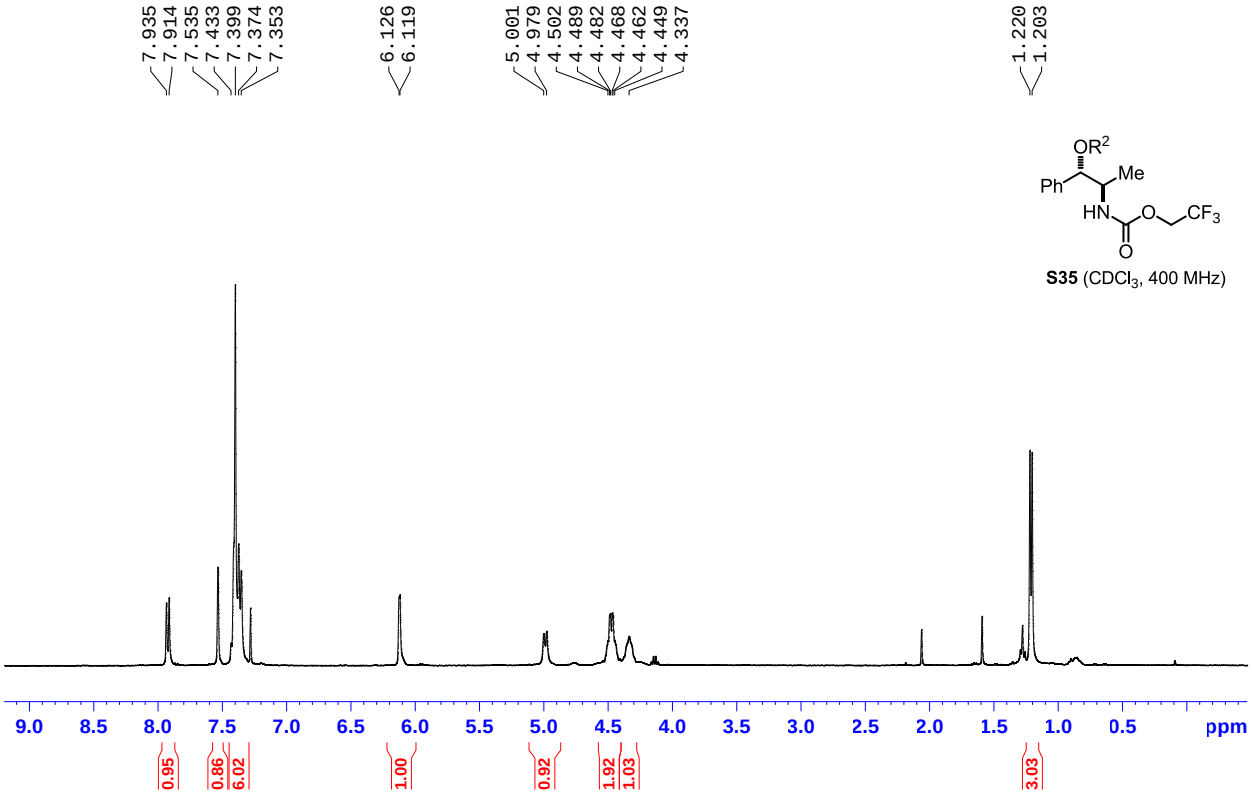
S34b ($CDCl_3$, 400 MHz)



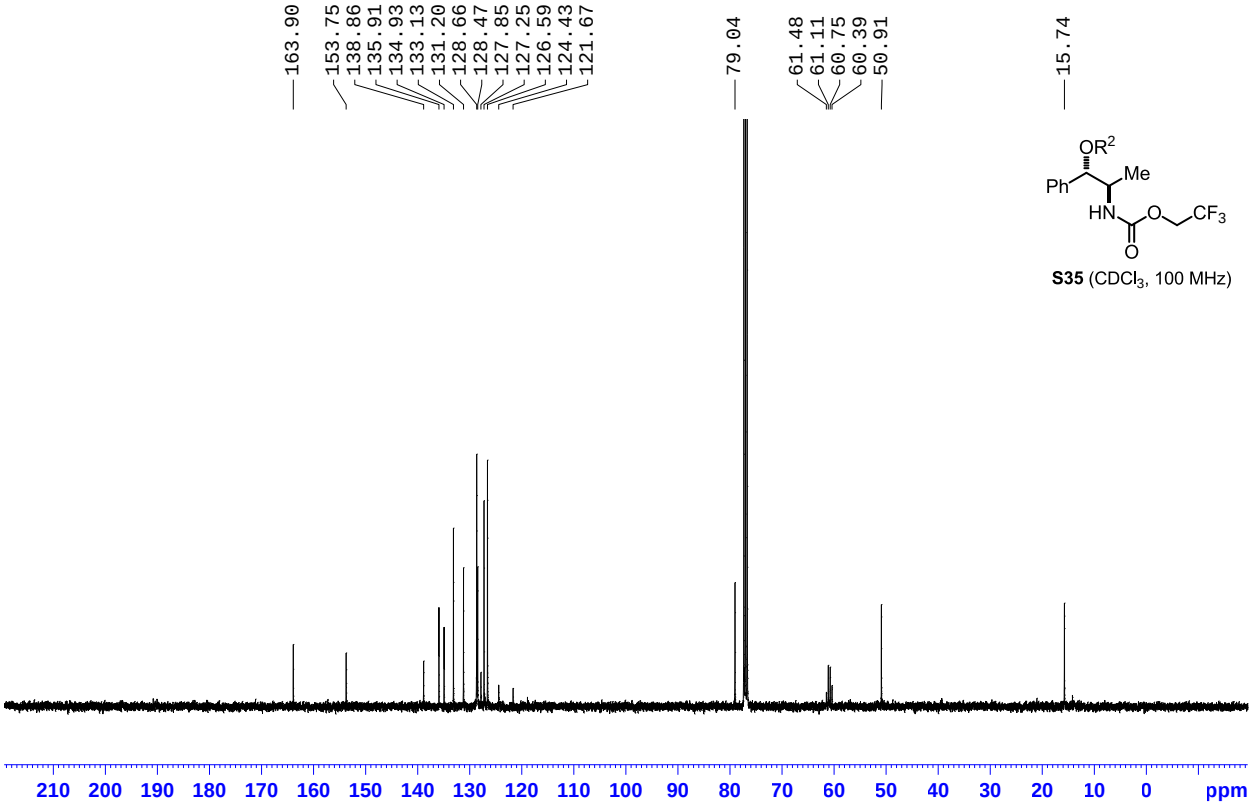
S34b ($CDCl_3$, 100 MHz)



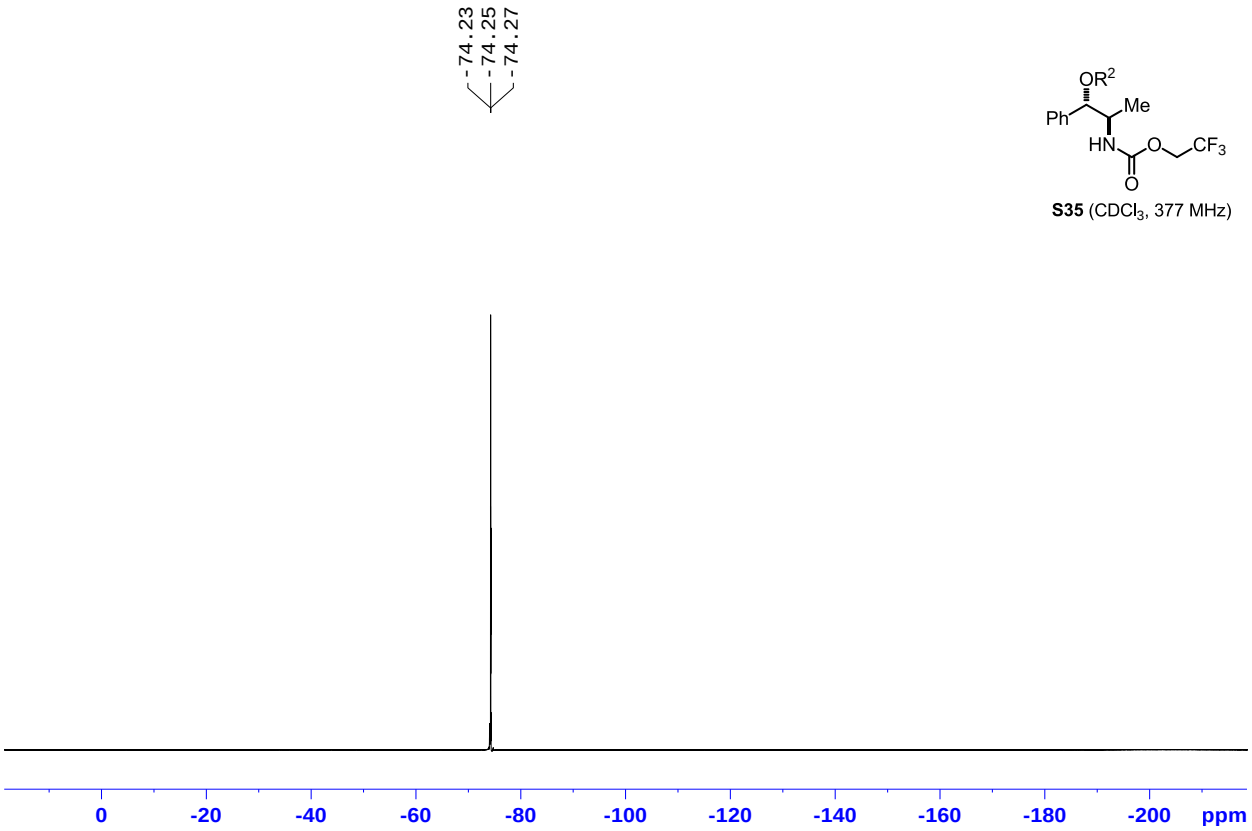
S34b ($CDCl_3$, 377 MHz)



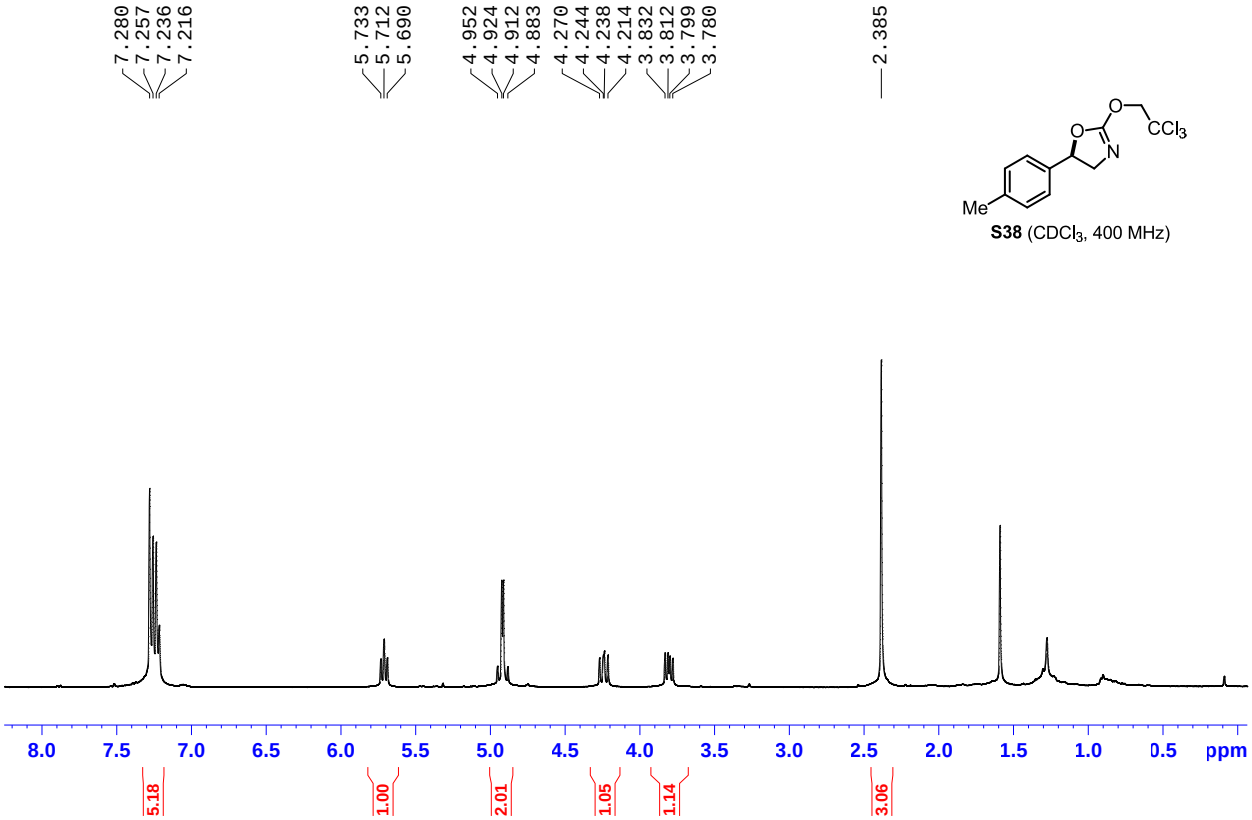
S35 ($CDCl_3$, 400 MHz)



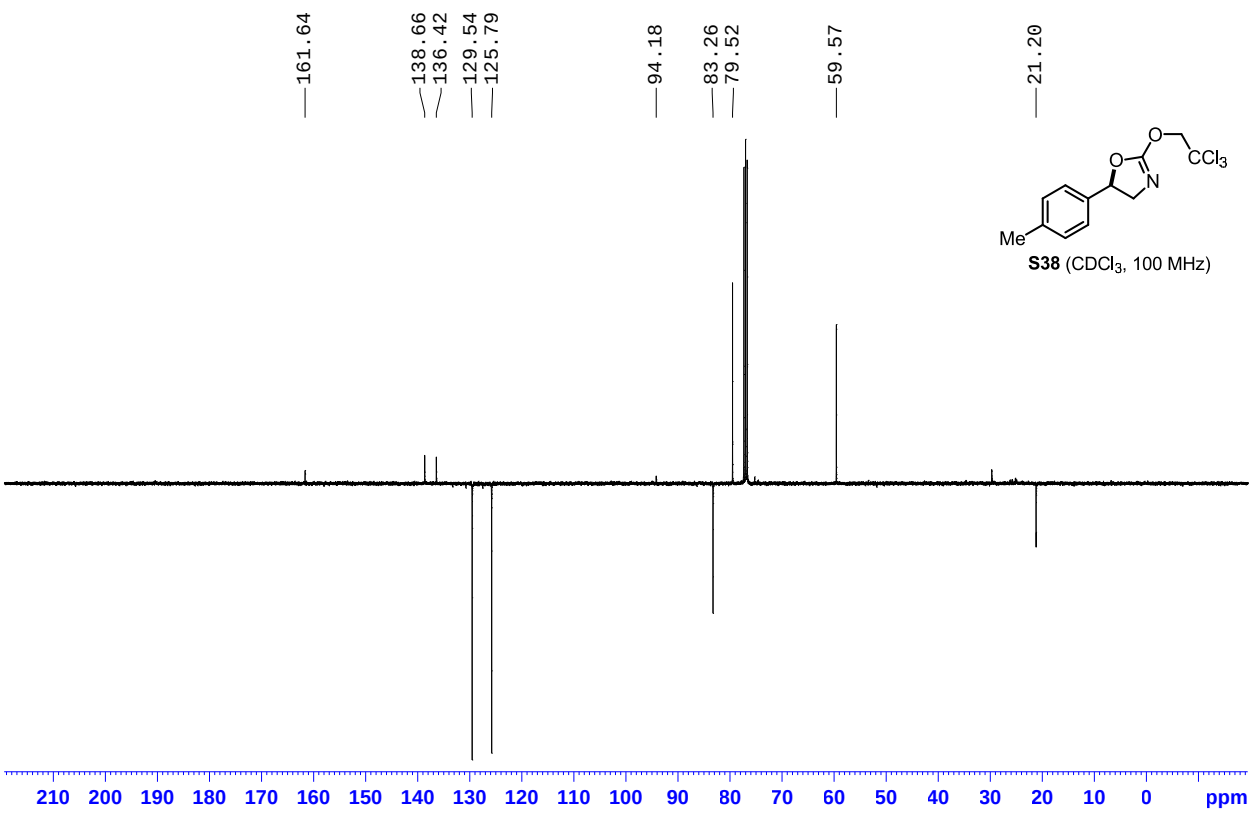
S35 ($CDCl_3$, 100 MHz)



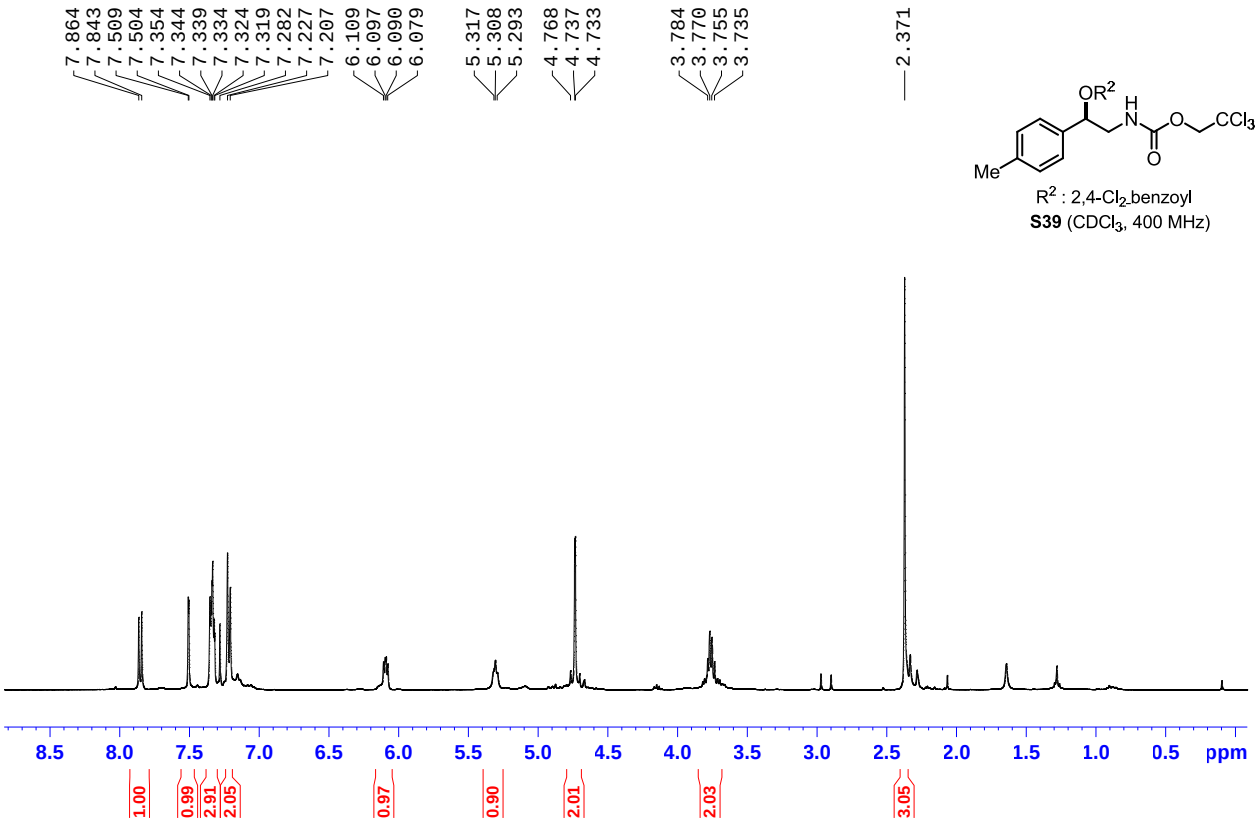
S35 ($CDCl_3$, 377 MHz)

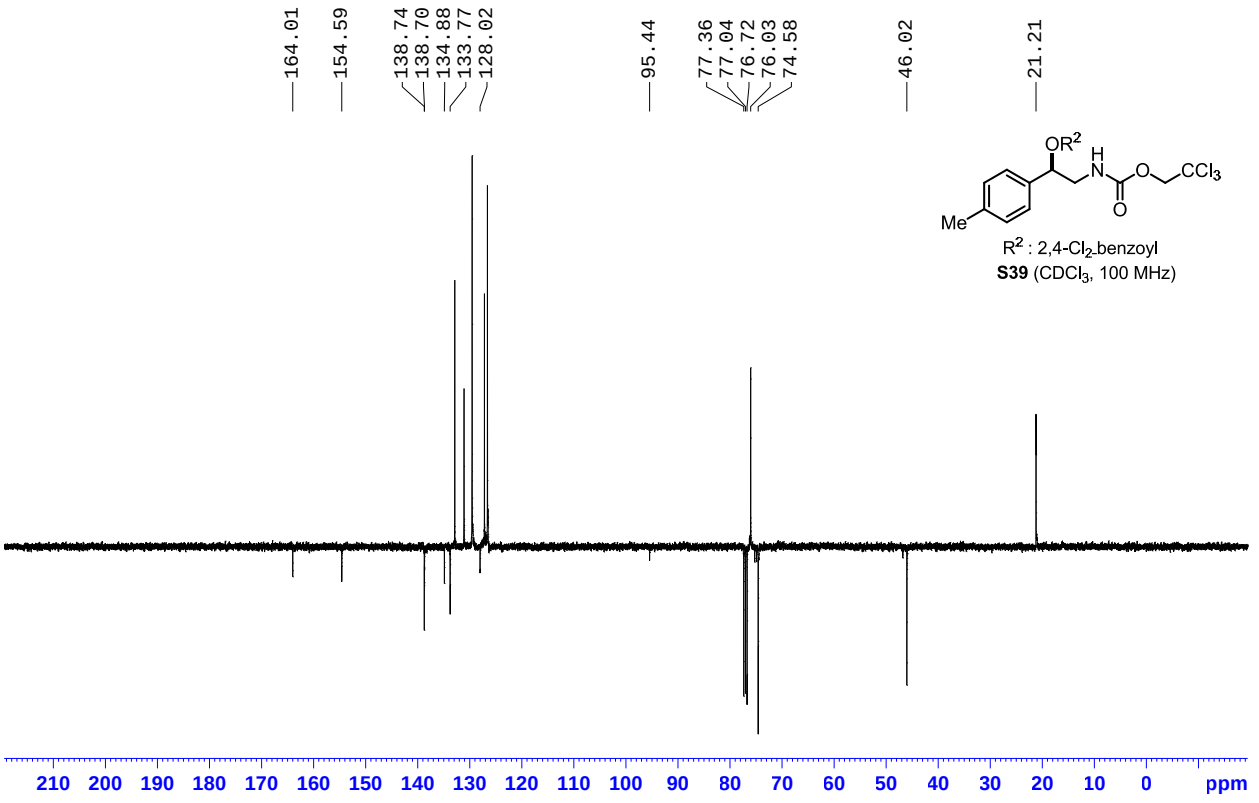


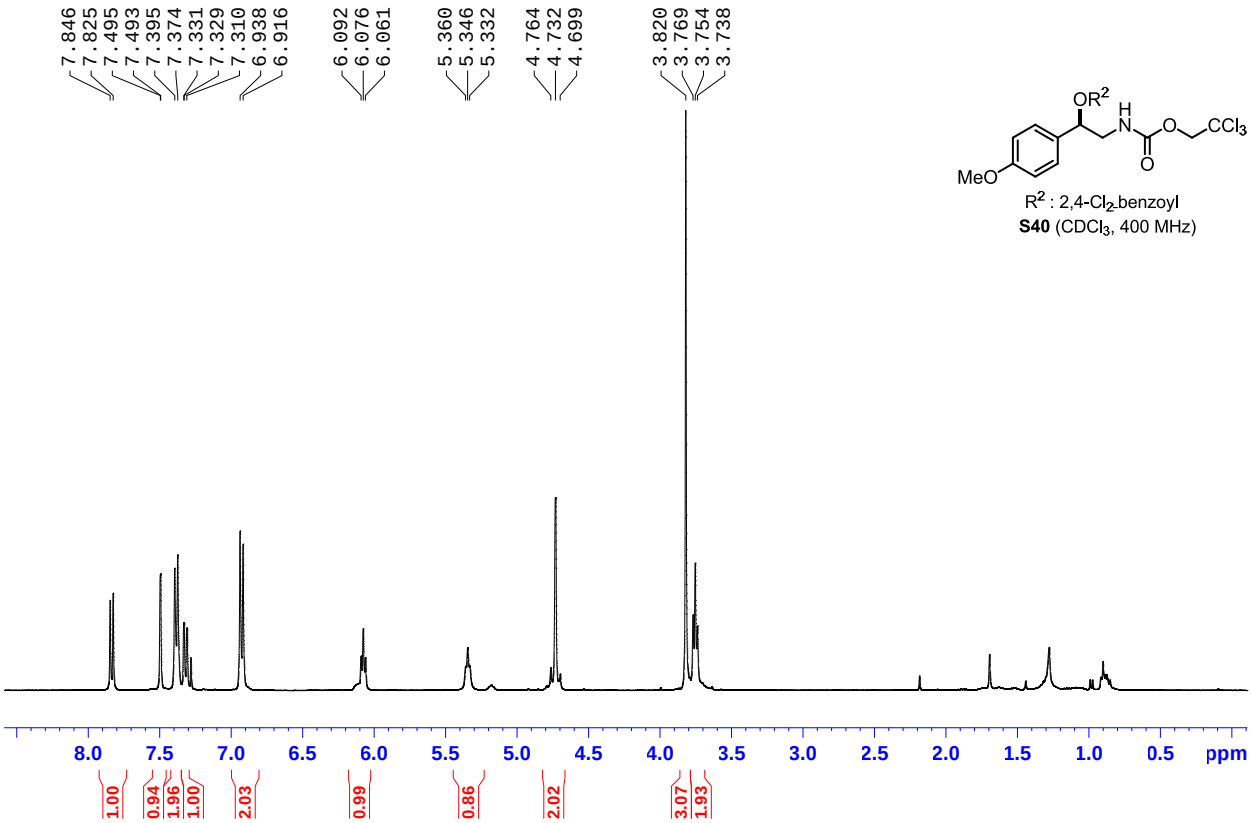
S38 ($CDCl_3$, 400 MHz)

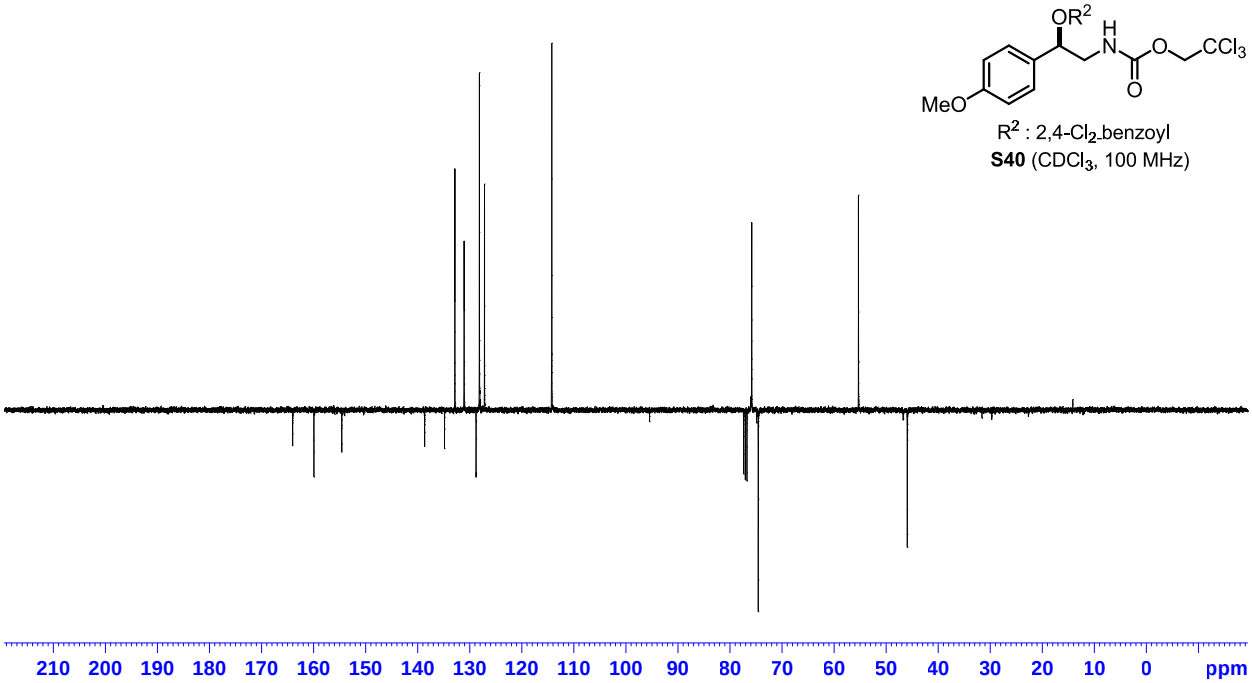


S38 ($CDCl_3$, 100 MHz)


7.864
7.843
7.509
7.504
7.354
7.344
7.339
7.334
7.324
7.319
7.282
7.227
7.207
6.109
6.097
6.090
6.079
5.317
5.308
5.293
4.768
4.737
4.733
3.784
3.770
3.755
3.735
2.371
OR2
H
N
O
O
CCl3
Me
R2 : 2,4-Cl2-benzoyl
S39 (CDCl3, 400 MHz)
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
ppm
1.00
0.99
2.91
2.05
0.97
0.90
2.01
2.03
3.05


164.01
154.59
138.74
138.70
134.88
133.77
128.02
95.44
77.36
77.04
76.72
76.03
74.58
46.02
21.21
OR2
H
N
O
O
CCl3
Me
R2 : 2,4-Cl2-benzoyl
S39 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.846
7.825
7.495
7.493
7.395
7.374
7.331
7.329
7.310
6.938
6.916
6.092
6.076
6.061
5.360
5.346
5.332
4.764
4.732
4.699
3.820
3.769
3.754
3.738
OR2
H
N
O
O
CCl3
MeO
O
R2 : 2,4-Cl2-benzoyl
S40 (CDCl3, 400 MHz)
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
ppm
1.00
0.94
1.96
1.00
2.03
0.99
0.86
2.02
3.07
1.93


164.03
159.94
154.59
138.68
134.85
132.86
131.08
128.79
128.15
127.17
114.23
95.45
77.38
77.06
76.74
75.83
74.57
55.32
45.94
OR2
H
N
O
O
CCl3
MeO
O
R2 : 2,4-Cl2-benzoyl
S40 (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm