Electronic Supplementary Information for:

A C-to-O atom-swapping reaction sequence enabled by Ni-catalyzed decarbonylation of lactones

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1. Materials and Methods

Room temperature is defined as 23 °C. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Acetonitrile, *N*,*N*-dimethylformamide, dichloromethane, tetrahydrofuran, diethyl ether and toluene were obtained from a 800L Solvent Purification System by Pure Process Technology, in which the solvent was dried over alumina and dispensed under an atmosphere of Ar. Where indicated, experiments were carried out in a nitrogen-filled mBraun glovebox. All other solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Rotary evaporation was carried out at 40 °C.

Routine ^{1}H NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers at ambient temperature unless otherwise stated. All NMR solvents were purchased from Cambridge Isotope Laboratories and used without further purification. Methanol-d_4, Chloroform-d_3, and dichloromethane-d_2, were stored at ambient temperature. Spectra were processed using MestReNova 14.0.1 using the automatic phasing and polynomial baseline correction capabilities. Splitting was determined using the automatic multiplet analysis function with manual intervention as necessary. Spectral data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplet of doublets (dtd), doublet of doublet of doublet of doublets (dddd), doublet of triplets (dt), triplet of doublets (td), etc.], coupling constant, integration). Chemical shifts are reported in ppm (δ), and coupling constants are reported in Hz. ^{1}H Resonances are referenced to solvent residual peaks for CD_3OD (3.31 ppm), $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), and CD_2Cl_2 (5.32 ppm). ^{13}C Resonances are referenced to solvent residual peaks for CD_3OD (49.00 ppm), $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), and CD_2Cl_2 (53.84 ppm). Note: Small deviations in chemical shifts may be observed depending on the concentration of NMR samples.

Analytical thin-layer chromatography was performed using 60 Å Silica Gel F_{254} pre-coated plates (0.25 mm thickness). TLC plates were visualized by irradiation with a UV lamp. Normal-phase column chromatography was performed using 60 Å Silica Gel (32–62 micron) with an appropriate mobile phase composition and gradient. Automated column chromatography was performed using a CombiFlash NextGen 300+ System by Teledyne ISCO on RediSep Rf Gold silica gel columns or RediSep Rf disposable flash columns. Positive (and/or negative) ion mode mass spectra were obtained using the Agilent (Santa Clara, CA) mass spectrometer. Agilent LC 1200 series system, equipped with Agilent autosampler was used. 1 µl of sample (concentration of approximately 10 ppm) was injected into the JetStream ESI ion source. Water/MeOH (0.1% Formic acid) 50/50 was used as effluent solvent. The mass range was kept constant from 100 to 1000 amu. The instrument was operated in the 4GHz HRes mode. Accurate mass measurement was achieved by constantly infusing a calibrant (masses: 121.0508 and 922.0098). In some cases, mass spectrometry was performed using the Agilent 7250 GC Q-TOF MSMS with FID detector. Infrared spectra were recorded on a Bruker Tensor 37 ATR/FT-IR spectrometer, and ν_{max} are reported in cm^{-1}.

2. Abbreviations

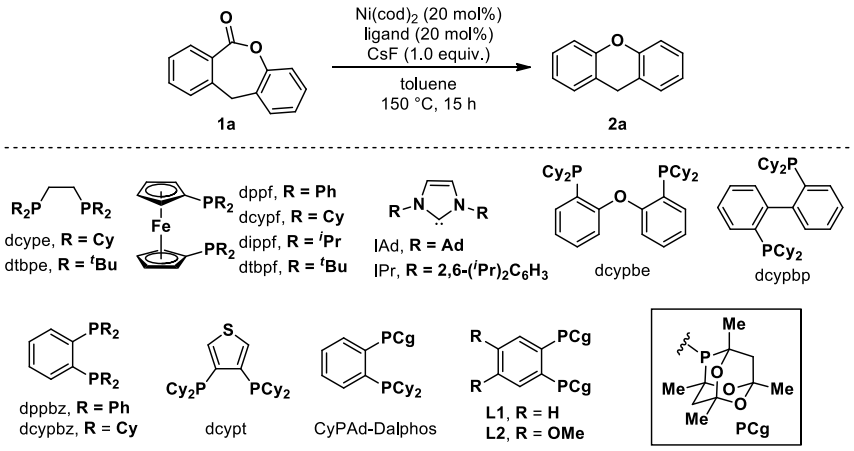
BnBr	Benzyl bromide
BrettPhos	2-Dicyclohexylphosphino-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl (CAS # 1070663-78-3)
MOMCl	Chloromethyl methyl ether
cod	Cyclooctadiene
Cy	Cyclohexyl
DCC	Dicyclohexylcarbodiimide
DCM	Dichloromethane
DIC	Diisopropylcarbodiimide
DMAP	4-(Dimethylamino)pyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethylsulfoxide
Et	Ethyl
EtOAc	Ethyl acetate
HRMS	High-resolution mass spectrometry
Hx	Hexanes
*i*Pr	Isopropyl
IR	Infrared
MeCN	Acetonitrile
mCPBA	*meta*-Chloroperoxybenzoic acid
MTBE	Methyl *tert*-butyl ether
NMR	Nuclear magnetic resonance
PCg	tetramethylphosphatrioxaadamantyl
Rac	racemic
rt	Room temperature
RuPhos	2-Dicyclohexylphosphino-2’,6’-diisopropoxybiphenyl (CAS # 787618-22-8)
SPhos	2-Dicyclohexylphosphino-2’,6’-dimethoxybiphenyl (CAS # 657408-07-6)
*t*Bu	*tert*-Butyl
*t*BuOH	*tert*-Butyl alcohol
TFA	Trifluoroacetic acid, trifluoroacetate
THF	Tetrahydrofuran
TLC	Thin-layer chromatography
Tosyl/Ts	*p*-Toluenesulfonyl
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (CAS # 161265-03-8)

3. Experimental procedures for additional optimization studies

3.1. Ligand screen (Table S1)

A 2-dram vial was charged with a magnetic stir bar, **1a** (0.0110 g, 0.050 mmol), and a ligand (see Figure 4 in the main text). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give **2a** as a white solid.

Table S1. Ligand screen.

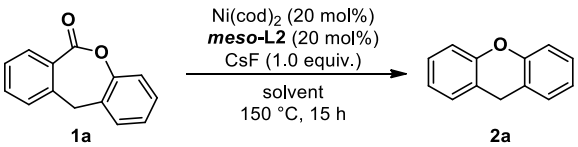


Entry	Ligand	Isolated yield (%)	Entry	Ligand	Isolated yield (%)
1	dcype	0	10	dcypbp	0
2	dtbpe	0	11	dppbz	0
3	dppf	0	12	dcypbz	29
4	dcypf	0	13	dcypt	25
5	dippf	0	14	Dalphos	22
6	dtbpf	0	15	***rac*-L1**	21
7	IAd	0	16	***meso*-L1**	60
8	IPr·HCl	0	17	***rac*-L2**	28
9	dcypbe	0	18	***meso*-L2**	80

3.2. Solvent screen (Table S2)

A 2-dram vial was charged with a magnetic stir bar, **1a** (11.0 mg, 0.050 mmol), ***meso*-L2** (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and a solvent (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give **2a** as a white solid.

Table S2. Solvent screen.

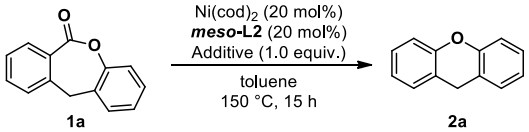


Entry	Solvent	isolated yield (%)
1	toluene	80
2	dioxane	<5
3	DMF	0
4	DMSO	0

3.3. Additive screen (Table S3)

A 2-dram vial was charged with a magnetic stir bar, **1a** (11.0 mg, 0.050 mmol), ***meso*-L2** (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), an additive (see **Table S3**, 0-1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give **2a** as a white solid.

Table S3. Additive screen.

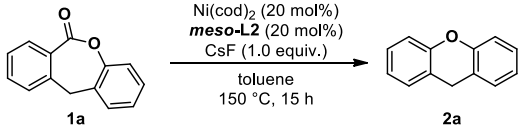


Entry	Additive	isolated yield (%)
1	CsF	80
2	KF	54
3	Cs_2CO_3	34
4	K_3PO_4	12
5	No additive	74

3.4. Reaction concentration screen (Table S4)

A 2-dram vial was charged with a magnetic stir bar, **1a** (11.0 mg, 0.050 mmol), ***meso*-L2** (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.25, 0.50, 0.70, 0.80, or 1.0 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 15 h. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give **2a** as a white solid.

Table S4. Concentration screen. The yields shown are averages of two runs.

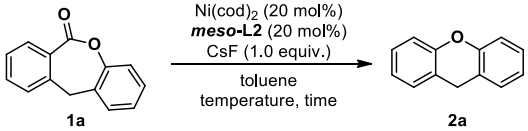


Entry	Toluene (mL)	Concentration (M)	isolated yield (%)
1	0.50	0.10	80
2	0.70	0.071	31
3	0.80	0.063	15
4	1.00	0.050	14

3.5. Temperature and reaction time screen (Table S5)

A 2-dram vial was charged with a magnetic stir bar, **1a** (0.0110 g, 0.050 mmol), ***meso*-L2** (0.0057 g, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 120, 130, 140, or 150 °C as indicated in Table S4. The mixture was stirred for a certain time (4 h, 15 h, 24 h, or 48 h) as indicated in Table S4. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (0.5 × 3.0 cm). The column was eluted with hexanes (5.0 mL) and the product containing fractions were collected. The solvent was then removed using rotary evaporator and high-vacuum oil pump to give **2a** as a white solid.

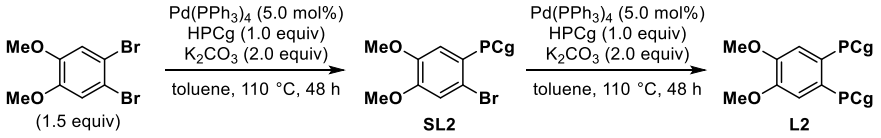
Table S5. Temperature and reaction time screen.

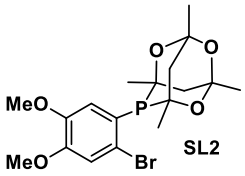


Entry	Temperature (°C)	Time (h)	isolated yield (%)	Entry	Temperature (°C)	Time (h)	isolated yield (%)
1	150	15	80	4	120	15	11
2	140	15	40	5	150	5	63
3	130	15	54	6	150	24	99

4. Synthesis and characterization data for ligands in Figure 4

Ligands ***rac***- and ***meso*-L1** were synthesized according to a literature procedure.[1] Ligands ***rac***- and ***meso*-L2** were synthesized in a similar manner as described below.

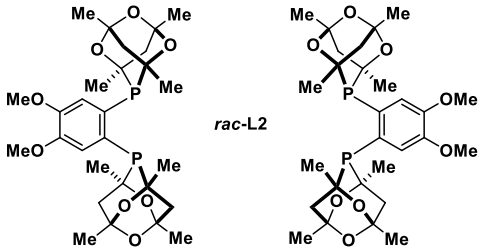




4-(tetramethylphosphatrioxaadamantyl)-5-bromo-1,2-dimethoxybenzene (SL2): A 40-mL vial was charged with a magnetic stir-bar, 4,5-dibromo-1,2-dimethoxybenzene (2.23 g, 7.50 mmol, 1.5 equiv), and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv). The vial was brought inside a glovebox. The phosphine HPCg (32% solution in toluene, 3.38 g, 5.0 mmol, 1.0 equiv), the catalyst $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol, 5.0 mol%), and toluene (10 mL) were then added. The vial was sealed with a Teflon-lined cap, brought outside of the glovebox, and placed on an aluminum heating block preheated at 110 °C. The reaction mixture was stirred at 110 °C for 48 h and was cooled to room temperature. Dichloromethane (10 mL) and water (20 mL) were added. The mixture was then transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic fractions were dried with Na_2SO_4 and concentrated using rotary evaporator. The resulting red oil was chromatographed (silica gel column, 5 × 20 cm, packed in hexanes, eluted with hexanes/ethyl acetate 90/10) to give the product **SL2** as a white solid (1.45 g, 3.36 mmol, 67%).

TLC (90/10 hexanes/ethyl acetate): R_f = 0.20 (visualized by UV).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.07 (br s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.10 (dd, *J* = 13.3, 7.4 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.51 (dd, *J* = 13.5, 4.0 Hz, 1H), 1.47 (d, *J* = 12.5 Hz, 3H), 1.41 (m, 9H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.6, 148.1, 125.2 (d, *J* = 27.5 Hz), 124.0 (d, *J* = 35.2 Hz), 116.6, 116.2 (d, *J* = 4.4 Hz), 96.8, 95.9, 74.4 (d, *J* = 9.9 Hz), 73.8 (d, *J* = 23.7 Hz), 56.1, 56.0, 45.7 (d, *J* = 18.7 Hz), 36.5, 28.3 (d, *J* = 19.8 Hz), 28.2, 27.8, 26.8 (d, *J* = 11.0 Hz).
^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ –30.90.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3092 (w), 2987 (m), 2931 (m), 2839 (w), 1591 (m), 1562 (w), 1499 (s), 1470 (m), 1440 (m), 1375 (m), 1349 (m), 1316 (w), 1243 (s), 1211 (s), 1198 (s), 1181 (s), 1135 (m), 1082 (m), 1043 (w), 1030 (m), 974 (m), 958 (m), 899 (m), 866 (w), 833 (m), 787 (m), 695 (w), 662 (w),
HRMS: Exact mass calculated for $C_{18}H_{24}BrO_5P$ requires m/z = 430.0545, found m/z = 430.0542 (EI).

Ligand L2: A 20-mL vial was charged with a magnetic stir-bar, **SL2** (0.180 g, 0.42 mmol, 1.0 equiv), and K_2CO_3 (0.118 g, 0.84 mmol, 2.0 equiv). The vial was brought inside a glovebox. The phosphine HPCg (32% solution in toluene, 0.284 g, 0.42 mmol, 1.0 equiv), the catalyst $Pd(PPh_3)_4$ (0.030 g, 0.021 mmol, 5.0 mol%), and toluene (2.0 mL) was then added. The vial was sealed with a Teflon-lined cap, brought outside of the glovebox, and placed on an aluminum heating block preheated at 110 °C. The reaction mixture was stirred at 110 °C for 48 h and was then cooled to room temperature. Dichloromethane (5 mL) and water (10 mL) were added. The mixture was transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were dried with Na_2SO_4 and concentrated using rotary evaporator. The resulting red oil was chromatograph (silica gel column, 3 × 15 cm, packed in hexanes, eluted with hexanes/ethyl acetate 95/5) to give the products ***rac*-L2** (0.111 g, 0.20 mmol, 48%, R_f = 0.15 (90/10 hexanes/ethyl acetate)) and ***meso*-L2** (0.067 g, 0.12 mmol, 29%, R_f = 0.10 (90/10 hexanes/ethyl acetate)) as white solids. The stereochemical configurations of the ligands were assigned based on the order of elution as compared to ligands **L1**.[1] The stereochemical configuration of ligand ***meso*-L2** was further confirmed by an X-ray crystal structure of a nickel complex ***meso*-L2-Ni-2a** (see section 5.3).



TLC (90/10 hexanes/ethyl acetate): R_f = 0.15 (visualized by UV)

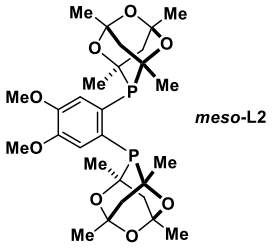
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (app t, *J* = 2.4 Hz, 2H), 3.89 (s, 6H), 2.12 (dt, *J* = 13.1, 3.5 Hz, 2H), 1.99 (d, *J* = 13.4 Hz, 2H), 1.95 (d, *J* = 13.2 Hz, 1H), 1.90 (d, *J* = 13.1 Hz, 1H), 1.46 – 1.34 (m, 26H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.1 (2C), 135.6 (d, *J* = 2.6 Hz, 2C), 116.2 (d, *J* = 2.3 Hz, 2C), 96.8 (2C), 95.8 (2C), 74.6 (2 × d, *J* = 6.3 Hz, 2C), 74.0 (d, *J* = 5.4 Hz), 73.9 (d, *J* = 5.0 Hz), 55.7 (2C), 46.1 (app t, *J* = 9.5 Hz, 2C), 36.3 (2C), 28.3 (2C), 27.70 (2C), 27.5 (app t, *J* = 11.8 Hz, 2C), 26.6 (app t, *J* = 5.4 Hz, 2C).

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ -41.20.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3128 (w), 3112 (w), 2983 (m), 2964 (m), 2931 (m), 2843 (w), 1585 (w), 1562 (m), 1503 (m), 1467 (m), 1441 (m), 1381 (m), 1349 (m), 1316 (m), 1260 (m), 1214 (s), 1188 (s), 1132 (s), 1089 (m), 1043 (m), 984 (s), 961 (m), 945 (w), 895 (s), 863 (m), 820 (w), 800 (m), 734 (w), 692 (m), 667 (w), 626 (w).

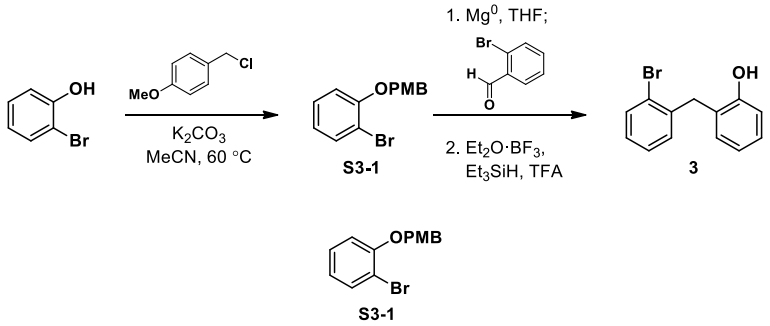
HRMS: Exact mass calculated for $[C_{28}H_{40}OP_2+H]^+$ requires m/z = 567.2271, found m/z = 567.2283. (ESI+).



TLC (90/10 hexanes/ethyl acetate): R_f = 0.10 (visualized by UV).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (t, *J* = 2.4 Hz, 2H), 3.90 (s, 6H), 2.26 (d, *J* = 13.5 Hz, 2H), 2.20 (dt, *J* = 13.1, 3.5 Hz, 2H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.89 (d, *J* = 13.1 Hz, 1H), 1.66 (dt, *J* = 13.6, 2.2 Hz, 2H), 1.45 (s, 6H), 1.38 (s, 6H), 1.32 (t, *J* = 6.3 Hz, 6H), 1.27 – 1.18 (m, 6H).
^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ -42.06.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.4, 136.5, 116.8, 97.2, 95.9, 75.63 – 74.01 (m, 2C), 55.8, 46.1 (t, *J* = 9.4 Hz), 37.2, 29.5 (t, *J* = 10.5 Hz), 28.6, 27.8, 26.6 (t, *J* = 5.2 Hz).
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3141 (w), 3119 (w), 2997 (m), 2964 (m), 2934 (m), 2915 (m), 2836 (w), 1585 (w), 1562 (w), 1496 (m), 1463 (m), 1440 (m), 1372 (m), 1345 9m), 1312 (m), 1260 (m), 1214 (s), 1191 (s), 1138 (m), 1083 (m), 1066 (w), 1036 (m), 981 (s), 961 (m), 941 (w), 892 (s), 849 (m), 826 (w), 790 (m), 744 (w), 685 (w), 665 (w), 629 (w).
HRMS: Exact mass calculated for $[C_{28}H_{40}OP_2+H]^+$ requires m/z = 567.2271, found m/z = 567.2286. (ESI+).

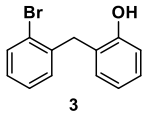
5. Experimental procedures and characterization data for compounds in Figure 3, 5, and 6

5.1. Synthesis of compound 3



1-bromo-2-((4-methoxybenzyl)oxy)benzene (S3-1): An oven-dried 100 mL Shclenk flask was charged with a stir bar, evacuated and back-filled with N_2 (× 3). 2-bromophenol (2.00 mL, 18.94 mmol, 1 equiv.) was added by syringe, followed by MeCN (35 mL). K_2CO_3 (5.44 g, 39.34 mmol, 2.08 equiv.) was added as a solid. Under vigorous stirring, PMB-Cl (3.2 mL, 23.60 mmol, 1.25 equiv.) via syringe. The reaction was heated in a 60 °C oil bath for 14 h. After cooling to RT, the reaction was quenched with 1:1 brine/H_2O (50 mL) and transferred to a separatory funnel with EtOAc (20 mL). After phase separation, the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organics were washed with brine, dried over Na_2SO_4, filtered, and concentrated with a rotary evaporator. The crude product was washed with hexanes (30 mL). The white solids were isolated by vacuum filtration, washed with hexanes (2 × 20 mL), and dried under high vacuum to give the pure product (5.13 g, 89%) as a white solid. This solid was used immediately for the next reaction.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.44-7.37 (m, 2H), 7.23 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 6.97-6.90 (m, 3H), 6.84 (ddd, *J* = 7.9, 7.4, 1.4 Hz, 1H), 5.09 (s, 2H), 3.82 (s, 3H).

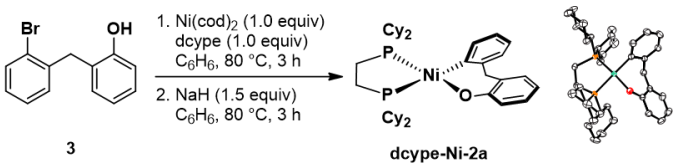


3

2-(2-bromobenzyl)phenol (3): A 3-neck round bottom flask, equipped with a reflux condenser, was charged with a stir bar, Mg turnings (0.629 g, 26.4 mmol, 1.5 equiv), and compound **S3-1** (5.14 g, 17.5 mmol, 1.0 equiv). The flask was evacuated and put under a N_2 atmosphere. THF (40 mL) was added, and the mixture was heated at 40 °C with vigorous stirring for 2 h. The mixture was then cooled to room temperature.
A Schlenk flask was charged with a stir bar, 2-bromobenzaldehyde (1.36 mL, 2.16 g, 11.7 mmol), and THF (40 mL) under a N_2 atmosphere. The solution was cooled to 0 °C in an ice bath. The Grignard reagent was then cannulated in a dropwise manner from the 3-neck round bottom flask to the Schlenk flask at 0 °C with stirring. After finishing addition, the mixture was warmed to room temperature and stirred for 12 h, and then quenched with water (10 mL). The mixture was transferred to a separatory funnel, then ethyl acetate (100 mL) and water (100 mL) were added. The organic layer was collected, and the aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic fractions were dried with Na_2SO_4 and concentrated by rotary evaporator to dryness to give a yellow solid. The yellow solid was dissolved in dichloromethane (14 mL). Triethylsilane (6.16 mL, 4.48 g, 39 mmol, 3.3 equiv) and $Et_2O{\cdot}BF_3$ (4.76 mL) were then added at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h and another 2.0 equiv of Et_3SiH (3.74 mL, 2.72 g, 23.4 mmol) was added followed by 1.0 mL of TFA. The solution was stirred for another 1.5 h at 0 °C and was warmed to room temperature. The reaction was quenched with 100 mL of a saturated aqueous NH_4Cl solution. The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were dried with Na_2SO_4, and the solvent was removed by rotary evaporator. The yellow residue was chromatographed (silica gel, 5 × 20 cm column, packed in hexanes, eluted with 95/5 hexanes/ethyl acetate) to give compound **3** as a colorless oil (1.27 g, 4.83 mmol, 41%). NMR data of **3** match with previously reported values.[2]

TLC (90/10 hexanes/ethyl acetate): R_f = 0.50 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.05 (m, 3H), 6.91 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.85 (br s, 1H), 4.11 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.7, 139.4, 132.9, 131.1, 130.8, 128.1 (2 × s), 127.7, 125.6, 125.0, 121.2, 115.7, 36.2.

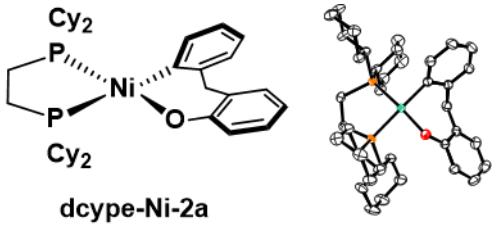
5.2. Synthesis of dcype-Ni-2a from 3



3 dcype-Ni-2a

A 20-mL vial was charged with a stir bar and **3** (0.066 g, 0.25 mmol). The vial was brought inside a glove box. The ligand dcype (0.110 g, 0.25 mmol), $Ni(cod)_2$ (0.070 g, 0.25 mmol), and benzene (5.0 mL) were then added. The vial was sealed, brought outside the glovebox, and placed in an aluminum heating block preheated at 80 °C. After 3 h, the vial was brought back inside the glovebox and NaH (0.0090 g, 0.38 mmol, 1.5 equiv) was added. The vial was sealed and was brought outside to heat again at 80 °C. After 3 h, the vial was brought back inside the glovebox and the mixture was filtered through a syringe filter. Pentane (5.0 mL) was added to the red filtrate and the resulting solution was let sit at room temperature in the glovebox. After 24 h, the orange crystals formed were collected and washed with pentane (5.0 mL). A specimen of the crystals was used for X-ray crystallographic analysis. The remaining were dried under vacuum for 5 h to give **dcype-Ni-2a·C_6H_6** (0.0611 g, 0.0825 mmol, 33%). Crystallographic parameters for **dcype-Ni-2a·C_6H_6** are provided below and are available free of charge from the Cambridge Crystallographic Data Center, CCDC 2116182.

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.35 (s, 6H, benzene), 7.02 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.83-6.66 (m, 3H), 6.36 (d, *J* = 7.9 Hz, 1H), 6.23 (t, *J* = 7.1 Hz, 1H), 5.99 (d, *J* = 12.2 Hz, 1H), 3.63 (d, *J* = 12.2 Hz, 1H), 3.19 (br s, 1H), 2.47 (d, *J* = 10.5 Hz, 2H), 2.26 (d, *J* = 8.1 Hz, 2H), 2.05 – 0.80 (multiple overlapping signals, 44H). The region 2.05 – 0.80 ppm may contain residual pentane and grease, leading to larger than expected integral values.
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 164.0, 151.0, 150.4, 135.8, 128.7 (benzene), 128.6, 128.1, 127.6, 124.5 (m), 123.6, 121.1 (2 × s), 112.2, 44.8, 36.5-25.0 (multiple overlapping signals for dcype).
^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2) δ 62.77 (d, *J* = 14.3 Hz), 55.77 (d, *J* = 14.3 Hz).
X-ray crystallographic data



dcype-Ni-2a

An orange block-like specimen of the crystals, approximate dimensions 0.020 mm × 0.080 mm × 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE diffractometer system equipped with a microfocus sealed tube (Cu Kα, λ = 1.54178 Å) and a multilayer mirror monochromator. The total exposure time was 4.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32358 reflections to a maximum θ angle of 66.65 (0.84 Å resolution), of which 7167 were independent (average redundancy 4.515, completeness = 100.0%, R_{int} = 5.75%, R_{sig} = 5.51%) and 6927

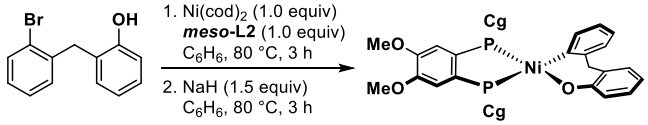
(96.65%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0475(15) Å, b = 18.2763(14) Å, c = 12.7484(11) Å, β = 105.437(9), volume = 2032.0(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9957 reflections above 20 σ(I) with $8.672 < 2\theta < 133.1$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.827. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8250 and 0.9670. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with Z = 2 for the formula unit, $C_{45}H_{64}NiOP_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 437 variables converged at R1 = 3.50%, for the observed data and wR2 = 8.01% for all data. The goodness-of-fit was 1.130. The largest peak in the final difference electron density synthesis was 0.621 $e^-/Å^3$ and the largest hole was –0.372$e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.212 g/cm^3 and F(000), 800 e^-. Additional details are provided in Table S6.

Table S6. Crystal and structural data for dcype-Ni-2a·C_6H_6

Chemical formula	$C_{45}H_{64}NiOP_2$
Formula weight	741.61 g/mol
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal size	0.020 × 0.080 × 0.120 mm
Crystal habit	orange block
Crystal system	monoclinic
Space group	P 1 2_1 1
Unit cell dimensions	a = 9.0475(15) Å α = 90°
	b = 18.2763(14) Å β = 105.437(9)°
	c = 12.7484(11) Å γ = 90°
Volume	2032.0(4) $Å^3$
Z	2
Density (calculated)	1.212 g/cm^3
Absorption coefficient	1.665 mm^{-1}
F(000)	800
Diffractometer	Bruker D8 VENTURE diffractometer
Radiation source	sealed tube microfocus sealed tube (Cu Kα, λ = 1.54178 Å)
Theta range for data collection	3.60 to 66.65°
Index ranges	-10<=h<=10, -21<=k<=21, -15<=l<=15
Reflections collected	32358
Independent reflections	7167 [R(int) = 0.0575]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9670 and 0.8250
Structure solution technique	direct methods

Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	7167 / 1 / 437	
Goodness-of-fit on F2	1.130	
Δ/σmax	0.002	
Final R indices	6927 data; I>2σ(I)	R1 = 0.0350, wR2 = 0.0793
	all data	R1 = 0.0363, wR2 = 0.0801
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0420P)^2+0.0200P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.002(10)	
Largest diff. peak and hole	0.621 and -0.372 eÅ^{-3}	
R.M.S. deviation from mean	0.054 eÅ^{-3}	

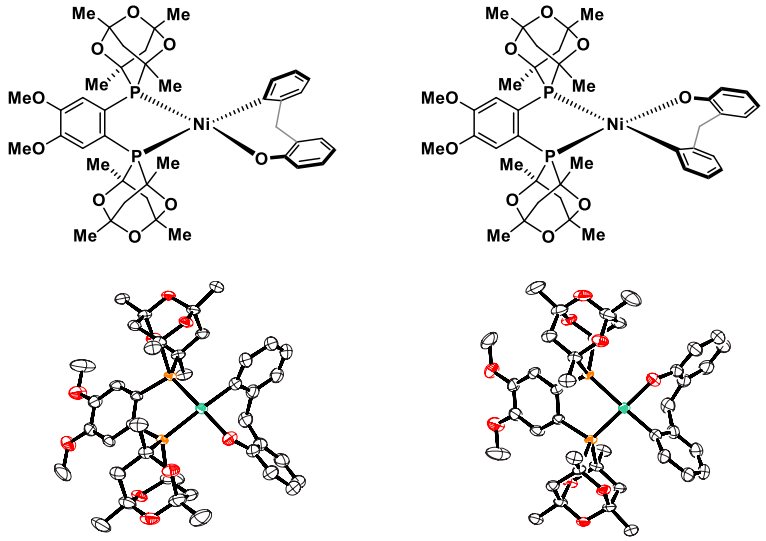
5.3. Synthesis of *meso*-L2-Ni-2a from 3



3 *meso*-L2-Ni-2a

A 20-mL vial was charged with a stir bar and **3** (0.066 g, 0.25 mmol). The vial was brought inside a glove box. The ligand ***meso*-L2** (0.140 g, 0.25 mmol), $Ni(cod)_2$ (0.070 g, 0.25 mmol), and benzene (5.0 mL) were then added. The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. After 3 h, the vial was brought back inside the glovebox and NaH (0.0090 g, 0.38 mmol, 1.5 equiv) was added. The vial was sealed and was brought outside to heat again at 80 °C. After 3 h, the vial was brought back inside the glovebox and the mixture was filtered through a syringe filter. Pentane (5.0 mL) was added to the red filtrate and the resulting solution was let sit at room temperature in the glovebox. After 24 h, the orange crystals formed were collected and washed with pentane (5.0 mL). A specimen of the crystals was used for X-ray crystallographic analysis and showed two isomers in the unit cell. Crystallographic parameters for ***meso*-L2-Ni-2a·C$_6$H$_6$** are provided below and are available free of charge from the Cambridge Crystallographic Data Center, CCDC 2116181. The remaining were dried under vacuum for 5 h to give ***meso*-L2-Ni-2a·C$_6$H$_6$** (0.0908 g, 0.103 mmol, 41%). ^{13}C and ^{1}H NMR of the crystals gave complex spectra of the two isomers. Therefore, no meaningful analyses were possible. Attempts to separate the isomers by fractional recrystallization in benzene/pentane were not successful. ^{31}P NMR spectrum gave two sets of signals (2 doublets each) for the isomers.
^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2) δ 25.23 (d, *J* = 9.5 Hz), 21.97 (d, *J* = 11.9 Hz), 2.86 (d, *J* = 14.3 Hz), 2.79 (d, *J* = 9.5 Hz).

X-ray crystallographic data



An orange block-like specimen of the crystals, approximate dimension 0.100 mm × 0.160 mm × 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 VENTURE diffractometer system equipped with a microfocus sealed tube (Cu Kα, λ = 1.54178 Å) and a multilayer mirror monochromator. The total exposure time was 3.71 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 57746 reflections to a maximum θ angle of 63.30 (0.86 Å resolution), of which 7735 were independent (average redundancy 7.466, completeness = 99.8%, R_{int} = 5.99%, R_{sig} = 3.66%) and 7224 (93.39%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.239(4) Å, b = 20.228(3) Å, c = 19.483(2) Å, β = 99.971(10), volume = 4750.6(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 9471 reflections above 20 σ(I) with 6.372 < 2θ < 133.1. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.750. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7540 and 0.8510. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{50}H_{59}NiO_9P_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 557 variables converged at R1 = 6.51%, for the observed data and wR2 = 18.18% for all data. The goodness-of-fit was 1.109. The largest peak in the final difference electron density synthesis was 2.020 $e^-/Å^3$ and the largest hole was –0.913 $e^-/Å^3$ with an RMS deviation of 0.078 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.293 g/cm^3 and F(000), 1956 e^-. Additional details are provided in Table S7.

Table S7. Crystal and structural data for *meso*-L2-Ni-2a·C_6H_6

Chemical formula	$C_{50}H_{59}NiO_9P_2$
Formula weight	924.62 g/mol
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal size	0.100 x 0.160 x 0.180 mm
Crystal habit	orange block
Crystal system	monoclinic

Space group	P 1 2_1/c 1	
Unit cell dimensions	a = 12.239(4) Å	α = 90°
	b = 20.228(3) Å	β = 99.971(10)°
	c = 19.483(2) Å	γ = 90°
Volume	4750.6(18) $Å^3$	
Z	4	
Density (calculated)	1.293 g/cm^3	
Absorption coefficient	1.666 mm^{-1}	
F(000)	1956	
Diffractometer	Bruker D8 VENTURE diffractometer	
Radiation source	sealed tube microfocus sealed tube (Cu Kα, λ = 1.54178 Å)	
Theta range for data collection	3.17 to 63.30°	
Index ranges	-14<=h<=14, -23<=k<=23, -22<=l<=22	
Reflections collected	57746	
Independent reflections	7735 [R(int) = 0.0599]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8510 and 0.7540	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	7735 / 543 / 557	
Goodness-of-fit on F2	1.109	
Δ/σmax	0.001	
Final R indices	7224 data; I>2σ(I)	R1 = 0.0651, wR2 = 0.1787
	all data	R1 = 0.0686, wR2 = 0.1818
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0900P)^2+9.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.020 and -0.913 $eÅ^{-3}$	
R.M.S. deviation from mean	0.078 $eÅ^{-3}$	

5.4. Stoichiometric experiments with dcype (Figure 3)

Stoichiometric experiment with dcype and 1a (Figure 3A): In a glove box, a 2-dram vial was charged with a stir bar, the ligand dcype (11.0 mg, 0.025 mmol), $Ni(cod)_2$ (7.0 mg, 0.025 mmol), and C_6D_6 (0.50 mL). The mixture was stirred at room temperature for 10 min then the lactone **1a** (5.5 mg, 0.025 mmol) was added. The vial was sealed and brought outside to place on a heating block preheated at 80 °C. After stirring for 3 h, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. The NMR tube was sealed then a ^{31}P NMR spectrum was acquired (Figure S1-B). The main signals matched with **dcype-Ni-2a** (Figure S1-A), and **dcype-Ni(CO)$_2$**. The ^{31}P signal of **dcype-Ni(CO)$_2$** at 64.00 ppm was assigned based on previously reported values.[3] The NMR tube was brought back inside the glovebox and the NMR solution was transferred back to the vial and the mixture was heated further at 150 °C for 3 h on a heating block. After cooling to room temperature, the vial was brought back inside the glovebox and the solution was transferred to another NMR tube. A ^{31}P NMR spectrum was acquired again (Figure S1-C). The signals for the complex **dcype-Ni(CO)$_2$** disappeared. A singlet appeared at 82.2 ppm, corresponding to an unknown species.

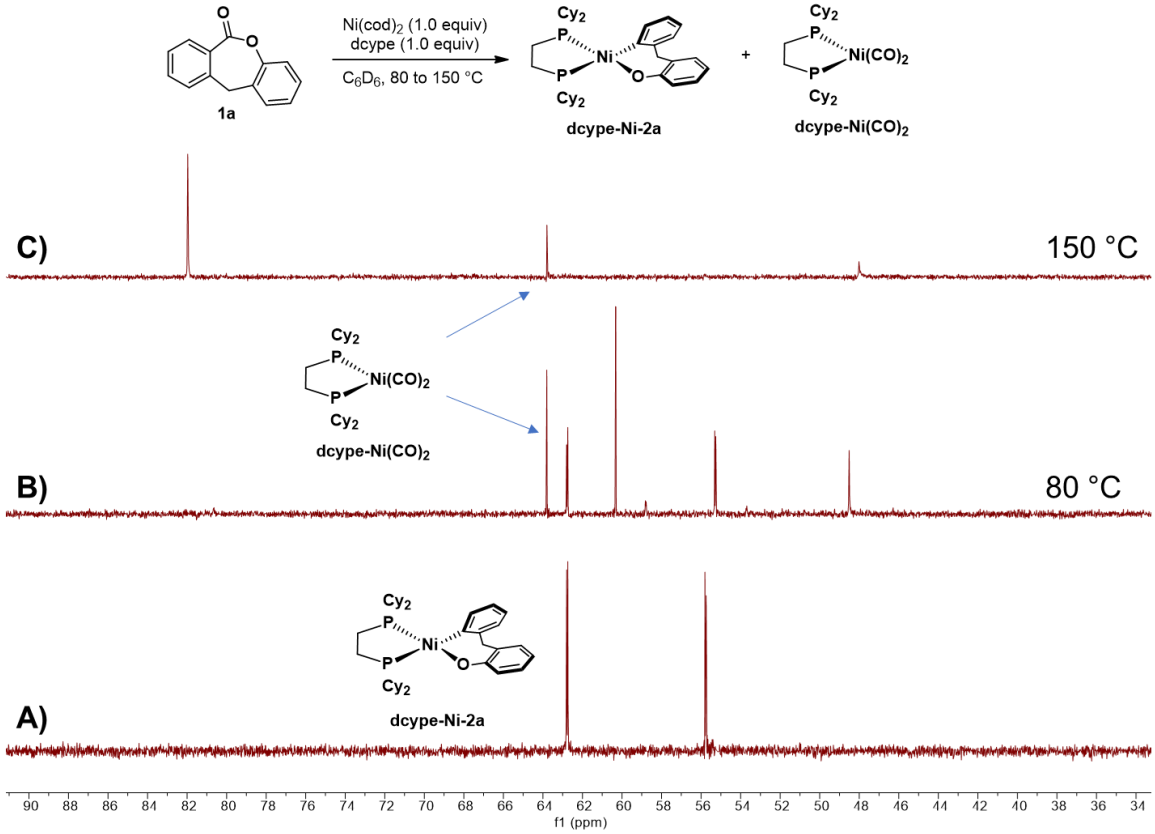


Figure S1. $^{31}P\{^1H\}$ NMR (253 MHz, C_6D_6) of A) **dcype-Ni-2a**, B) stoichiometric reaction at 80 °C, and C) stoichiometric reaction at 150 °C (top).

Stoichiometric reductive elimination test with dcype-Ni-2a (Figure 3B): In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, **dcype-Ni-2a** (0.037 g, 0.050 mmol), and toluene (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 150 °C. The reaction was stirred at 150 °C for 3 h. After cooling to room temperature,

the reaction was analyzed by TLC (100% hexanes). No product spot was observed under UV. The reaction was then concentrated by rotary evaporator and $CDCl_3$ (0.50 mL) was added. The black solids were removed by syringe filter. A ^1H NMR spectrum was then acquired for the filtrate and showed no signals corresponding to the product **2a** or the complex **dcype-Ni-2a**.

5.5. Stoichiometric experiments with *meso*-L2 (Figure 5):

Stoichiometric experiment with *meso*-L2 and 1a: In a glovebox, a 2-dram vial was charged with a stir bar, the ligand ***meso*-L2** (0.014 g, 0.025 mmol), $Ni(cod)_2$ (0.0070 g, 0.025 mmol), and C_6D_6 (0.50 mL). The mixture was stirred at room temperature for 10 min then the lactone **1a** (0.0055 g, 0.025 mmol) was added. The vial was sealed and brought outside to place on a heating block preheated at 110 °C. After stirring for 3 h, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. The NMR tube was sealed then ^1H and ^{31}P NMR spectra were acquired (Figure S2-A and S3-A). The main signals were lactone **1a**. In the glovebox, the solution in the NMR tube was transferred back to the vial and the mixture was heated further at 120 °C for 3 h on a heating block. After cooling to room temperature, the vial was brought back inside the glovebox and the solution was transferred to an NMR tube. ^1H and ^{31}P NMR spectra were acquired again to show a 40:60 ratio of **2a**:**1a** (Figure S2-B) and ***meso*-L2-Ni(CO)$_2$**. (Figure S3-B). The complex ***meso*-L2-Ni-2a** was not detected (Figure S3-A and S3-B vs. S3-E). The mixture was again heated in the manner described above at 150 °C for 3 h to give **2a**:**1a** = 100:0 (Figure S2-C).

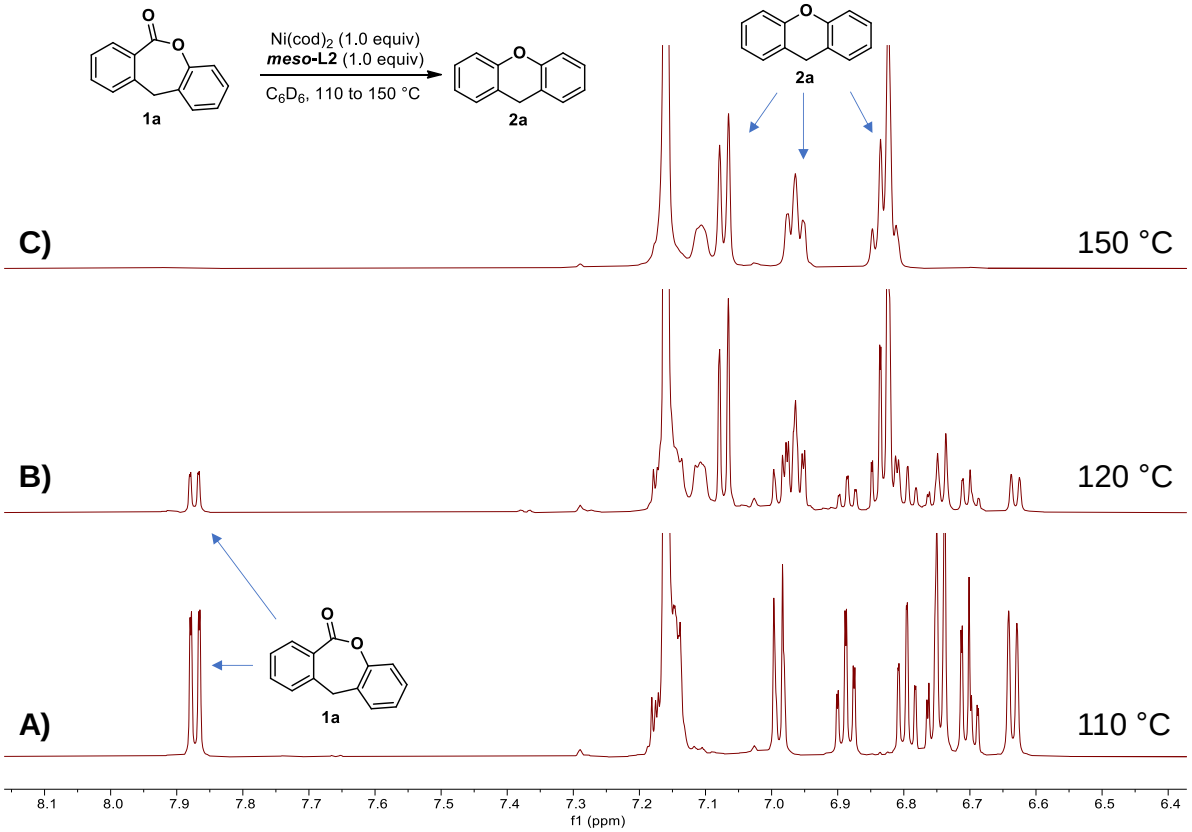


Figure S2. ^1H NMR (600 MHz, C_6D_6) spectra for the stoichiometric reaction using ***meso*-L2** and **1a** at A) 110 °C, B) 120 °C, and C) 150 °C.

***In situ* generation and observation of *meso*-L2-Ni(CO)$_2$ in ^{31}P NMR:** In a glovebox, a 2-dram vial was charged with a stir bar, ***meso*-L2** (0.0070 g, 0.0125 mmol), $(Ph_3P)_2Ni(CO)_2$ (0.0075 g, 0.0125 mmol), and C_6D_6 (0.50 mL). The solution was stirred at room temperature in the glovebox for 1 h and was filtered by syringe filter into an NMR tube. The NMR tube was sealed and brought outside to acquire a ^{31}P NMR spectrum. The signal for ***meso*-L2-Ni(CO)$_2$** was seen at 36.76 ppm (Figure S3-D).

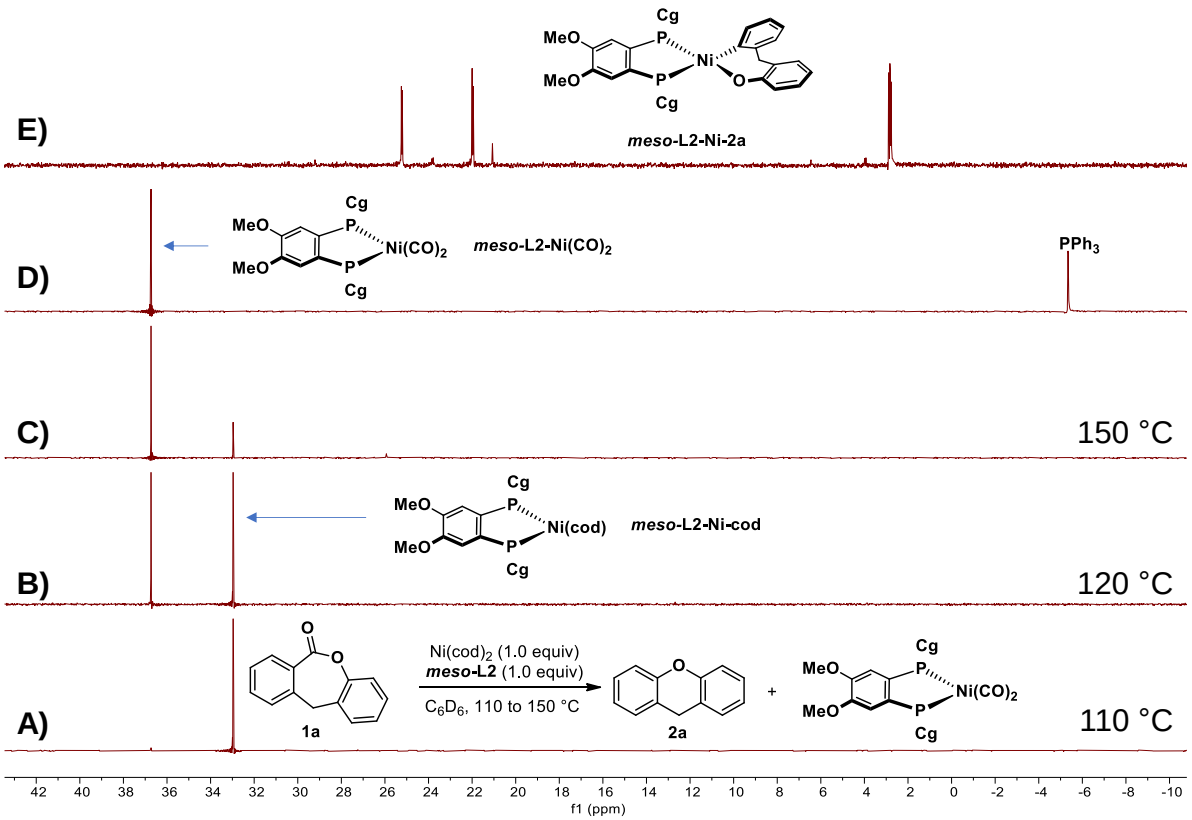


Figure S3. $^{31}P\{^1H\}$ NMR (253 MHz, C_6D_6) spectra of A) stoichiometric reaction at 110 °C, B)120 °C, C) 150 °C, D) ***meso*-L2-Ni(CO)$_2$**, and E) ***meso*-L2-Ni-2a**.

Stoichiometric reductive elimination test with *meso*-L2-Ni-2a·C$_6$H$_6$: In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, ***meso*-L2-Ni-2a·C$_6$H$_6$** (0.088 g, 0.050 mmol), and toluene (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 110 °C. The reaction was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). The product **2a** was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 5 cm). The column was eluted with 50 mL of hexanes. The product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give **2a** (0.0091 g, 0.050 mmol, >99%). Characterization data for **2a** is provided in section 6.2.

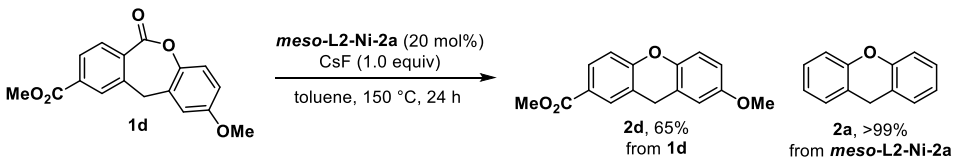
The same reaction carried out at 80 °C for 24 h gave 0% of **2a**.

5.6. Carbonylation tests (Figure 6A)

Stoichiometric carbonylation test with dcype-Ni-2a·C_6H_6: In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, **dcype-Ni-2a·C_6H_6** (0.037 g, 0.050 mmol), $Cr(CO)_6$ (0.011 g, 0.050 mmol, 1.0 equiv), and C_6D_6 (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. The reaction was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). A spot matching with **1a** was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 10 cm, packed in hexanes). The column was eluted with 100 mL of 90/10 hexanes/ethyl acetate. The fractions containing **1a** was collected and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give **1a** as a white solid (0.0095 g, 0.045 mmol, 90%). NMR data of **1a** matched with previously reported values.[4]

Stoichiometric carbonylation test with *meso*-L2-Ni-2a·C_6H_6: In a glovebox, an oven-dried 2-dram vial was charged with a stir bar, ***meso*-L2-Ni-2a·C_6H_6** (0.088 g, 0.050 mmol), $Cr(CO)_6$ (0.011 g, 0.050 mmol, 1.0 equiv), and C_6D_6 (0.50 mL). The vial was sealed and brought outside to place on an aluminum heating block preheated at 80 °C. The reaction was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was analyzed by TLC (100% hexanes). A spot matching with **2a** was visualized under UV. The reaction was then loaded directly onto a silica gel column (1 × 10 cm, packed in hexanes). The column was eluted with 100 mL of hexanes. The fractions containing **2a** was collected and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give **2a** as a white solid (0.0089 g, 0.049 mmol, 98%). Characterization data for **2a** are provided in section 6.2.

5.7. Catalytic experiments with *meso*-L2-Ni-2a:



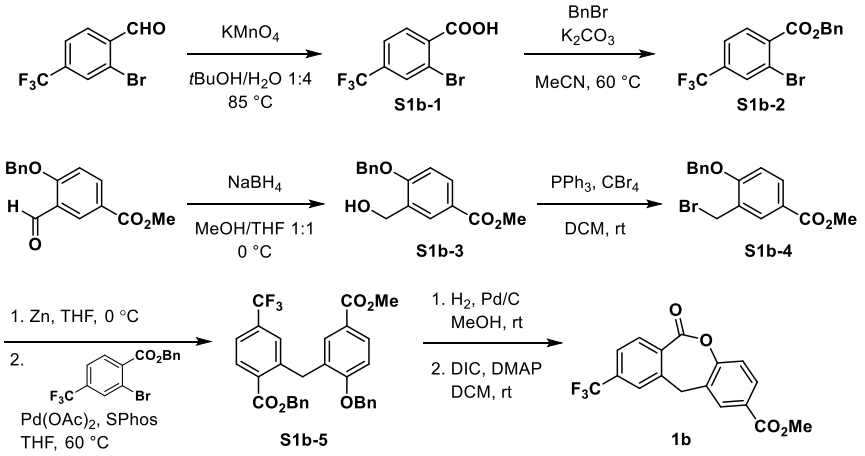
An oven-dried 2-dram vial was charged with a stir bar, and **1d** (0.030 g, 0.100 mmol). The vial was brought inside a glovebox, then ***meso*-L2-Ni-2a·C_6H_6** (0.018 g, 0.020 mmol), CsF (0.015 g, 0.100 mmol), and toluene (1.00 mL) were added. The vial was sealed and brought outside to place on an aluminum heating block preheated at 150 °C. The reaction was stirred at 150 °C for 24 h. After cooling to room temperature, the reaction was loaded directly onto a silica gel column (2 × 15 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 80/20 hexanes/ethyl acetate. The products containing fractions were collected and concentrated by rotary evaporator. The residues were dried under vacuum using an oil pump to give **2d** as a white solid (0.0175 g, 0.065 mmol, 65% from **1d**) and **2a** (0.0036 g, 0.020 mmol, >99% from ***meso*-L2-Ni-2a·C_6H_6**). Characterization data for **2a** and **2d** are provided in section 6.

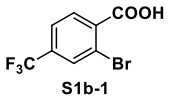
6. Experimental procedures and characterization data for compounds in Figure 7

6.1. Synthesis of substrates and characterization data for substrates

Substrates **1a**, **1f**, **1h**, and **1n** were synthesized according to a literature procedure.[4]

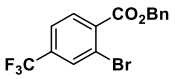
6.1.1. Synthesis of substrate 1b





2-bromo-4-(trifluoromethyl)benzoic acid (S1b-1): To a solution of $KMnO_4$ (1.42 g, 9 mmol, 2.25 equiv.) in H_2O (20 mL) was added 2-bromo-4-(trifluoromethyl)benzaldehyde (1.01 g, 4 mmol, 1 equiv.) in *t*BuOH (4 mL) at RT. The reaction was stirred at 85 °C for 2 h. The reaction was cooled to RT, then the pH was adjusted to 14 with 10% aq. NaOH. The green solution with brown precipitate was filtered through Celite, rinsing with H_2O. The pH of the aqueous filtrate was adjusted to 1 with 4N HCl and extracted with Et_2O (50 mL × 2). The combined organics were dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator to give **S1b-1** as a white solid (973 mg, 90% yield). ^{1}H NMR data match reported data.[5]

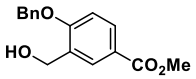
TLC (50% EtOAc/hexanes): R_f = 0.15 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 135.3, (q, *J* = 33.6 Hz), 133.8, 132.8, 132.0 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 3.7 Hz), 123.0, 122.7 (q, *J* = 273 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.34.



S1b-2

2-bromo-4-(trifluoromethyl)benzoic acid (S1b-2): To a solution of **S1b-1** (958 mg, 3.56 mmol, 1 equiv.) in MeCN (10 mL) in a 25 mL Schlenk flask was added K_2CO_3 (750 mg, 5.43 mmol, 1.53 equiv.) followed by BnBr (0.52 mL, 4.38 mmol, 1.23 equiv.) at RT. The reaction was stirred at 60 °C for 14 h, then cooled to RT. The reaction was diluted with 1:1 H_2O/brine (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (Combiflash, 0 → 10% EtOAc/hexanes) to give **S1b-2** as a colorless oil (941 mg, 72%).

TLC (15% EtOAc/hexanes): R_f = 0.42 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.40 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 5.40 (s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.2, 135.7, 135.2, 134.3 (q, *J* = 33.4 Hz), 131.8, 131.4 (q, J = 3.8 Hz), 128.8 (2C), 128.7, 124.2, 122.8 (q, *J* = 273 Hz), 68.0.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -63.20.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3089 (w), 3069 (w), 3037 (w), 2961 (w), 1736 (s), 1611 (w), 1572 (w), 1493 (w), 1460 (w), 1388 (m), 1322 (s), 1296 (s), 1250 (s), 1175 (s), 1132 (s), 1083 (s), 1040 (s), 951 (w), 892 9w), 846 (w), 777 (w), 754 (w), 695 (m), 666 (w), 639 (w).
HRMS: Exact mass calculated for $C_{15}H_{10}O_2BrF_3$ requires m/z = 357.9816, found m/z = 357.9807 (EI)

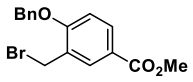


S1b-3

Methyl 4-(benzyloxy)-3-(hydroxymethyl)benzoate (S1b-3): Methyl 4-(benzyloxy)-3-formylbenzoate[6] (600 mg, 2.22 mmol, 1.0 equiv.) was dissolved in 2:1 MeOH/THF (7.5 mL) and cooled to 0 °C. $NaBH_4$ (99.7 mg, 2.44 mmol, 1.2 equiv.) was added portionwise over 5 min. The reaction was stirred at 0 °C for 2 h. Another portion of $NaBH_4$ (16.8 mg, 0.44 mmol, 0.2 equiv.) was added and the reaction stirred for another 2 h, then quenched with brine. The mixture was partially concentrated by rotary evaporation. The aqueous phase was extracted with MTBE (20 mL × 3). Brine was added to aid phase separation. The combined DCM layers were washed with 0.5N HCl (15 mL), brine, dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (20%-40% EtOAc/hexanes) to give **S1b-3** as a colorless oil (578 mg, 96%).

TLC (30% EtOAc/hexanes): R_f = 0.21 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.2 Hz, 1H), 7.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.44 – 7.32 (m, 5H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 4.76 (s, 2H), 3.88 (s, 3H), 2.07 (br s, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.9, 160.2, 136.1, 131.2, 130.2, 129.6, 129.0, 128.5, 127.5, 122.9, 111.2, 70.4, 61.6, 52.1.

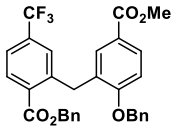
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3445 (br s), 3069 (w), 3036 (w), 2951 (w), 2882 (w), 1716 (s), 1608 (m), 1499 (m), 1440 (m), 1387 (w), 1299 (m), 12260 (s), 1194 (m), 1132 (m), 1109 (w), 1147 (w), 1023 (m), 918 (m), 829 (w), 773 (m), 734 (m), 702 (m), 652 (w), 626 (w).
HRMS: Exact mass calculated for $C_{16}H_{16}O_4$ requires m/z = 272.1049, found m/z = 272.1049 (EI).



S1b-4

Methyl 4-(benzyloxy)-3-(bromomethyl)benzoate (S1b-4): A 50 mL Schlenk flask was charged with **S1b-3** (578 mg, 2.12 mmol, 1.0 equiv.), evacuated, and back-filled with N_2 (×3). DCM (16 mL) was added, followed by CBr_4 (1.33 g, 4.03 mmol, 1.9 equiv.). The solution was cooled to 0 °C, then a solution of PPh_3 (834 mg, 3.18 mmol, 1.5 equiv.) in DCM (8 mL) was added. The reaction was stirred for 1 h at 0 °C, then quenched with saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was extracted with DCM (20 mL × 2). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes-8% EtOAc/hexanes) to give **S1b-4** as a white solid (624 mg, 88%).

TLC (15% EtOAc/hexanes): R_f = 0.21 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.41 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.38 – 7.34 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.22 (s, 2H), 4.60 (s, 2H), 3.89 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.5, 160.2, 136.1, 132.6, 132.3, 128.8, 128.3, 127.3, 126.7, 122.9, 111.8, 70.5, 52.1, 28.3.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3056 (w), 3026 (w), 2961 (w), 2938 (w), 2924 (w), 2972 (w), 2943 (w), 1707 (s), 1611 (m), 1506 (m), 1456 (w), 1231 (m), 1414 (m), 1387 (w), 1325 (m), 1309 (m), 1273 (s), 1266 (s), 1221 (m), 1194 (m), 1152 (m), 1122 (m), 1010 (m), 984 (w), 938 (w), 912 (w), 879 (w), 863 (w), 840 (w), 767 (m), 741 (m), 698 (m), 652 (w), 616 (w).
HRMS: Exact mass calculated for $C_{16}H_{15}BrO_3$ requires m/z = 334.0205, found m/z = 334.0204 (EI).

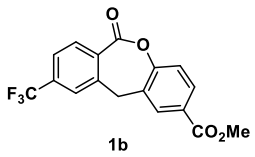


S1b-5

benzyl 2-(2-(benzyloxy)-5-(methoxycarbonyl)benzyl)-4-(trifluoromethyl)benzoate (S1b-5): The formation of the organozinc solution was adapted from a published procedure.[7] A 50 mL Schlenk tube was charged with Zn dust (654 mg, 10 mmol, 2.5 equiv.) and a stir bar. The tube was sealed with a rubber septum and evacuated. The Zn dust was heated with a heat gun under vacuum for 5 min, then cooled to RT. THF (5 mL) was added, followed by 1 drop of 1,2-dibromoethane. The mixture was heated to reflux, then 2 drops of trimethylchlorosilane was added. The mixture was stirred vigorously for 15 min, then cooled to 0 °C. A solution of **S1b-4** (1.61 g, 4.80 mmol, 1 equiv.) in THF (1.5 mL) was added dropwise over 5 min. After the addition, the ice/water bath

was removed, and the reaction stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.25 M after titration with I_2 (49.9 mg, 0.20 mmol) in THF (1 mL). A separate Schlenk flask was charged with aryl bromide **S1b-2** (770 mg, 2.14 mmol, 1 equiv.), $Pd(OAc)_2$ (21.9 mg, 0.0965 mmol, 0.045 equiv. wrt aryl bromide **S1b-2**), and SPhos (79.2 mg, 0.193 mmol, 0.09 equiv.). The flask was sealed with a rubber septum under N_2. THF (5 mL) was added. The organozinc solution prepared above (11 mL, 2.75 mmol, 1.29 equiv.) was added dropwise at RT. After the addition, the reaction mixture was stirred at 40 °C for 2 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with MTBE (20 mL × 3). The grey solid that was poorly soluble in the organic phase was discarded. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give a yellow oil. Trituration with MeOH and removal of the MeOH gives **S1b-5** a white solid (1.13 g, 95% wrt **S1b-2**).

TLC (100% hexanes): R_f = 0.35 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.74 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* = 6.2 Hz, 1H), 7.40 (s, 1H), 7.36 – 7.28 (m, 8H), 7.20 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.29 (s, 2H), 5.07 (s, 2H), 4.45 (s, 2H), 3.84 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.9, 166.8, 160.3, 142.5, 136.3, 135.5, 133.7, 133.5 (q, *J* = 32.2 Hz), 132.0, 131.0, 130.5, 128.8, 128.7 (2C), 128.5, 128.4, 128.2, 127.8 (q, *J* = 3.8 Hz), 127.2, 123.7 (q, *J* = 272.8 Hz), 123.1 (q, *J* = 3.1 Hz), 122.8, 111.3, 70.2, 67.3, 52.0, 34.3.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3069 (w), 3037 (w), 2958 (w), 2905 (w), 2872 (w), 2839 (w), 1716 (s), 1601 (m), 1503 (m), 1456 9w), 1427 (m), 1411 (w), 1385 (w), 1335 (w), 1303 (m), 1260 (s), 1194 (w), 1171 (m), 1122 (s), 1092 (m), 1066 (w), 1027 (w), 977 (w), 954 (w), 941 (w), 905 (w), 853 (w), 793 (w), 771 (w), 754 (m), 721 (w), 695 (w), 649 (w).
HRMS: Exact mass calculated for $[C_{31}H_{25}F_3O_5+H]^+$ requires m/z = 535.1732, found m/z = 535.1726 (ESI+).

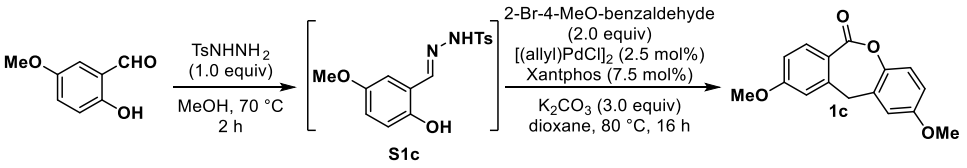


1b

methyl 6-oxo-9-(trifluoromethyl)-6,11-dihydrodibenzo[b,e]oxepine-2-carboxylate (1b): S1b-5 (816 mg, 1.53 mmol, 1 equiv.) was dissolved in MeOH/THF 3:1 (40 mL) and 10% Pd/C (245 mg) was added). The flask was evacuated briefly and back-filled with H_2 from a H_2-filled balloon. The reaction was stirred at RT for 4 h, then purged with N_2 for 15 min. The reaction mixture was filtered through Celite, rinsing with EtOAc. The filtrate was concentrated on a rotary evaporator to give a light-yellow solid which was suspended in DCM (60 mL). DMAP (17 mg, 2.30 mmol, 0.1 equiv.) was added, followed by DIC (0.36 mL, 2.32 mmol, 1.52 equiv.) under ambient atmosphere and temperature. The reaction was stirred at RT for 20 h, then Celite was added. The crude product was adsorbed onto Celite by removal of the solvent on a rotary evaporator. Purification by silica gel column chromatography (100% hexanes – 10% – 15% EtOAc/hexanes gave the product **1b** was a white solid (428 mg, 83% over 2 steps).

TLC (20% hexanes): R_f = 0.35 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.94 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 4.12 (s, 2H), 3.91 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.9, 164.1, 153.9, 142.8, 135.2 (q, *J* = 33.0 Hz), 133.5, 131.3, 130.5, 130.2, 128.2, 124.7 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 274 Hz), 121.2, 52.5, 36.4.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -63.3.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3052 (w), 3010 (w), 2964 (w), 1723 (s), 1615 (w), 1588 (w), 1496 9w), 1447 (m), 1424 (m), 1339 (m), 1322 (m), 1266 (m), 1234 (m), 1198 (m), 1178 (m) 1132 (m), 1112 (m), 1983 (m), 1056 (m), 997 (w), 951 (w), 932 (w), 692 (w), 863 (w), 803 (w), 774 (w), 757 (w), 708 (w), 664 (w), 626 (w).
HRMS: Exact mass calculated for $[C_{17}H_{11}F_3O_4+H]^+$ requires m/z = 337.0682, found m/z = 337.0685 (ESI+).

6.1.2. Synthesis of substrate 1c

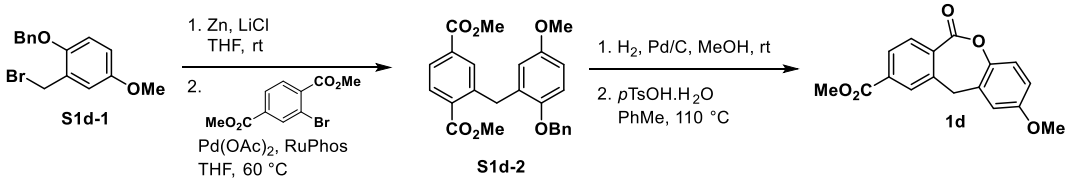


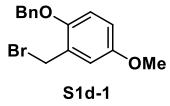
2,9-Dimethoxydibenzo[b,e]oxepin-6(11H)-one (1c): The synthesis of **c**ompound **1c** was adapted from a reported procedure for **1a**.[4]
Step 1: A 40-mL vial was charged with a stir bar, *N*-Tosyl hydrazide (3.7246 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and 5-methoxy salicylaldehyde (2.50 mL, 3.04 g, 20 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (–36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give **S1c** and was used directly in the next step without further purification.
Step 2: A 40-mL vial was charged with a stir bar, **S1c** (1.60 g, 5.00 mmol, 2.0 equiv), 2-bromo-4-methoxy benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and K_2CO_3 (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then $[(allyl)PdCl]_2$ (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give **1c** as a yellow solid (0.230 g, 0.83 mmol, 33%).

TLC (90/10 hexanes/ethyl acetate): R_f = 0.20 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.85 – 6.65 (m, 4H), 3.92 (s, 2H), 3.84 (s, 3H), 3.77 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 166.4, 163.5, 157.2, 144.9, 144.6, 135.5, 133.7, 121.7, 120.4, 113.6, 112.9, 112.7, 112.6, 55.8, 55.6, 38.2.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 2990 (w), 2954(w), 2918 (w), 2843 (w), 1716 (s), 1605 (m), 1496 (m), 1450 (w), 1424 (w), 1322 (w), 1257 (m), 1204 (m), 1122 (m), 1099 (m), 1066 (m), 1026 (m), 954 (w), 865 (w), 826 (w), 804 (w), 761 (w).
HRMS: Exact mass calculated for $[C_{16}H_{14}O_4+H]^+$ requires m/z = 271.0965, found m/z = 271.0969. (ESI+).

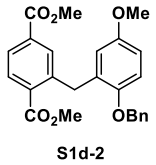
6.1.3. Synthesis of substrate 1d





1-(benzyloxy)-2-(bromomethyl)-4-methoxybenzene (S1d-1): S1d-1 was synthesized according to literature procedure.[8]

TLC (15% EtOAc/hexanes): R_f = 0.33 (visualized by UV)
^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.37 – 7.31 (m, 2H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.81 (dd, *J* = 9.0, 3.1 Hz, 1H), 5.12 (s, 2H), 4.59 (s, 2H), 3.78 (s, 3H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 153.8, 150.8, 137.2, 128.7, 128.0, 127.6, 127.4, 116.5, 115.2, 113.9, 70.4, 55.9, 28.6.



Dimethyl 2-(2-(benzyloxy)-5-methoxybenzyl)terephthalate (S1d-2): A 10 mL Schlenk tube was charged with LiCl (267 mg, 6.3 mmol, 2.57 equiv.) and a stir bar. The flask was sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N_2 and cooled to RT. Zn dust (330 mg, 5.04 mmol, 2.07 equiv.) was then added. The flask was re-sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N_2 and cooled to RT. THF (1 mL) was added. A solution of **S1d-1** (753 mg, 2.45 mmol, 1 equiv.) in THF (2 mL mL) was added dropwise over 5 min. The reaction stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.63 M after titration with I_2 (25.4 mg, 0.10 mmol) in THF (0.5 mL). A separate Schlenk flask was charged with dimethyl 2-bromoterephthalate[9] (286 mg, 1.05 mmol, 1 equiv.), $Pd(OAc)_2$ (11.9 mg, 0.0525 mmol, 0.05 equiv. wrt aryl bromide), and RuPhos (49.0 mg, 0.105 mmol, 0.1 equiv.). The flask was sealed with a rubber septum under N_2. THF (6 mL) was added. The organozinc solution prepared above (2.5 mL, 1.58 mmol, 1.5 equiv.)

was added dropwise at RT. After the addition, the reaction mixture was stirred at 60 °C for 5 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with diethyl ether (10 mL × 3). The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give **S1d-2** a yellow oil (453 mg, quantitative).

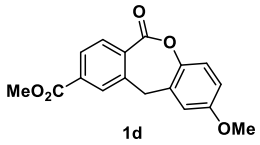
TLC (15% EtOAc/hexanes): R_f = 0.16 (visualized by UV)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 3H), 7.34 – 7.28 (m, 5H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 5.01 (s, 2H), 4.40 (s, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.8, 166.5, 153.8, 150.8, 142.1, 137.6, 134.5, 132.9, 132.5, 130.7, 130.4, 128.6, 127.8, 127.2 (2C), 117.0, 113.0, 111.5, 70.7, 54.8, 52.4, 52.3, 34.2.

IR (FT-ATR, cm^{-1}, neat) ν_{max}

HRMS: Exact mass calculated for $[C_{25}H_{24}O_6+H]^+$ requires m/z = 421.1646, found m/z = 421.1656. (ESI+).



1d

Methyl 2-methoxy-6-oxo-6,11-dihydrodibenzo[b,e]oxepine-9-carboxylate (1d): A suspension of **S1d-2** (435 mg, 1.03 mmol, 1.0 equiv) and 10% Pd/C (43.5 mg) was stirred overnight at RT under an atmosphere of H_2 (H_2 balloon). TLC showed incomplete conversion. The reaction was purged with N_2, then another portion of 10% Pd/C (21.5 mg) was added. The reaction was evacuated briefly and back-filled with H_2 from a balloon. After stirring for another 3 h at RT, TLC showed complete conversion. The reaction was purged with N_2 and filtered through Celite and silica gel. The filtrate was concentrated on a rotary evaporator and suspended in PhMe (30 mL). *p*TsOH·H_2O (39.2 mg, 0.206 mmol, 0.2 equiv.) was added, and the reaction refluxed for 6 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (30 mL). After phase separation, the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (50% – 80% DCM/hexanes) to give **1d** as a white solid (223 mg, 73% over 2 steps).

TLC (30% EtOAc/hexanes): R_f = 0.29 (visualized by UV)

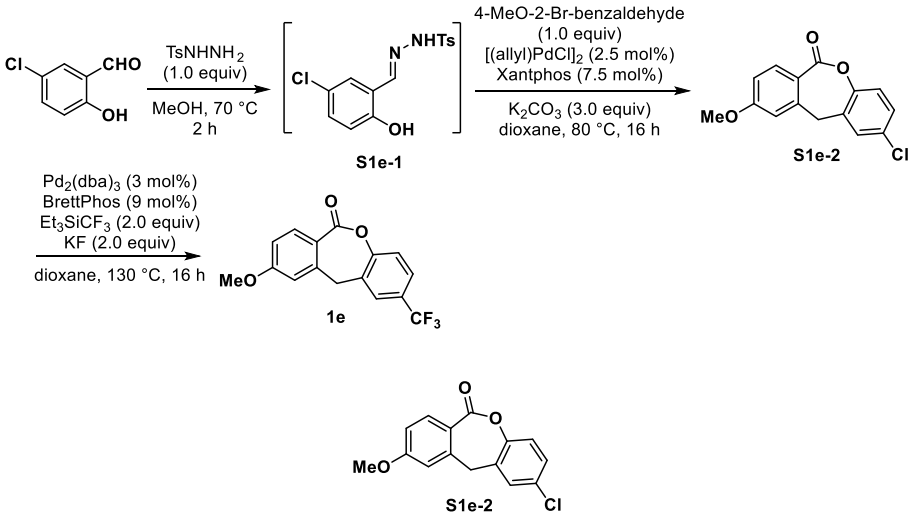
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.72 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.00 (br s, 2H), 3.93 (s, 3H), 3.77 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.0, 165.8, 157.4, 144.3, 142.7, 134.2, 133.4, 133.0, 132.2, 128.5, 128.4, 121.7, 113.6, 113.0, 56.3, 52.7, 37.0.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3064 (w), 3024 (w), 2965 (w), 2945 (w), 2916 (w), 2844 9w), 1740 (s), 1714 (s), 1616 (w), 1497 (m), 1455 (w), 1434 (m), 1415 (m), 1278 (m), 1241 (m), 1198 (s), 1152 (w), 1120 (m), 1100 (m), 1053 (m), 1038 (w), 978 (m), 942 (w), 916 (w), 896 (w), 857 (m), 811 (m), 788 (w), 771 (w), 742 (m), 706 (w), 630 (w), 611 (w).

HRMS: Exact mass calculated for $[C_{17}H_{14}O_5+H]^+$ requires m/z = 299.0914, found m/z = 299.0916. (ESI+).

6.1.4. Synthesis of substrate 1e



2-chloro-9-methoxydibenzo[b,e]oxepin-6(11H)-one (S1e-2): The synthesis of **c**ompound **S1e-2** was adapted from a reported procedure for **1a**.[4]

Step 1: A 40-mL vial was charged with a stir bar, *N*-tosyl hydrazide (3.72 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and 5-chloro salicylaldehyde (3.13 g, 20 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (–36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give **S1e-1** and was used directly in the next step without further purification.

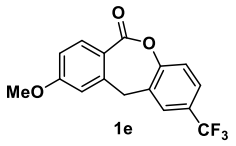
Step 2: A 40-mL vial was charged with as stir bar, **S1e-1** (1.62 g, 5.00 mmol, 2.0 equiv), 2-bromo-4-methoxy benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and K_2CO_3 (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then $[(allyl)PdCl]_2$ (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 25 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give **S1e-2** as a yellow solid with ca. 1% impurities seen in NMR (0.303 g, 1.10 mmol, ca. 44%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.23 – 7.12 (m, 2H), 6.84 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 2H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 163.8, 149.7, 144.1, 136.0, 134.2, 131.0, 128.2 (2 × s), 122.3, 120.0, 113.1, 112.9, 55.7, 37.9.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3096 (w), 2977 (w) 2846 (w), 1726 (s), 1601 (s), 1476 (m), 1431 (w), 1414 (w), 1319 (m), 1263 (s), 1230 (m), 1181 (m), 1115 (m), 1056 (w), 1023 (m), 905 (w), 872 (w), 820 (m), 757 (w), 702 (w), 639 (w), 612 (w).
HRMS: Exact mass calculated for $[C_{15}H_{11}ClO_3+H]^+$ requires m/z = 275.0469, found m/z = 275.0466. (ESI+).

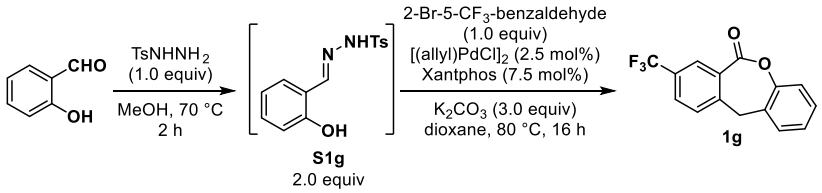


1e

9-Methoxy-2-(trifluoromethyl)dibenzo[b,e]oxepin-6(11H)-one (1e): The synthesis of compound **1e** was adapted from a reported trifluoromethylation method.[10]
In a glovebox, a vial (vial A) was charged with a stir bar, KF (0.058 g, 1.0 mmol, 2.0 equiv), and **S1e-2** (0.137 g, 0.50 mmol). Another vial (vial B) was charged with a stir bar, $Pd_2(dba)_3$ (0.018 g, 0.015 mmol, 3.0 mol%), BrettPhos (0.024 g, 0.045 mmol, 9.0 mol%), Et_3SiCF_3 (0.19 mL, 0.184 g, 1.0 mmol, 2.0 equiv), and dioxane (1.5 mL). The solution in vial B was stirred at room temperature in the glovebox for 10 min and was then transferred to vial A. Vial A was sealed and brought outside the glovebox to place on the heating block preheated at 130 °C. The reaction was stirred at 130 °C for 16 h and was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a plug of Celite. The filtrate was concentrated by rotary evaporator. The residue was loaded on a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 99/1 hexanes/ethyl acetate. The product containing fractions were concentrated using rotary evaporator and the residue was dried under vacuum using an oil pump to give **1e** as a white solid with ca. 5% impurities seen in NMR (0.0695 g, 0.23 mmol, ca. 45%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.20 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 1H), 7.54 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 4.03 (s, 2H), 3.86 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.0, 153.5, 143.9, 135.8, 133.3, 128.2 (q, *J* = 33.1 Hz), 125.7-125.6 (m, 2C), 123.8 (q, *J* = 272.6 Hz), 121.6, 119.8, 113.2, 113.0, 55.7, 37.9.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -62.09.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 2954 (w), 2921 (m), 2854 (w), 1714 (s), 1608 (m), 1575 (w), 1502 (w), 1484 (w), 1466 (w), 1442 (w), 1339 (m), 1327 (m), 1293 (w), 1260 (s), 1239 (w), 1184 (w), 1160 (s), 1117 (s), 1105 (s), 1081 (w), 1060 (m), 1033 (m), 957 (w), 936 (w), 908 (w), 890 (w), 842 (w), 820 (m), 760 (m), 745 (w), 705 (m), 675 (w), 620 (w).
HRMS: Exact mass calculated for $C_{16}H_{11}F_3O_3$ requires m/z = 308.0660, found m/z = 308.0655 (EI)

6.1.5. Synthesis of substrate 1g



Step 1: A 40-mL vial was charged with a stir bar, *N*-tosyl hydrazide (3.7246 g, 20 mmol, 1.0 equiv), and MeOH (10 mL). The suspension was stirred vigorously, and salicylaldehyde (2.40 mL, 3.04 g, 22 mmol, 1.1 equiv) was added. The vial was sealed with a Teflon-lined cap and was placed on an aluminum heating block preheated at 70 °C. The mixture was stirred at 70 °C for 2 h and was cooled to room temperature. Hexanes (10 mL) was added, and the vial was placed in a freezer (–36 °C). After 12 h, the white crystals were collected by filtration and washed with hexanes (10 mL). The crystal was dried under vacuum using an oil pump to give **S1g** and was used directly in the next step without further purification.

Step 2: A 40-mL vial was charged with as stir bar, **S-1g** (1.60 g, 5.00 mmol, 2.0 equiv), 2-bromo-5-(trifluoromethyl) benzaldehyde (0.538 g, 2.5 mmol, 1.0 equiv), and K_2CO_3 (1.04 g, 7.5 mmol). The vial was brought inside a glovebox, then $[(allyl)PdCl]_2$ (23 mg, 0.063 mmol, 2.5 mol%), Xantphos (0.108 g, 0.19 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give **1g** as an off-white solid (0.318 g, 1.18 mmol, 47%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.40 (visualized by UV).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.13 (m, 1H), 4.05 (s, 2H).

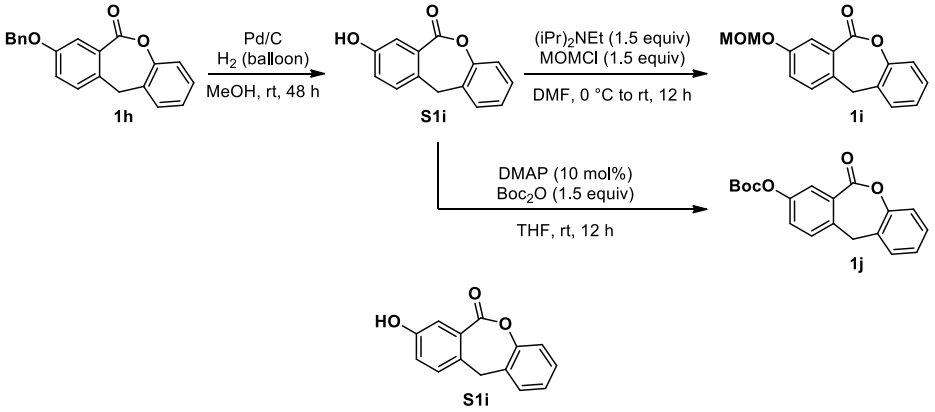
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 150.4, 146.2, 131.6, 130.3 (q, *J* = 33.4 Hz), 130.1-129.8 (m, 2C), 128.9, 128.7, 128.4, 127.9, 126.3, 123.4 (q, *J* = 272.1 Hz), 120.9, 37.3.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -62.81.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3079 (w), 3043 (w), 2924 (w), 2856 (w), 1716 (s), 117 (w), 1585 (w), 1493 (w), 1476 (w), 1457 (w), 1427 (w), 1414 (w), 1332 (m), 1312 (m), 1283 (w), 1243 (m), 1171 (m), 1129 (s), 1079 (m), 1033 (w), 997 (w), 954 (w), 918 (w), 865 (w), 842 (w), 787 (w), 757 (m), 728 (w), 667 (w), 646 (w), 613 (w).

HRMS: Exact mass calculated for $C_{15}H_9F_3O_2$ requires m/z = 278.0555, found m/z = 278.0554 (EI).

6.1.6. Synthesis of substrate 1i and 1j



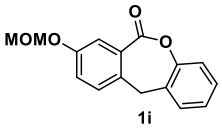
8-hydroxydibenzo[b,e]oxepin-6(11H)-one (**S1i)**: A three-neck round bottom flask was charged with a stir bar, **1h** (0.566 g, 1.79 mmol), and Pd/C (100 mg). The round bottom flask was placed under a H_2 atmosphere and MeOH (10 mL) was added. The mixture was stirred at room temperature for 48 h and the black solid was filtered off using a pad silica gel and Celite (2 cm silica gel on top of 10 cm Celite). The solid was washed with dichloromethane (10 mL) and the filtrate was concentrated to give **S1i** as a white solid (0.398 g, 1.76 mmol). Compound **S1i** was used directly in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD) δ 7.27 (s, 1H), 7.23 – 7.14 (m, 3H), 7.13 – 7.04 (m, 2H), 6.92 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.88 (s, 2H), 2.57 (br s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/CD_3OD) δ 166.9, 156.4, 150.7, 134.2, 133.4, 128.7, 128.4, 128.1, 128.0, 126.0, 121.2, 120.6, 118.6, 36.6.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3414 (broad s), 3069 (w), 2974 (w), 2915 (w), 2853 (w), 1733 (s), 1697 (s), 1614 (m), 1578 (m), 1490 (m), 1447 (s), 1299 (s), 1260 (m), 1230 (s), 1181 (s), 1119 (m), 1066 (m), 944 (m), 899 (w), 885 (m), 862 (w), 838 (m), 793 (m), 764 (m), 734 (w), 698 (w), 655 (w), 626 (w), 606 (m).

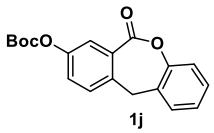
HRMS: Exact mass calculated for $[C_{14}H_{10}O_3+H]^+$ requires m/z = 227.0703, found m/z = 227.0701. (ESI+).



8-(Methoxymethoxy)dibenzo[b,e]oxepin-6(11H)-one (1i):

A round bottom flask was charged with a stir bar, **S1i** (0.398 g, 1.76 mmol), and DMF (2.0 mL). The resulting solution was cooled to 0 °C in an ice bath. Diisopropylethylamine (0.46 mL, 0.341 g, 2.64 mmol, 1.5 equiv) was then added followed by chloromethyl methyl ether (0.20 mL, 0.212 g, 2.64 mmol). The mixture was warmed to room temperature. After stirring for 12 h, water (20 mL) was added followed by dichloromethane (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were washed with water (3 × 10 mL), dried with Na_2SO_4 and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give **1i** as a white solid (0.454 g, 1.68 mmol, 95%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.50 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.6 Hz, 1H), 7.25 – 7.07 (m, 7H), 5.14 (s, 2H), 3.94 (s, 2H), 3.43 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.9, 156.5, 150.8, 136.3, 133.2, 129.1, 128.5, 128.2 (2C), 126.0, 121.7, 120.8, 119.9, 94.6, 56.2, 36.7.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3059 (w), 3000 (w), 2964 (w), 2908 (w), 2852 (w), 2830 (w), 1720 (s), 1615 (w), 1675 (w), 1493 (m), 1454 (m), 1427 (w), 1286 (m), 1259 (m), 1227 (m), 1177 (m), 1128 (m), 1085 (m), 1063 (m), 1004 (s), 922 9m), 899 (w), 859 (w), 823 (w), 784 (w), 757 (m), 731 (w), 708 (w), 662 (w), 639 (w).
HRMS: Exact mass calculated for $[C_{16}H_{14}O_4+H]^+$ requires m/z = 271.0965, found m/z = 271.0959. (ESI+).

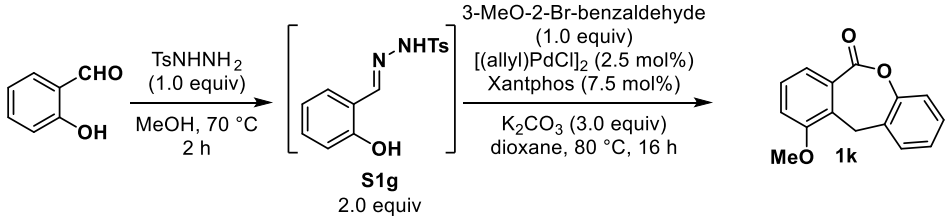


1j

tert-butyl (6-oxo-6,11-dihydrodibenzo[b,e]oxepin-8-yl) carbonate (1j): A round bottom flask was charged with a stir bar, **S1i** (0.398 g, 1.00 mmol), DMAP (0.012 g, 0.1 mmol, 10 mol%), and THF (5.0 mL). The mixture was stirred at room temperature and di*tert*-butyl decarbonate (Boc_2O, 0.327 g, 1.50 mmol, 1.5 equiv) was added. The reaction was stirred at room temperature for another 12 h and water (10 mL) was added followed by ethyl acetate (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were washed with brine (10 mL), dried with Na_2SO_4 and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product containing fractions were combined and concentrated by rotary evaporator. The residue was dried under vacuum using an oil pump to give **1j** as a white solid (0.326 g, 1.00 mmol, >99%).

TLC (90/10 hexanes/ethyl acetate): R_f = 0.10 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 1.5 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.13 (m, 1H), 4.00 (s, 2H), 1.55 (s, 9H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 151.6, 150.7, 150.3, 140.2, 132.5, 129.3, 128.5, 128.4, 128.3, 126.5, 126.2, 125.6, 121.0, 84.3, 36.9, 27.8.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3000 (w), 2981 (w), 2938 (w), 2872 (w), 1756 (s), 1730 (s), 1612 (w), 1582 (w), 1493 (w), 1457 (w), 1428 (w), 1391 (w), 1365 (w), 1282 (m), 1243 (s), 1207 (w), 1175 (m), 1155 (s), 1122 (m), 1096 (w), 1066 (w), 1050 (w), 1023 (w), 938 (w), 902 (w), 872 (w), 838 (w), 810 (w), 780 (w), 754 (w), 702 (w), 662 (w), 623 (w).
HRMS: Exact mass calculated for $[C_{19}H_{18}O_5+H]^+$ requires m/z = 327.1227, found m/z = 327.1227. (ESI+).

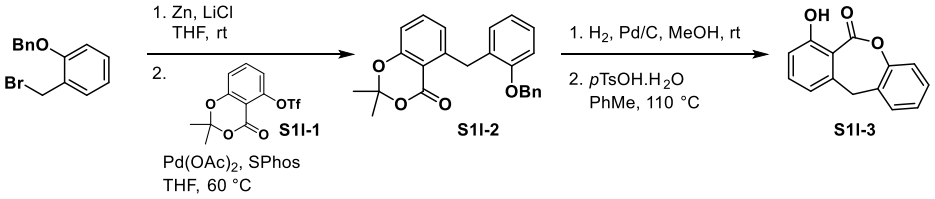
6.1.7. Synthesis of substrate 1k

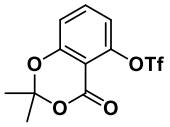


Step 1: **S1g** was synthesized according to the procedure described in section 6.1.5.
Step 2: A 40-mL vial was charged with as stir bar, **S1g** (1.18 g, 4.06 mmol, 2.0 equiv), 3-methoxy-2-bromo benzaldehyde (0.437 g, 2.03 mmol, 1.0 equiv), and K_2CO_3 (0.842 g, 6.09 mmol, 3.0 equiv). The vial was brought inside a glovebox, then $[(allyl)PdCl]_2$ (19 mg, 0.051 mmol, 2.5 mol%), Xantphos (0.087 g, 0.15 mmol, 7.5 mol%), and dioxane (5.0 mL) were added. The vial was sealed and brought outside and placed on an aluminum heating block preheated at 80 °C. The mixture was vigorously stirred at 80 °C for 16 h and was cooled to room temperature. Ethyl acetate (50 mL) was added and the solid was filtered off using a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was loaded onto a silica gel column (5 × 20 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give **1k** as a yellow solid (0.250 g, 1.04 mmol, 51%).

TLC (90/10 hexanes/ethyl acetate): R_f = 0.25 (visualized by UV).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.13 – 7.06 (m, 1H), 7.02 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.09 (s, 2H), 3.89 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.3, 154.8, 151.4, 133.0, 131.6, 129.7, 128.6, 128.0, 127.9, 125.8, 124.1, 120.55, 115.0, 56.3, 27.6.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3069 (w), 3016 (w), 2974 (w), 2948 (w), 2921 (w), 2846 (w), 1739 (s), 1565 (m), 1476 (m), 1457 (m), 1434 (m), 1335 (w), 1309 (w), 1269 (s), 1230 (m), 1204 (m), 1174 (w), 1161 (w), 1108 (m), 1065 (w), 1049 (m), 1033 (w), 915 (w), 833 (w), 796 (w), 761 (w), 741 (m), 737 (w), 715 (w), 679 (w), 639 (w), 610 (w).
HRMS: Exact mass calculated for $[C_{15}H_{12}O_3+H]^+$ requires m/z = 241.0859, found m/z = 241.0855. (ESI+).

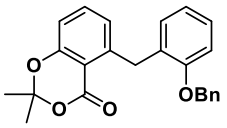
6.1.8. Synthesis of substrates 1l and 1m





S1l-1

2,2-dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl trifluoromethanesulfonate (S1l-1):
A 100 mL Schlenk flask was charged with 2,2-dimethyl-5-hydroxy-4-oxo-benzo-1,4-dioxin[11] (1.94 g, 10 mmol, 1.0 equiv.), DMAP (122 mg, 1 mmol, 0.1 equiv.), and a stir bar. The flask was sealed, evacuated, and back-filled with N_2 (3×). DCM (50 mL) and NEt_3 (7 mL, 50 mmol, 5.0 equiv.) were added sequentially. *N*-Phenyl-bis(trifluoromethanesulfonimide) (3.57 g, 10 mmol, 1.0 equiv.) was then added portionwise under a flow of N_2 at RT. The reaction was stirred at RT for 18 h, then quenched with the slow addition of 0.5N HCl (40 mL). The mixture was transferred to a separatory funnel. After phase separation, the organic phase was washed with 0.5N HCl (40 mL). The combined aqueous phase was extracted with DCM (40 mL). The DCM layers were washed with saturated $NaHCO_3$ (aq.), dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified partially by silica gel chromatography (40% – 50% DCM/hexanes). The fractions containing the product were concentrated and further purified by recrystallization from EtOAc/hexanes (~ 1:10 v/v) to afford **S1l-1** as a white crystalline solid (2.89 g, 89%). ^{1}H NMR and ^{13}C NMR match reported data in the literature.[12]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.00 (dq, *J* = 8.3, 0.7 Hz, 1H), 1.76 (s, 6H)
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 157.6, 157.3, 148.8, 136.4, 118.9 (q, *J* = 321 Hz), 118.0, 116.7 (q, *J* = 1 Hz), 108.5, 107.0, 25.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -73.15.

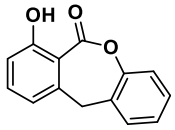


S1l-2

5-(2-(benzyloxy)benzyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one:
A 10 mL Schlenk tube was charged with LiCl (106 mg, 2.5 mmol, 2.5 equiv.) and a stir bar. The flask was sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N_2 and cooled to RT. Zn dust (131 mg, 2.00 mmol, 2.0 equiv.) was then added. The flask was re-sealed and evacuated. The flask was heated with a heat gun for 5 min, then back-filled with N_2 and cooled to RT. THF (1 mL) was added. A solution of **S1l-1** (277 mg, 1.00 mmol, 1 equiv.) in THF (1 mL) was added dropwise over 5 min. The reaction was stirred at RT for 2 hours. The concentration of the organozinc solution was calculated to be 0.40 M after titration with I_2 (30.7 mg, 0.121 mmol) in THF (2 mL). A separate Schlenk flask was charged with 1-(benzyloxy)-2-(bromomethyl)benzene[13] (150 mg, 0.46 mmol, 1 equiv.), $Pd(OAc)_2$ (5.2 mg, 0.023 mmol, 0.05 equiv. wrt aryl bromide), and SPhos (18.9 mg, 0.046 mmol, 0.1 equiv.). The flask was sealed with a rubber septum under N_2. THF (3 mL) was added. The organozinc solution prepared above (1.2 mL, 0.48 mmol, 1.04 equiv.) was added dropwise at RT. After the addition, the reaction mixture was stirred at 60 °C for 3 h. After cooling to RT, the reaction was quenched with 0.5N HCl (20 mL) and the aqueous layer extracted with diethyl ether (10 mL × 3). The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The

crude product was purified by silica gel column chromatography (100% Hexanes - 10% EtOAc/hexanes - 15% EtOAc/hexanes) to give **S1l-2** a yellow oil (162 mg, 94%).

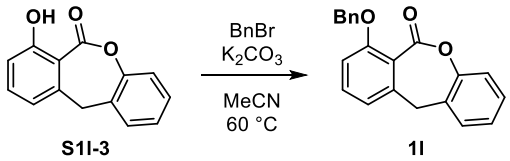
TLC (15% EtOAc/hexanes): R_f = 0.28 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 7.24 – 7.18 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.05 (s, 2H), 4.59 (s, 2H), 1.66 (s, 6H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.6, 157.1, 156.8, 146.4, 137.4, 135.1, 130.9, 129.2, 128.5, 127.8, 127.3, 124.9, 120.9, 115.2, 112.6, 111.9, 105.2, 70.0, 34.3, 25.7.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3063 (m), 3027 (m), 3004 (m), 2954 (m), 2921 (w), 1736 (s), 1608 (m), 1585 (m), 1496 (m), 1476 (m), 1453 (m), 1385 (m), 1316 (m), 1270 (m), 1273 (m), 1237 (m), 1211 (m), 1161 (w), 1142 (w), 1109 (m), 1179 (m), 1043 (m), 1023 (m), 970 (w), 928 (m), 849 (w), 823 (w), 777 (w), 751 (m), 731 (m), 702 (m), 642 (w), 620 (w).
HRMS: Exact mass calculated for $[C_{24}H_{22}O_4+H]^+$ requires m/z = 375.1591, found m/z = 375.1602 (ESI+).



S1l-3

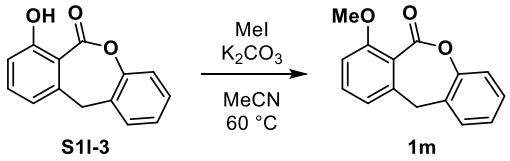
7-hydroxydibenzo[b,e]oxepin-6(11H)-one (S1l-3): S1l-2 (1.29 g, 3.44 mmol, 1.0 equiv.) was dissolved in MeOH/EtOAc 5:3 (80 mL) and 10% Pd/C (206 mg) was added). The flask was evacuated briefly and back-filled with H_2 from a H_2-filled balloon. The reaction was stirred at RT for 16 h, then purged with N_2 for 15 min. The reaction mixture was filtered through Celite, rinsing with EtOAc. The filtrate was concentrated on a rotary evaporator. The white solid obtained was suspended in PhMe (50 mL) and *p*TsOH·H_2O (129 mg, 0.68 mmol, 0.2 equiv.) was added. The reaction was refluxed for 22 h, then cooled to RT. After filtration through Celite and rinsing with EtOAc, the filtrate was concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 10% EtOAc/hexanes) to give **S1l-3** as a white solid (740 mg, 95% over 2 steps).

TLC (30% EtOAc/hexanes): R_f = 0.56 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.36 (dd, *J* = 8.4, 7.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.22 (m, 2H), 7.17 (ddd, *J* = 7.4, 5.5, 3.2 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.78 (dd, *J* = 7.4, 1.1 Hz, 1H), 3.99 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.9, 162.5, 150.2, 144.3, 135.9, 132.2, 128.3 (2C), 126.7, 120.6, 119.0, 116.8, 111.3, 38.1.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3352 (br s), 3089 (w), 3053 (w), 2971 (w), 2922 (w), 1684 (s), 1608 (m), 1582 (m), 1490 (m), 1454 (s), 1355 (m), 1299 (m), 1250 (m), 1231 (m), 1185 (m), 1159 (m), 1103 (m), 1080 (m), 1053 (w), 1011 (w), 952 (w), 912 (w), 893 (w), 840 (w), 791 (m), 761 (m), 732 (w), 698 (w), 679 (w), 650 (w), 610 (w).
HRMS: Exact mass calculated for $[C_{14}H_{10}O_3+H]^+$ requires m/z = 227.0703, found m/z = 227.0703. (ESI+).



7-(benzyloxy)dibenzo[b,e]oxepin-6(11H)-one (1l):
A 50 mL Schlenk tube was charged with **S1l-3** (226 mg, 1.0 mmol, 1.0 equiv.), sealed with a rubber septum, evacuated, and back-filled with N_2 (×2). MeCN (5 mL) was added, followed by K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv.) under a flow of N_2. BnBr (140 μL, 1.18 mmol, 1.2 equiv.) was added neat at RT. The reaction was stirred in a 60 °C oil bath for 13 h, then cooled to RT. 1:1 brine/H_2O (20 mL) was added, and the mixture was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic phase was extracted with brine, dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 20% EtOAc/hexanes) to give the product **1l** as a white solid (314 mg, 99%).

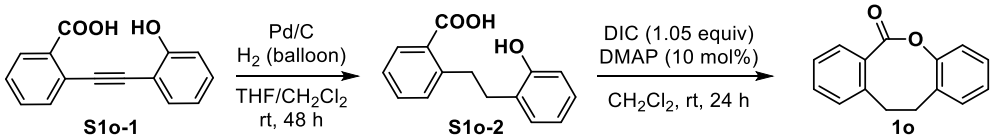
TLC (30% EtOAc/hexanes): R_f = 0.41 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.41 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 7.11 (ddd, *J* = 7.3, 6.2, 2.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.18 (s, 2H), 3.93 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.8, 158.8, 151.6, 144.7, 137.9, 133.2, 132.6, 130.3, 128.7, 128.2 (2C), 128.0, 127.0, 125.5, 121.1, 119.0, 117.7, 111.1, 70.9, 37.4.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3092 (w), 3069 (w), 3033 (w), 2924 (w), 2902 (w), 2878 (w), 2846 (w), 1742 (s), 1598 (m), 1581 (m), 1482 (m), 1450 (m), 1388 (w), 1289 (m), 1263 (m), 1227 (s), 1181 (m), 1154 (w), 1105 (m), 1085 (m), 1069 (m), 1043 (m), 1019 (m), 964 (w), 908 (w), 872 (w), 826 (w), 767 (m), 737 (m), 724 (m), 691 (m), 652 (w), 639 (w), 616 (w).
HRMS: Exact mass calculated for $C_{21}H_{16}O_3$ requires m/z = 316.1099, found m/z = 316.1100 (EI).



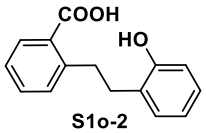
7-methoxydibenzo[b,e]oxepin-6(11H)-one (1m):
A 50 mL Schlenk tube was charged with **S1l-3** (226 mg, 1.0 mmol, 1.0 equiv.), sealed with a rubber septum, evacuated, and back-filled with N_2 (×2). MeCN (5 mL) was added, followed by K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv.) under a flow of N_2. MeI (80 μL, 1.3 mmol, 1.3 equiv.) was added neat at RT. The reaction was stirred in a 60 °C oil bath for 13 h, then cooled to RT. 1:1 brine/H_2O (20 mL) was added, and the mixture was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic phase was extracted with brine, dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography (100% hexanes – 20% – 25% EtOAc/hexanes) to give the product **1m** as a white solid (220 mg, 92% yield).

TLC (30% EtOAc/hexanes): R_f = 0.32 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.19 (qd, *J* = 6.6, 2.8 Hz, 3H), 7.07 (td, *J* = 7.0, 2.1 Hz, 1H), 6.83 (t, *J* = 8.7 Hz, 2H), 3.88 (s, 2H), 3.85 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 159.7, 150.7, 144.6, 133.3, 133.0, 128.2 (2C), 125.6, 120.4, 118.7, 116.9, 110.6, 56.3, 36.8.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3092 (w), 3024 (w), 2981 (w), 2948 (w), 2846 (w), 1745 (s), 1594 9m), 1471 (m), 1454 (m), 1441 (m), 1270 (m), 1224 (s), 1178 (m), 1155 (w), 1102 (m), 1069 (m), 1040 (m), 1020 (m), 961 (w), 905 (w), 872 (w), 820 (w), 777 (m), 738 (w), 705 (w), 675 (w), 639 (w).
HRMS: Exact mass calculated for $[C_{15}H_{12}O_3+H]^+$ requires m/z = 241.0859, found m/z = 241.0860. (ESI+).

6.1.9. Synthesis of substrate 1o

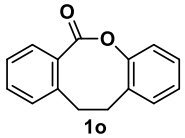


The starting material **S1o-1** was synthesized according to a reported procedure.[14]



A three-neck round bottom flask was charged with a stir bar, 10% Pd/C (100 mg), **S1o-1** (1.14 g, 4.52 mmol), THF (5.0 mL), and dichloromethane (5.0 mL). The flask was put under a H_2 atmosphere (H_2-filled balloon). The reaction mixture was stirred at rt for 48 h. The black solids were filtered off using a pad of Celite and the filtrate was concentrated by rotary evaporator. The residue was loaded directly onto a silica gel column (3 × 30 cm, packed in hexanes). The column was eluted with 90/10 hexanes/ethyl acetate followed by 80/20 hexanes/ethyl acetate. The product-containing fractions were combined, and the solvents were removed by rotary evaporator. The residue was dried under vacuum using an oil pump to give **S1o-2** as a white solid (0.521 g, 2.15 mmol, 48%).

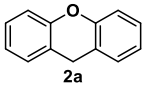
TLC (80/20 hexanes/ethyl acetate): R_f = 0.60 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.99 (br s, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42-7.33 (m, 2H), 7.23-7.15 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 3.23 – 3.14 (m, 2H), 2.96 – 2.87 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.9, 154.0, 145.1, 133.8, 132.6, 131.8, 130.6, 128.2, 127.3, 126.9 (2 × s), 121.0, 116.3, 36.8, 34.2.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3332 (s), 3158 (m), 3079 (m), 2960 (w), 2862 (w), 2658 (w), 1699 (s), 1585 (m), 1489 (m), 1460 (w), 1407 (w), 1338 (w), 1299 (m), 1270 (m), 1243 (m), 1217 (m), 1165 (w), 1165 (w), 1138 (w), 1105 (w), 1076 (w), 1043 (w), 1003 (w), 931 (w), 836 (m), 793 (m), 751 (s), 702 9w), 649 (w), 620 (w).
HRMS: Exact mass calculated for $C_{15}H_{14}O_3$ requires m/z = 242.0943, found m/z = 242.0939 (EI).



1o

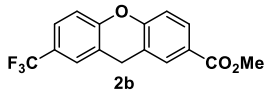
11,12-Dihydro-6H-dibenzo[b,f]oxocin-6-one (1o):
A round bottom flask was charged with a stir bar, **S1o-2** (0.521 g, 2.15 mmol), DMAP (0.026 g, 0.215 mmol, 10 mol%), and dichloromethane (21.5 mL). DIC (0.35 mL, 0.285 g, 2.25 mmol, 1.05 equiv) was then added with stirring. The solution was stirred at room temperature for 24 h and was then concentrated using rotary evaporator to 10 mL. The residue was then loaded directly onto a silica gel column (3 × 25 cm, packed in hexanes). The column was eluted with dichloromethane. The product-containing fractions were combined. The solvents were removed by rotary evaporator and the residue was dried under vacuum using an oil pump to give **1o** as a white solid (0.173 g, 0.77 mmol, 36%). NMR data match with previously reported values.[15]
TLC (80/20 hexanes/ethyl acetate): R_f = 0.50 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6. 1.4 Hz, 1H), 7.25 (td, *J* = 7.8, 1.6 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.10 – 7.04 (m, 2H), 7.04 – 6.98 (m, 2H), 3.25 (t, *J* = 7.4 Hz, 2H), 3.17 (t, *J* = 7.4 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 171.0, 151.9, 137.1, 132.3, 132.1, 131.3, 132.1, 129.3, 127.9, 127.8, 126.9, 126.6, 122.1, 32.8, 30.6.

6.2. General procedure and characterization data for decarbonylation products
General procedure: An oven-dried 2-dram vial was charged with a magnetic stir bar, a lactone **1** (0.200 mmol), and the ligand ***meso*-L2** (0.023 g, 0.040 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (0.011 g, 0.040 mmol, 20 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column and chromatographed as described below for each compound. The product containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product.



2a

9*H*-Xanthene (2a): Compound **2a** was isolated as a white solid (0.0306 g, 0.17 mmol, 85%) from the reaction of **1a** (0.0440 g, 0.20 mmol). A 1.00 mmol scale reaction of **1a** (0.220 g, 1.00 mmol) gave **2a** in 58% yield (0.106 g, 0.58 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 200 mL of hexanes. NMR data match with previously reported values.[16]
TLC (100% hexanes): R_f = 0.50 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.16 (m, 4H), 7.05-7.01 (m, 4H), 4.06 (s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 152.1, 129.1, 127.8, 123.1, 120.7, 116.6.



2b

Methyl 7-(trifluoromethyl)-9H-xanthene-2-carboxylate (2b): Compound **2b** was isolated as a white solid (0.0331 g, 0.11 mmol, 54%) from the reaction of **1b** (0.067 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90/10 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV).

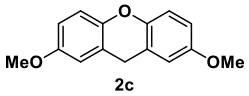
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), 7.48 – 7.43 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 9.1 Hz, 1H), 4.10 (s, 2H), 3.91 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.5, 154.8, 153.8, 131.1, 129.9, 126.6 (q, *J* = 3.9 Hz), 125.9 (q, *J* = 33.0 Hz), 125.7, 125.3 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 271.2 Hz), 120.6, 119.7, 117.2, 116.8, 52.2, 27.5.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –61.89.

IR (FT-ATR, cm^{-1}, neat) ν_{max} 3003 (w), 2960 (w), 2928 (w), 2855 (w), 1716 (s), 1614 (m), 1585 (w), 1496 (m), 1440 (m), 1421 (m), 1332 (s), 1289 (s), 1270 (s), 1204 (m), 1181 (m), 1161 (s), 1122 (s), 1073 (s), 990 (w), 961 (w), 954 (w), 896 (w), 846 (w), 830 (m), 810 (w) 767 (m), 731 (w), 708 (w), 656 (w), 616 (w).

HRMS: Exact mass calculated for $C_{16}H_{11}F_3O_3$ requires m/z = 308.0660, found m/z = 308.0655. (ESI+).



2c

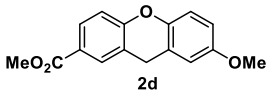
2,7-dimethoxy-9H-xanthene (2c):

Compound **2c** was isolated as a white solid (0.0157 g, 0.065 mmol, 32%) from the reaction of **1c** (0.054 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.[17]

TLC (90/10 hexanes/ethyl acetate): R_f = 0.25 (visualized by UV).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.9 Hz, 1H), 6.75 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.2, 146.4, 120.9, 117.2, 113.5, 113.4, 55.8, 28.9.



2d

Methyl 7-methoxy-9H-xanthene-2-carboxylate (2d):

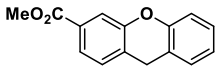
Compound **2d** was isolated as a white solid (0.0362 g, 0.13 mmol, 67%) from the reaction of **1d** (0.060 g, 0.200 mmol). Chromatography conditions: silica gel column (2 × 25 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 80/20 hexanes/ethyl acetate.

TLC (80/20 hexanes/ethyl acetate): R_f = 0.50 (bright blue spot visualized by UV).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 9.1 Hz, 1H), 6.68 (s, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.8, 155.8, 145.4, 131.1, 129.6, 124.6, 120.7, 119.9, 117.4, 116.5, 113.8, 113.4, 55.8, 52.1, 28.0.

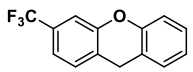
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3016 (w), 2960 (m), 2928 (m), 2855 (m), 1713 (s), 1621 (m), 1581 (m), 1493 (s), 1460 (m), 1427 (m), 1312 (m), 1292 (s), 1266 (s), 1247 (s), 1211 (m), 1194 (m), 1178 (m), 1158 (w), 1122 (m), 1099 (m), 1046 (m), 977 (w), 957 (w), 905 (w), 839 (m), 823 (m), 770 (m), 734 (w), 708 (w), 681 (w), 626 (w), 606 (w).
HRMS: Exact mass calculated for $C_{16}H_{14}O_4$ requires m/z = 270.0887, found m/z = 270.0889 (EI).



2f

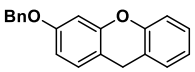
Methyl 9*H*-xanthene-3-carboxylate (2f): Compound **2f** was isolated as an off-white solid (0.0151 g, 0.063 mmol, 63%) from the reaction of **1f** (0.0270 g, 0.10 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90:10 hexanes/ethyl acetate): R_f = 0.60 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.24-7.19 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.08-7.02 (m, 2H), 4.09 (s, 2H), 3.92 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.7, 152.0, 151.8, 130.0, 129.1, 129.0, 128.1, 126.1, 124.1, 123.5, 119.9, 117.9, 116.7, 52.3, 28.2.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3072 (w), 3036 (w), 2997 (w), 2954 (m), 2924 (m), 2856 (m), 1710 (s), 1670 (w), 1601 (w), 1572 (m), 1508 (w), 1487 (m), 1457 (m), 1434 (m), 1296 (s), 1243 (m), 1213 9m), 1191 (m), 1181 (m), 1149 (w), 1129 (m), 1092 (m), 1033 (w), 987 (m), 958 (m), 895 (w), 869 (w), 849 (w), 813 (w), 809 (w), 770 (s), 715 (w), 688 (w).
HRMS: Exact mass calculated for $C_{15}H_{12}O_3$ requires m/z = 240.0786, found m/z = 240.0773 (EI).



2g

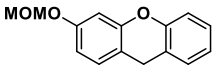
3-(Trifluoromethyl)-9H-xanthene (2g): Compound **2g** was isolated as a white solid (0.0168 g, 0.068 mmol, 67%) from the reaction of **1g** (0.014 g, 0.10 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. ^{1}H NMR data match with previously reported values.[18]
TLC (100% hexanes): R_f = 0.50 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.27 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 8.1, 5.2 Hz, 2H), 4.09 (s, 2H).
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -62.61.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 152.2, 151.6, 130.4 (q, *J* = 32.9 Hz), 129.6, 129.0, 128.2, 124.7, 124.0 (q, *J* = 272.2 Hz), 123.7, 119.8, 119.6 (q, *J* = 3.7 Hz), 116.7, 114.0 (q, *J* = 4.0 Hz), 28.0



2h

3-(benzyloxy)-9H-xanthene (2h): Compound **2h** was isolated as a white solid (0.023 g, 0.080 mmol, 67%) from the reaction of **1h** (0.032 g, 0.100 mmol). Chromatography conditions: silica

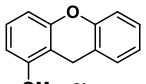
gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.
TLC (100% hexanes): R_f = 0.40 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.23 – 7.16 (m, 2H), 7.09 – 7.00 (m, 3H), 6.71 (m, 2H), 5.08 (s, 2H), 4.00 (s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 158.6, 152.6, 151.9, 137.1, 129.5, 129.1, 128.7, 128.1, 127.7, 127.6, 123.1, 120.9, 116.5, 112.9, 110.6, 102.8, 70.3, 27.3
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3063 (w), 3037 (w), 2954 (m), 2921 (m), 2852 (m), 1716 (w), 1630 (m), 1608 (m), 1578 (m), 1506 (m), 1489 (m), 1460 (m), 1391 (m), 1332 (w), 1309 (w), 1276 (w), 1236 (s), 1210 (m), 1187 (w), 1158 (s), 1102 (m), 1017 (m), 967 (m), 905 (w), 879 (w), 839 (m), 816 (m), 751 (m), 695 (m), 655 (w), 616 (w).
HRMS: Exact mass calculated for $C_{20}H_{16}O_2$ requires m/z = 288.1145, found m/z = 288.1150 (EI).



2i

3-(methoxymethoxy)-9H-xanthene (2i): Compound **2i** was isolated as a white solid (0.020 g, 0.083 mmol, 41%) from the reaction of **1i** (0.054 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

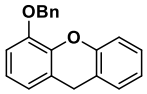
TLC (90/10 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.17 (s, 2H), 4.00 (s, 2H), 3.50 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 156.9, 152.6, 151.9, 129.5, 129.1, 127.7, 123.1, 120.8, 116.6, 114.0, 111.6, 104.5, 94.7, 56.1, 27.4.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3079 (w), 3000 (w), 2974 (w), 2928 (w), 2852 (w), 2829 (w), 1650 (m), 1611 (s), 1506 (w), 1483 (w), 1470 (m), 1450 (m), 1361 (w), 1322 9m), 1253 (m), 1230 (m), 1213 (w), 1177 (w), 1161 (s), 1099 (w), 1076 (s), 997 (s), 958 (m), 921 (m), 875 (w), 855 (w), 838 (w), 787 (w), 761 (m), 708 (w), 668 (w), 633 (w).
HRMS: Exact mass calculated for $C_{15}H_{14}O_3$ requires m/z = 242.0943, found m/z = 242.0945 (EI).



2k

1-(methoxy)-9H-xanthene (2k): Compound **2k** was isolated as a white solid (0.023 g, 0.11 mmol, 55%) from the reaction of **1k** (0.048 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.[19]

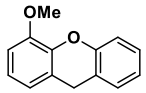
TLC (90/10 hexanes/ethyl acetate): R_f = 0.40 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 3H), 7.05 – 6.99 (m, 2H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 8.2, 1H), 3.96 (s, 2H), 3.87 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 157.7, 152.5, 151.6, 129.5, 127.7, 127.5, 123.0, 120.2, 116.5, 109.5, 109.1, 104.2, 55.8, 22.8.



2l

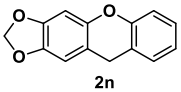
4-Benzyloxy-9H-xanthene (2l): Compound **2l** was isolated as a white solid (0.026 g, 0.090 mmol, 45%) from the reaction of **1l** (0.063 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate.

TLC (90/10 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.09 – 7.00 (m, 1H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.82 (dd, *J* = 16.7, 6.2 Hz, 2H), 5.22 (2, 4H), 4.06 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.0, 147.3, 142.6, 137.4, 128.9, 128.7, 128.0, 127.7, 127.4, 123.2, 122.6, 122.0, 121.5, 120.7, 117.0, 113.5, 71.7, 28.1.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3065 (w), 3032 (w), 2954 (w), 2924 (w), 2879 (w), 2852 (w), 2826 (w), 1582 (m), 1483 (m), 1463 (m), 1391 (w), 1335 (w), 1302 (w), 1273 (m), 1237 (s), 1204 9m), 1112 (m), 1085 (w), 1062 (m), 1032 (w), 967 (w), 915 (w), 883 (w), 859 (w), 840 (w), 747 (s0, 728 (w), 695 (w), 623 (w).
HRMS: Exact mass calculated for $C_{20}H_{16}O_2$ requires m/z = 288.1145, found m/z = 288.1151 (EI).



2m

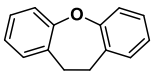
4-Methoxy-9H-xanthene (2m): Compound **2m** was isolated as a white solid (0.021 g, 0.097 mmol, 48%) from the reaction of **1m** (0.048 g, 0.200 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 200 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.[20]
TLC (90/10 hexanes/ethyl acetate): R_f = 0.25 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 3H), 7.03 (ddd, *J* = 7.6, 5.9, 2.6 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.82 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.78 (ddt, *J* = 7.7, 1.6, 0.9 Hz, 1H), 4.06 (t, *J* = 0.9 Hz, 2H), 3.94 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.9, 148.2, 141.7, 128.9, 127.7, 123.3, 122.7, 121.7, 120.8, 120.5, 117.0, 110.3, 56.3, 28.0.



2n

10*H*-[1,3]Dioxolo[4,5-b]xanthene (2n): Compound **2n** was isolated as an off-white solid (0.016 g, 0.071 mmol, 36%) from the reaction of **1n** (0.052 g, 0.20 mmol). Chromatography conditions: silica gel column (1 × 20 cm), packed in hexanes, eluted with 100 mL of hexanes, followed by 100 mL of 90/10 hexanes/ethyl acetate. NMR data match with previously reported values.[21]
TLC (90/10 hexanes/ethyl acetate): R_f = 0.40 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.60 (d, *J* = 0.9 Hz, 2H), 5.93 (s, 2H), 3.96 (s, 2H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 152.1, 146.9, 146.6, 143.4, 128.9, 127.7, 123.0, 120.3, 116.4, 112.2, 107.6, 101.3, 98.7, 28.2.



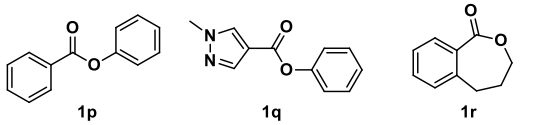
2o

10,11-Dihydrodibenzo[*b,f*]oxepine (2o): Compound **2o** was isolated as a colorless oil (0.0166 g, 0.085 mmol, 42%) from the reaction of **1o** (0.0440 g, 0.20 mmol). Chromatography conditions: silica gel column (1 × 15 cm), packed in hexanes, eluted with 200 mL of hexanes. ^{1}H NMR data match with previously reported values.[22]

TLC (100% hexanes): R_f = 0.50 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.16 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.04-6.99 (apparent t, *J* = 7.0 Hz, 2H), 3.16 (s, 4H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.2, 132.0, 130.5, 127.4, 124.0, 121.2, 31.3.

6.3. Unsuccessful substrates

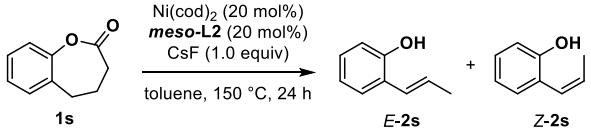
Substrates **1p**, **1q**, and **1r** were synthesized according to literature methods.[23-25] Applying the general procedure for decarbonylation (section 6.2) to **1p**, **1q**, and **1r** did not lead to the corresponding ether products.



1p (85% recovery) **1q** (89% recovery) **1r** (>99% recovery)

Decarbonylation of 1s

Substrate **1s** was synthesized according to a literature procedure.[26]

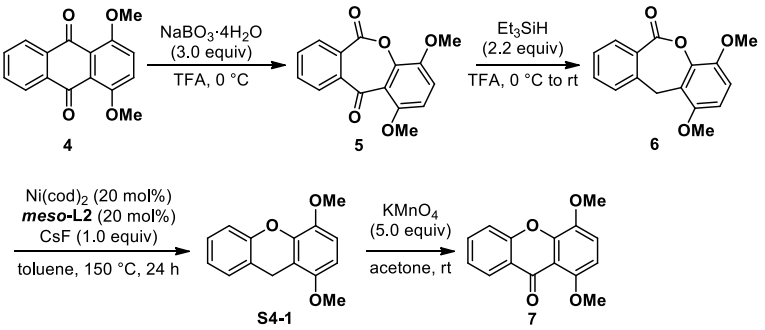


1s *E*-**2s** *Z*-**2s**
E/*Z* = 82:18

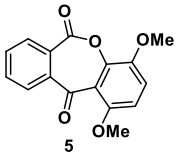
An oven dried 2-dram vial was charged with a magnetic stir bar, **1s** (8.1 mg, 0.050 mmol), ***meso*-L2** (5.7 mg, 0.010 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 20 mol%), CsF (7.6 mg, 0.050 mmol, 1.0 equiv.), and toluene (0.50 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred for 24 h. After cooling to room temperature, the reaction mixture was transferred to a 40-mL vial using CH_2Cl_2 and ethyl acetate. The solvents were then removed by rotary evaporator. The residue was dissolved in $CDCl_3$. ^{1}H NMR spectrum of the sample was obtained and showed full conversion of **1s** along with signals for *E*-**2s** and *Z*-**2s** in 82:18 ratio. The NMR spectrum is provided on page S88 and matches with a previously reported spectrum of a 88:12 mixture of *E*-**2s** and *Z*-**2s**.[27]

7. Experimental procedures for Figure 8

7.1. Synthesis of xanthone 7 from Quinizarin

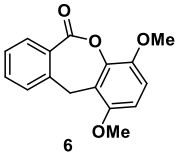


Dimethylquinizarin **4** was synthesized from quinizarin following a reported procedure.[28]



1,4-Dimethoxydibenzo[b,e]oxepine-6,11-dione (5): Compound **5** (0.623 g, 2.19 mmol, 75%) was obtained as a yellow solid from dimethylquinizarin **4** (0.784 g, 2.92 mmol) following a literature procedure.[28] NMR data match with previously reported values.[28]

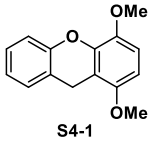
TLC (100% hexanes): R_f = 0.50 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.9 Hz, 1H), 7.76 - 7.62 (m, 3H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.2, 163.2, 150.1, 145.0, 142.6, 139.3, 134.5, 133.3, 132.6, 127.4, 124.8, 124.1, 116.1, 109.6, 57.0, 56.9.



1,4-dimethoxydibenzo[b,e]oxepin-6(11H)-one (6):
A Schlenk flask was charged with a stir bar and the lactone **5** (0.142 g, 0.500 mmol). The flask was put under an N_2 atmosphere and TFA (0.50 mL) was added. The solution was cooled to 0 °C in an ice bath and Et_3SiH (0.18 mL, 0.128 g, 1.10 mmol, 2.2 equiv) was added dropwise. The solution was then warmed to room temperature and stirred for 12 h. The reaction was quench with a saturated solution of $NaHCO_3$ (10 mL) and diluted with dichloromethane (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic fractions were dried with

Na_2SO_4 and concentrated using a rotary evaporator. The residue was loaded directly onto a silica gel column (1 × 20 cm, packed in 50/50 hexanes/ethyl acetate). The column was eluted with 50/50 hexanes/ethyl acetate and the product-containing fractions were collected. The solvents were removed by rotary evaporation and the residue was dried under vacuum using an oil pump to give **6** as a white solid (0.124 g, 0.46 mmol, 91%).

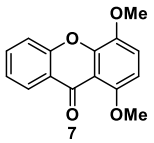
TLC (85/15 hexanes/ethyl acetate): R_f = 0.50 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.85 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.26 (m, 2H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 1H), 4.07 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.6, 149.5, 145.1, 143.1, 140.6, 133.3, 132.7, 128.3, 127.5, 127.3, 123.8, 110.5, 107.8, 56.5, 56.4, 28.8.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3020 (w), 2997 (w), 2957 (w), 2937 (w), 2836 (w), 1733 (s), 1673 (w), 1608 (w), 1499 (s), 1453 (m), 1319 (w), 1273 (m), 1243 (m), 1213 (m), 1181 (m), 1119 (m), 1089 (m), 1066 (m), 1036 (w), 981 (w), 954 (w), 793 (m), 777 (w), 754 (w), 741 (w), 718 (m), 646 (w), 620 (w).
HRMS: Exact mass calculated for $[C_{16}H_{14}O_4+H]^+$ requires m/z = 271.0965, found m/z = 271.0965. (ESI+).



S4-1

1,4-dimethoxy-9H-xanthene (S4-1):
An oven-dried 2-dram vial was charged with a magnetic stir bar, **6** (0.054 g, 0.200 mmol), and the ligand ***meso*-L2** (0.023 g, 0.040 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (0.011 g, 0.040 mmol, 20 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 100 mL of hexanes, 50 mL of 90/10 hexanes/ethyl acetate followed by 50 mL 80/20 hexanes/ethyl acetate. The product containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product **S4-1** as a white solid (0.0251 g, 0.104 mmol, 52%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.50 (visualized by UV)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.47 (d, *J* = 8.8 Hz, 1H), 3.96 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.4, 151.3, 142.4, 142.1, 129.3, 127.7, 123.3, 119.9, 117.2, 110.9, 110.3, 102.9, 56.9, 55.8, 23.0.
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3066 (w), 3020 (w), 2934 (m), 2852 (w), 2839 (w), 1608 (w), 1586 (m), 1499 (s), 1463 (m), 1312 (w), 1258 (s), 1240 (s), 1197 (w), 1115 (m), 1095 (s), 947 (w), 879 (w), 793 (w), 777 (m), 751 (m), 728 (w), 718 (w), 679 (w), 623 (w).
HRMS: Exact mass calculated for $C_{15}H_{14}O_3$ requires m/z = 242.0943, found m/z =242.0941 (EI).



7

1,4-dimethoxy xanthone (7):

A round bottom flask was charged with a stir bar, **S4-1** (0.0251 g, 0.104 mmol), and acetone (3.0 mL). The resulting solution was stirred vigorously and $KMnO_4$ (0.082 g, 0.52 mmol, 5.0 equiv) was added at once. After stirring at room temperature for 1 h, the brown solid was filtered off using a pad of Celite. The solid was washed with 10 mL of acetone and the pink filtrate was concentrated by rotary evaporator to give a brown solid. Dichloromethane (10 mL) was added, and the mixture was filtered through a pad of Celite. The filtrate was concentrated by rotary evaporator and the residue was dried under vacuum using an oil pump to give **7** as an orange solid (0.0226 g, 0.0881 mmol, 85%).

TLC (80/20 hexanes/ethyl acetate): R_f = 0.35 (visualized by UV)

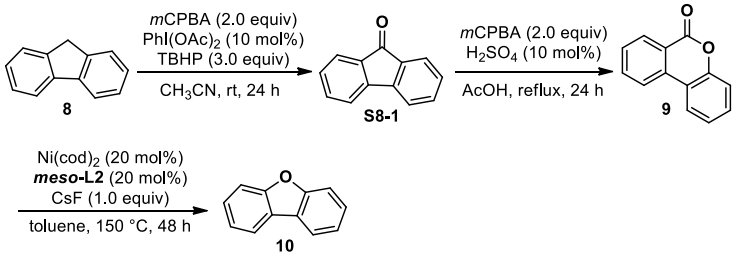
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.68 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.35 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.7, 155.0, 154.0, 148.1, 142.4, 134.4, 126.9, 124.2, 123.0, 117.7, 116.7, 104.5, 57.1, 56.7.

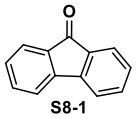
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3010 (w), 2961 (m), 2931 (m), 2889 (m), 1663 (s), 1598 (s), 1578 (m), 1489 (s), 1466 (s), 1440 (m), 1355 (w), 1316 (s), 1260 (s), 1287 (m), 1187 (w), 1145 (w), 1089 (m), 1072 (m), 974 (m), 934 (w), 892 (w), 865 (w), 800 (m), 754 (m), 728 (w), 682 (w), 633 (w).

HRMS: Exact mass calculated for $[C_{15}H_{12}O_4+H]^+$ requires m/z = 257.0808, found m/z = 257.0809. (ESI+).

7.2. Synthesis of dibenzofuran 10 from fluorene



8 S8-1 9 10

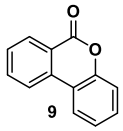

S8-1

Fluorenone (S8-1): Fluorenone (0.178 g, 0.98 mmol, 98%) was obtained as a yellow solid from fluorene (0.166 g, 1.00 mmol) following a literature procedure[29] with the reaction time increased to 24 h. NMR data match with previously reported values.[29]

TLC (80/20 hexanes/ethyl acetate): R_f = 0.45 (visualized by UV)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 5.1 Hz, 4H), 7.25 (dq, *J* = 8.6, 4.4 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 193.8, 144.3, 134.7, 134.1, 129.0, 124.2, 120.3.



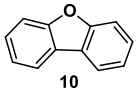
9

Benzocoumarin (9): Lactone **9** (0.118 g, 0.60 mmol, 60%) was obtained as a white solid from **s8-1** (0.180 g, 1.00 mmol) following a literature procedure.[30] NMR data match with previously reported values.[30]

TLC (80/20 hexanes/ethyl acetate): R_f = 0.30 (visualized by UV)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.34 – 7.24 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.2, 151.3, 134.9, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.0, 117.8.



10

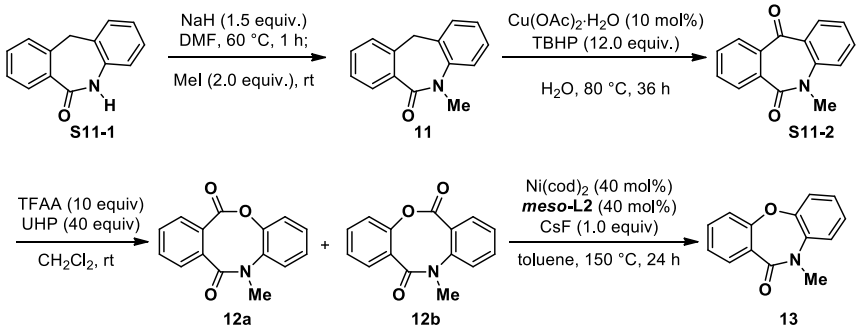
Dibenzo[*b,d*]furan (10): An oven-dried 2-dram vial was charged with a stir bar, **9** (19.6 mg, 0.10 mmol), and ***meso*-L2** (12.0 mg, 0.020 mmol, 20 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (6.5 mg, 0.020 mmol, 20 mol%), CsF (15.0 mg, 0.100 mmol, 1.0 equiv.), and toluene (1.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 48 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 15 cm, packed in hexanes). The column was eluted with 200 mL of hexanes. The product containing fractions were collected. The solvent was evaporated by rotary evaporation and the residue was dried under vacuum using an oil pump to give the product **10** as a white solid (0.0142 g, 0.084 mmol, 84%). NMR data match with previously reported values.[31]

TLC (100% hexanes): R_f = 0.50 (visualized by UV).

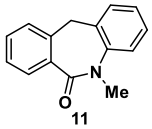
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 156.3, 127.3, 124.4, 122.8, 120.8, 111.8.

7.3. Synthesis of dibenzoxazepinone 13 from dibenzazepinone



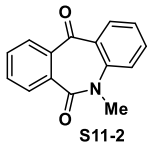
Compound **S11-1** was synthesized following a previously reported procedure.[32]



11

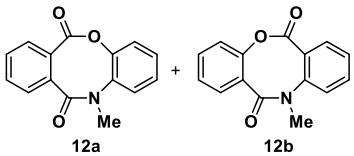
5-methyl-5H-dibenzo[b,e]azepin-6(11H)-one (11): A 20-mL vial was charged with a stir bar, **S11-1** (0.245 g, 1.00 mmol), and NaH (0.036 g, 1.50 mmol, 1.5 equiv). The vial was then placed under a N_2 atmosphere and DMF (5.0 mL) was added via syringe. The vial was placed in heating block preheated at 60 °C and the reaction was stirred at 60 °C for 1 h. The solution turned orange after 1 h and iodomethane (0.12 mL, 0.284 g, 2.0 mmol, 2.0 equiv) was added dropwise. After finishing addition, the reaction was again stirred at 60 °C for 12 h. After cooling to room temperature, water (10 mL) was added followed by dichloromethane (10 mL) and the mixture was transferred to a separatory funnel. The organic layer was collected and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with water (200 mL), dried with Na_2SO_4 and concentrated using rotary evaporator. The residue was loaded onto a silica gel column (3 × 15 cm), packed in dichloromethane. The column was eluted with dichloromethane. The product containing fractions were collected and concentrated using rotary evaporator. The residue was dried under vacuum using an oil pump to give **11** as an off-white solid (0.194 g, 0.87 mmol, 87%). NMR data match with previously reported values.[33]

TLC (100% dichloromethane): R_f = 0.40 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.14 (m, 5H), 7.08 (m, 1H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.63 (s, 3H), 3.55 (d, *J* = 13.3 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.9, 142.5, 141.4, 137.1, 132.6, 131.7, 131.1, 127.6, 127.3, 127.0, 126.1, 125.8, 122.5, 39.0, 37.9



S11-2

5-methyl-5H-dibenzo[b,e]azepine-6,11-dione (S11-2): Compound **S11-2** (0.201 g, 0.85 mmol, 85%) was obtained as a white solid from **11** (0.220 g, 1.00 mmol) using a literature procedure.[33] NMR data match with previously reported values.[33]
TLC (100% dichloromethane): R_f = 0.20 (visualized by UV).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz 1H), 7.64 (m, 4H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 3.64 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 195.3, 166.6, 140.4, 140.3, 136.5, 132.6, 132.5, 132.4, 132.2, 131.0, 128.2, 126.5, 125.6, 122.4, 38.9.

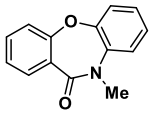


12a 12b

12-methyl-6H-dibenzo[b,f][1,4]oxazocine-6,11(12H)-dione (12a and 12b):
A Schlenk flask was charged with a stir bar and **S11-2** (0.0685 g, 0.25 mmol). The flask was placed under a N_2 atmosphere and dichloromethane (5.0 mL) was added followed by urea·hydrogen

peroxide complex (UHP, 0.84 g, 10 mmol, 40 equiv). The resulting mixture was vigorously stirred and TFAA (0.38 mL, 2.5 mmol, 10 equiv) was added dropwise at room temperature. The reaction was stirred for 12 h and turned light pink with white precipitates. Dichloromethane (10 mL) was added followed by water (10 mL). The mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic fractions were dried with Na_2SO_4 and concentrated by rotary evaporator to give an off-white solid. The solid was chromatographed (silica gel column (1 × 20 cm, packed in hexanes), eluted with 200 mL 80/20 hexanes/ethyl acetate) to give a mixture of **12a** and **12b** as a white solid (0.057 g, 0.23 mmol, 90%). The product ratio was determined to be 3:1 by ^{1}H NMR. Attempts to isolate the two regioisomers to determine the major product were not successful.

TLC (80/20 hexanes/ethyl acetate): R_f = 0.33 (visualized by UV as one spot)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, major + minor isomer integral value = 15), 7.31 – 7.27 (m, 2H from minor isomer), 7.25 – 7.13 (m, major + minor isomer integral value = 14), 7.03 (dd, *J* = 8.2, 1.1 Hz, 1H from minor isomer), 3.46 (s, 3H from major isomer, integral value = 9), 3.44 (s, 3H from minor isomer, integral value = 3).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.9 (major), 167.2 (major), 166.6 (2C, minor), 149.1 (major), 148.7 (minor), 140.7 (minor), 136.5 (major), 133.4, 132.5, 132.0 (major), 131.7, 130.6 (major, 129.4 (major), 129.2 (minor), 129.1 (minor), 128.7 (2C), 128.3, 127.5 (2C, major), 127.4 (major), 127.2 (2C), 127.0, 125.7, 122.3 (major), 121.0, 36.8 (minor), 36.5 (major).
IR (FT-ATR, cm^{-1}, neat) ν_{max} 3385 (w), 3319 (w), 3217 (w), 3069 (w), 2931 (w), 2859 (w), 1756 (s), 1706 (w), 1663 (s), 1601 (w), 1499 (m), 1459 (w), 1417 (w), 1374 (m), 1315 (w), 1283 (m), 1244 (m), 1201 (m), 1188 (w), 1105 (m), 1092 (m), 1056 (m), 1030 (m), 1007 (w), 981 (w), 905 (w), 885 (w), 865 (w), 780 (m), 728 (m), 669 (w), 639 (w).
HRMS: Exact mass calculated for $[C_{15}H_{11}NO_3+H]^+$ requires m/z = 254.0812, found m/z = 254.0814. (ESI+).



13

10-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (13):
An oven-dried 2-dram vial was charged with a magnetic stir bar, the mixture of **12a** and **12b** (0.057 g, 0.200 mmol), and the ligand ***meso*-L2** (0.046 g, 0.080 mmol, 40 mol%). The vial was brought into a glovebox, then $Ni(cod)_2$ (0.022 g, 0.080 mmol, 40 mol%), CsF (0.030 g, 0.200 mmol, 1.0 equiv.), and toluene (2.00 mL) were added. The vial was sealed and brought outside and placed in an aluminum heating block preheated at 150 °C. The mixture was stirred (700 rpm) for 24 h at 150 °C. After cooling to room temperature, the mixture was directly loaded onto a silica gel column (1 × 20 cm, packed in hexanes). The column was eluted with 100 mL of hexanes, 200 mL of 90/10 hexanes/ethyl acetate. The product containing fractions were collected. The solvent was evaporated by rotary evaporator and the residue was dried under vacuum using an oil pump to give the product **13** as a white solid (0.0432 g, 0.192 mmol, 96%). A reaction using 20 mol% $Ni(cod)_2$ and 20 mol% ***meso*-L2** gave **13** in 51% yield (0.0230 g, 0.102 mmol). NMR data match with previously reported values.[34]

TLC (80/20 hexanes/ethyl acetate): R_f = 0.40 (visualized by UV)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.17 (m, 5H), 7.14 (dt, *J* = 7.6, 1.7 Hz, 1H), 3.59 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.6, 160.8, 153.8, 136.2, 133.7, 132.4, 126.4 (2 × s), 125.9, 125.4, 122.7, 121.6, 120.0, 37.0.

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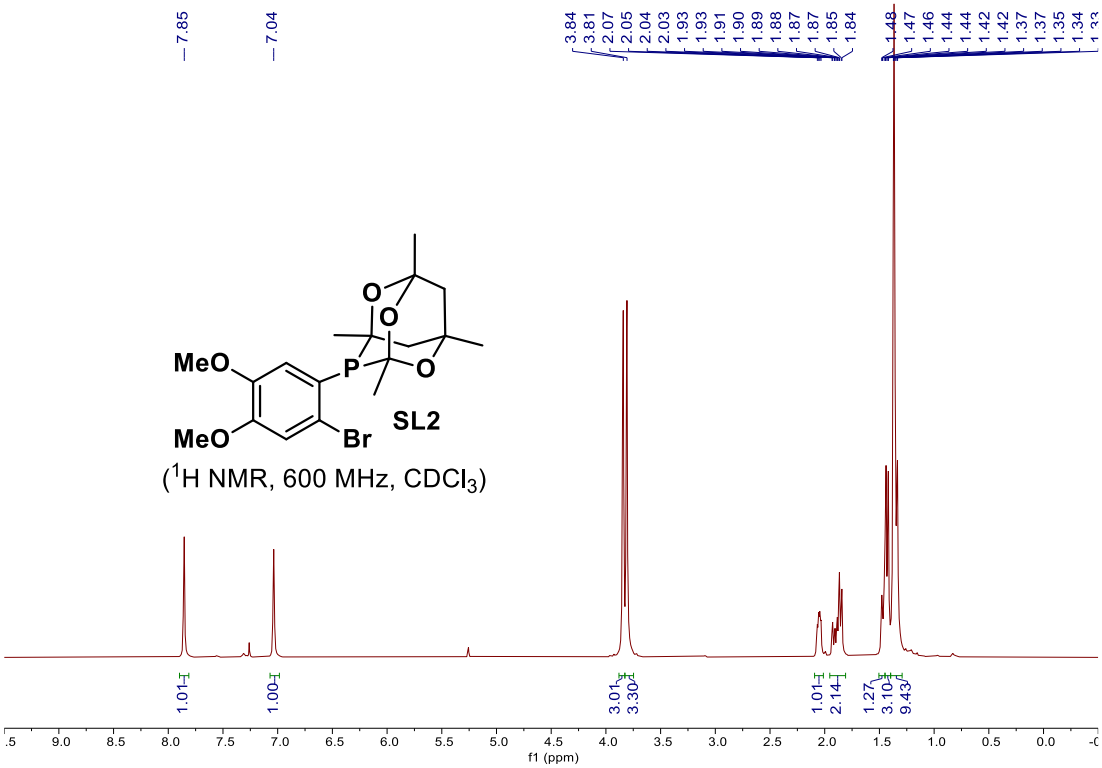
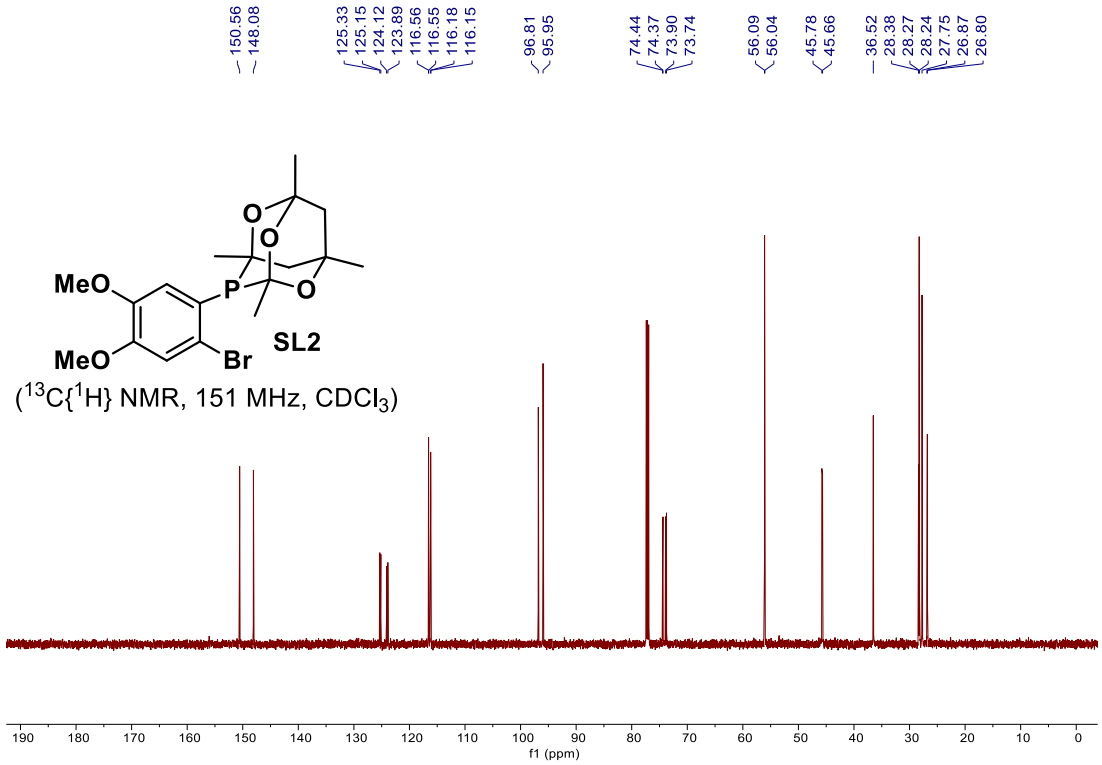
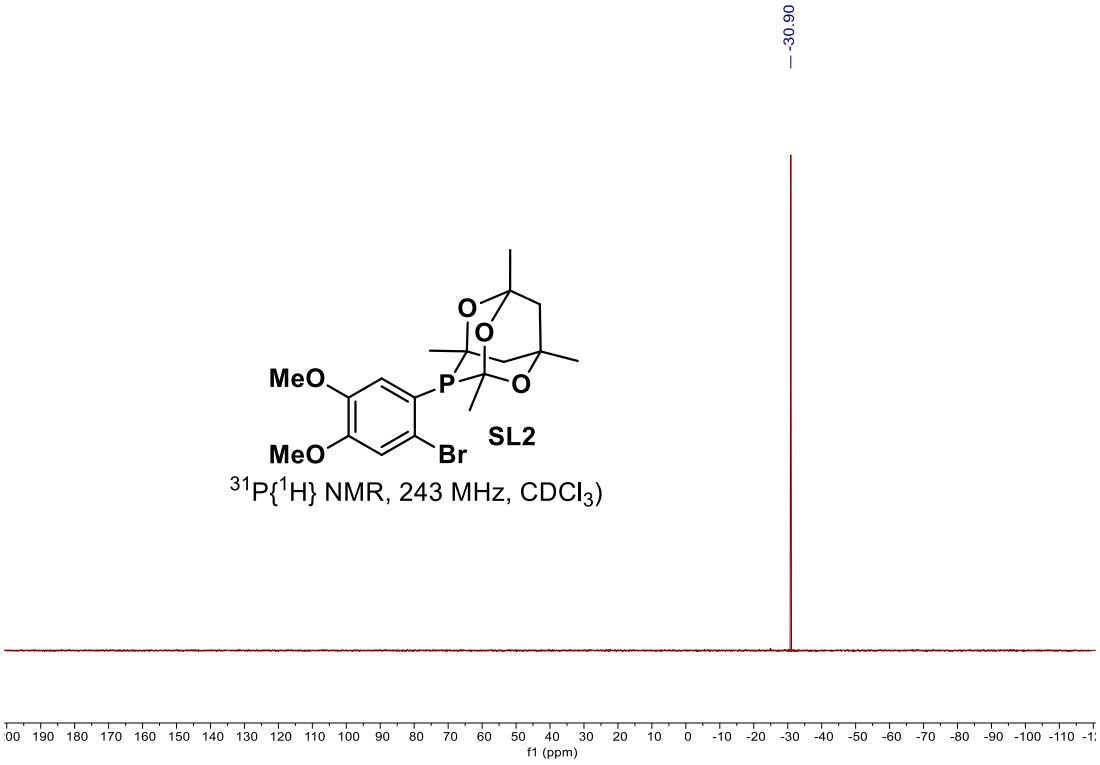
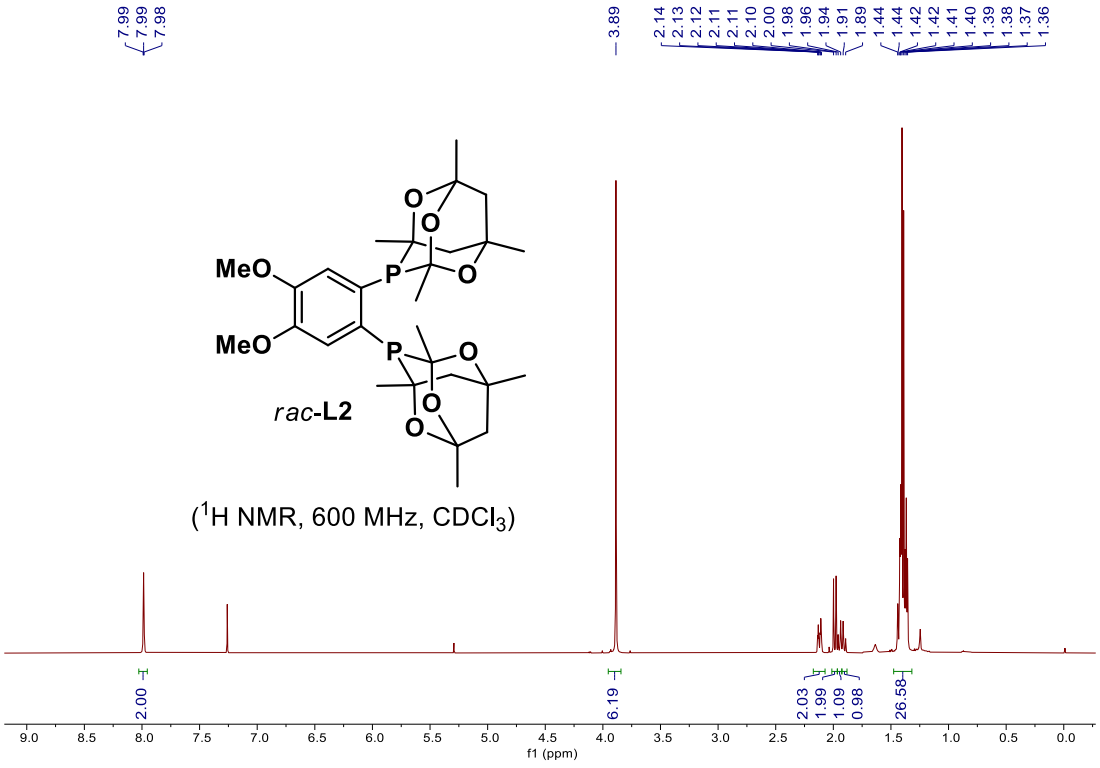
9. NMR spectra of new compounds



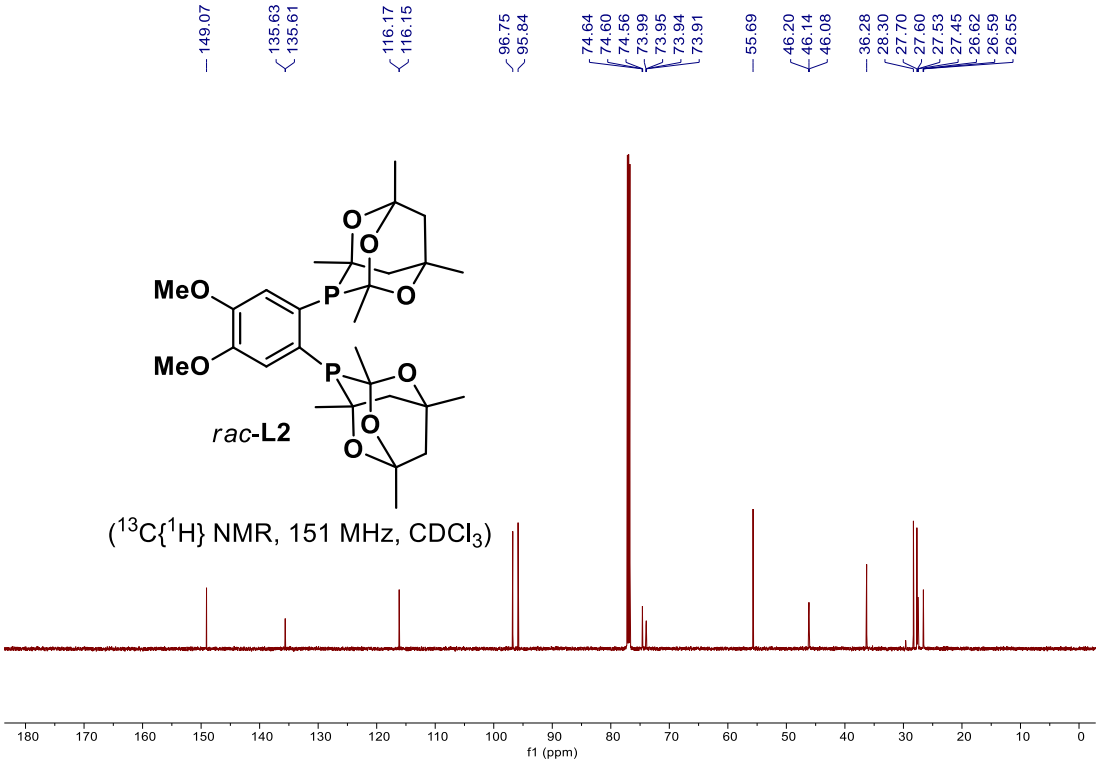




$^{31}P\{^{1}H\}$ NMR, 243 MHz, $CDCl_3$)



(^{1}H NMR, 600 MHz, $CDCl_3$)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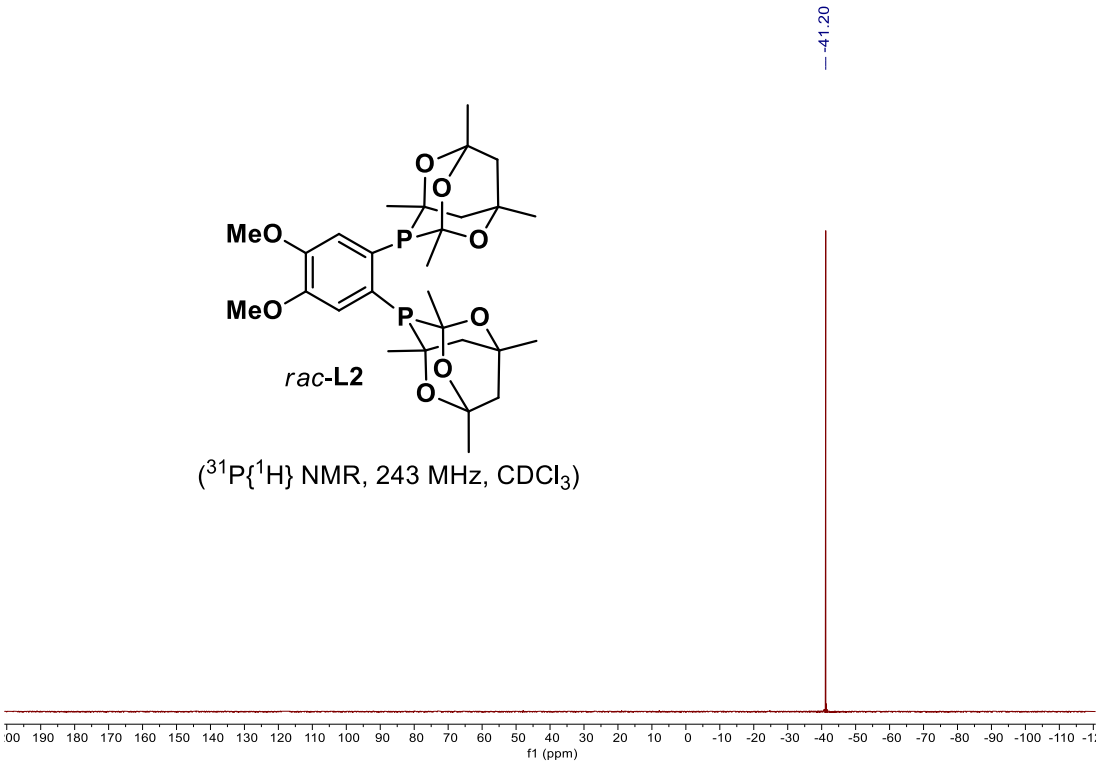
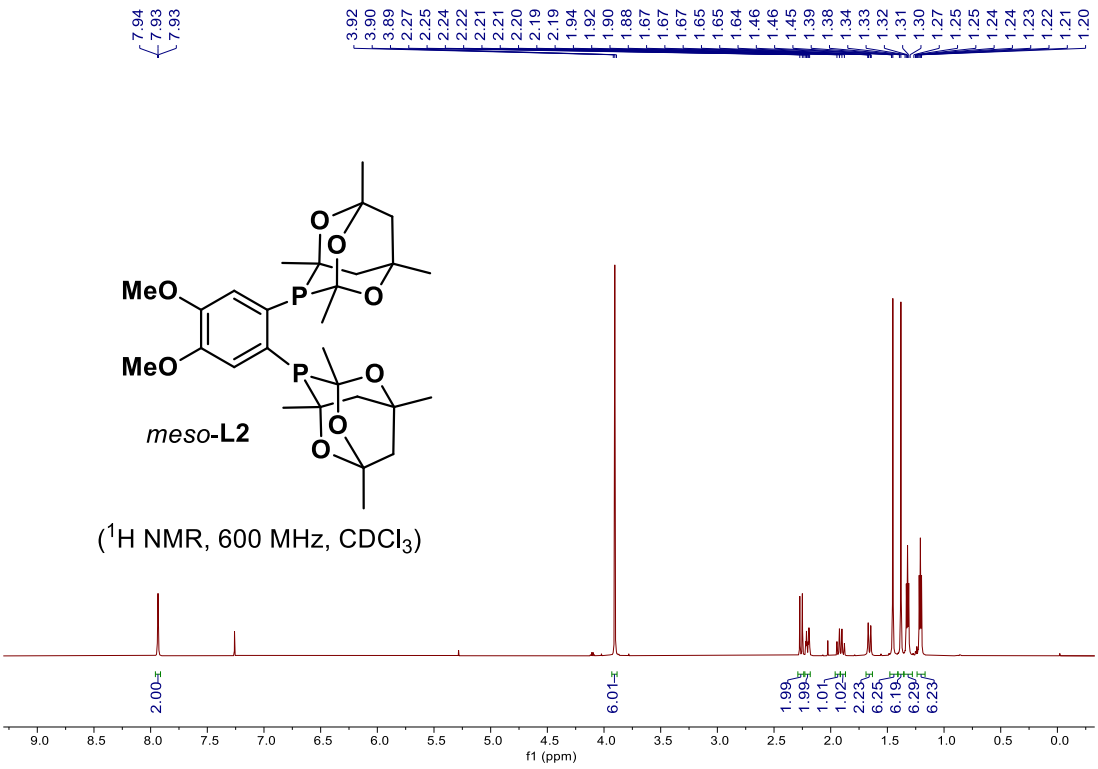
135.63
135.61
116.17
116.15
96.75
95.84
74.64
74.60
74.56
73.99
73.95
73.94
73.91
55.69
46.20
46.14
46.08
36.28
28.30
27.70
27.60
27.53
27.45
26.62
26.59
26.55
MeO
MeO
rac-L2
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)


-41.20
MeO
MeO
rac-L2
(31P{1H} NMR, 243 MHz, CDCl3)
f1 (ppm)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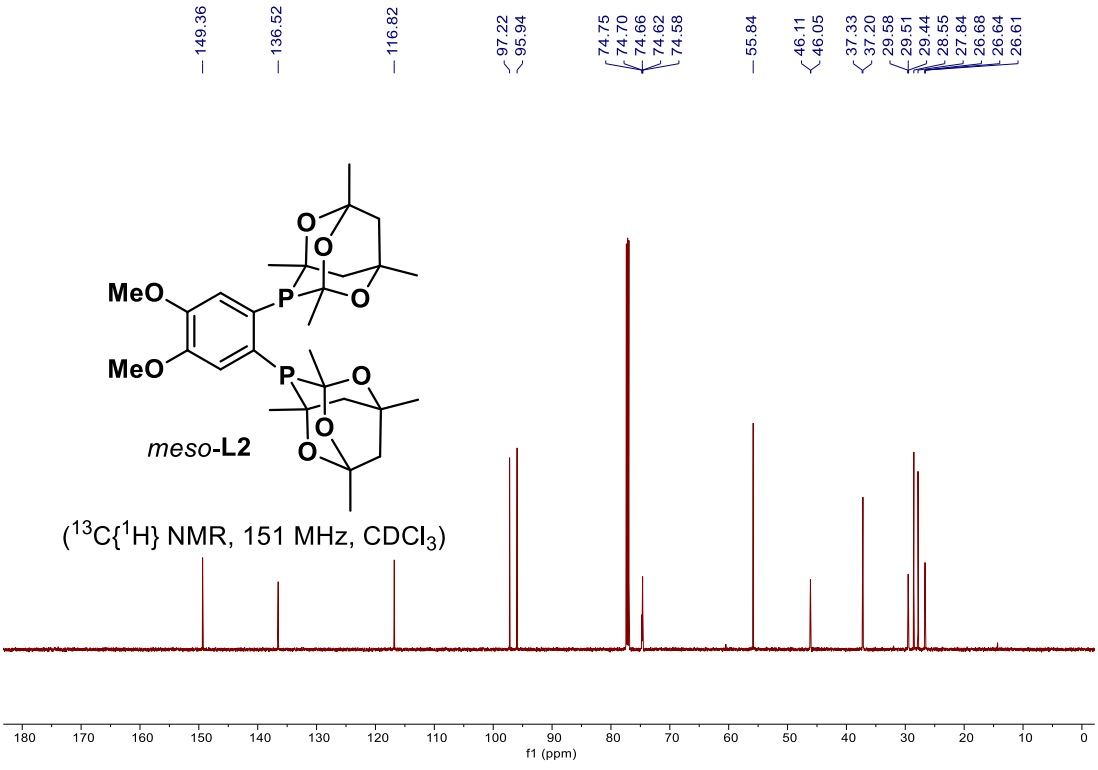
7.93
7.93
3.92
3.90
3.89
3.27
2.25
2.24
2.22
2.21
2.21
2.20
2.19
2.19
1.94
1.92
1.90
1.88
1.67
1.67
1.67
1.65
1.65
1.64
1.46
1.45
1.39
1.38
1.34
1.33
1.32
1.31
1.30
1.27
1.25
1.25
1.24
1.24
1.23
1.22
1.21
1.20
MeO
MeO
P
O
meso-L2
(1H NMR, 600 MHz, CDCl3)
2.00
6.01
1.99
1.99
1.01
1.02
2.23
6.25
6.19
6.29
6.23
f1 (ppm)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74.75
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74.66
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74.58
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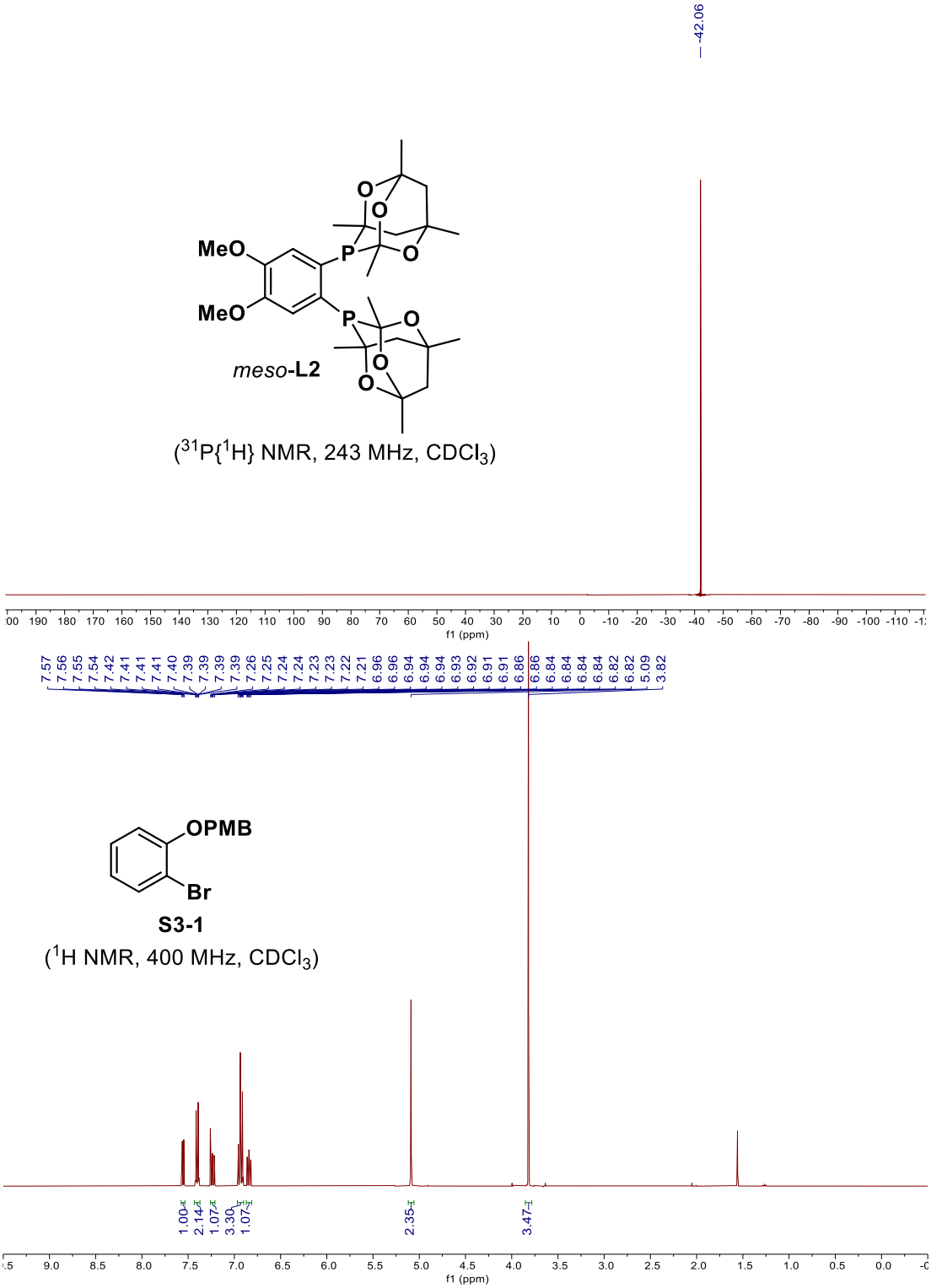
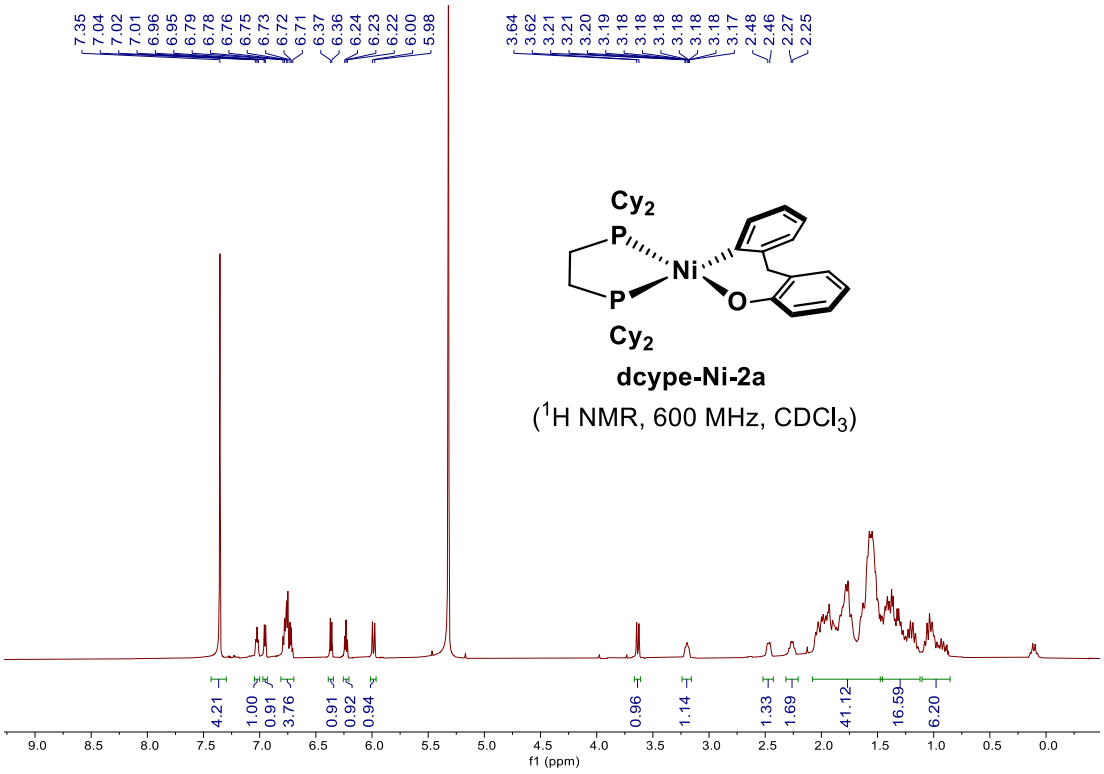
46.11
46.05
37.33
37.20
29.58
29.51
29.44
28.55
27.84
26.68
26.64
26.61
MeO
MeO
P
O
meso-L2
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)



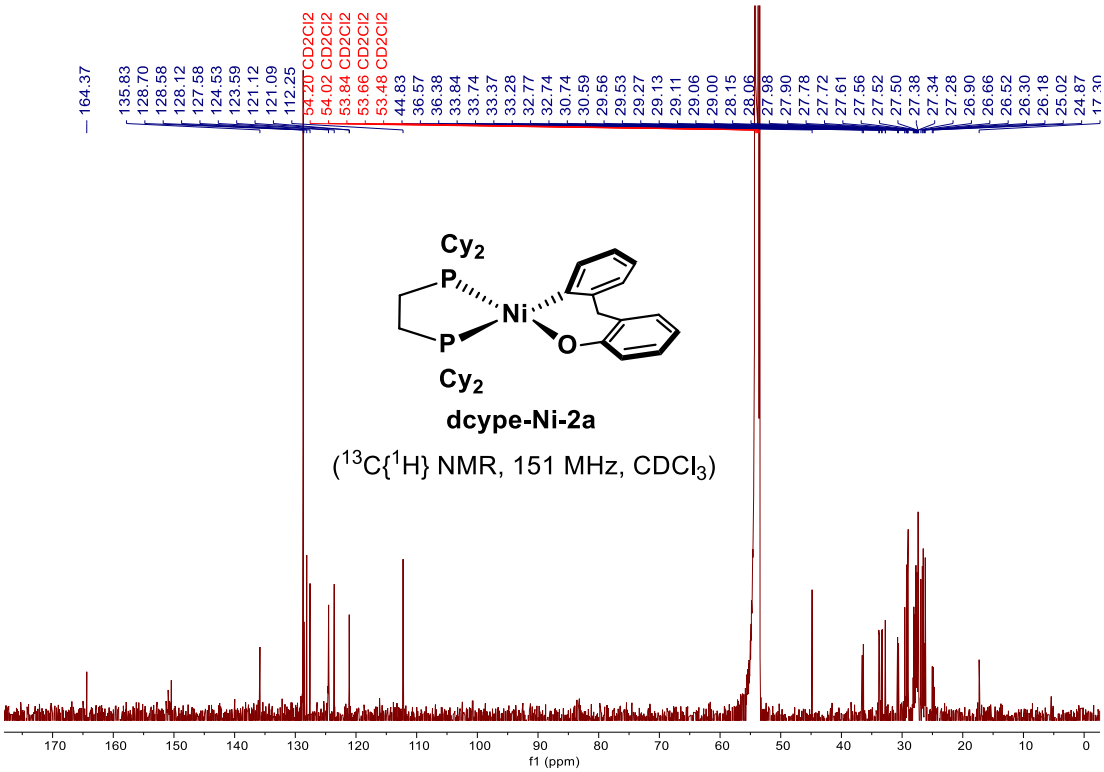
($^{31}P\{^{1}H\}$ NMR, 243 MHz, $CDCl_3$)

(^{1}H NMR, 400 MHz, $CDCl_3$)



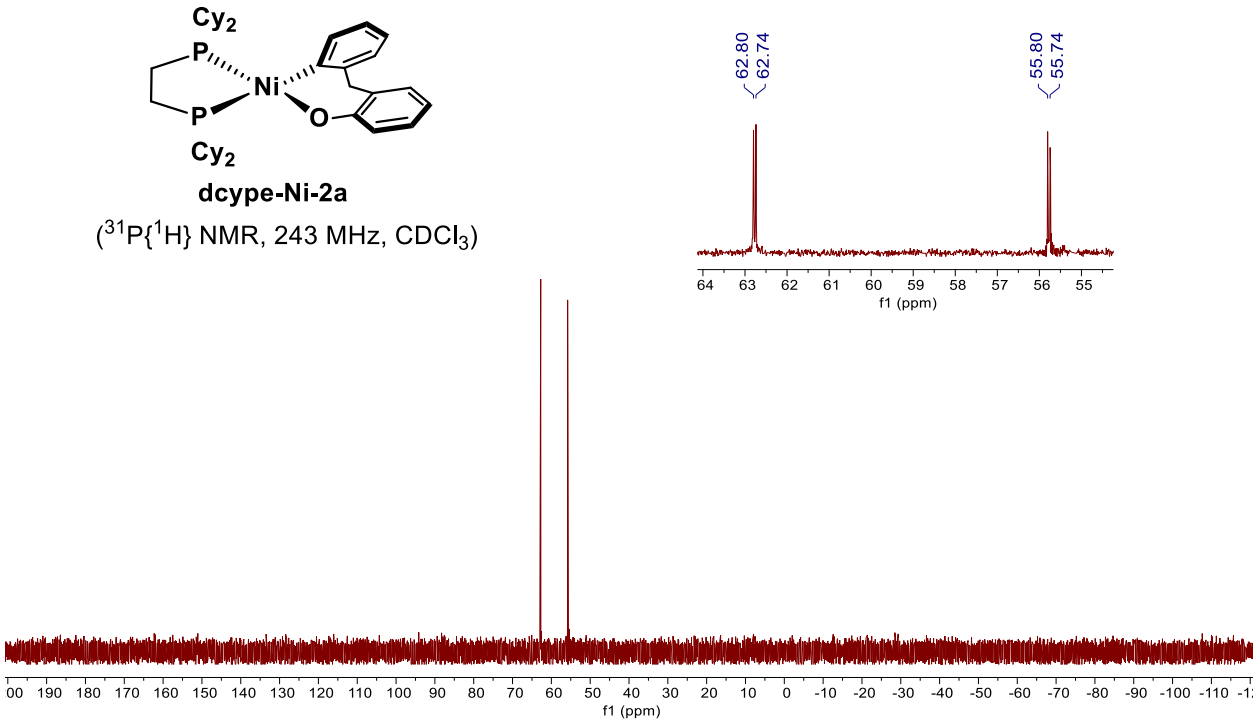
dcype-Ni-2a

(^{1}H NMR, 600 MHz, $CDCl_3$)



dcype-Ni-2a

($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)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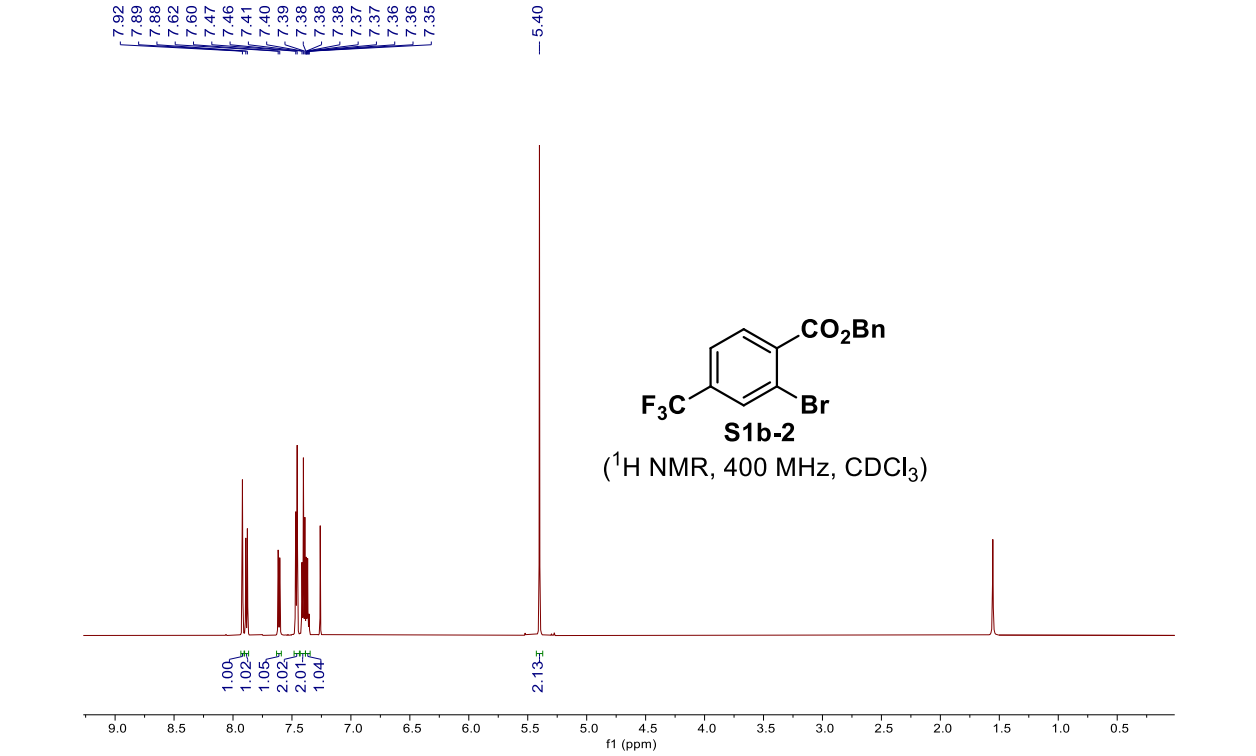
62.74
55.80
55.74
Cy2
P
Ni
P
O
Cy2
dcype-Ni-2a
(31P{1H} NMR, 243 MHz, CDCl3)
f1 (ppm)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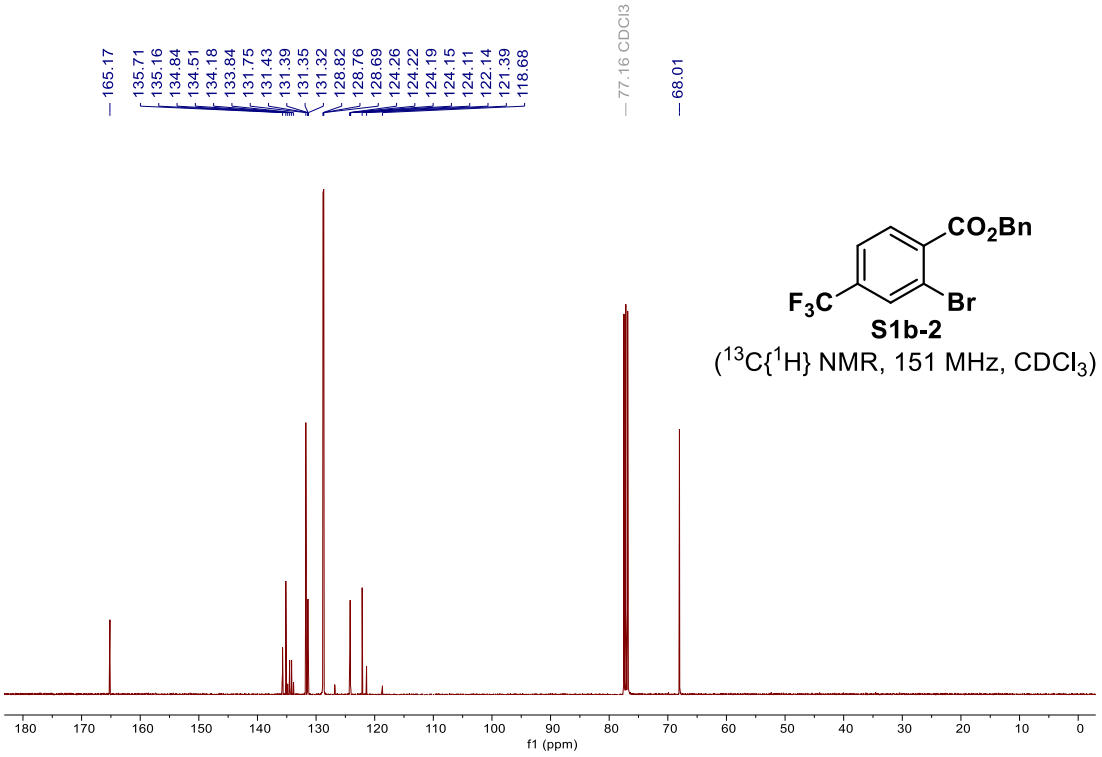
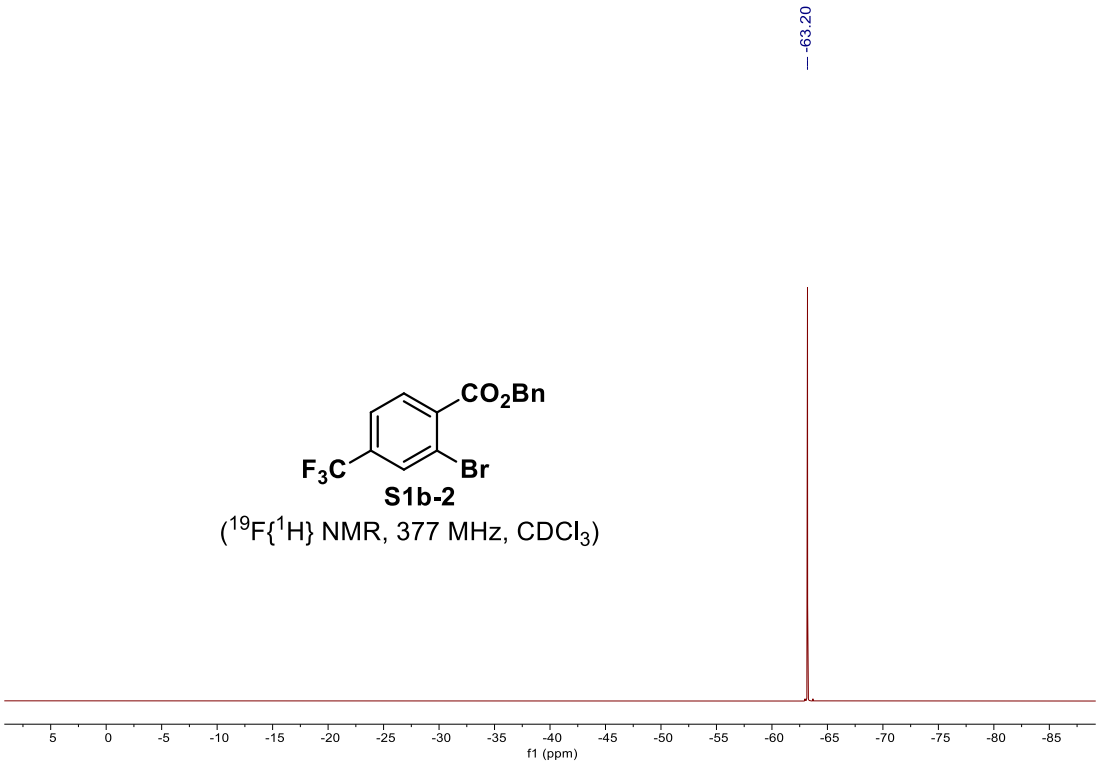
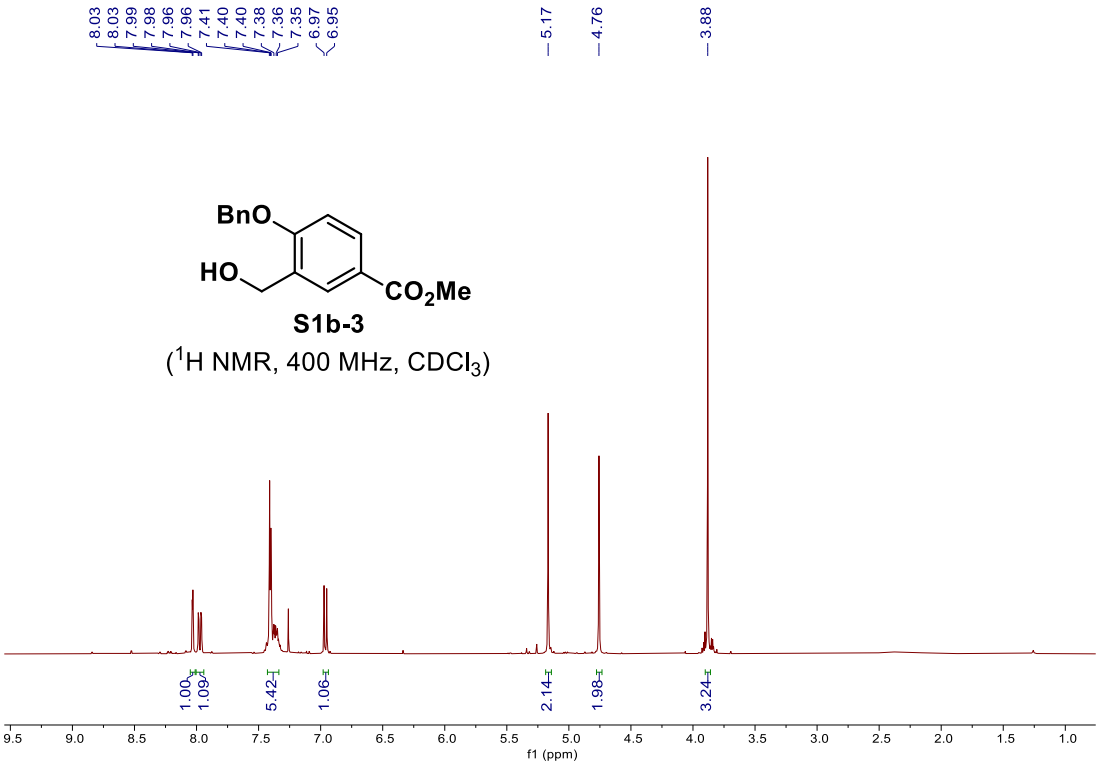
7.41
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
5.40
CO2Bn
F3C
Br
S1b-2
(1H NMR, 400 MHz, CDCl3)
1.00
1.02
1.05
2.02
2.01
1.04
2.13
f1 (ppm)



($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)

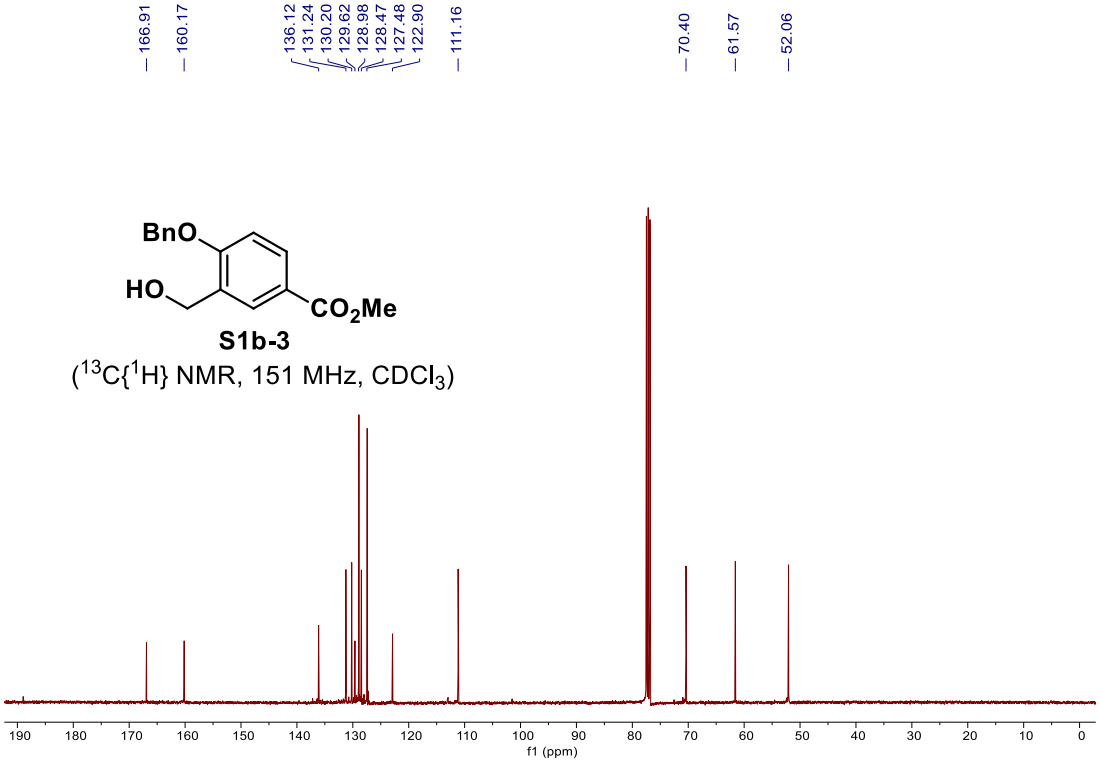


($^{19}F\{^{1}H\}$ NMR, 377 MHz, $CDCl_3$)



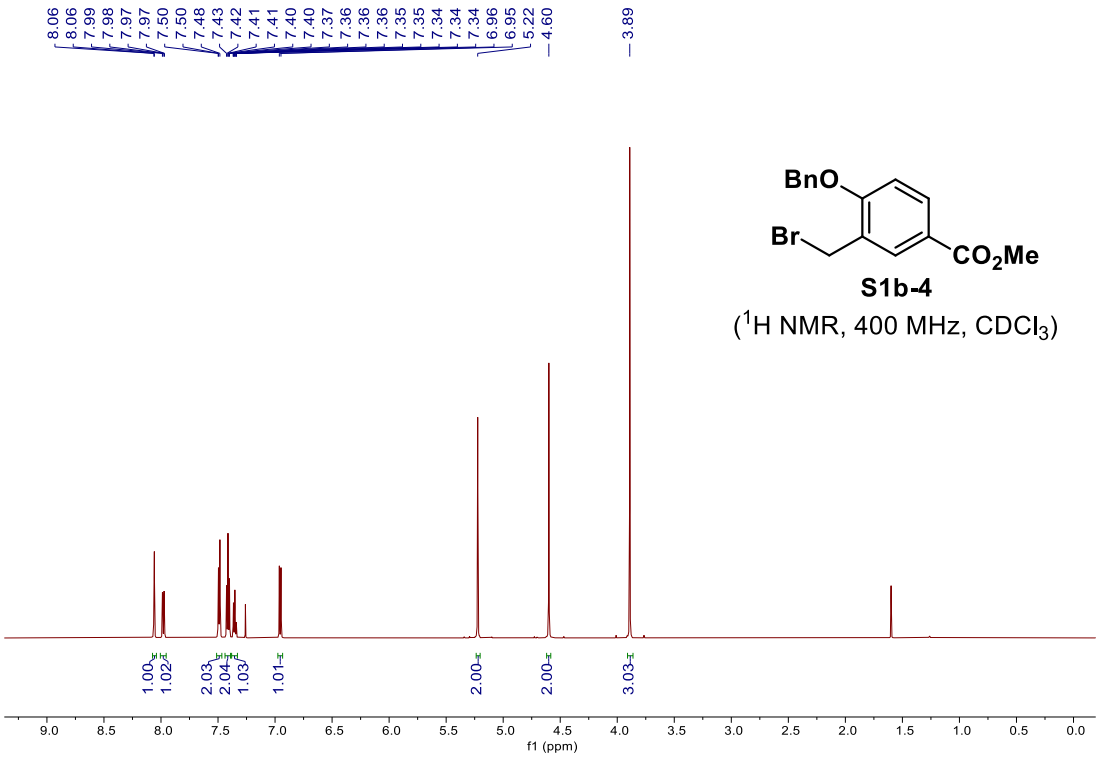
S1b-3

(^{1}H NMR, 400 MHz, $CDCl_3$)



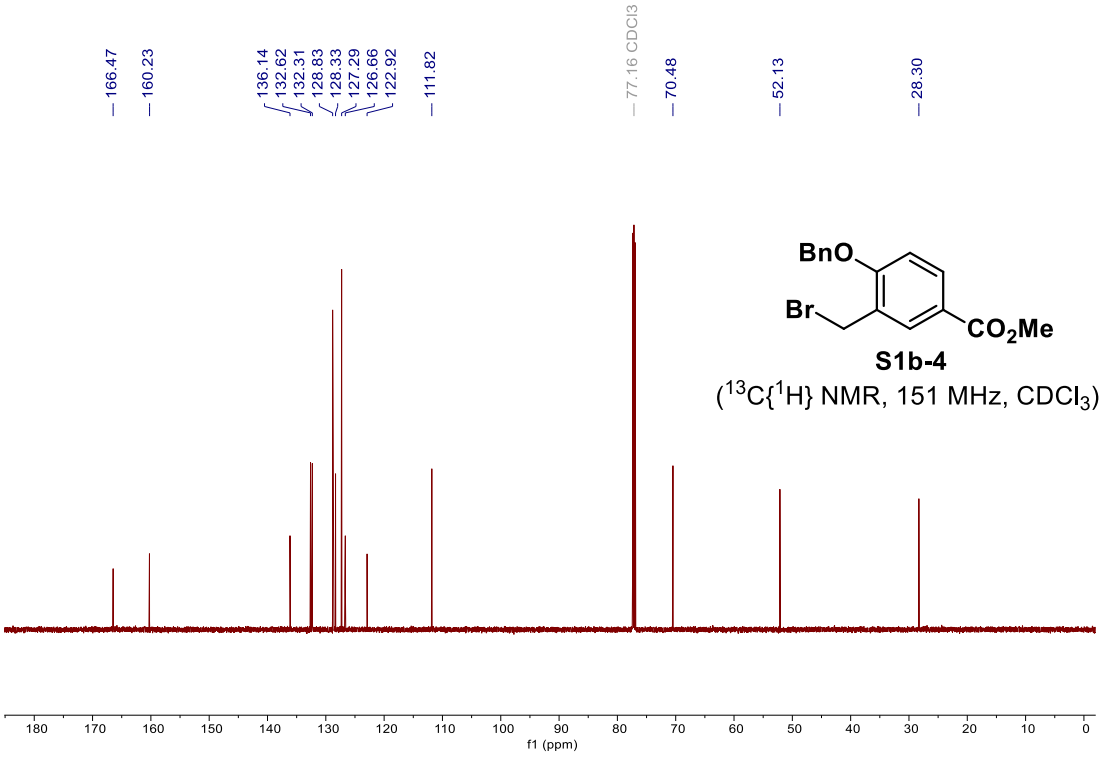
S1b-3

(^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$)



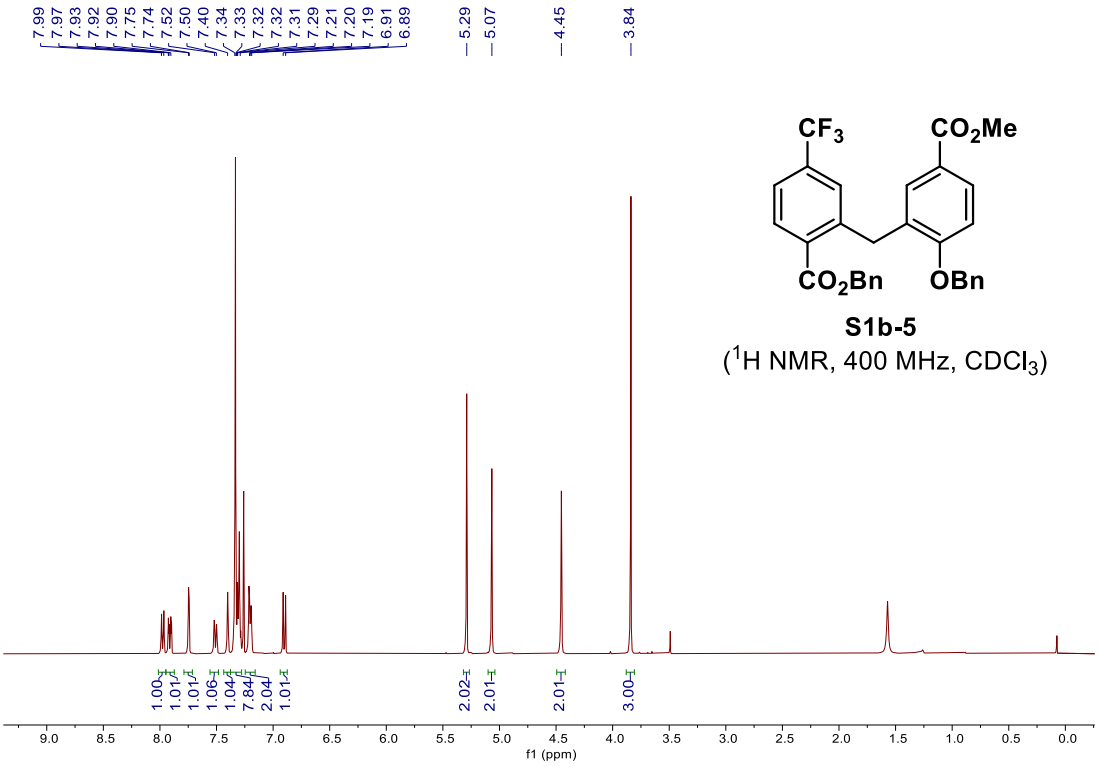
S1b-4

(^{1}H NMR, 400 MHz, $CDCl_3$)



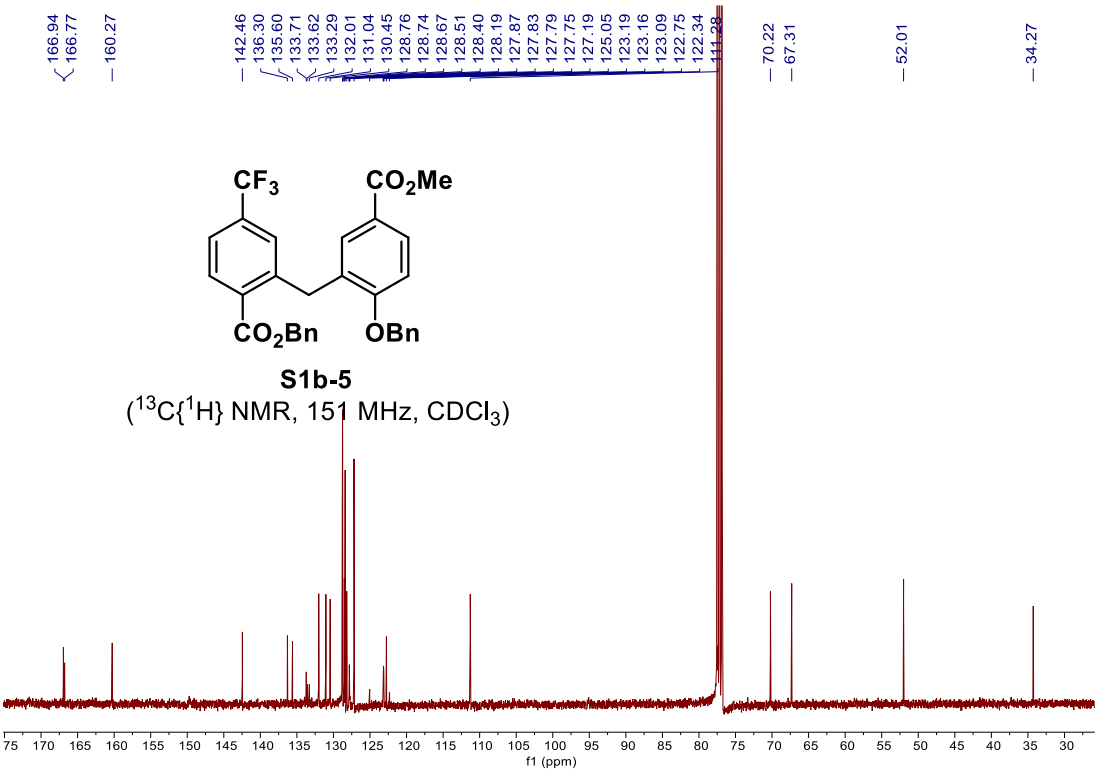
S1b-4

($^{13}C\{^1H\}$ NMR, 151 MHz, $CDCl_3$)



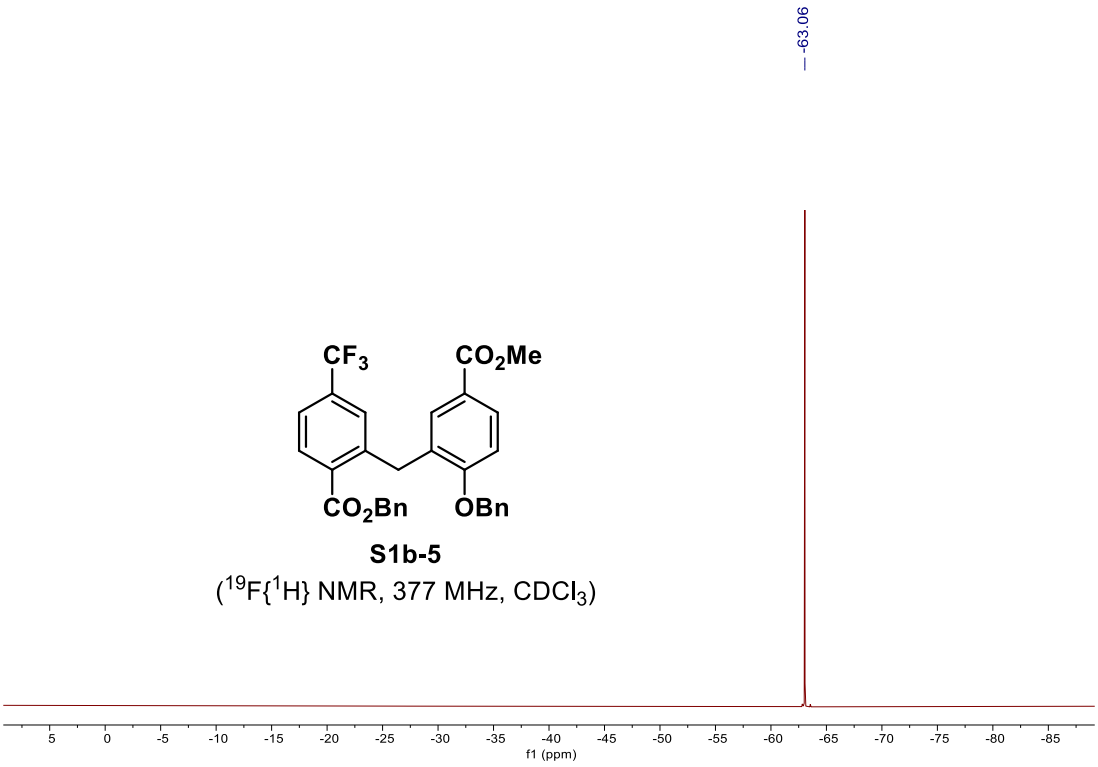
S1b-5

(^{1}H NMR, 400 MHz, $CDCl_3$)



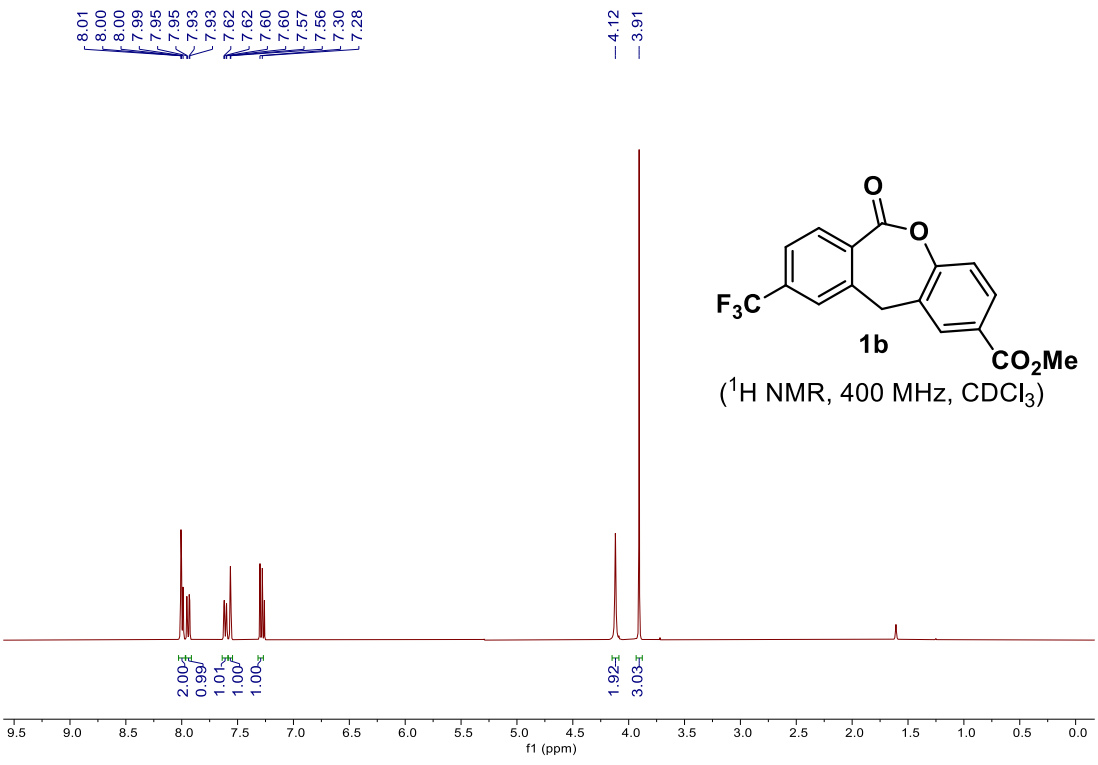
S1b-5

(^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$)



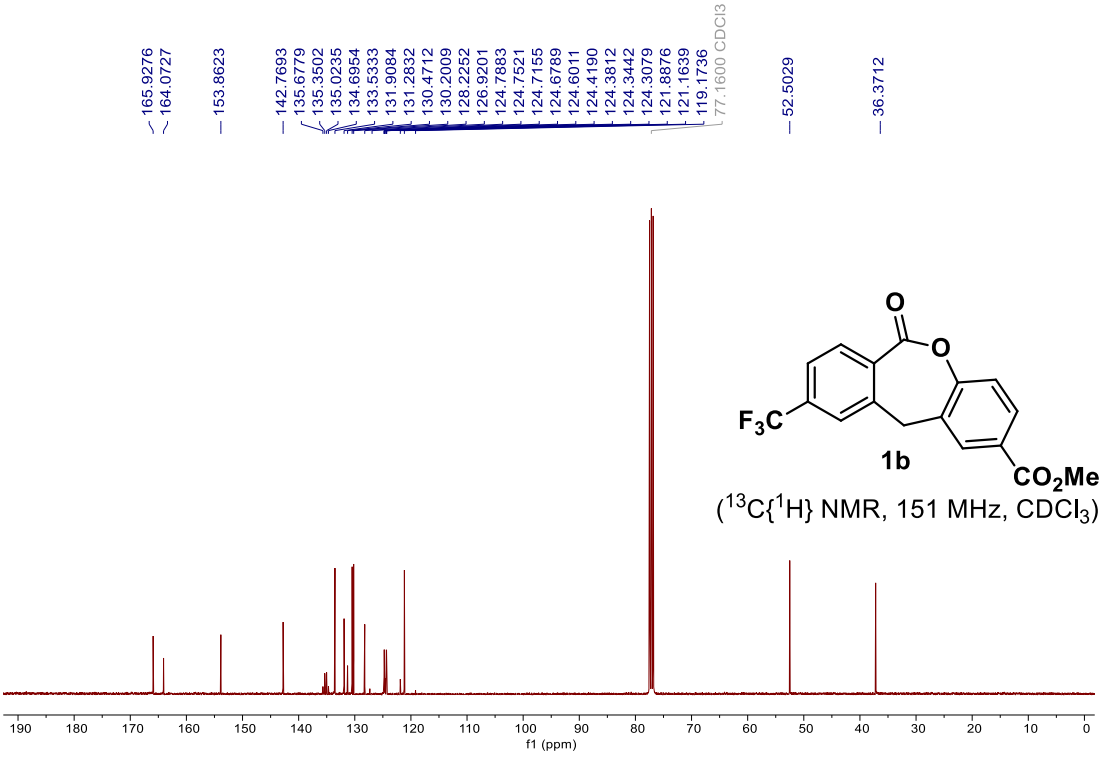
S1b-5

($^{19}F\{^{1}H\}$ NMR, 377 MHz, $CDCl_3$)

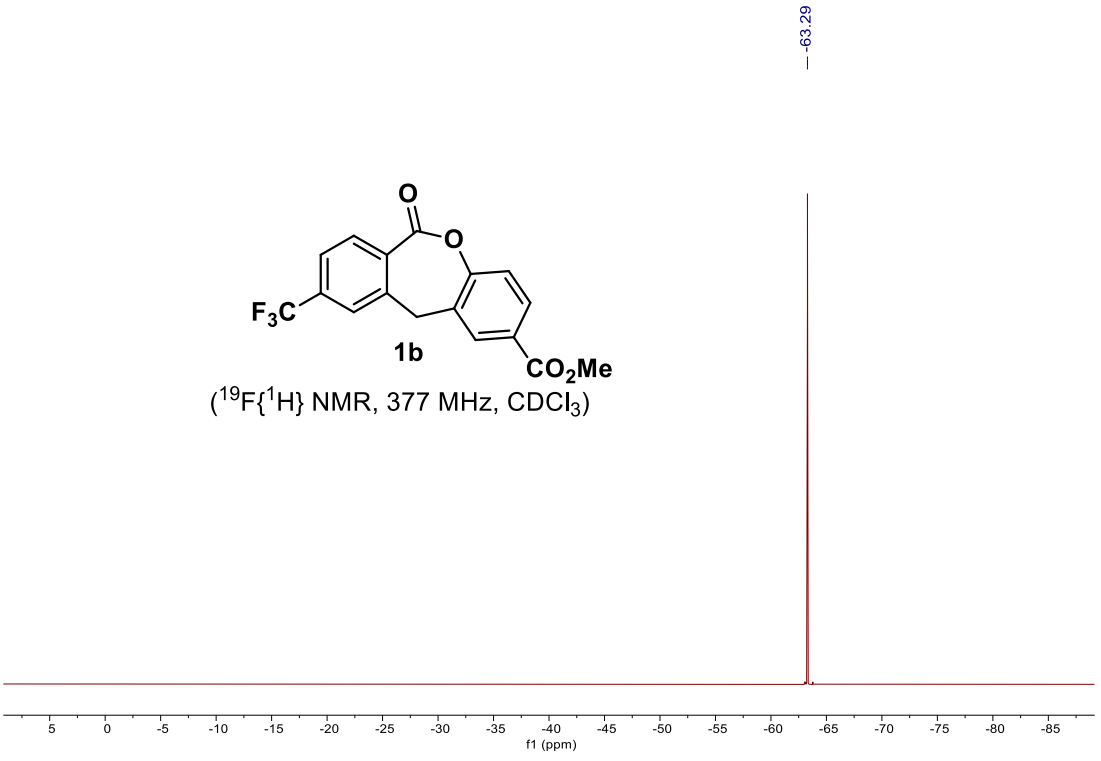


1b

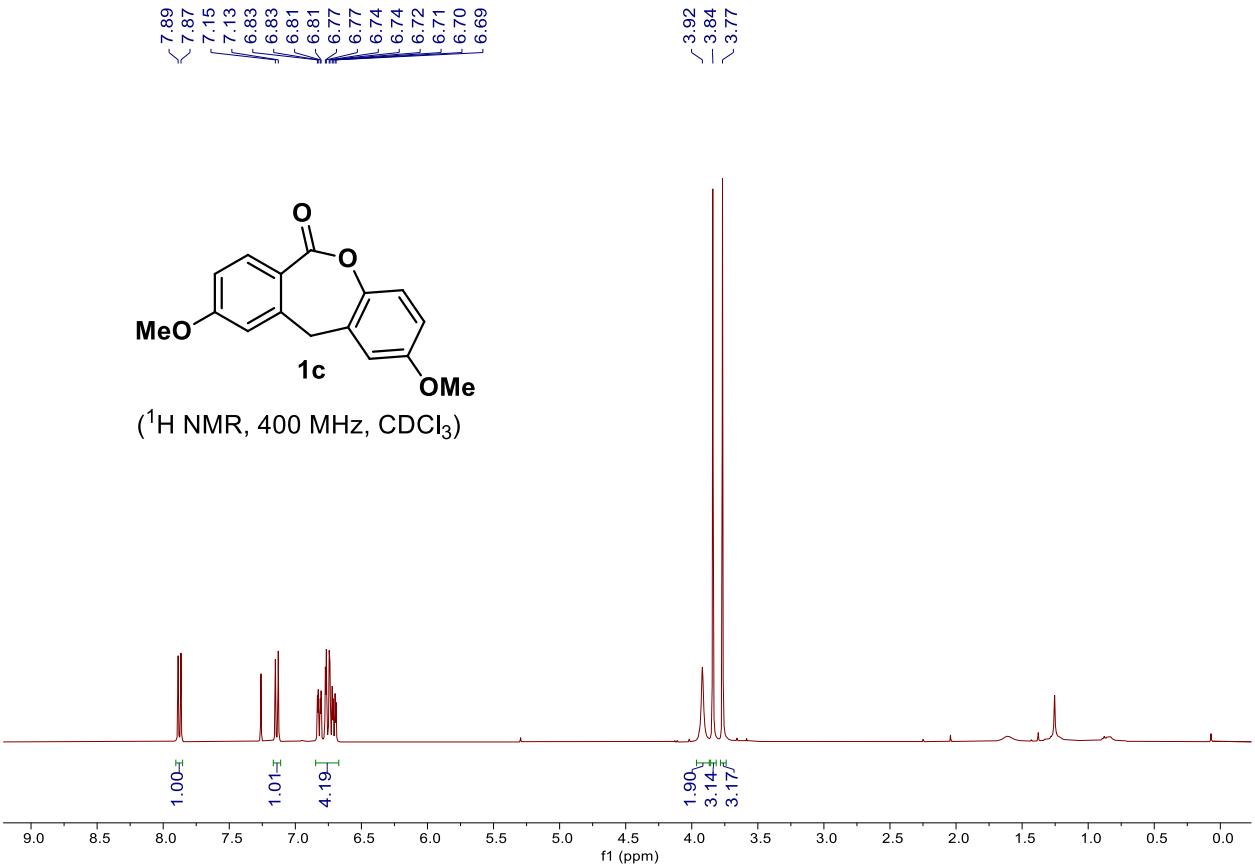
(^{1}H NMR, 400 MHz, $CDCl_3$)



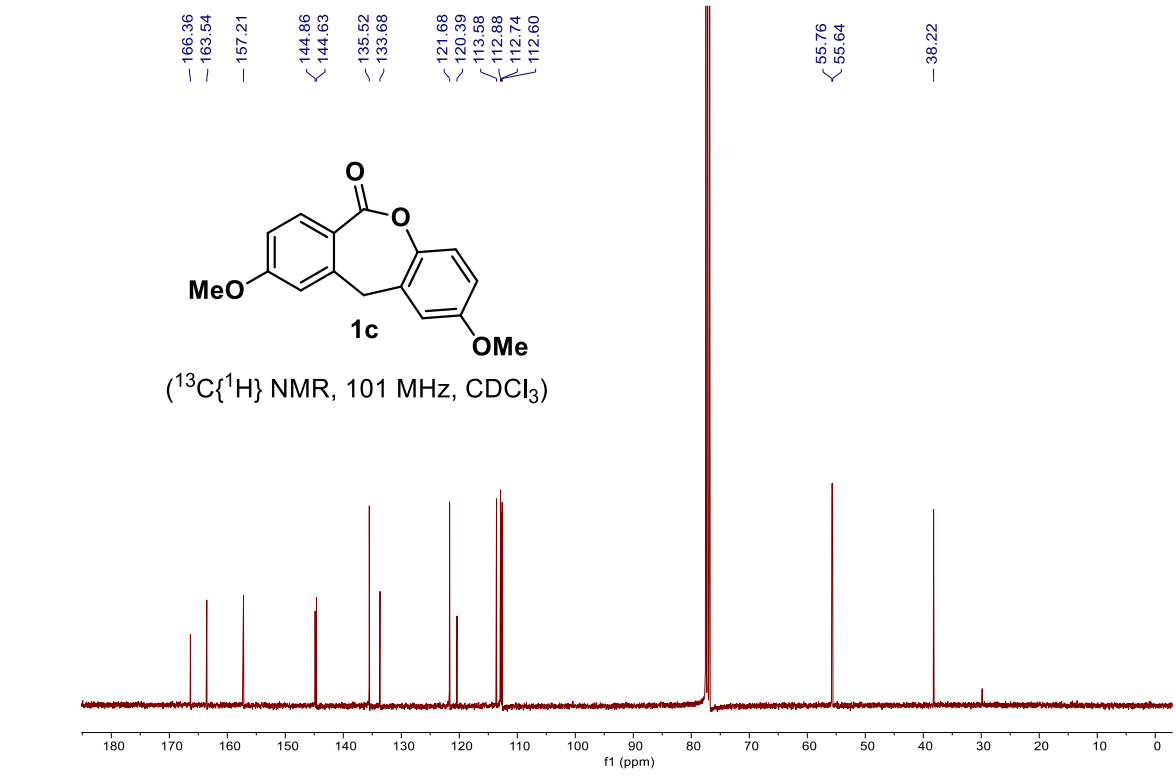
($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)



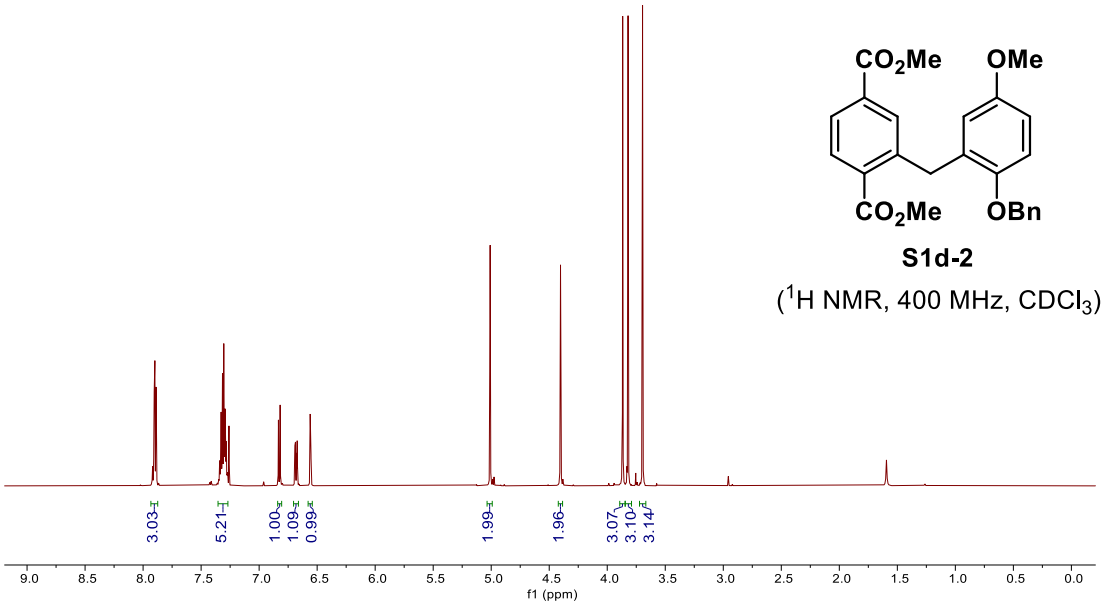
($^{19}F\{^{1}H\}$ NMR, 377 MHz, $CDCl_3$)



(^{1}H NMR, 400 MHz, $CDCl_3$)

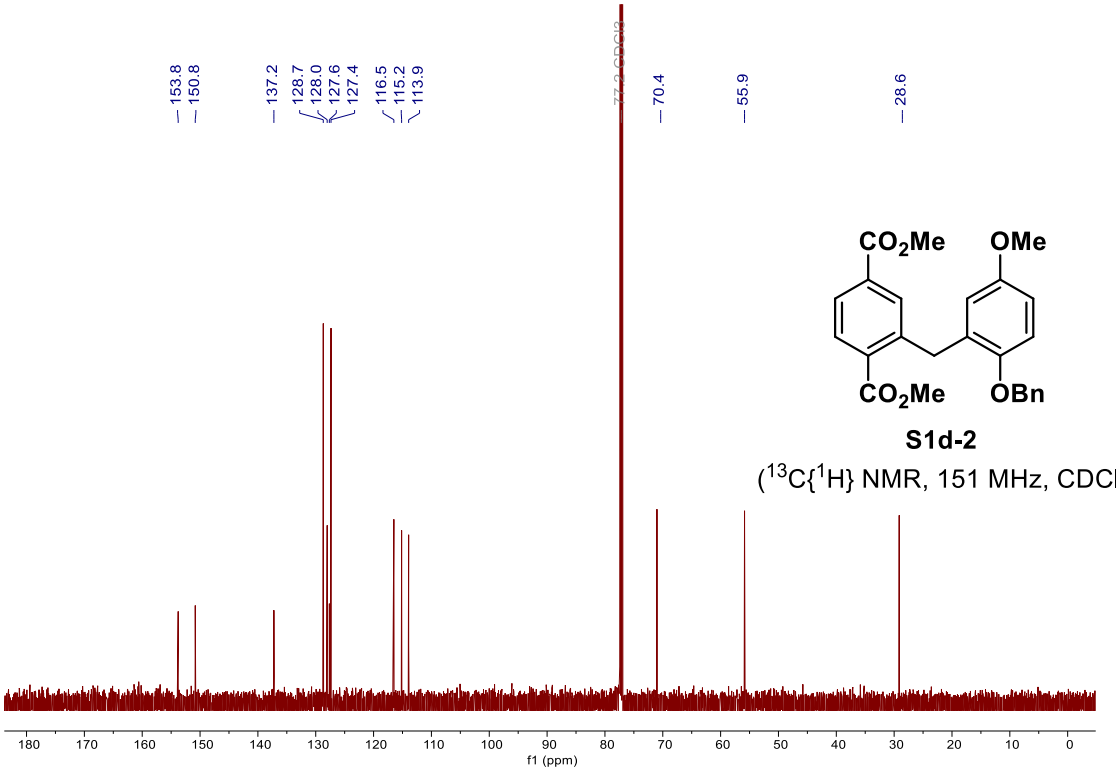


(^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$)



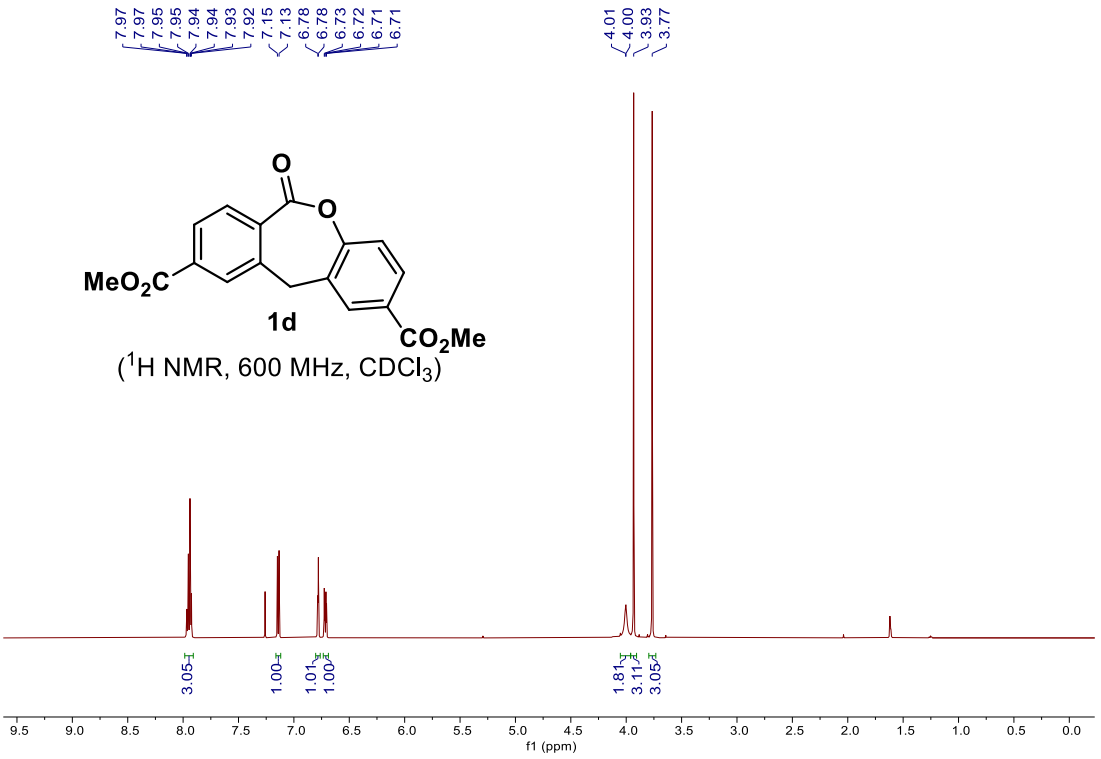
S1d-2

(^{1}H NMR, 400 MHz, $CDCl_3$)



S1d-2

($^{13}C\{^1H\}$ NMR, 151 MHz, $CDCl_3$)



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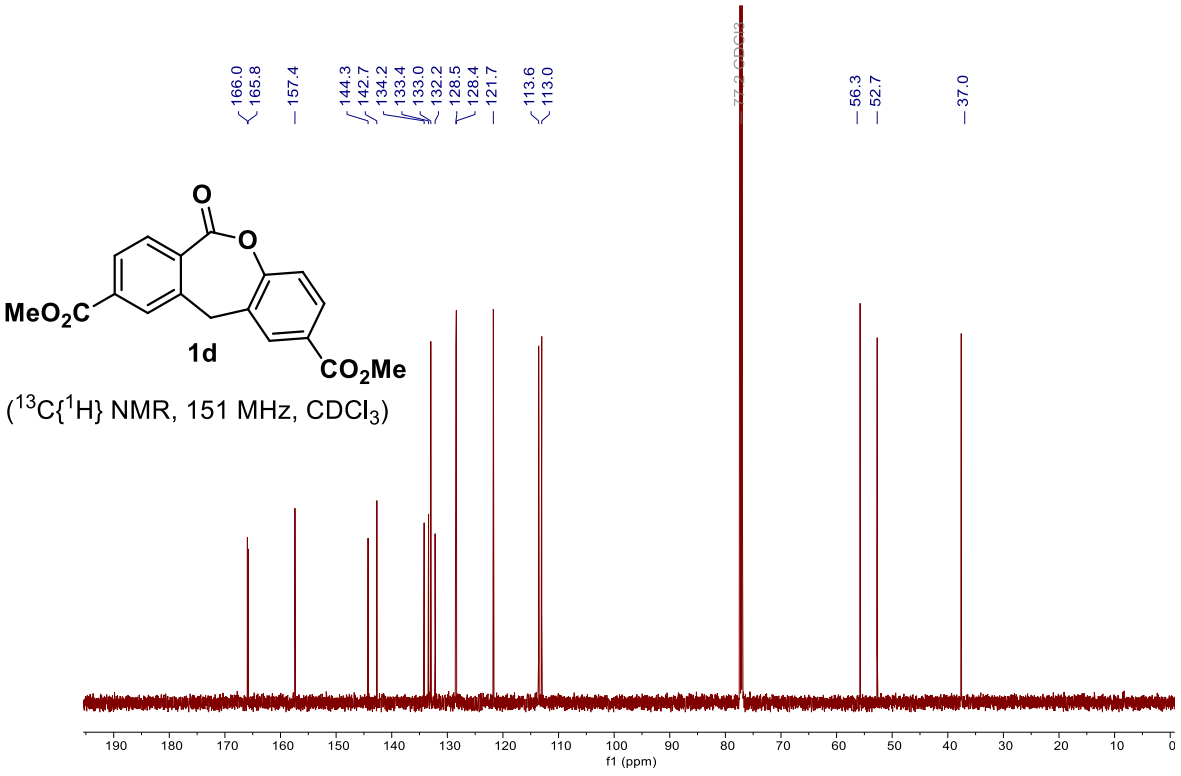
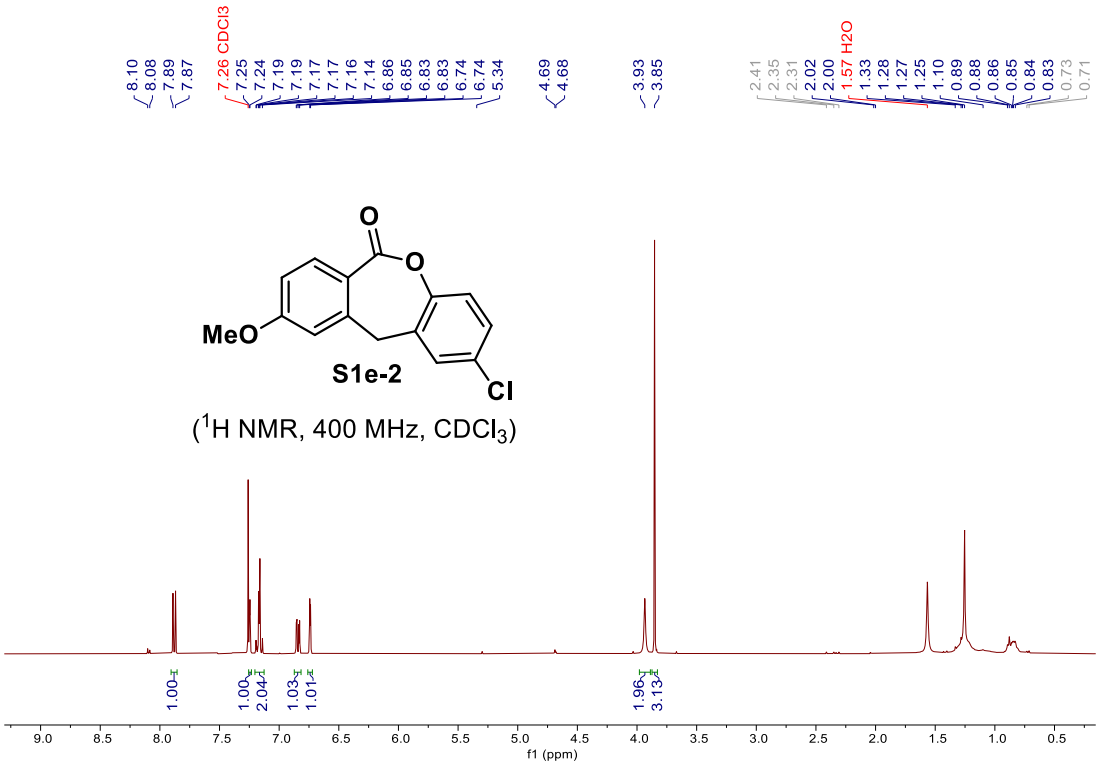
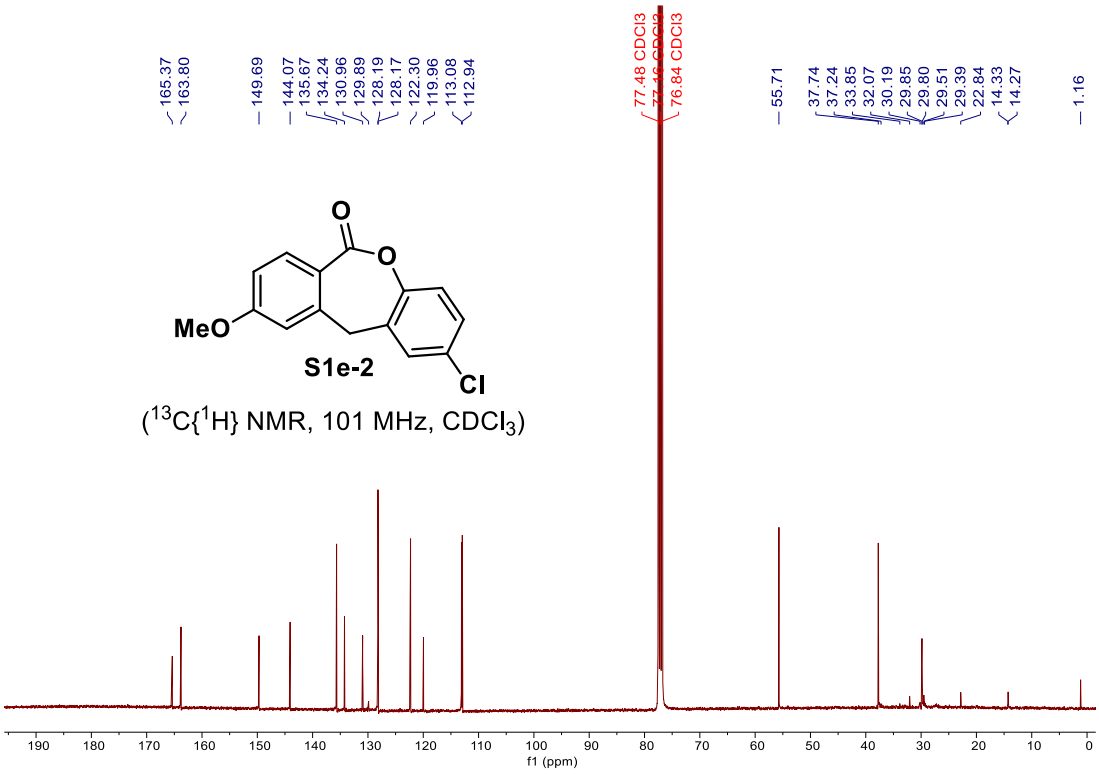


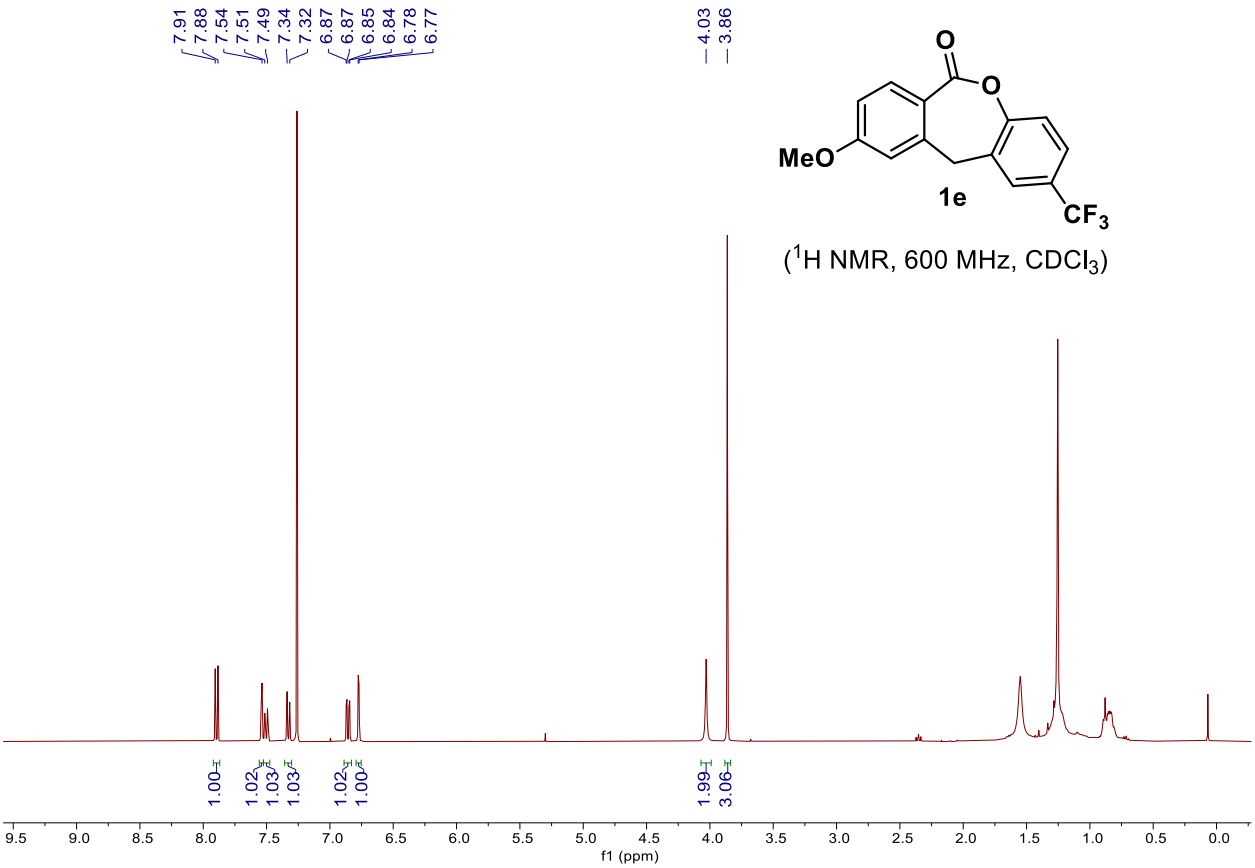
(^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$)



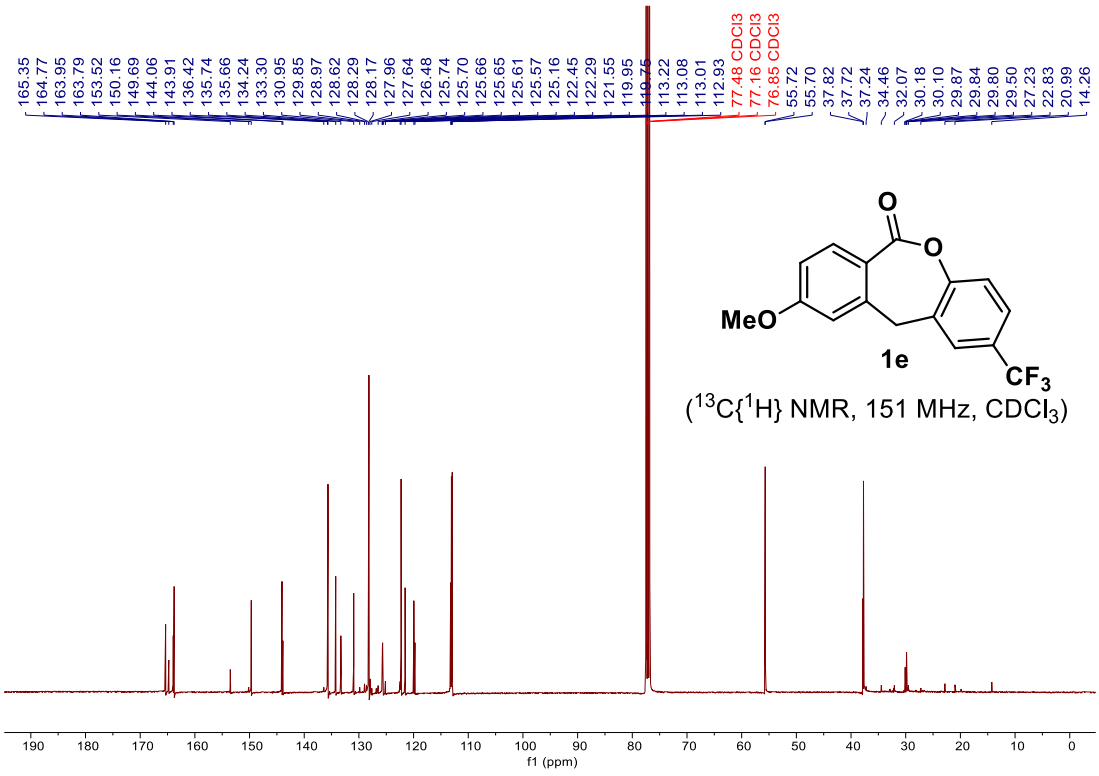
(^{1}H NMR, 400 MHz, $CDCl_3$)



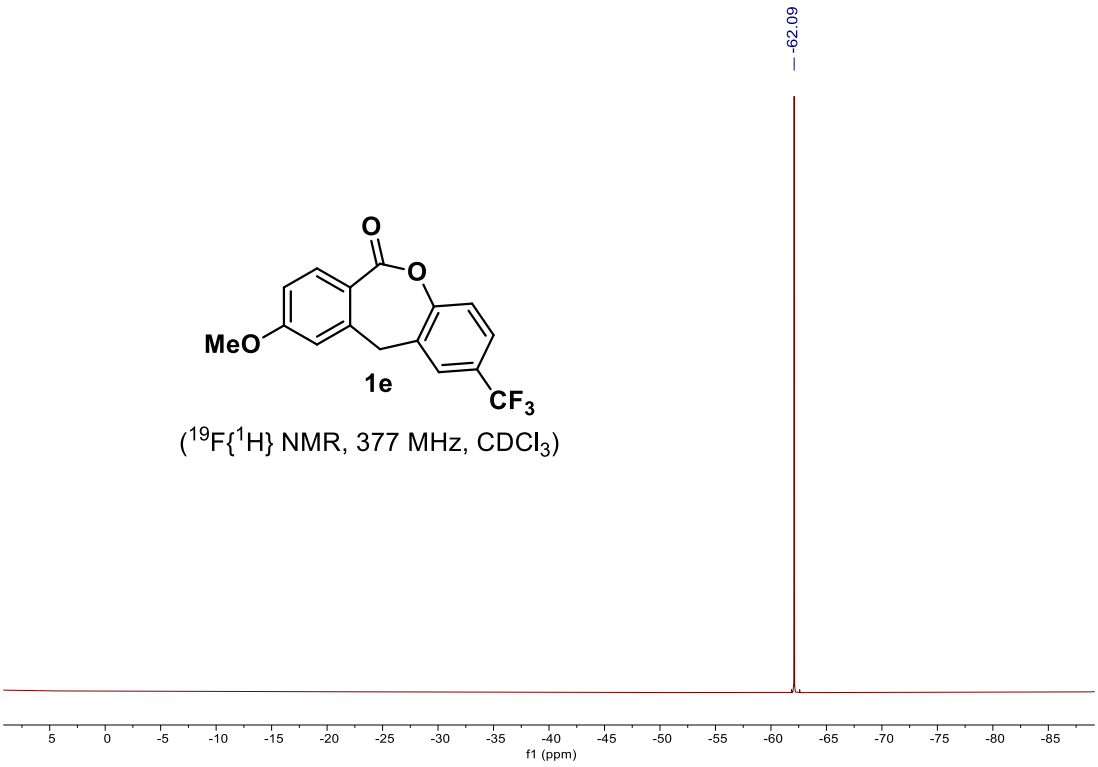
(^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$)



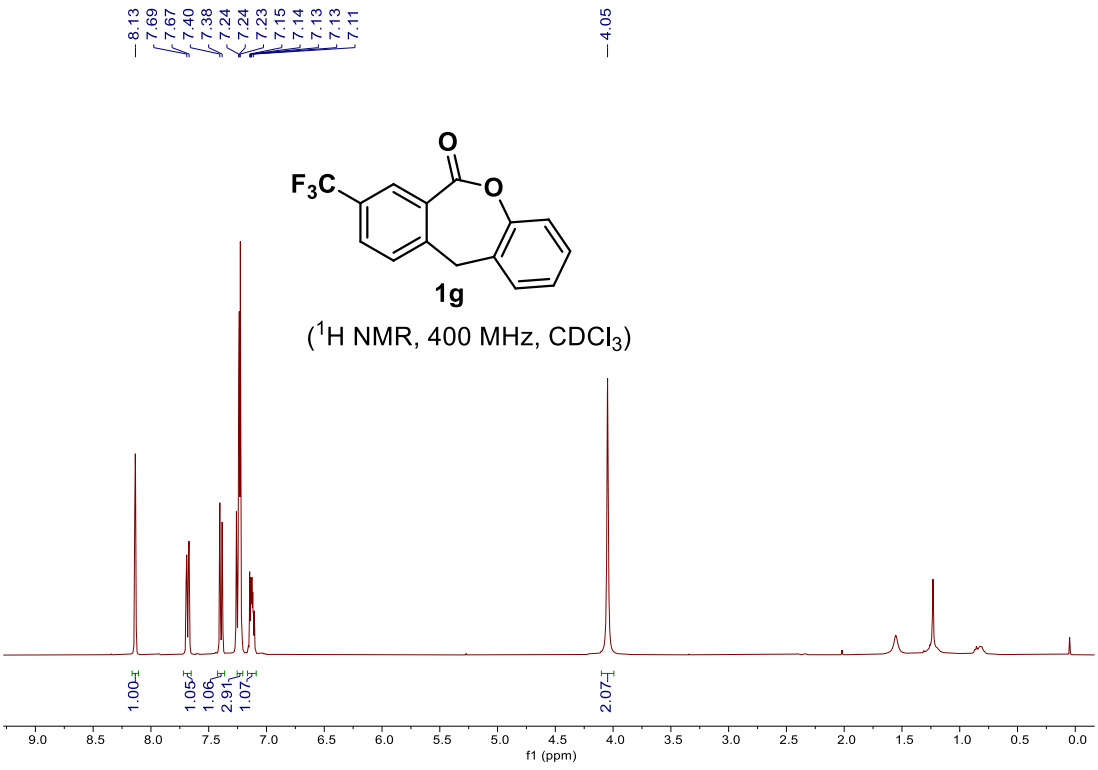
(^{1}H NMR, 600 MHz, $CDCl_3$)



(^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$)



($^{19}F\{^{1}H\}$ NMR, 377 MHz, $CDCl_3$)



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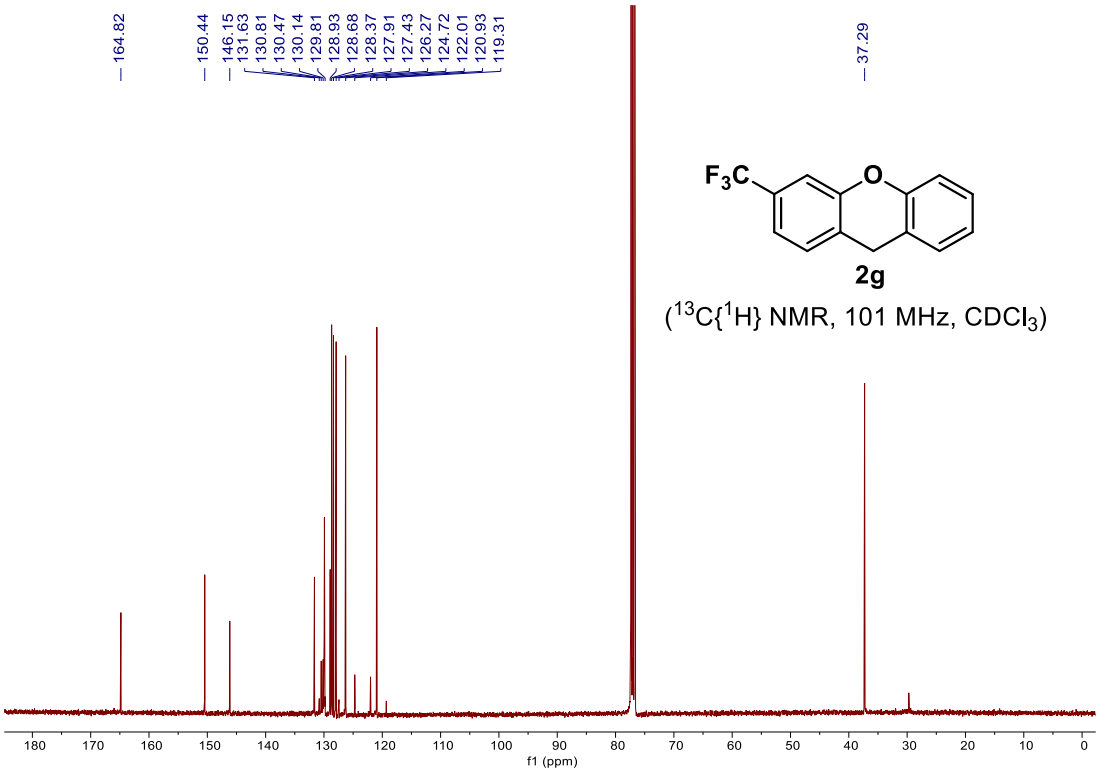
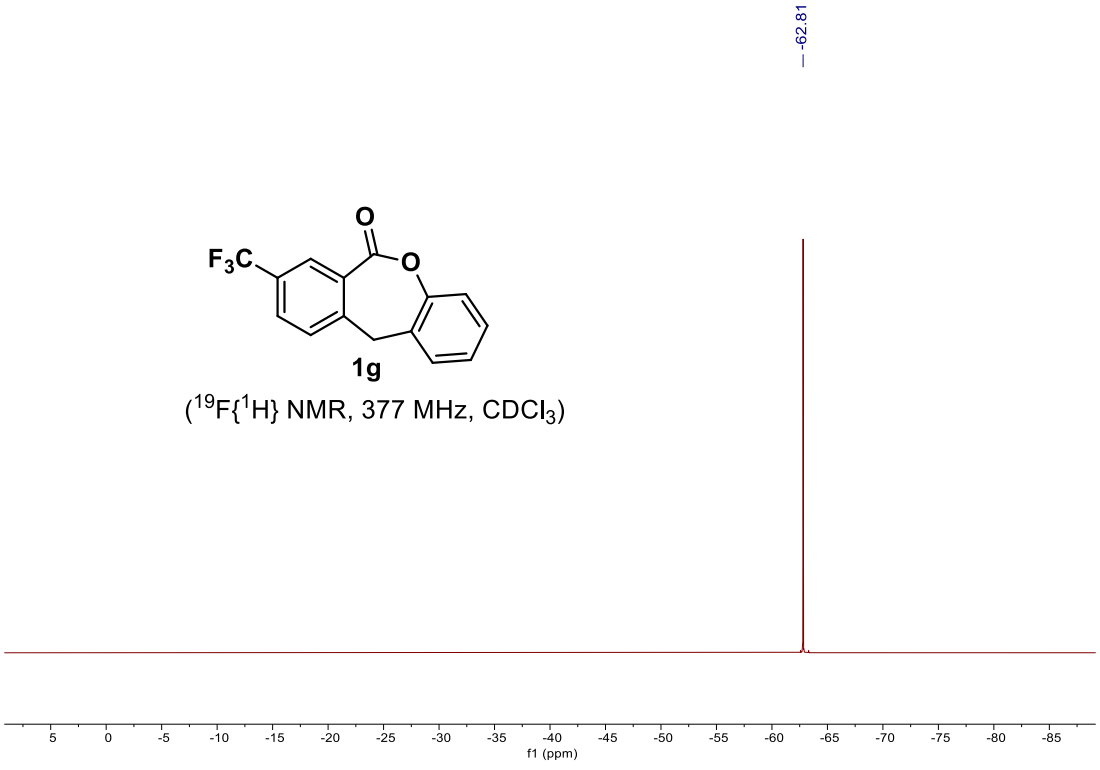


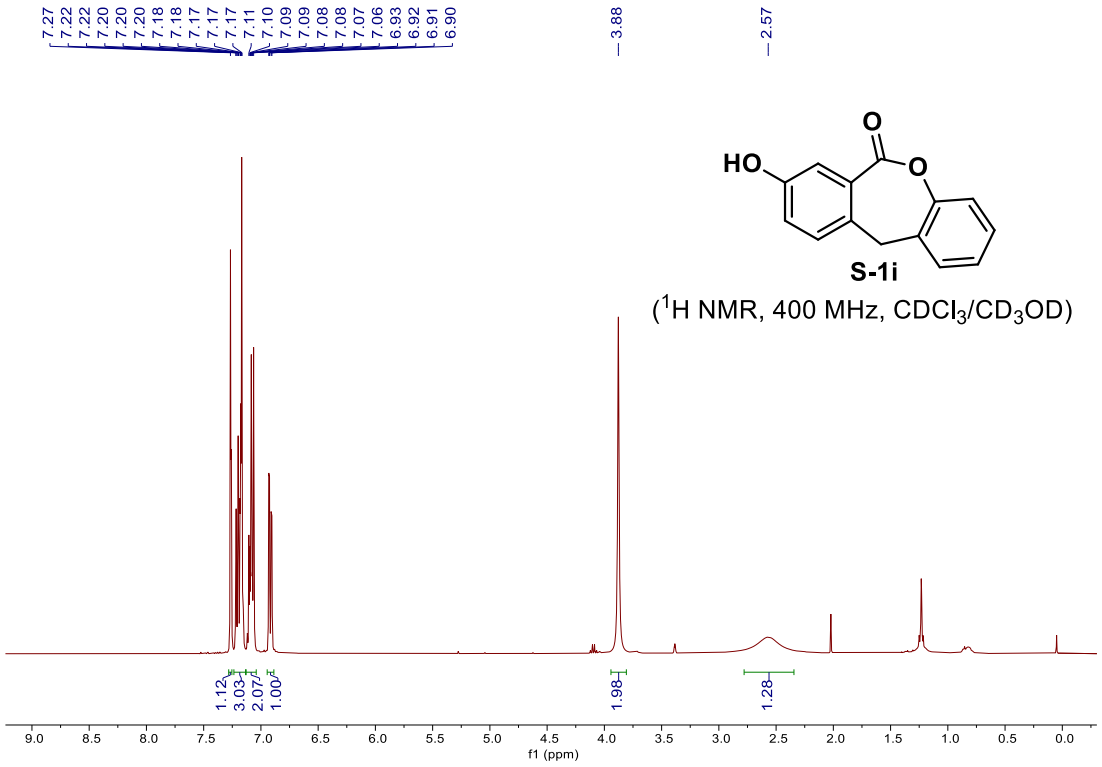
2g

($^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$)



1g

($^{19}F\{^{1}H\}$ NMR, 377 MHz, $CDCl_3$)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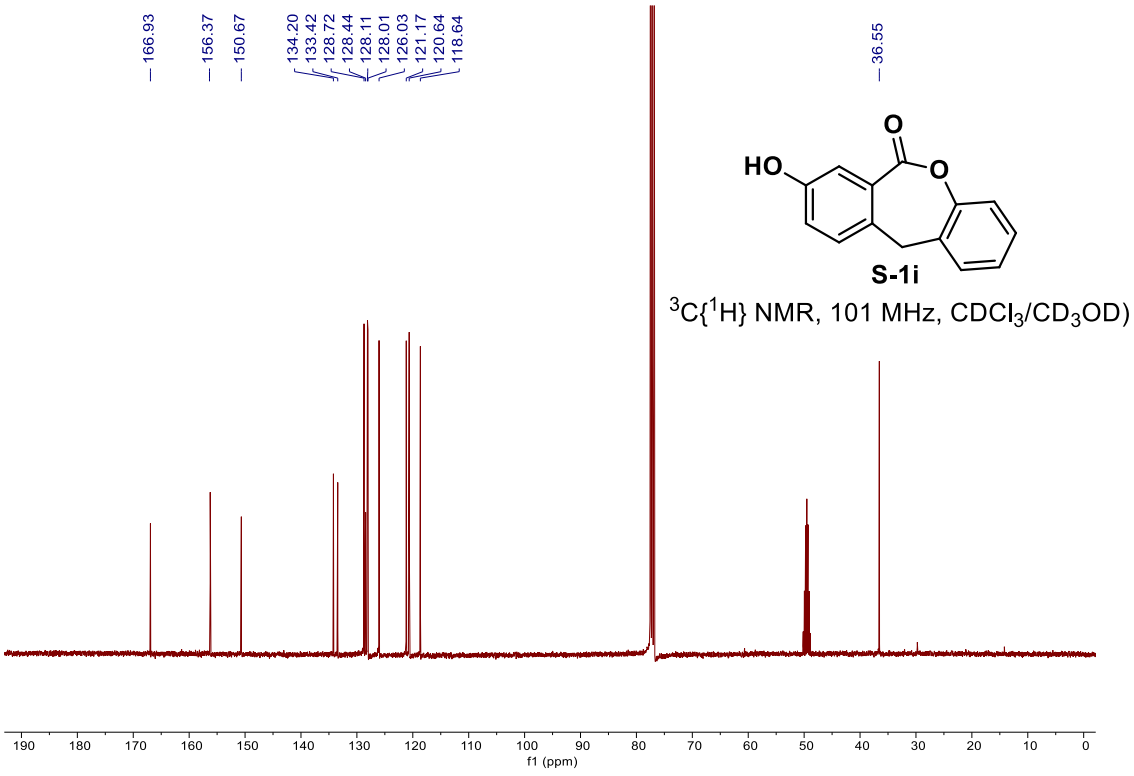
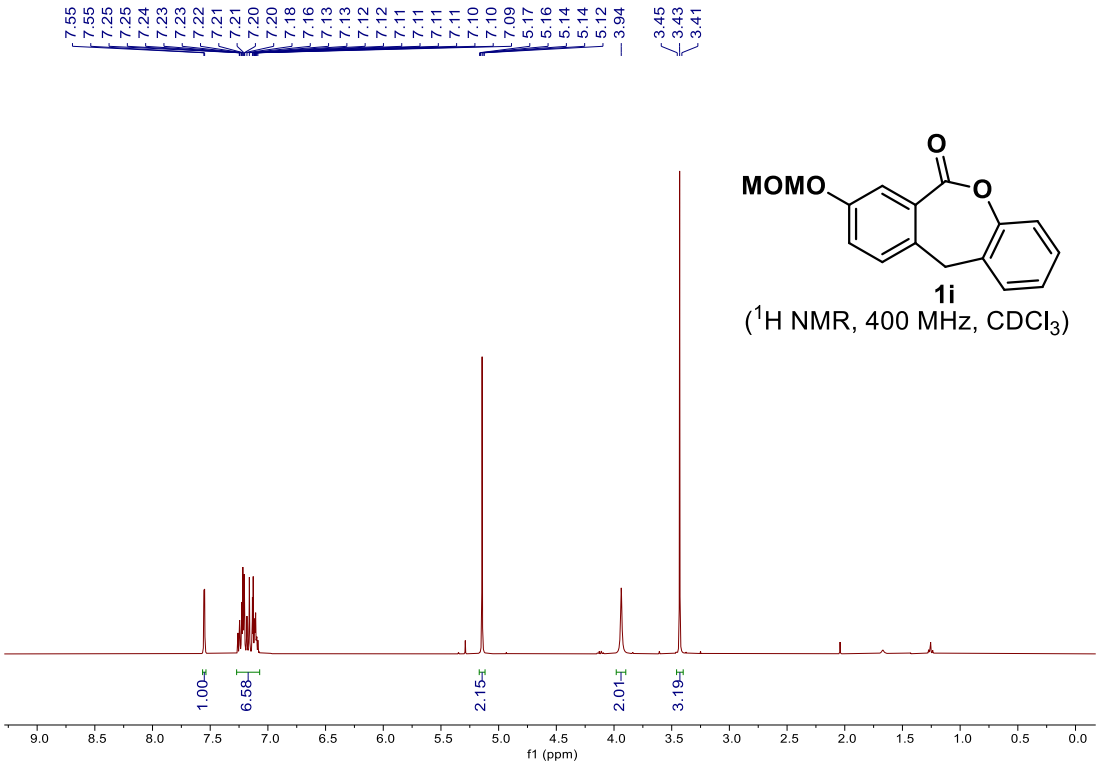
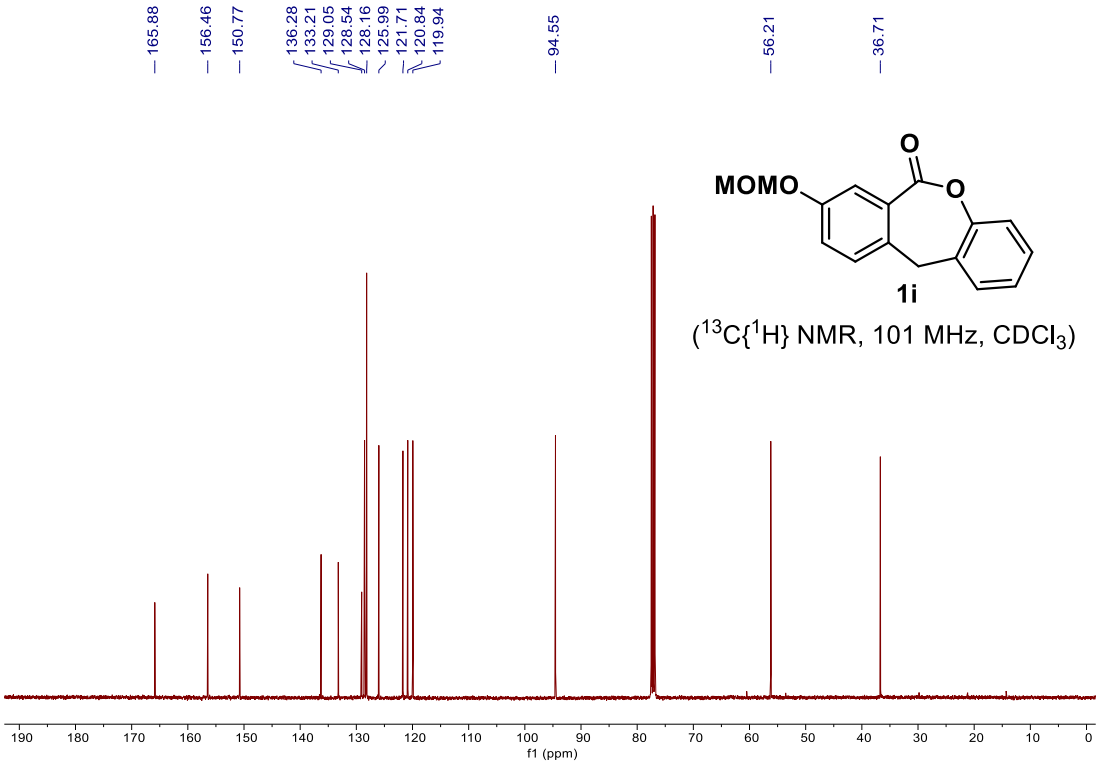
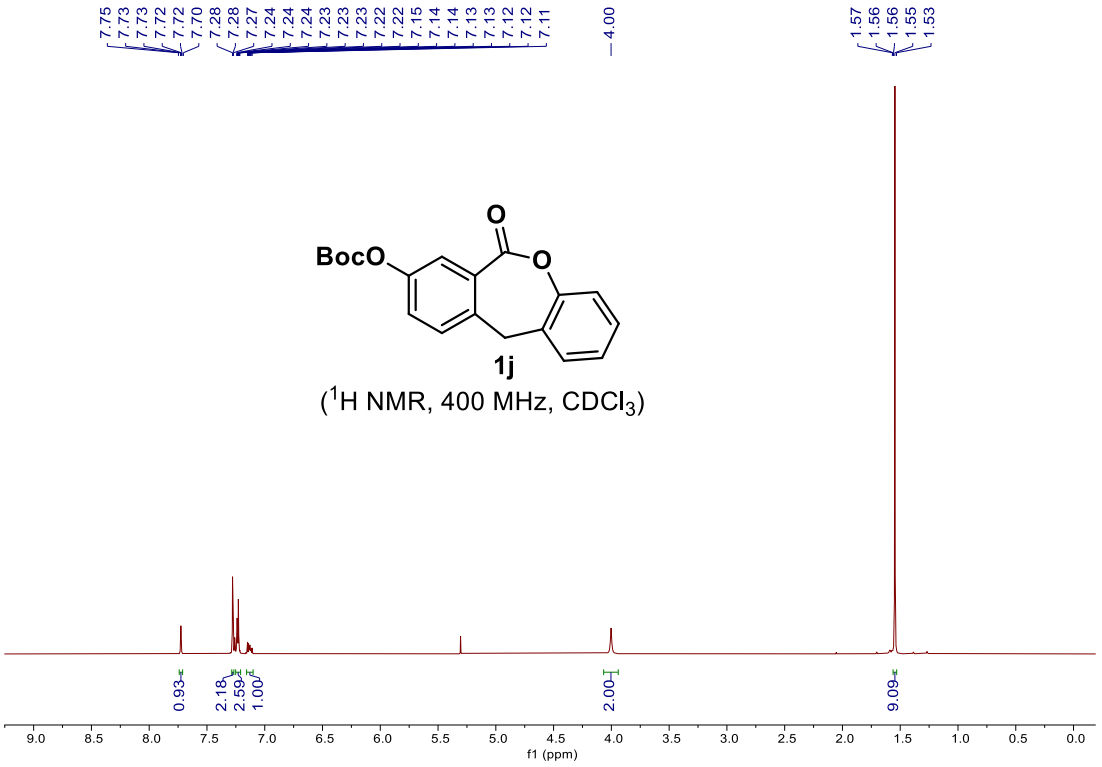
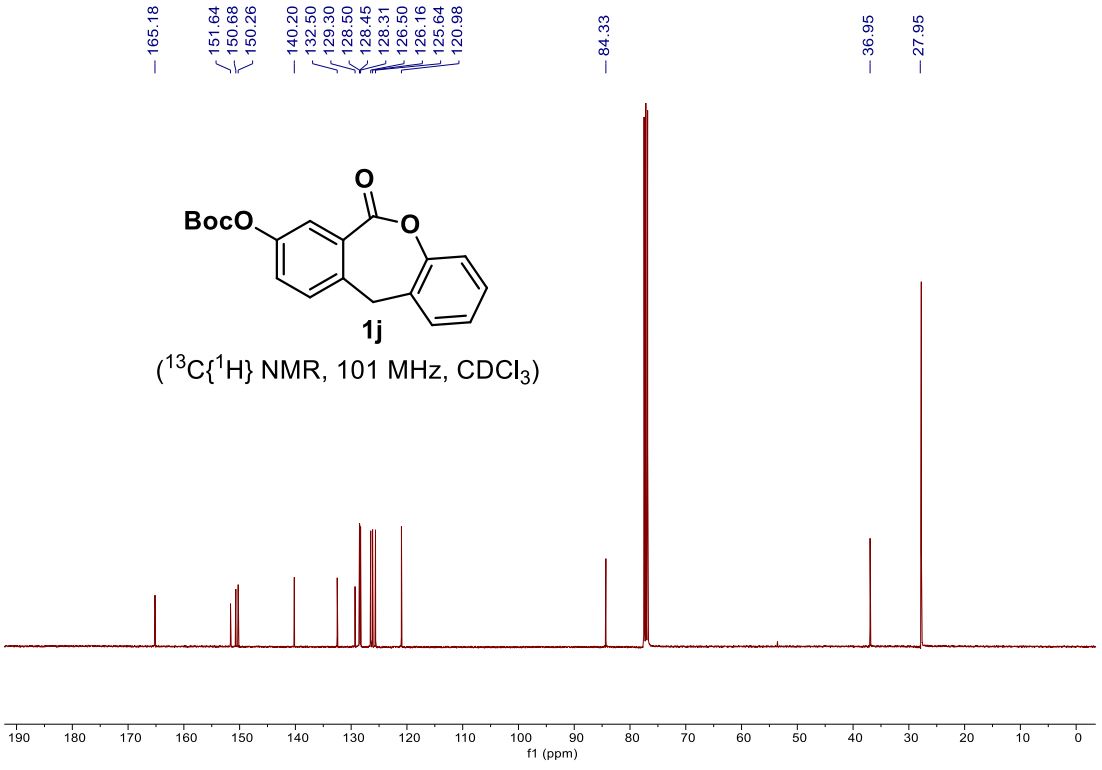
6.93
6.92
6.91
6.90
3.88
2.57
HO
O
O
S-1i
(1H NMR, 400 MHz, CDCl3/CD3OD)
1.12
3.03
2.07
1.00
1.98
1.28
f1 (ppm)

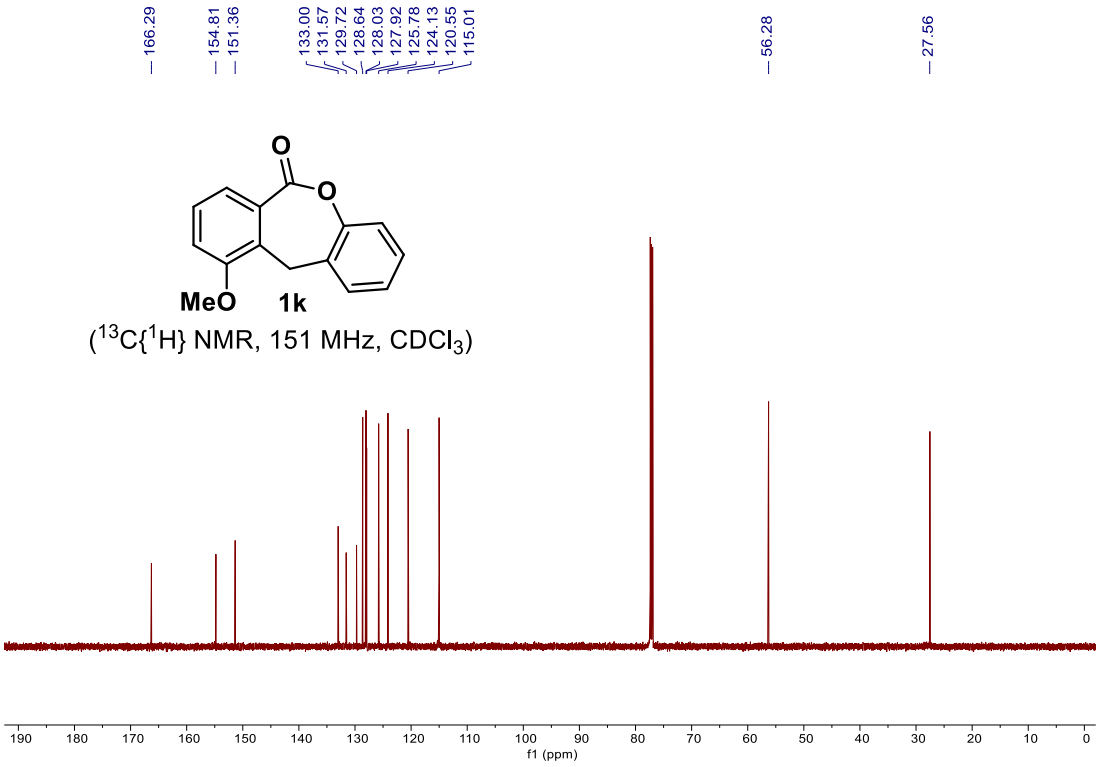

166.93
156.37
150.67
134.20
133.42
128.72
128.44
128.11
128.01
126.03
121.17
120.64
118.64
36.55
HO
O
O
S-1i
3C{1H} NMR, 101 MHz, CDCl3/CD3OD)
f1 (ppm)

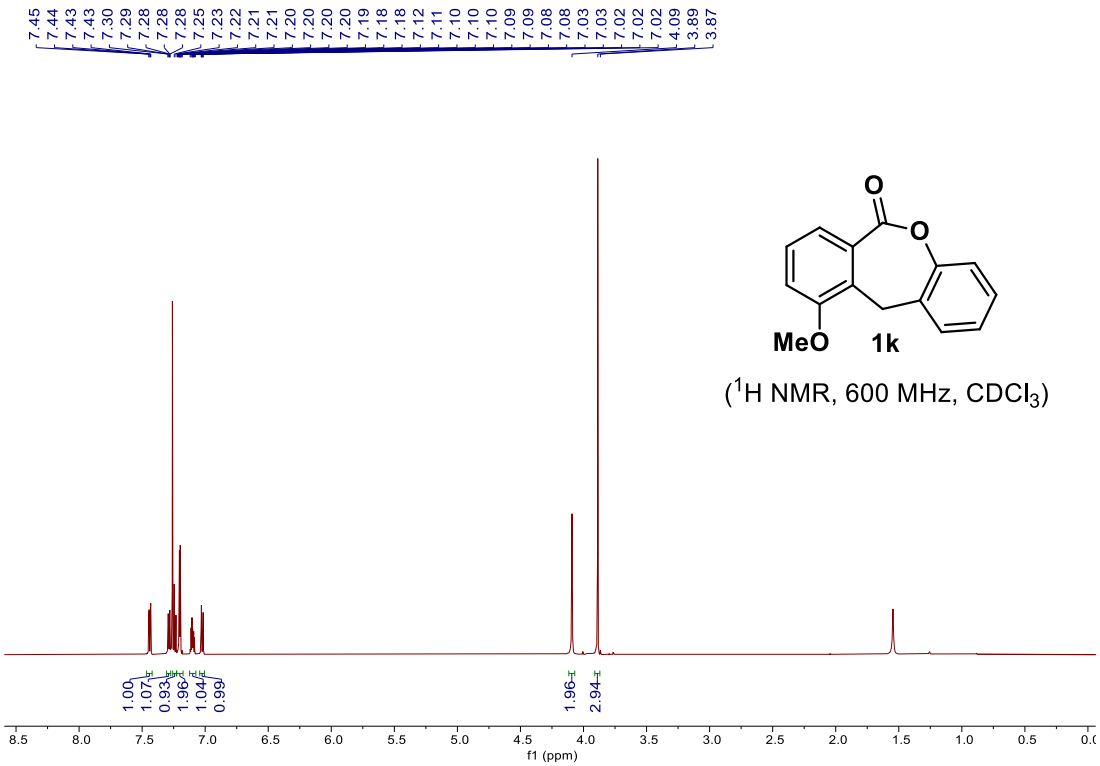

7.55
7.55
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.18
7.16
7.13
7.13
7.12
7.12
7.11
7.11
7.11
7.11
7.10
7.10
7.09
5.17
5.16
5.14
5.14
5.12
3.94
3.45
3.43
3.41
MOMO
O
O
1i
(1H NMR, 400 MHz, CDCl3)
1.00
6.58
2.15
2.01
3.19
f1 (ppm)

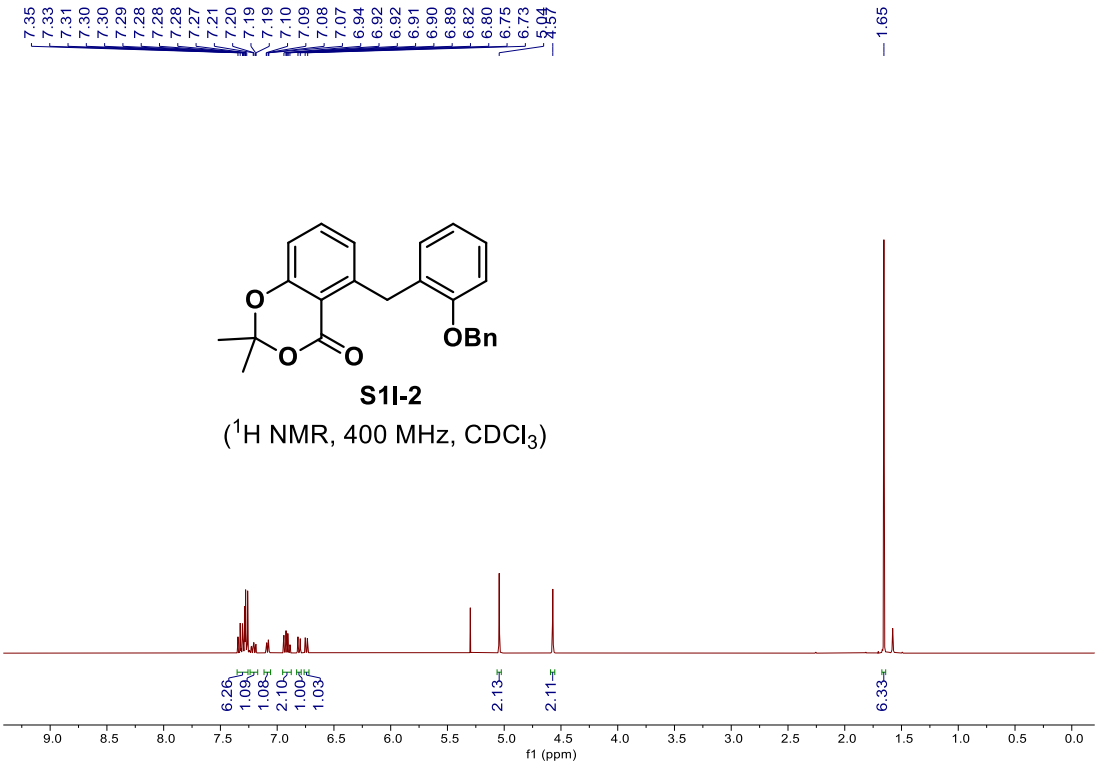

165.88
156.46
150.77
136.28
133.21
129.05
128.54
128.16
125.99
121.71
120.84
119.94
94.55
56.21
36.71
MOMO
O
O
1i
(13C{1H} NMR, 101 MHz, CDCl3)
f1 (ppm)


7.75
7.73
7.73
7.72
7.72
7.70
7.28
7.28
7.27
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
4.00
1.57
1.56
1.56
1.55
1.53
BocO
O
O
1j
(1H NMR, 400 MHz, CDCl3)
0.93
2.18
2.59
1.00
2.00
9.09
f1 (ppm)


165.18
151.64
150.68
150.26
140.20
132.50
129.30
128.50
128.45
128.31
126.50
126.16
125.64
120.98
84.33
36.95
27.95
BocO
O
O
1j
(13C{1H} NMR, 101 MHz, CDCl3)
f1 (ppm)

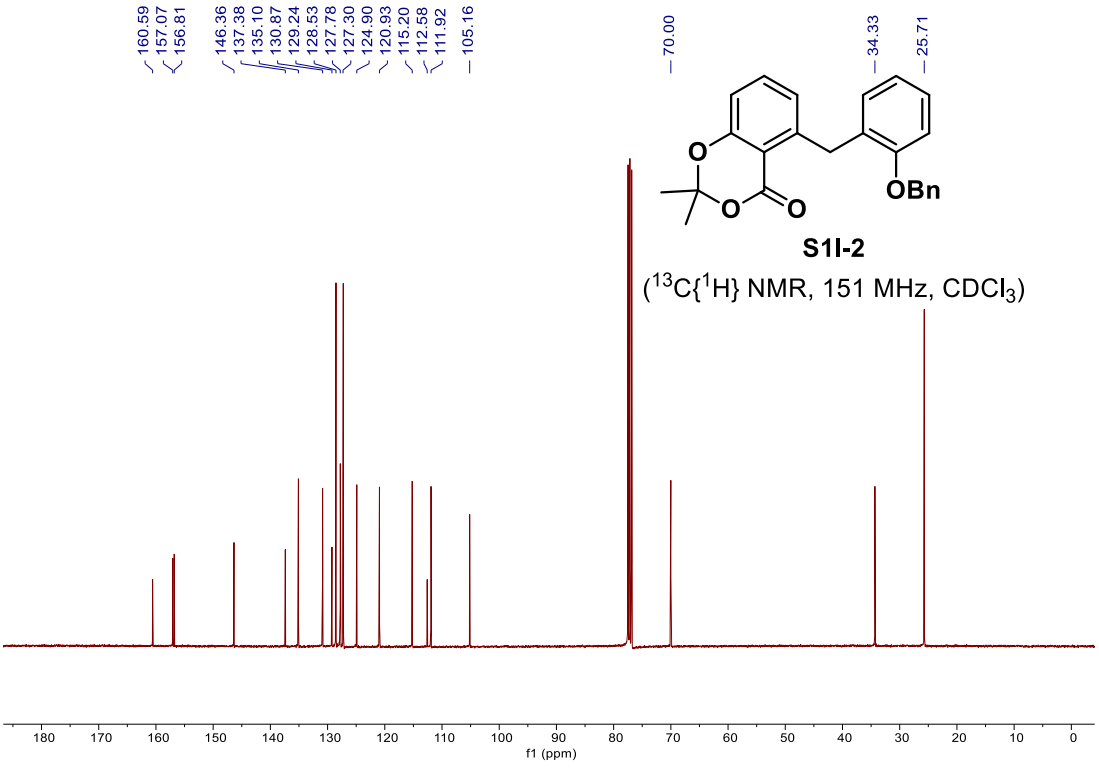

166.29
154.81
151.36
133.00
131.57
129.72
128.64
128.03
127.92
125.78
124.13
120.55
115.01
56.28
27.56
O
O
MeO
1k
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)


7.45
7.44
7.43
7.43
7.30
7.29
7.28
7.28
7.28
7.25
7.23
7.22
7.21
7.21
7.20
7.20
7.20
7.20
7.19
7.18
7.18
7.12
7.11
7.10
7.10
7.10
7.09
7.09
7.08
7.08
7.03
7.03
7.02
7.02
7.02
4.09
3.89
3.87
O
O
MeO
1k
(1H NMR, 600 MHz, CDCl3)
1.00
1.07
0.93
1.96
1.04
0.99
1.96
2.94
f1 (ppm)



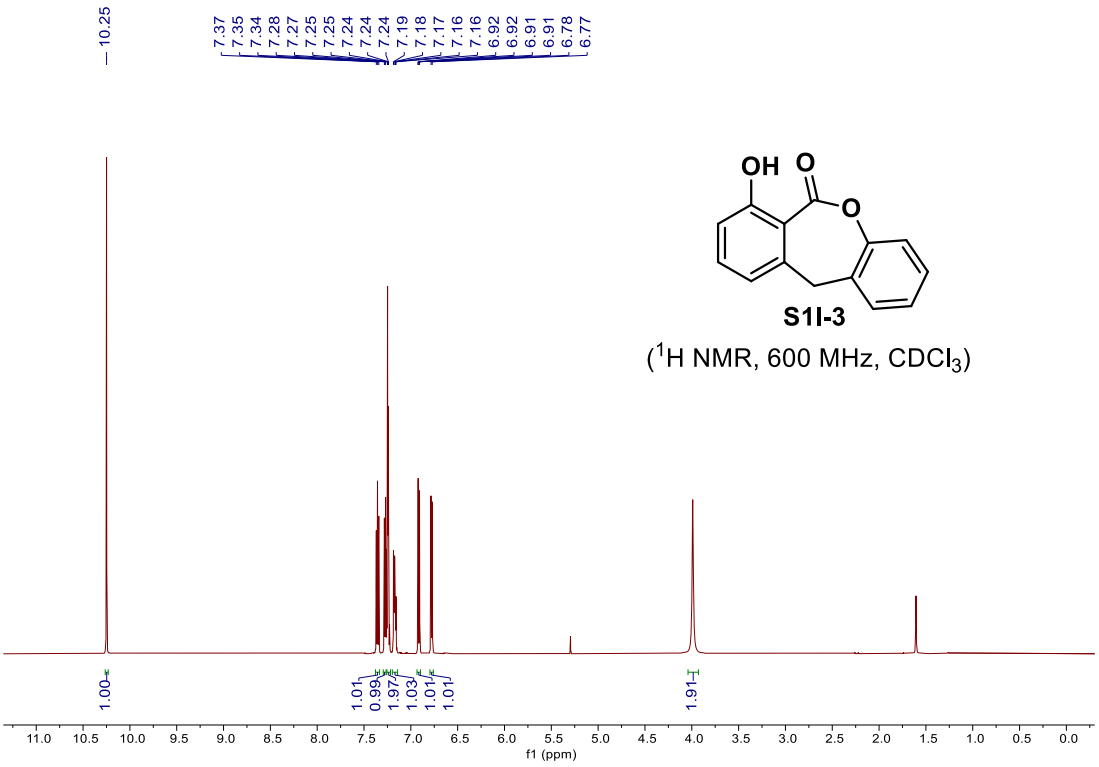
S1I-2

(^{1}H NMR, 400 MHz, $CDCl_3$)



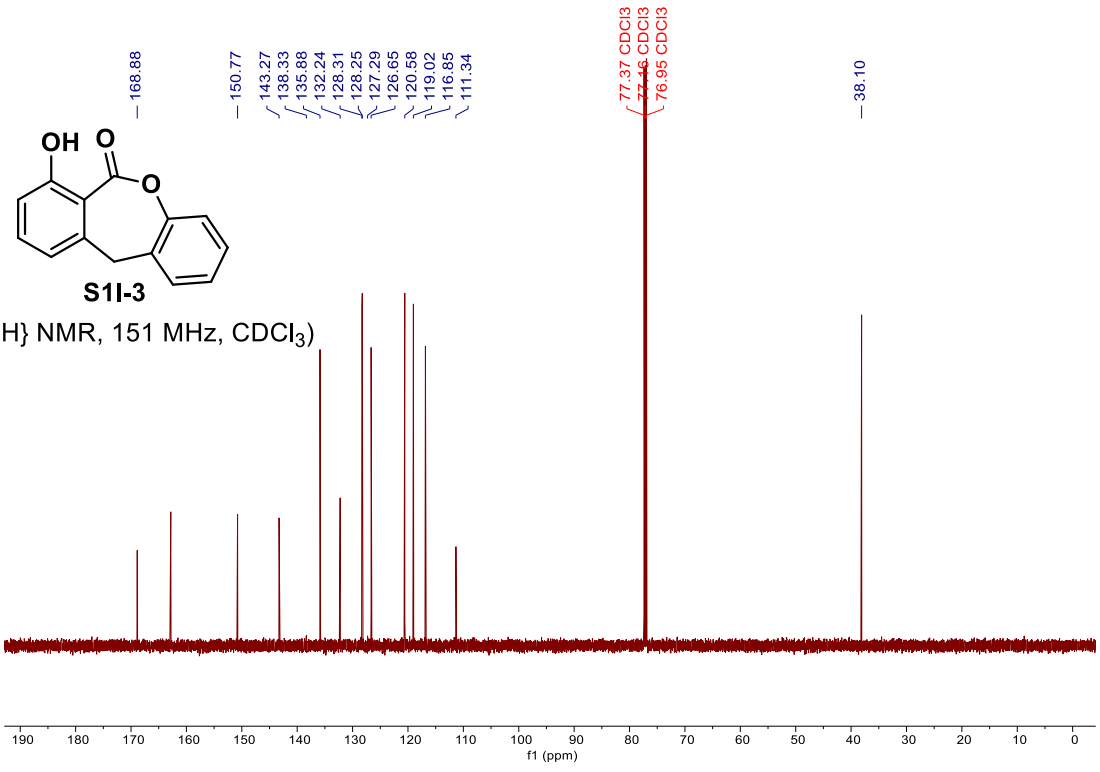
S1I-2

($^{13}C\{^1H\}$ NMR, 151 MHz, $CDCl_3$)



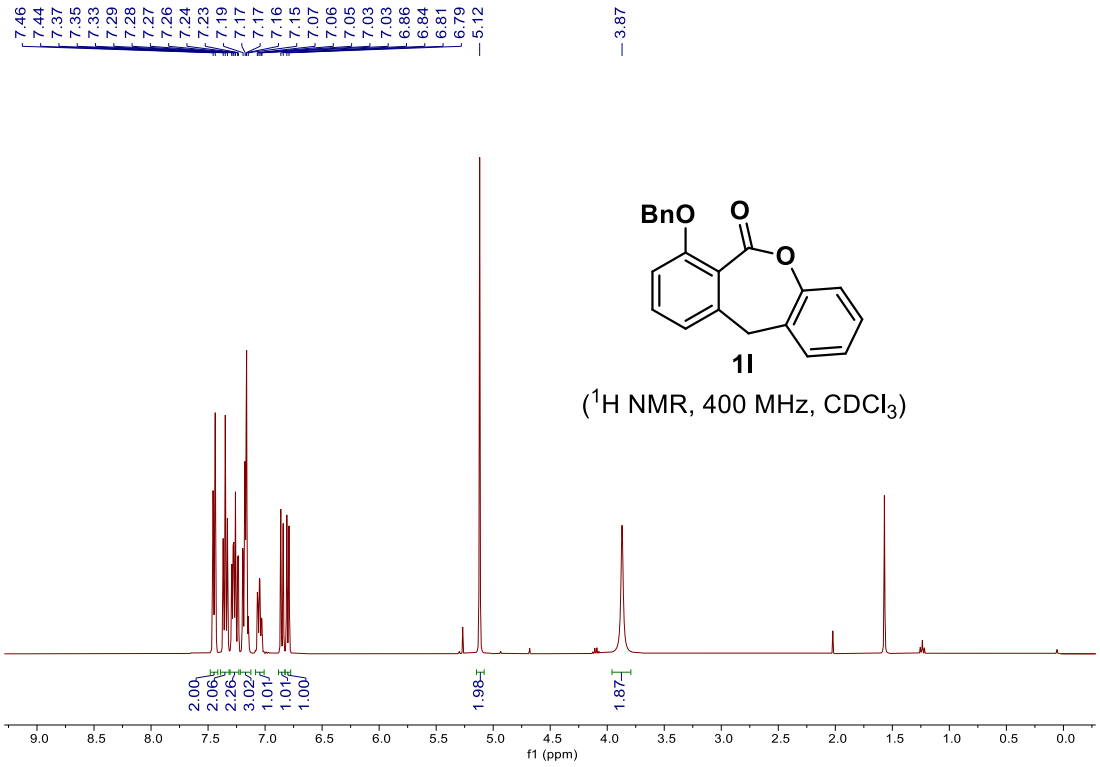
S1l-3

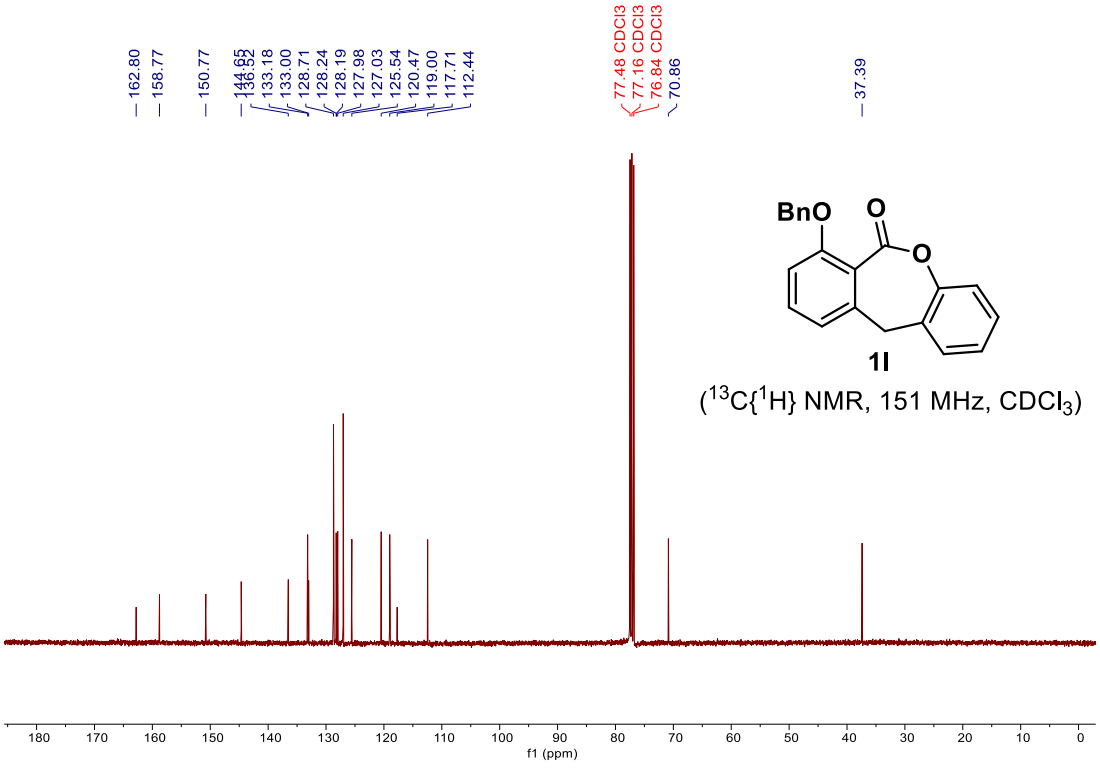
(^{1}H NMR, 600 MHz, $CDCl_3$)

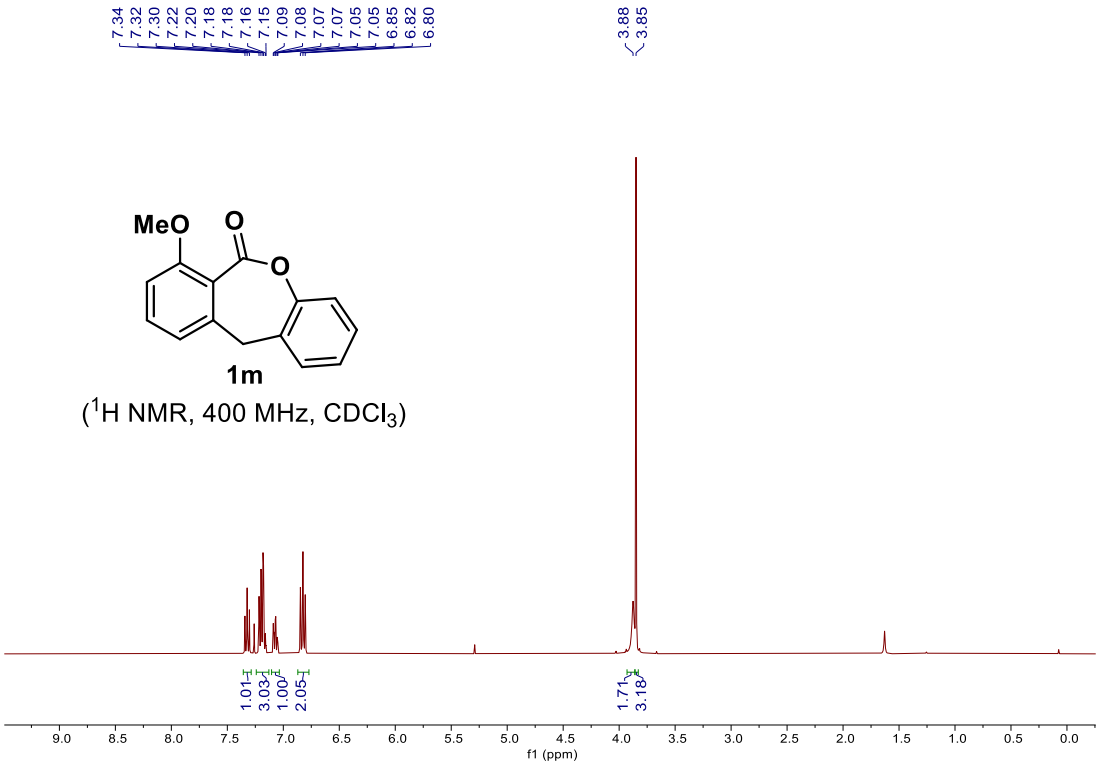


S1l-3

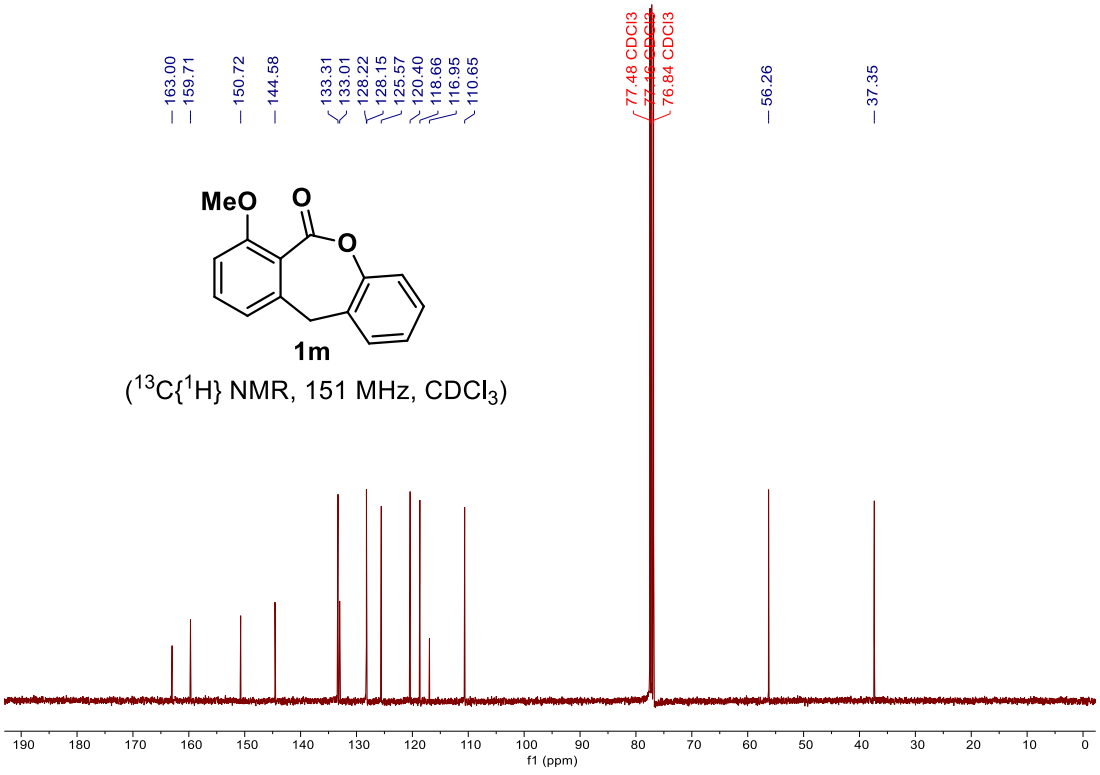
($^{13}C\{^1H\}$ NMR, 151 MHz, $CDCl_3$)


7.46
7.44
7.37
7.35
7.33
7.29
7.28
7.27
7.26
7.24
7.23
7.19
7.17
7.17
7.16
7.15
7.07
7.06
7.05
7.03
7.03
6.86
6.84
6.81
6.79
5.12
3.87
BnO
O
O
1l
(1H NMR, 400 MHz, CDCl3)
2.00
2.06
2.26
3.02
1.01
1.01
1.00
1.98
1.87
f1 (ppm)

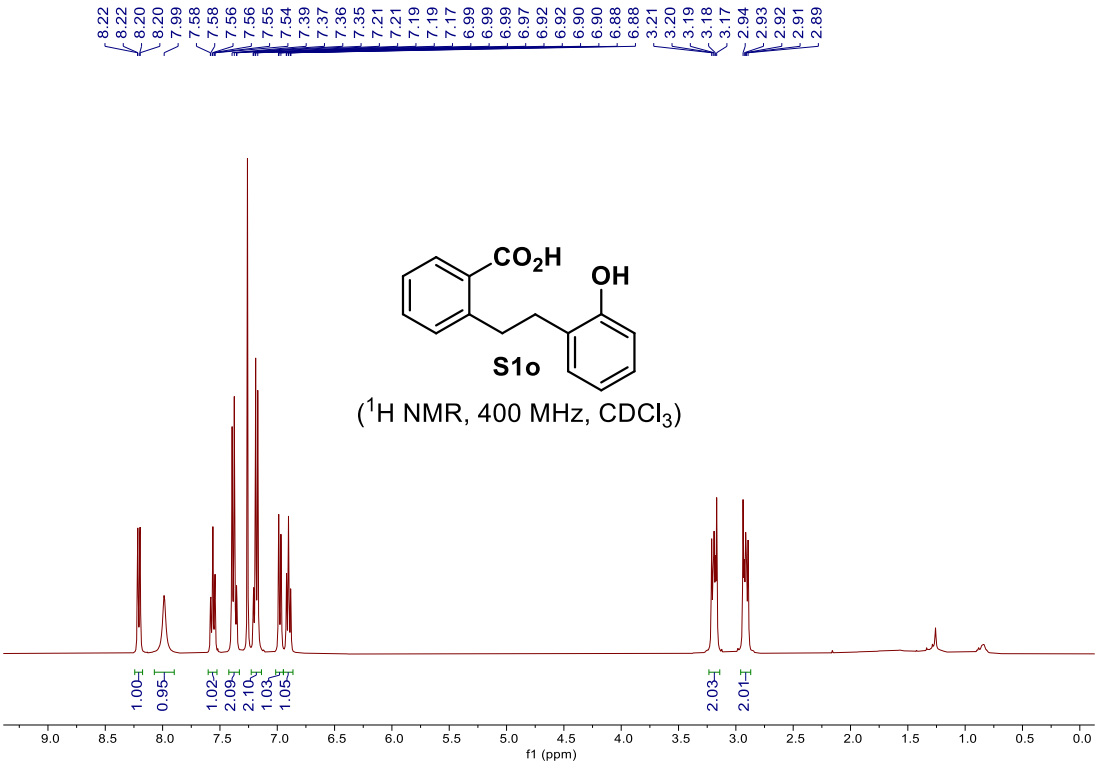

162.80
158.77
150.77
144.65
136.52
133.18
133.00
128.71
128.24
128.19
127.98
127.03
125.54
120.47
119.00
117.71
112.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.86
37.39
BnO
O
O
1l
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)

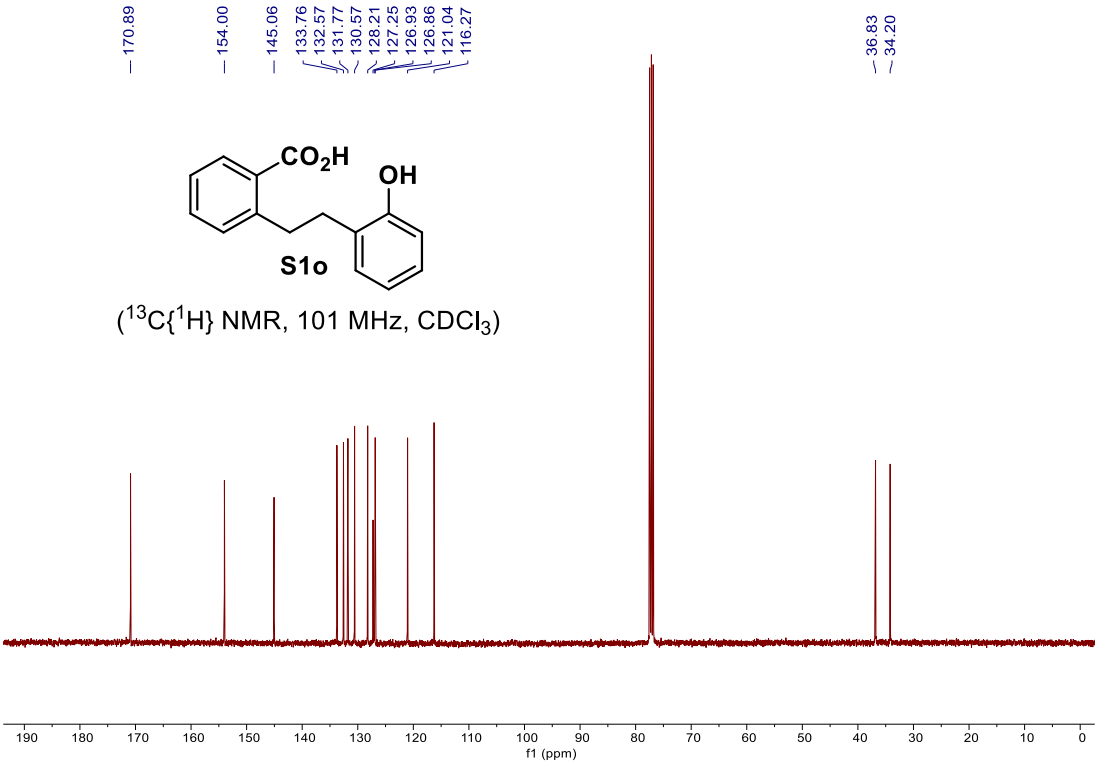


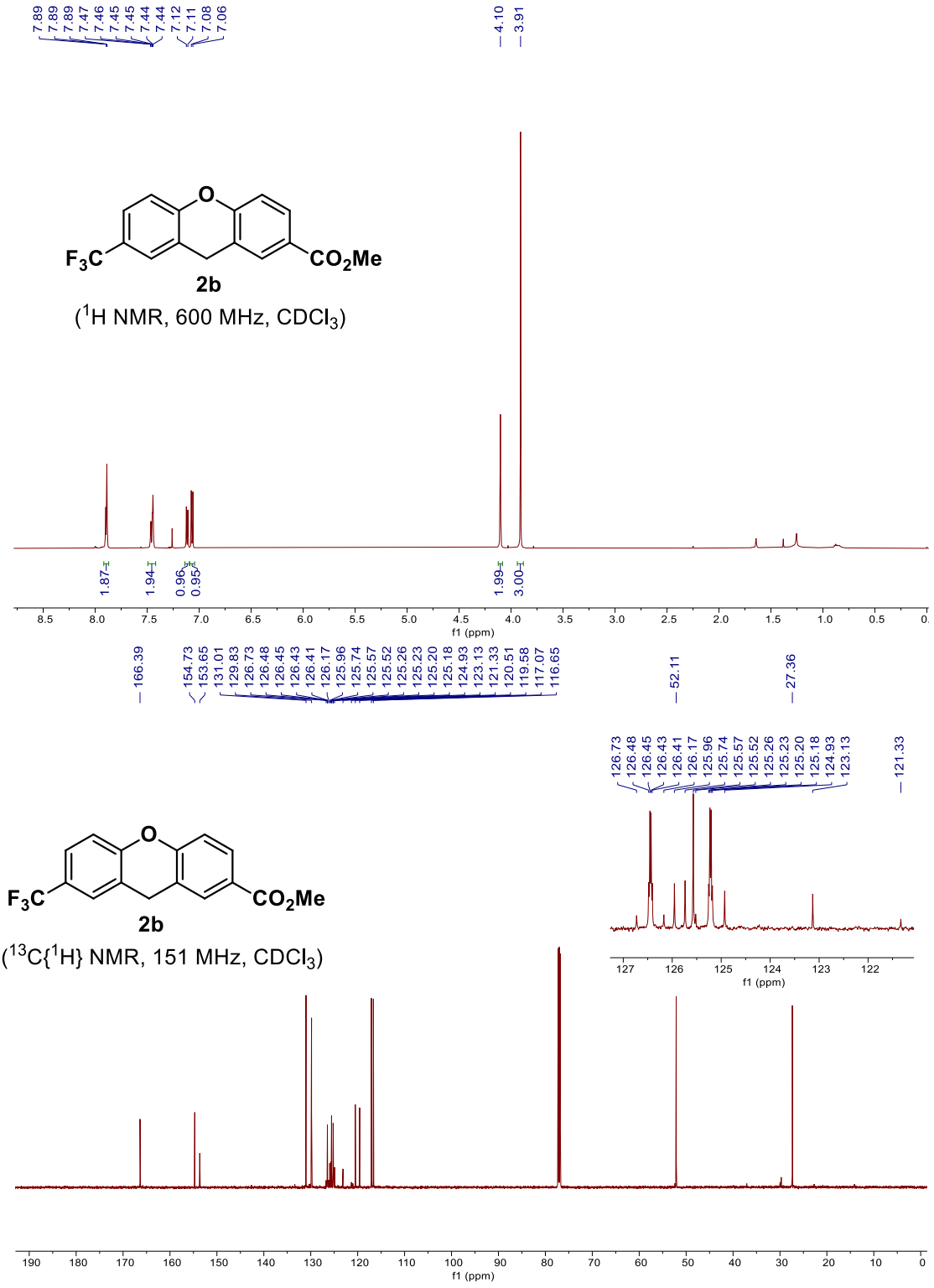
(^{1}H NMR, 400 MHz, $CDCl_3$)

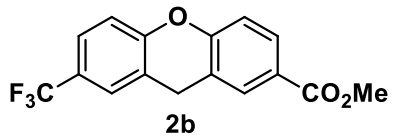


(^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$)


8.22
8.22
8.20
8.20
7.99
7.58
7.58
7.56
7.56
7.55
7.54
7.39
7.37
7.36
7.35
7.21
7.21
7.19
7.19
7.17
6.99
6.99
6.99
6.97
6.92
6.92
6.90
6.90
6.88
6.88
3.21
3.20
3.19
3.18
3.17
2.94
2.93
2.92
2.91
2.89
CO2H
OH
S1o
(1H NMR, 400 MHz, CDCl3)
1.00
0.95
1.02
2.09
2.10
1.03
1.05
2.03
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

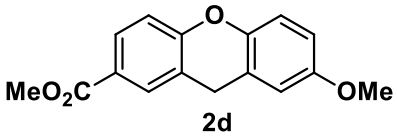

170.89
154.00
145.06
133.76
132.57
131.77
130.57
128.21
127.25
126.93
126.86
121.04
116.27
36.83
34.20
CO2H
OH
S1o
(13C{1H} NMR, 101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.89
7.89
7.89
7.47
7.46
7.45
7.45
7.44
7.44
7.12
7.11
7.08
7.06
4.10
3.91
O
F3C
CO2Me
2b
(1H NMR, 600 MHz, CDCl3)
1.87
1.94
0.96
0.95
1.99
3.00
f1 (ppm)
166.39
154.73
153.65
131.01
129.83
126.73
126.48
126.45
126.43
126.41
126.17
125.96
125.74
125.57
125.52
125.26
125.23
125.20
125.18
124.93
123.13
121.33
120.51
119.58
117.07
116.65
52.11
27.36
O
F3C
CO2Me
2b
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)



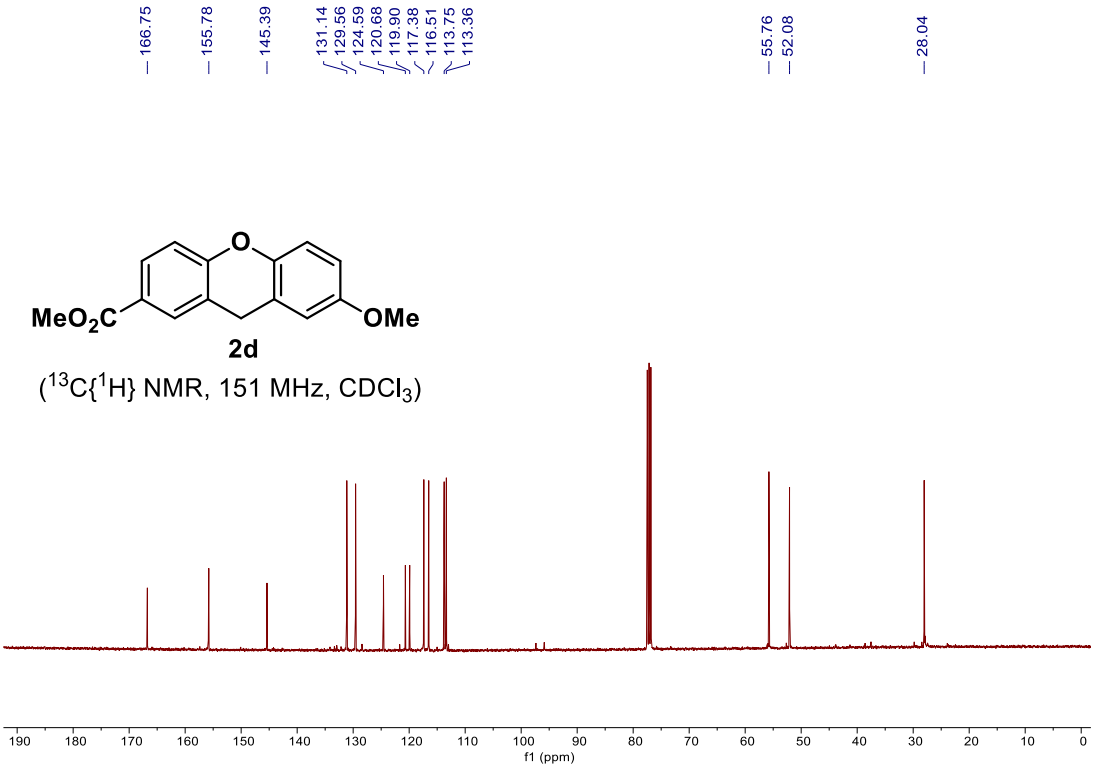
2b

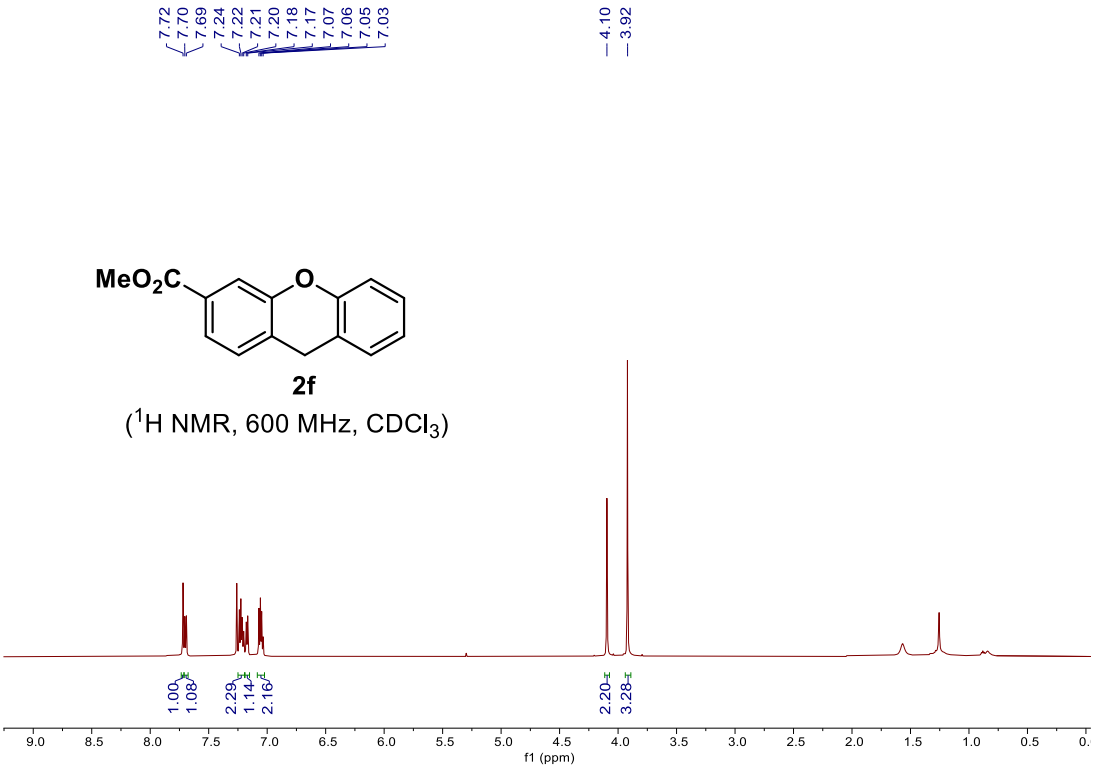
($^{19}F\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)

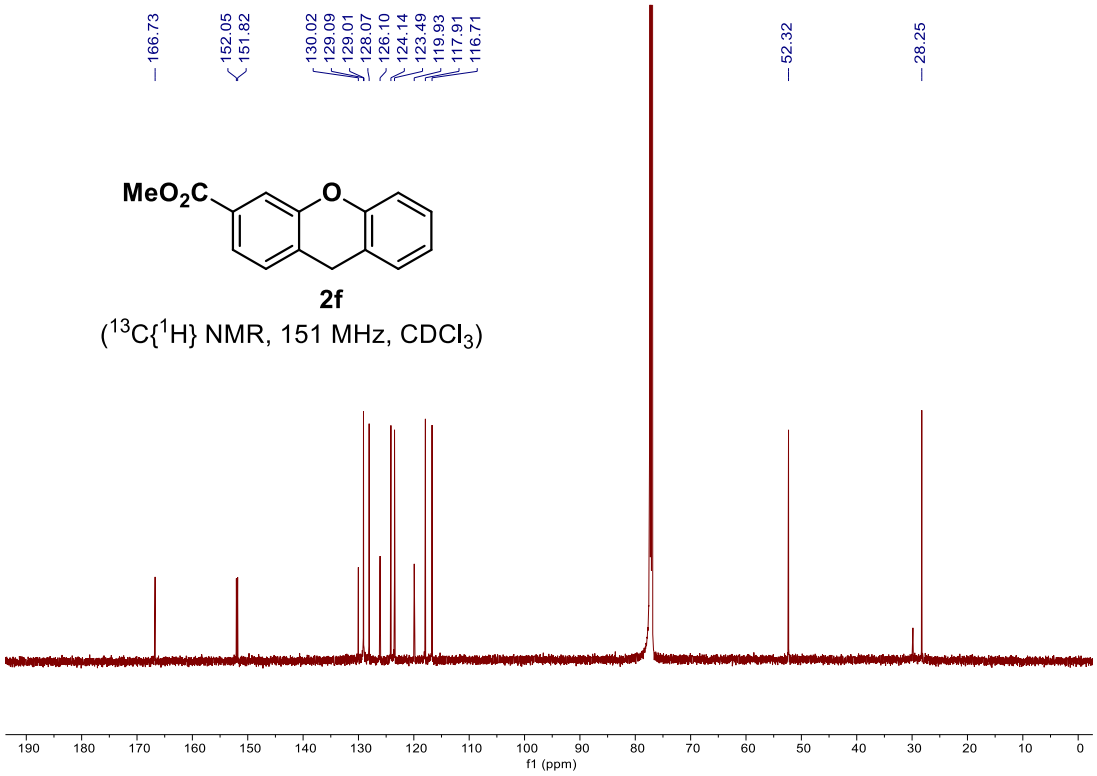


2d

(^{1}H NMR, 600 MHz, $CDCl_3$)

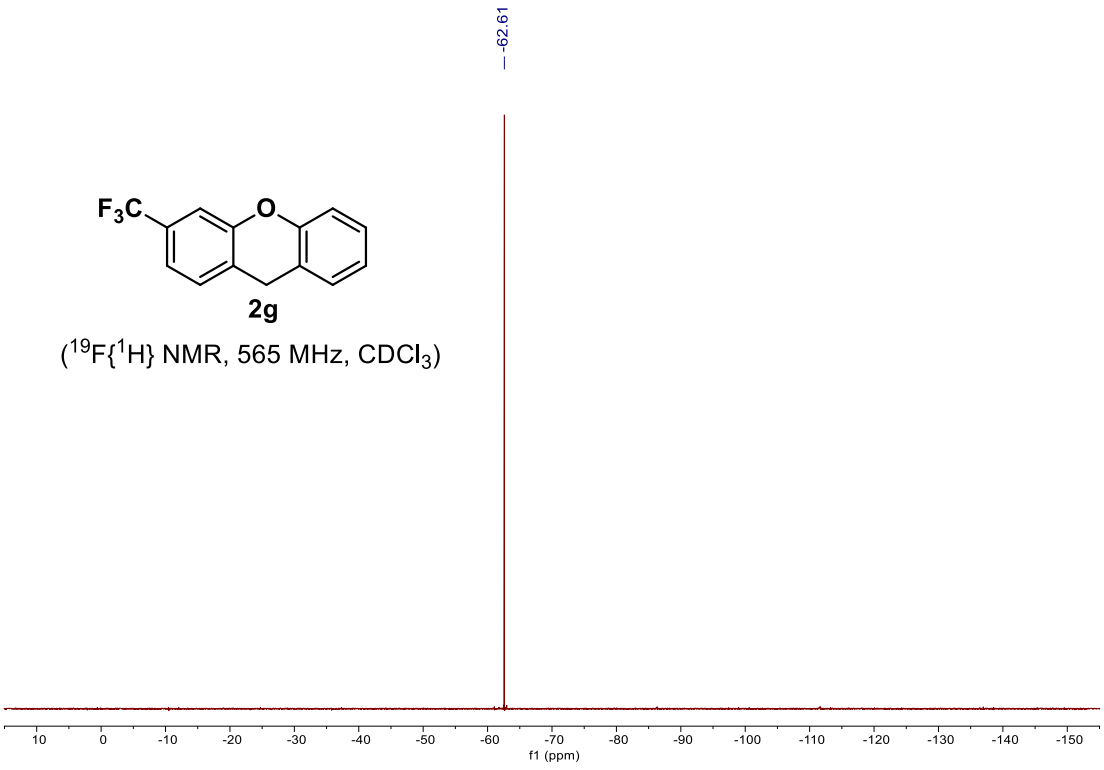

166.75
155.78
145.39
131.14
129.56
124.59
120.68
119.90
117.38
116.51
113.75
113.36
55.76
52.08
28.04
O
MeO2C
OMe
2d
(13C{1H} NMR, 151 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.72
7.70
7.69
7.24
7.22
7.21
7.20
7.18
7.17
7.07
7.06
7.05
7.03
4.10
3.92
MeO2C
O
2f
(1H NMR, 600 MHz, CDCl3)
1.00
1.08
2.29
1.14
2.16
2.20
3.28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



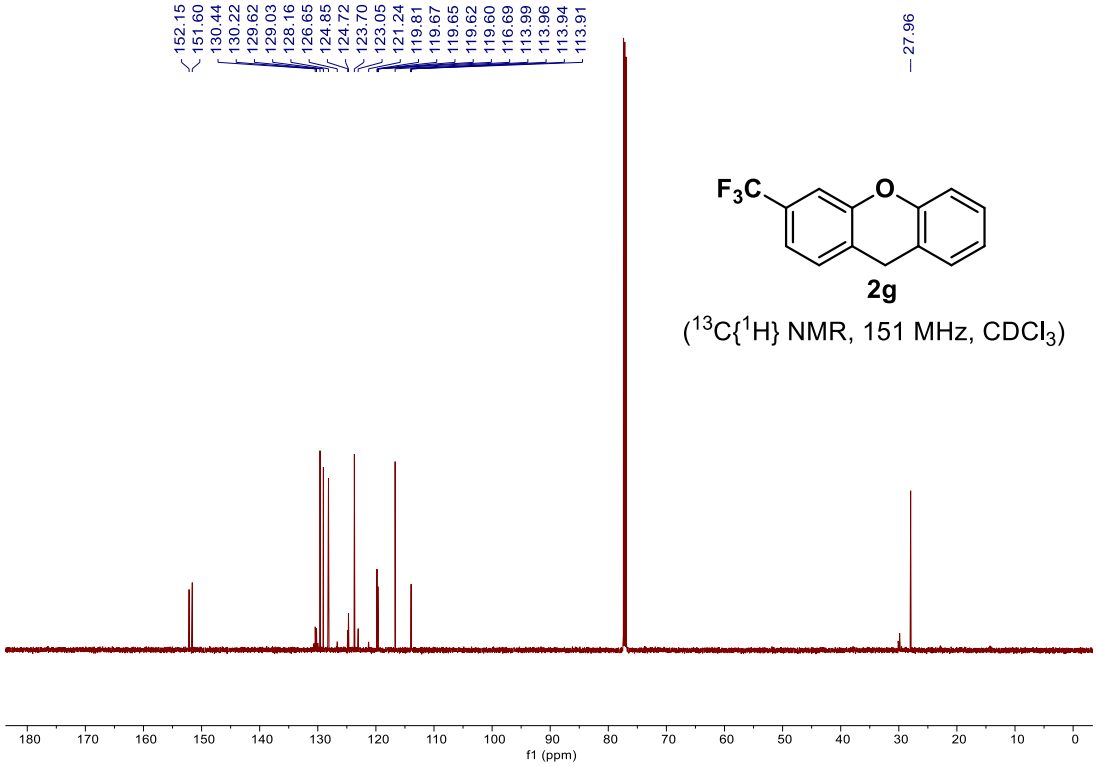
2f

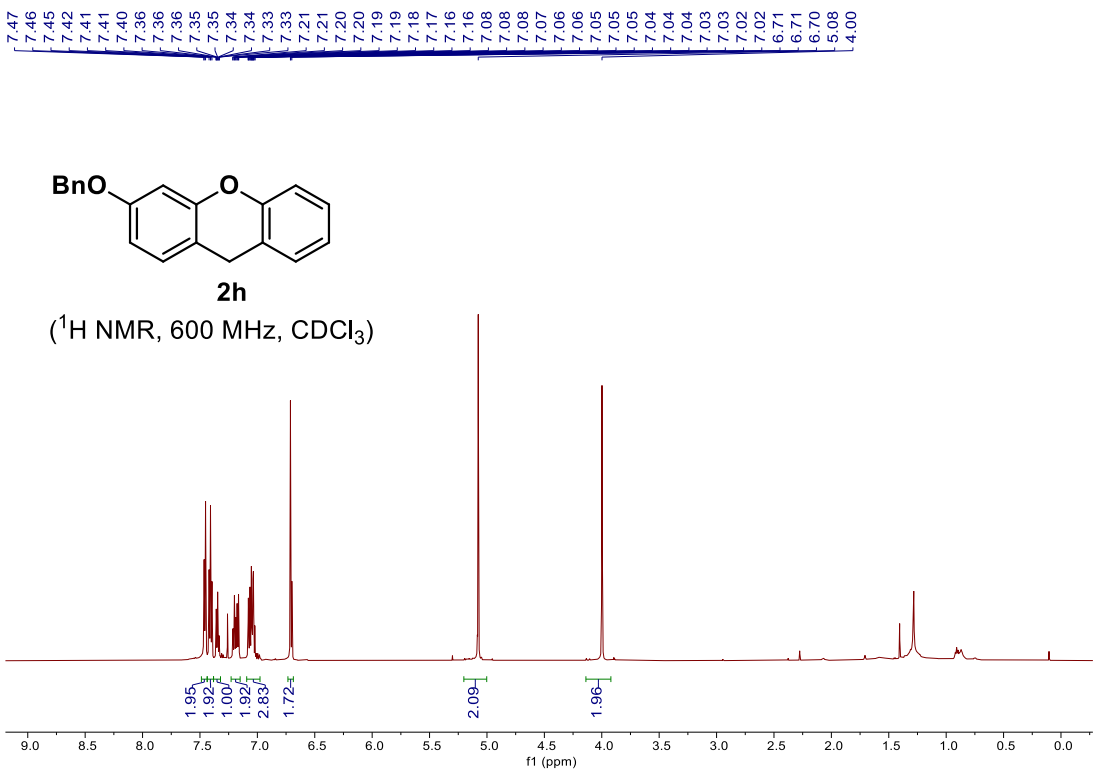
($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)

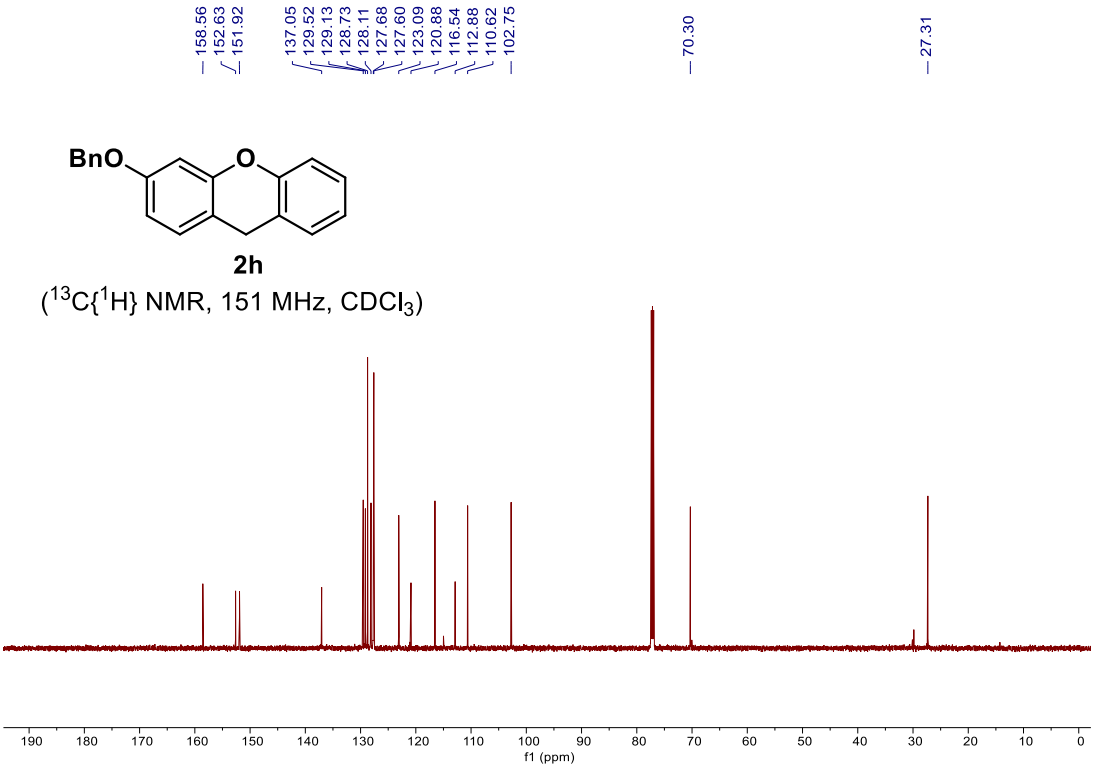


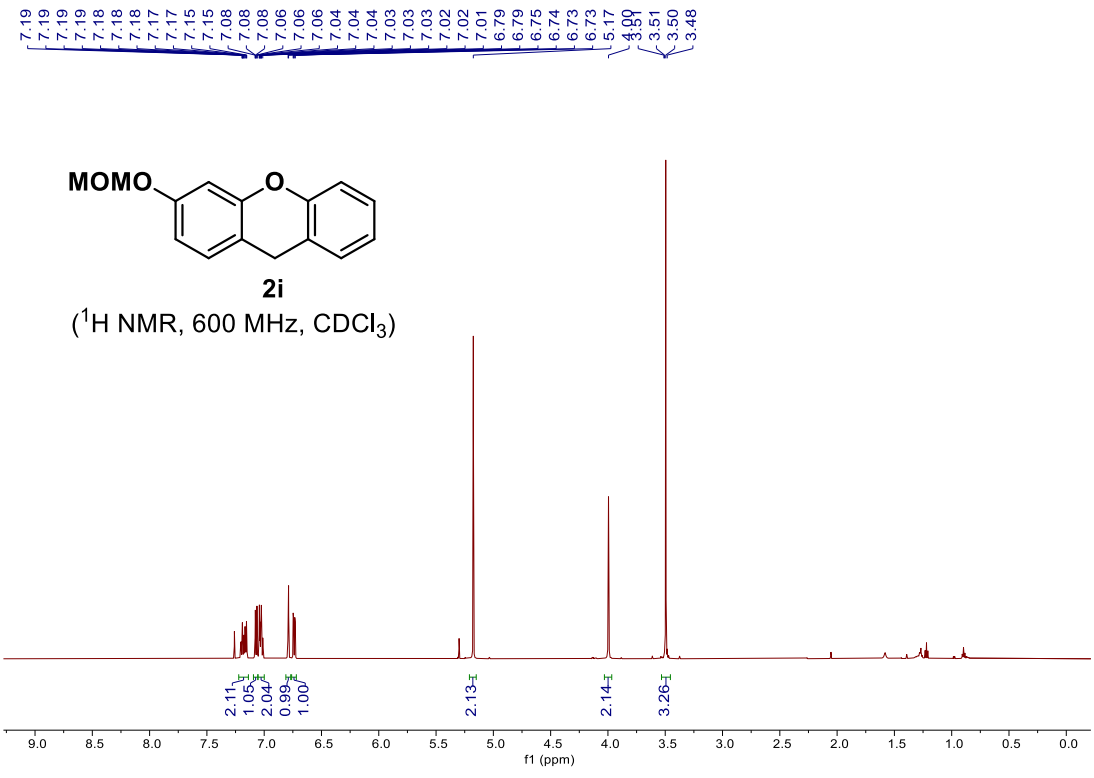
2g

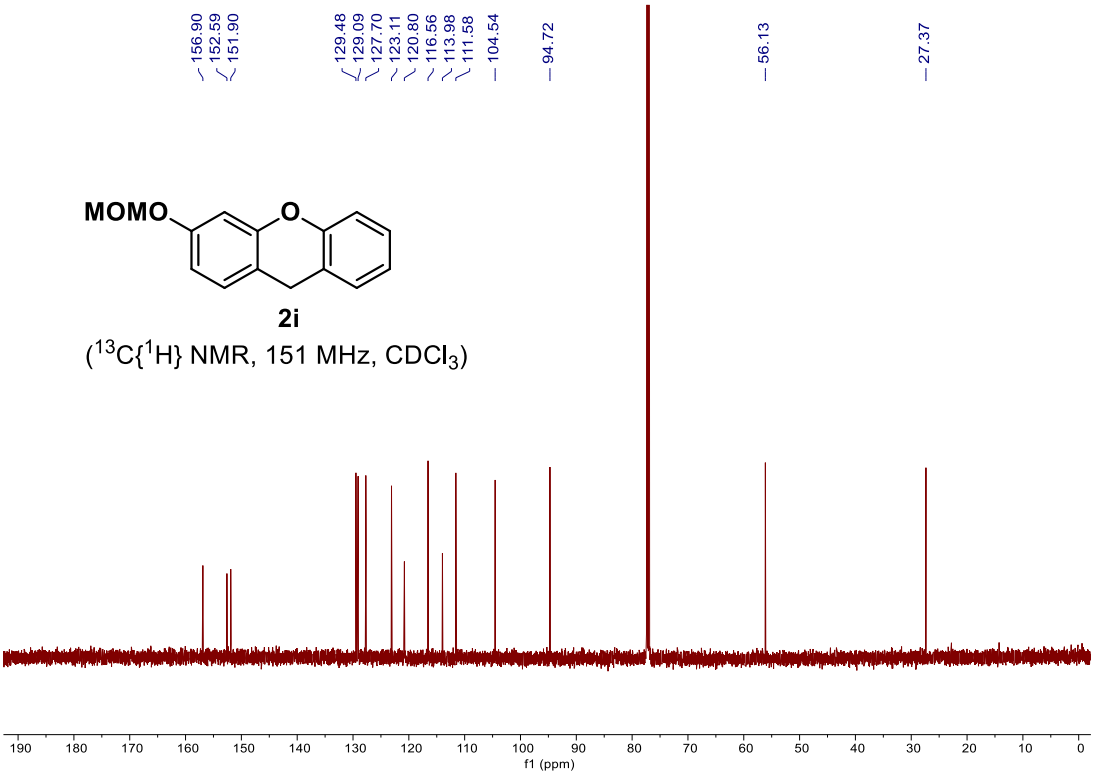
($^{19}F\{^{1}H\}$ NMR, 565 MHz, $CDCl_3$)


152.15
151.60
130.44
130.22
129.62
129.03
128.16
126.65
124.85
124.72
123.70
123.05
121.24
119.81
119.67
119.65
119.62
119.60
116.69
113.99
113.96
113.94
113.91
27.96
F3C
O
2g
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)


7.47
7.46
7.45
7.42
7.41
7.41
7.40
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.08
7.08
7.08
7.07
7.06
7.06
7.05
7.05
7.05
7.04
7.04
7.04
7.03
7.03
7.02
7.02
6.71
6.71
6.70
5.08
4.00
BnO
O
2h
(1H NMR, 600 MHz, CDCl3)
1.95
1.92
1.00
1.92
2.83
1.72
2.09
1.96
f1 (ppm)

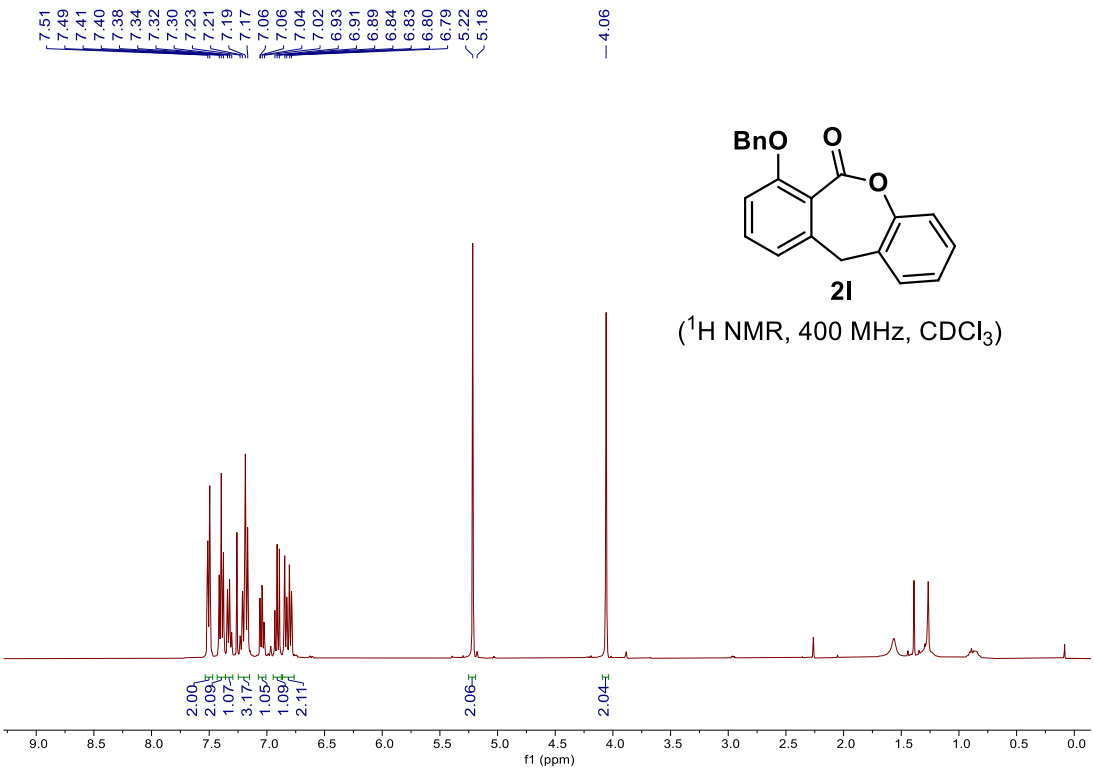

158.56
152.63
151.92
137.05
129.52
129.13
128.73
128.11
127.68
127.60
123.09
120.88
116.54
112.88
110.62
102.75
70.30
27.31
BnO
O
2h
($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)
f1 (ppm)


7.19
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.15
7.08
7.08
7.08
7.06
7.06
7.06
7.04
7.04
7.04
7.03
7.03
7.03
7.02
7.02
7.01
6.79
6.79
6.75
6.74
6.73
6.73
5.17
4.00
3.51
3.50
3.48
MOMO
O
2i
(^{1}H NMR, 600 MHz, $CDCl_3$)
2.11
1.05
2.04
0.99
1.00
2.13
2.14
3.26
f1 (ppm)



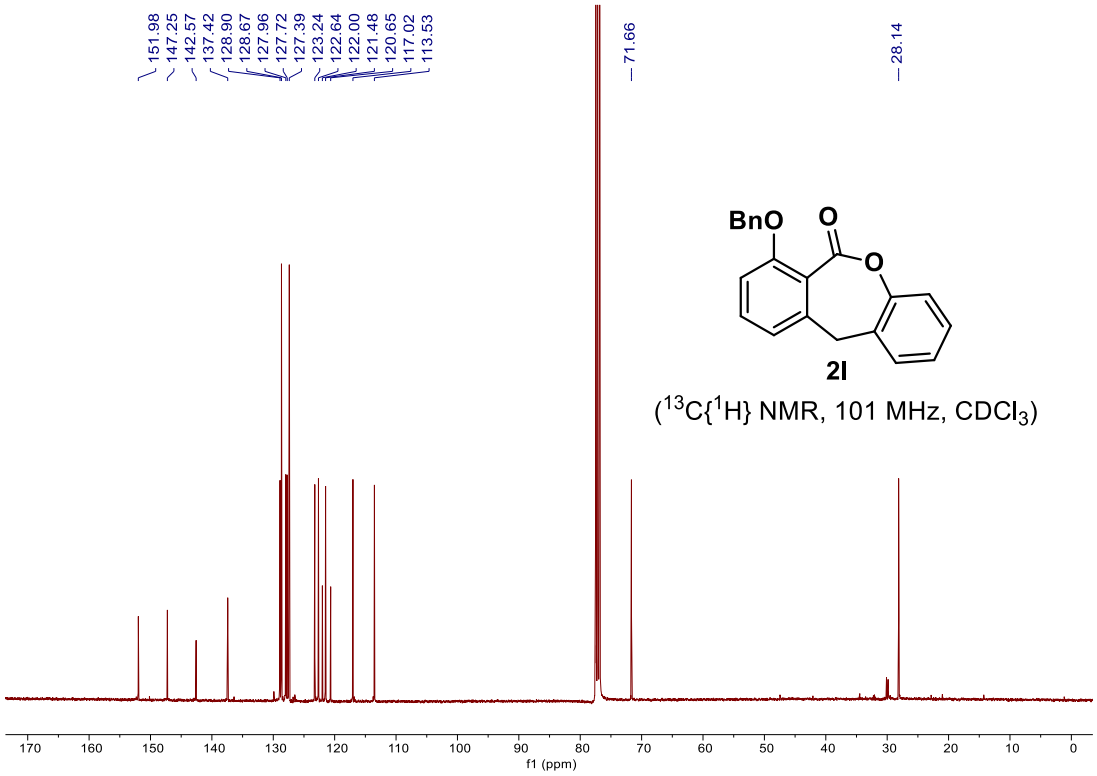
2i

($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)



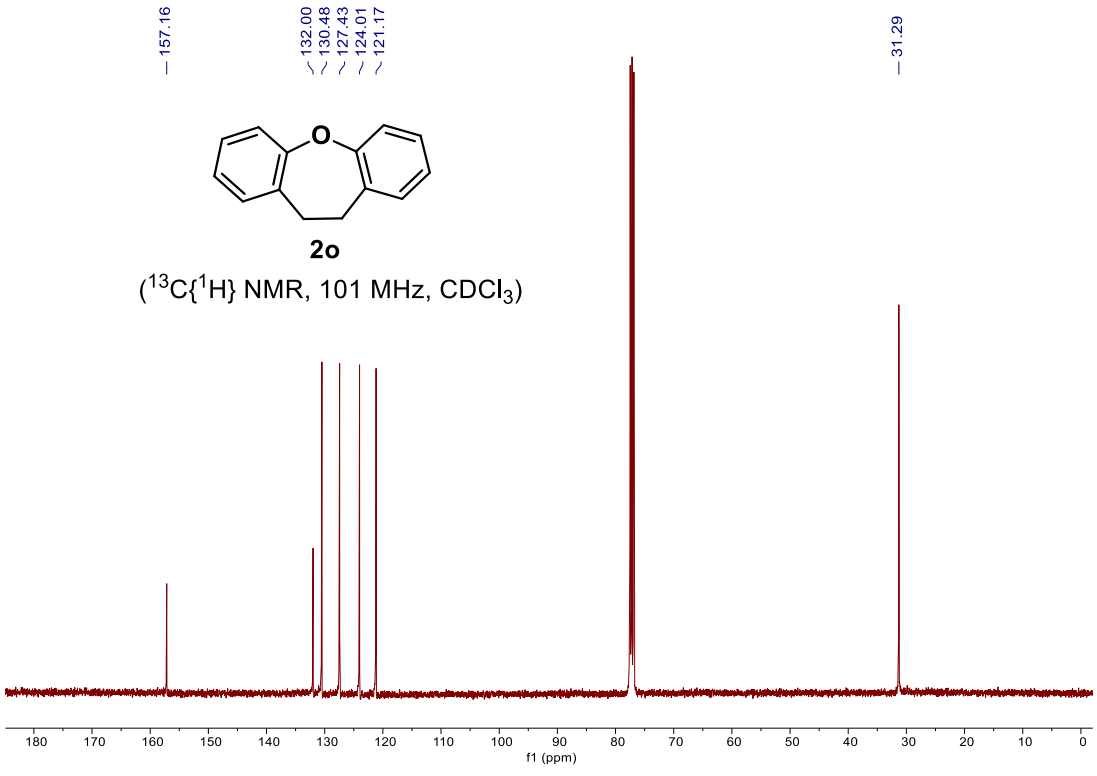
2l

(^{1}H NMR, 400 MHz, $CDCl_3$)



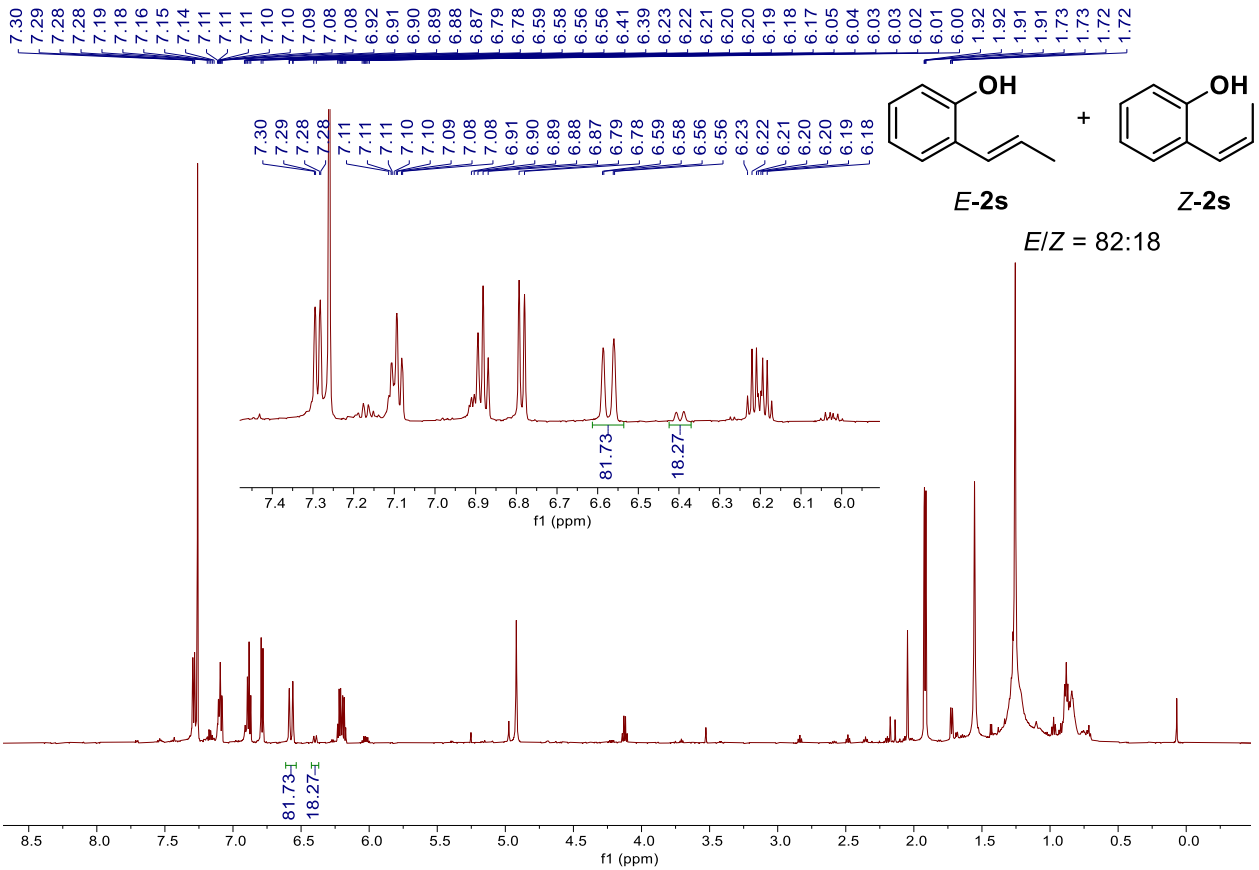
2l

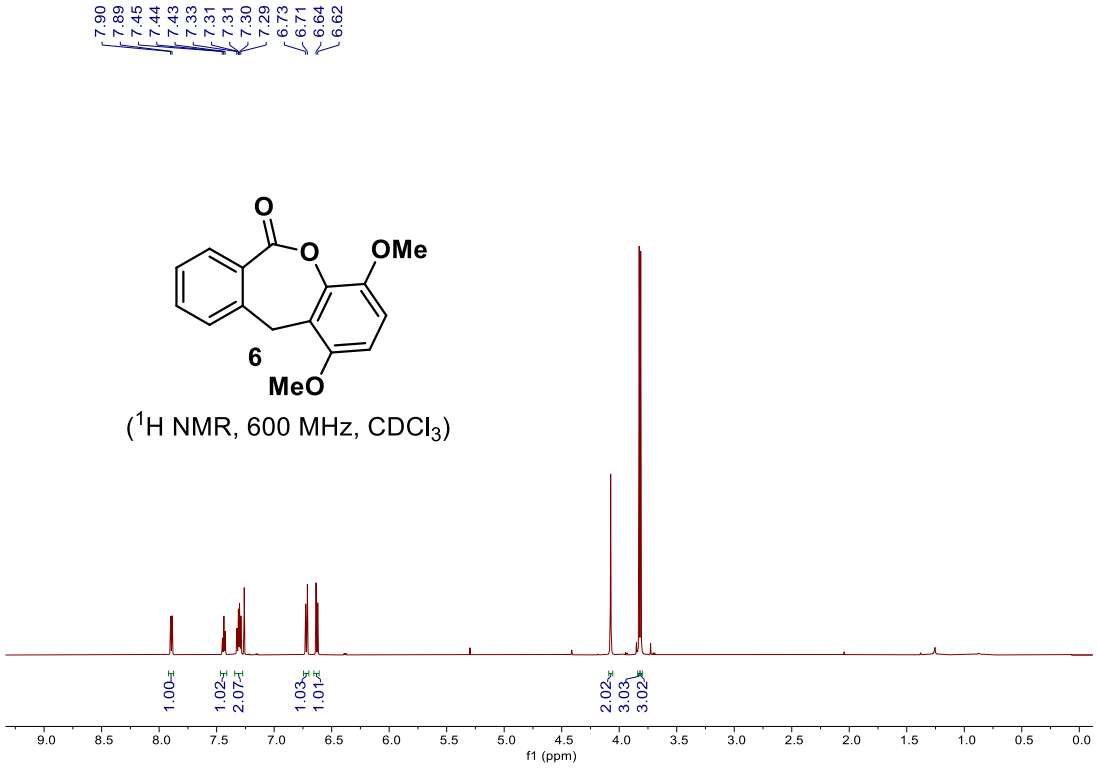
($^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$)

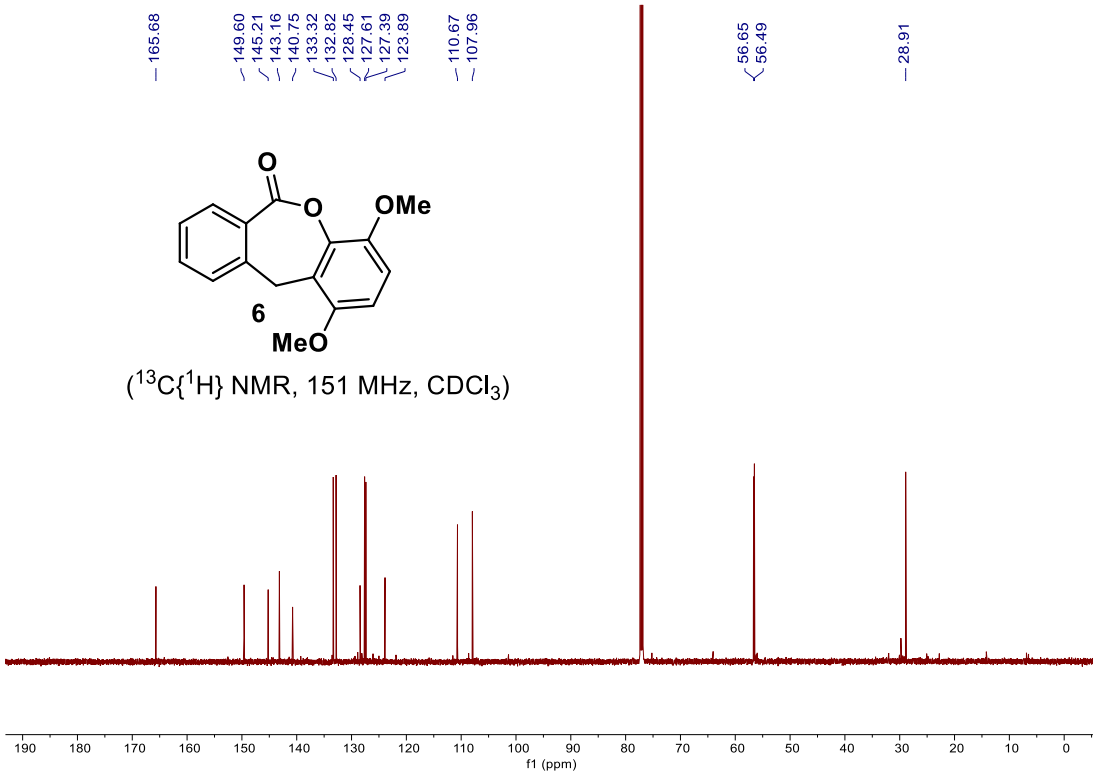


2o

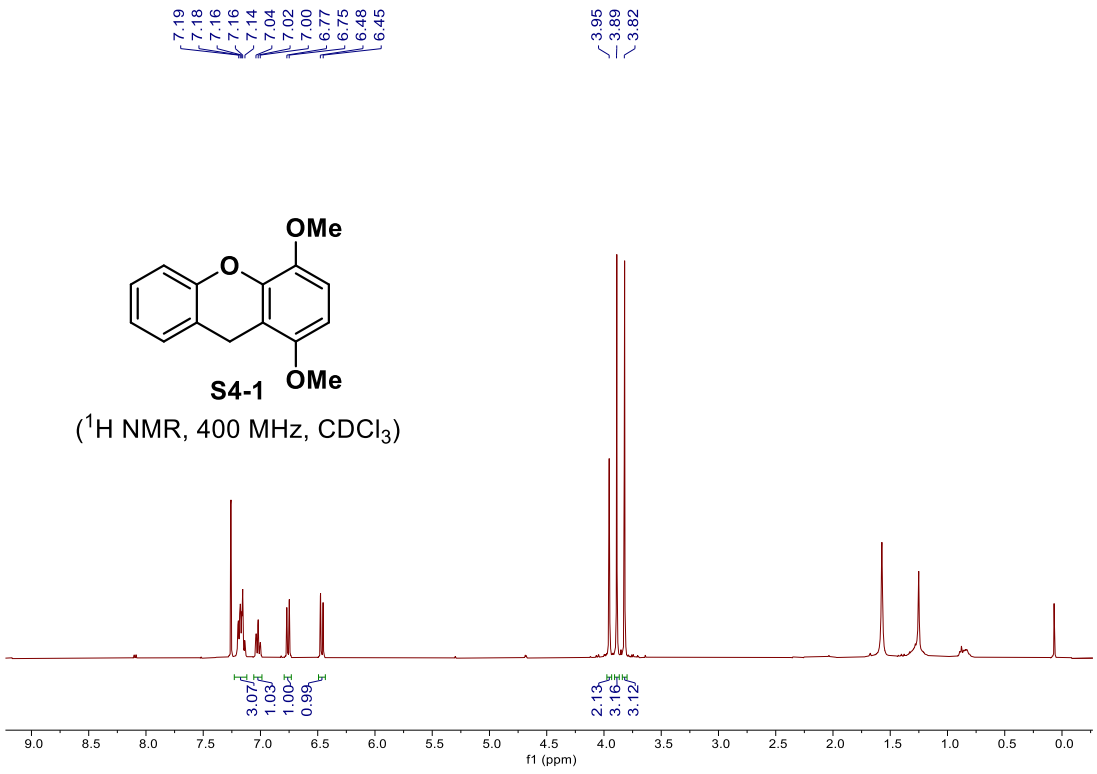
($^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$)


OH
OH
E-2s
Z-2s
E/Z = 82:18
81.73
18.27
f1 (ppm)


O
O
OMe
6
MeO
(1H NMR, 600 MHz, CDCl3)
f1 (ppm)

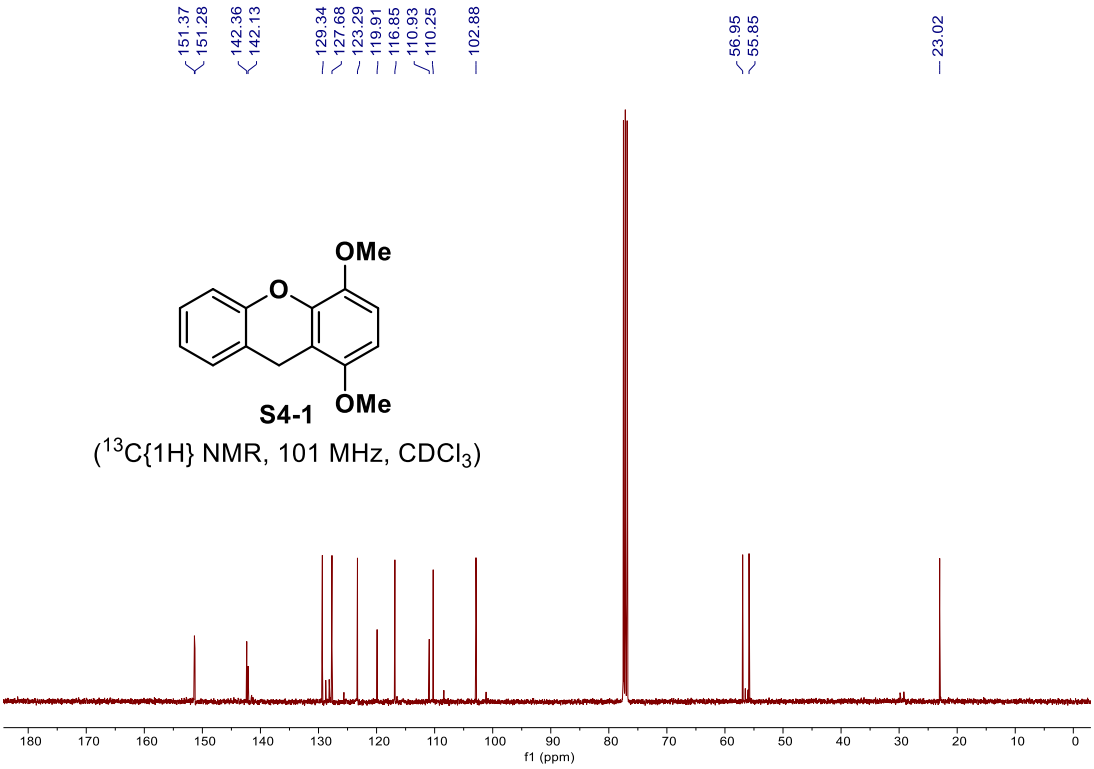


($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)



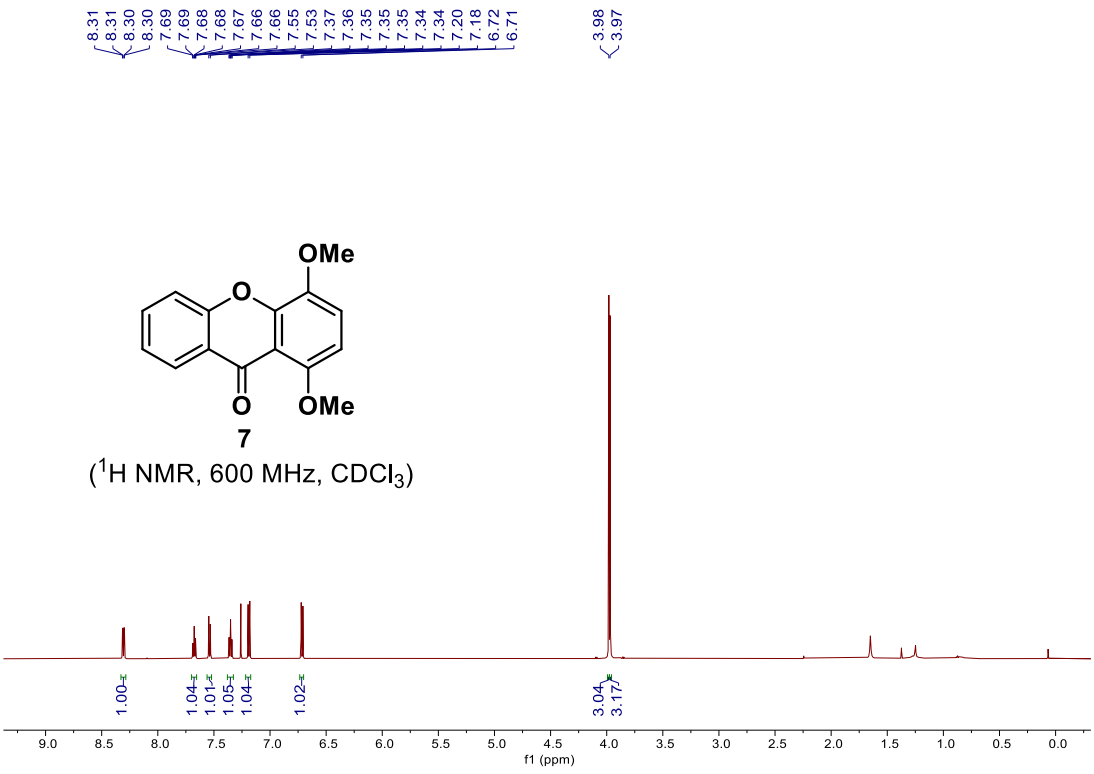
S4-1

(^{1}H NMR, 400 MHz, $CDCl_3$)



S4-1

($^{13}C\{1H\}$ NMR, 101 MHz, $CDCl_3$)



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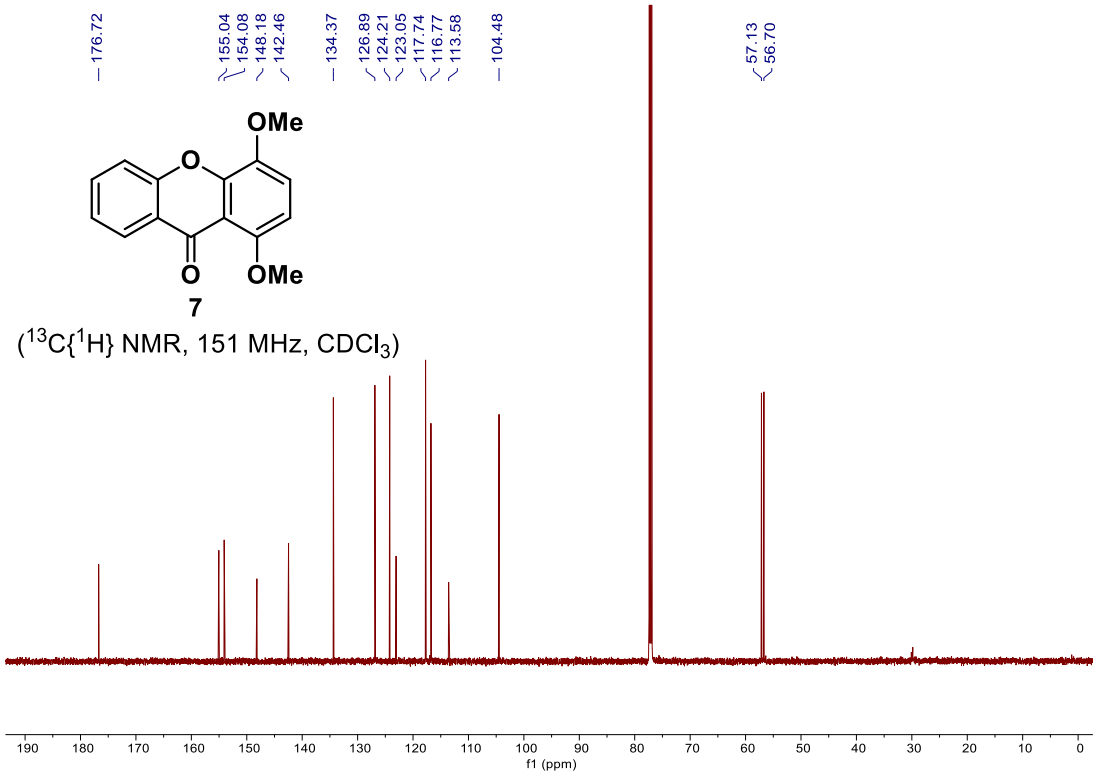
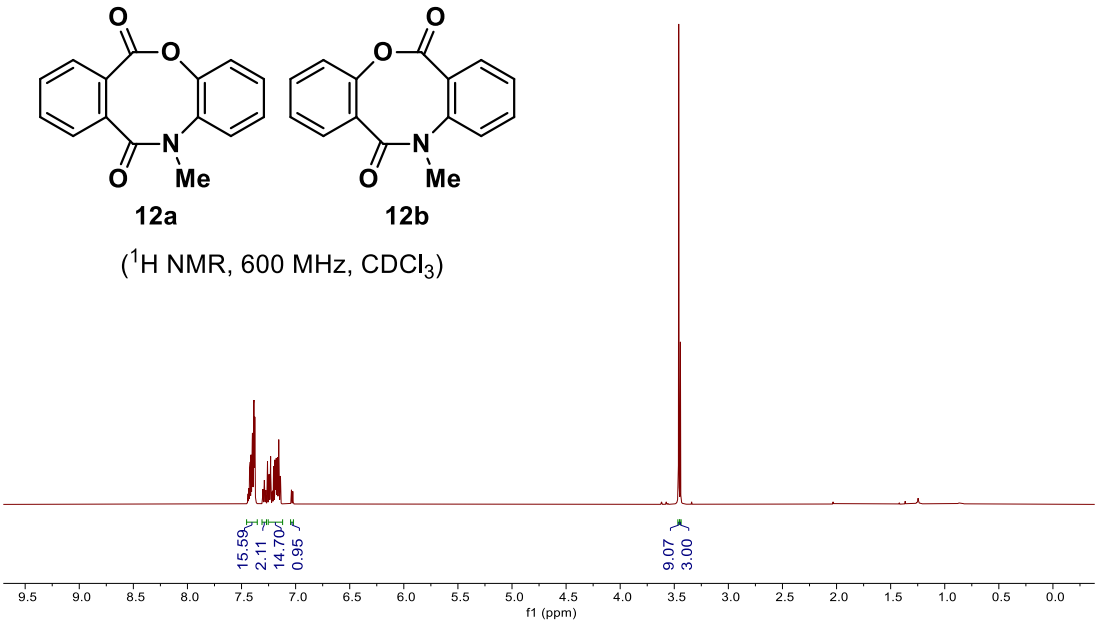
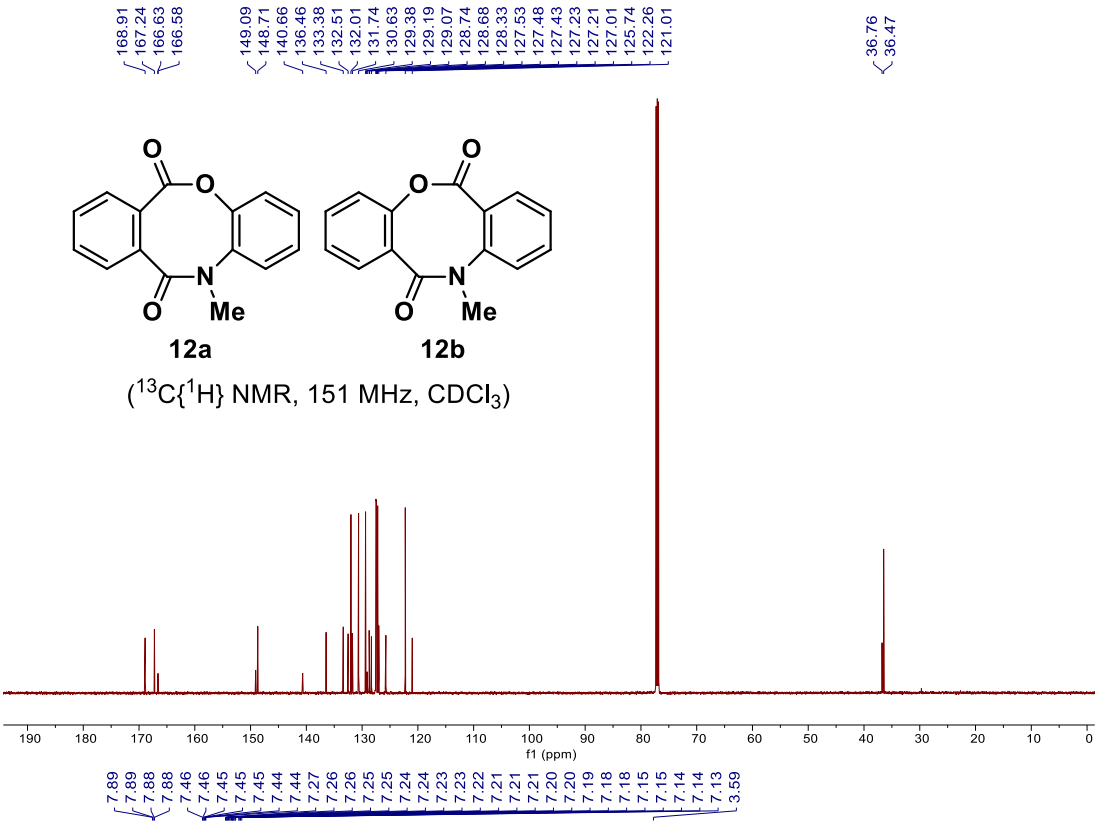
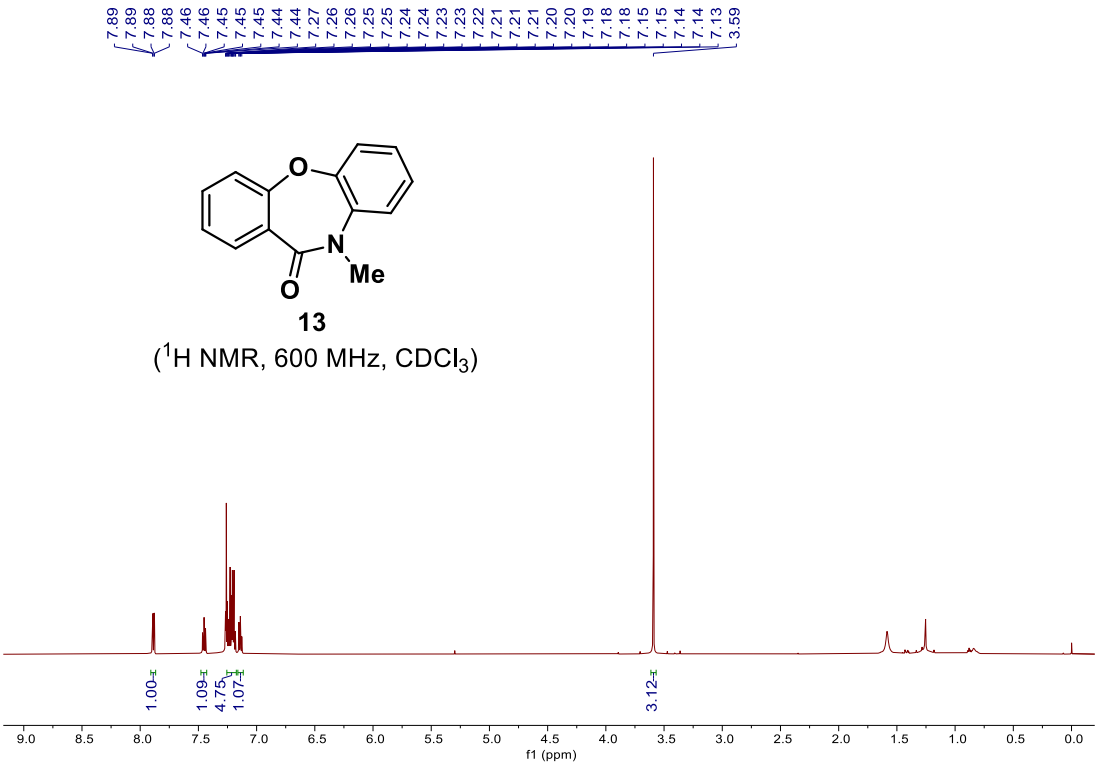
(^{1}H NMR, 600 MHz, $CDCl_3$)

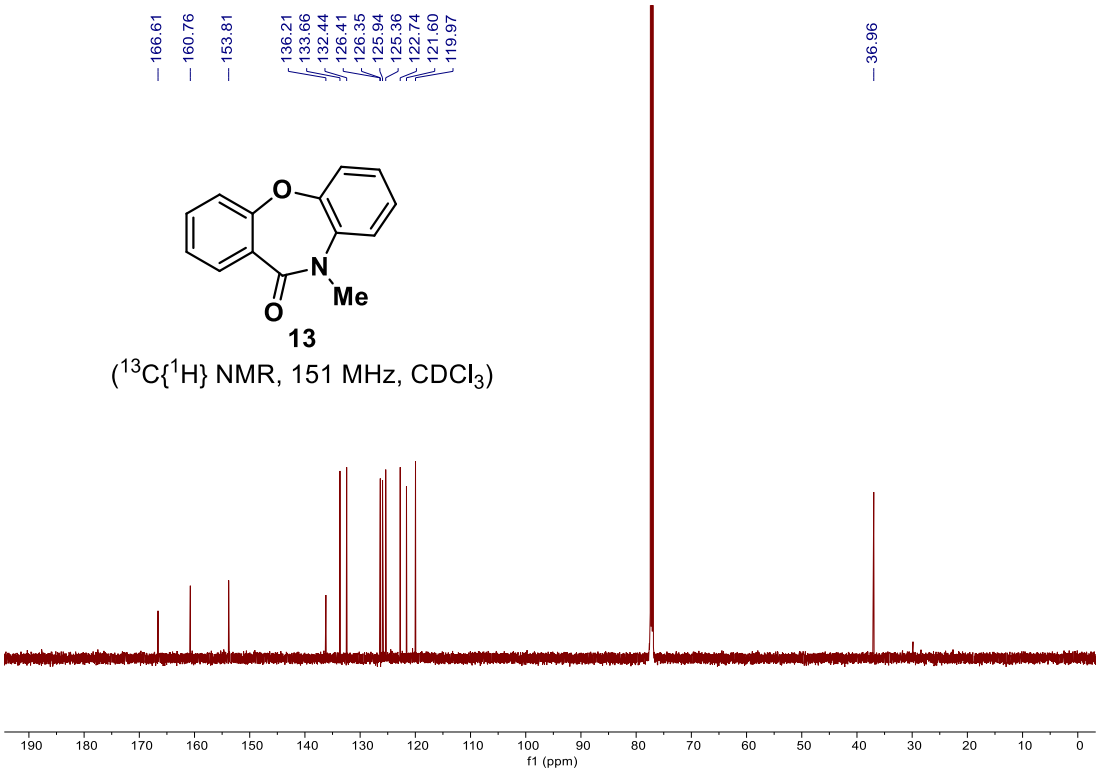

176.72
155.04
154.08
148.18
142.46
134.37
126.89
124.21
123.05
117.74
116.77
113.58
104.48
57.13
56.70
OMe
O
O
OMe
7
(13C{1H} NMR, 151 MHz, CDCl3)
f1 (ppm)


QL-366A-IV-79-1H.1.fid


O
O
N
Me
12a
12b
(1H NMR, 600 MHz, CDCl3)
15.59
2.11
14.70
0.95
9.07
3.00
f1 (ppm)


168.91
167.24
166.63
166.58
149.09
148.71
140.66
136.46
133.38
132.51
132.01
131.74
130.63
129.38
129.19
129.07
128.74
128.68
128.33
127.53
127.48
127.43
127.23
127.21
127.01
125.74
122.26
121.01
36.76
36.47
O
O
N
Me
O
12a
12b
(13C{1H} NMR, 151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.89
7.89
7.88
7.88
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.15
7.15
7.14
7.14
7.13
3.59
O
N
Me
O
13
(1H NMR, 600 MHz, CDCl3)
1.00
1.09
4.75
1.07
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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($^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$)