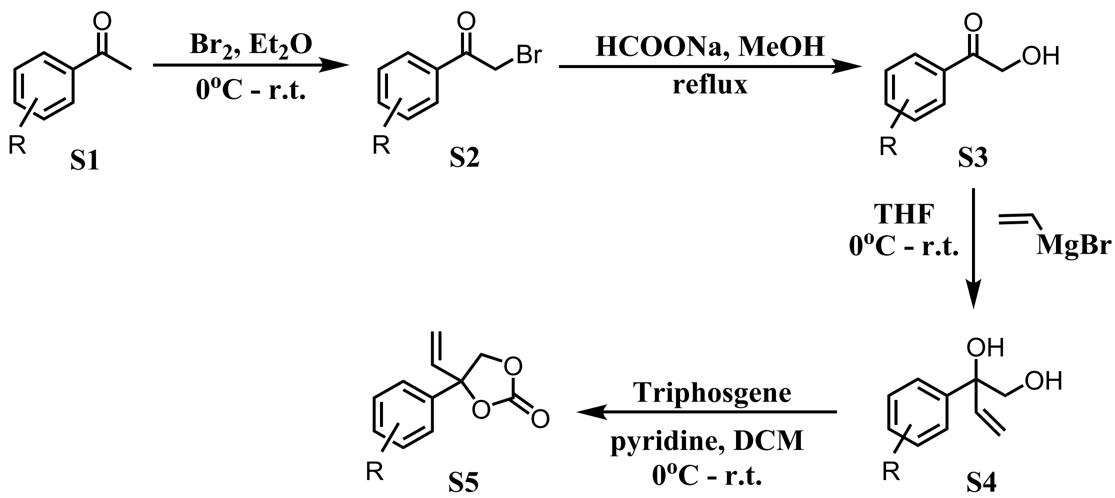
Divergent Synthesis of *N*-heterocycles by Pd-catalyzed Controllable Cyclization of Vinylethylene Carbonates

Contents:

General comments:

NMR spectra were recorded at room temperature on the following spectrometers: Bruker Avance III 400 Spectrometer (400 MHz) and Bruker Avance III 500 (Cryo) Spectrometer (500 MHz). Chemical shifts are given in ppm and coupling constants in Hz. ^{1}H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents. The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. For HRMS data, the ESI-positive method was applied on the Agilent G6520 Q-TOF, or EI method was applied on the Themo Fisher Scientific Thermo DFS. Chemicals were purchased from commercial suppliers. Unless stated otherwise, all the substrates and solvents were purified and dried according to standard methods prior to use.

Typical procedure for the preparation of vinylethylene carbonates



Bromine (5 mmol, 1eq) was added to a solution of the respective ketone (5 mmol, 1eq) in Et_2O (6 mL) at 0 °C. And then 15 minutes later, the solution was stirred for 6-12 h (until the color of the solution changed from red to light-yellow) at r.t.. The reaction progress was monitored by TLC or HPLC/MS. When the starting material disappeared, the reaction was quenched with ice water (6 mL), and extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution (10 mL), brine (10 mL), and dried over Na_2SO_4. After being filtered and concentrated, the residue was used for the next step without further purification (the crude **S2**).[1]

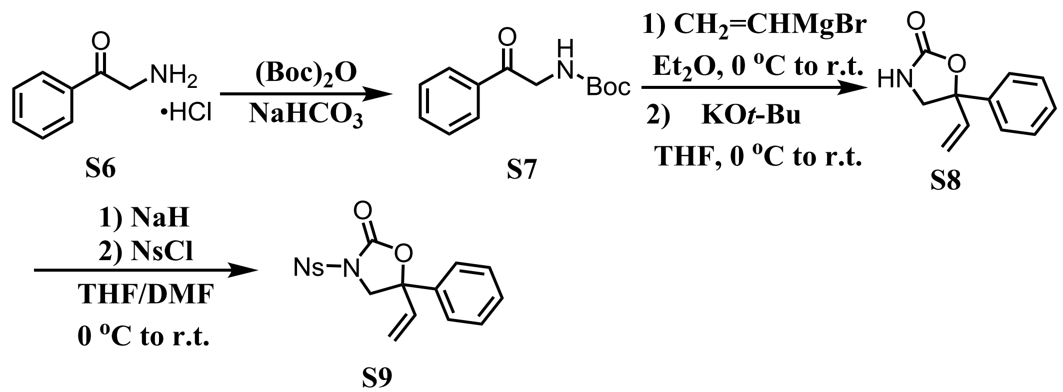
To a solution of resultant crude **S2** (1 eq) in methanol (3 mL/mmol) was added sodium formate (3 eq) at r.t.. The reaction mixture was refluxed until TLC shows the end, and then was filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved with ethyl acetate, washed with water and brine solution, dried over Na_2SO_4 and evaporated. The crude material was purified by column chromatography to get **S3**.

To a solution of the **S3** (1 eq) in THF (4 mL/mmol) was added vinylmagnesium bromide (1.0 M in THF, 2.5 eq) at 0 °C. The reaction was stirred under an N_2

atmosphere at room temperature for 2-3 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. Then the crude product was purified by FCC to get the **S4**.[2]

To a solution of **S4** in DCM (1.5 mL/mmol) added pyridine (4 eq) and triphosgene (0.5 eq) at 0 °C. The reaction was stirred under an N_2 atmosphere at room temperature for 1-2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, washed with H_2O, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford the corresponding carbonate (**S5**).[2]

Typical procedure for the formation of vinyloxazolidin-2-ones[3]



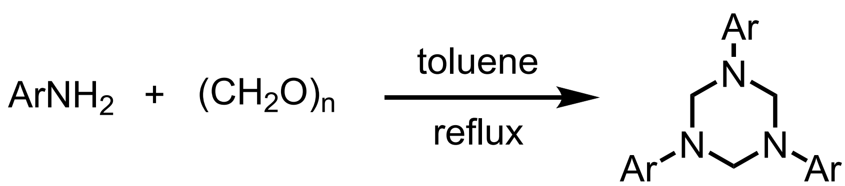
To a solution of **S6** (0.50 g, 1 eq) and $NaHCO_3$ (0.57 g, 2.5 eq) in H_2O/CH_3OH (v/v = 6.5 mL/6.5 mL) was added $(Boc)_2O$ (0.88 g, 1.5 eq). After stirring for 2-3 h, the reaction mixture was quenched with cooled water, and then the mixture filtrated. The residue was washed with brime and evaporated to afford **S7** (0.58 g).

To a solution of **S7** (0.6 g, 1 eq) in THF (3 mL) was added vinylmagnesium bromide (1.0 M THF solution, 6.0 mL) at 0 ºC under N_2. The mixture was warmed up to room temperature and the stirring was maintained for 3-5 h. The reaction mixture was then quenched with NH_4Cl (aq) at 0 ºC and extracted with ethyl acetate three times. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. This concentrate was passed through a short silica gel pad to remove the polar compounds to get the crude material.

To a solution of this crude material (0.33 g, 1 eq) in THF (3.6 mL) was added KO^{t}Bu (0.40 g, 3 eq) at 0 ºC under N_2 and the resulting mixture was stirred at room temperature for 5 h. The reaction mixture was then quenched by the slow addition of a saturated aqueous solution of NH_4Cl at 0 ºC, and the mixture was extracted with ethyl acetate three times, and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude product, which was purified by FCC to afford **S8** (200 mg).

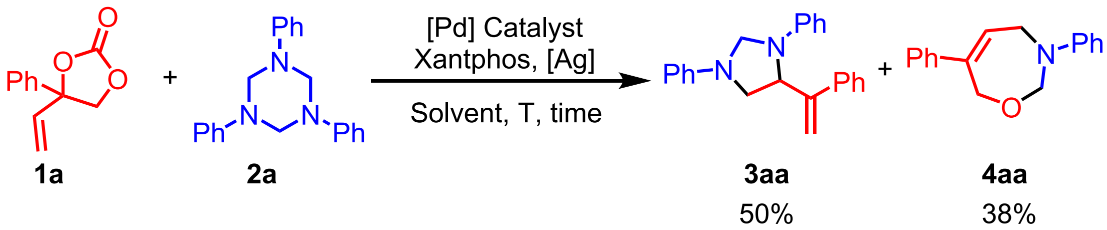
To a solution of **S8** (200 mg, 1eq) in THF (1 mL) and DMF (2.5 mL) was slowly added NaH (60%, 79 mg, 2eq) at 0 ºC under N_2 and the mixture was stirred for 15 min. Then, 4-nitrobenzenesulfonyl chloride (280 mg, 1.3 eq) was added, and the reaction mixture was stirred over night at room temperature. And then a saturated aqueous solution of NH_4Cl was slowly added at 0 ºC and extracted with ethyl acetate three times. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the residue by FCC gave the product **S9** (1.49 g, 4.77 mmol, 63% yield) as a white solid.

General procedure for synthesis of triazine compounds[4]



In a 100 mL round-bottomed flask equipped with a Dean-Stark apparatus, a mixture of aniline (30 mmol), paraformaldehyde (33 mmol), and toluene (50 mL) was heated with refluxing for 2 hours. Then the solvent was concentrated under reduced pressure at 50°C, a precipitate came out from the mixture. The precipitate was collected by filtration, washed with n-hexane several times, and dried to obtain 1,3,5-triazine.

Table S1. Screening Reaction Conditions for Pd-Catalyzed [3 + 2] Cycloaddition And [5 + 2] Cycloaddition[a]

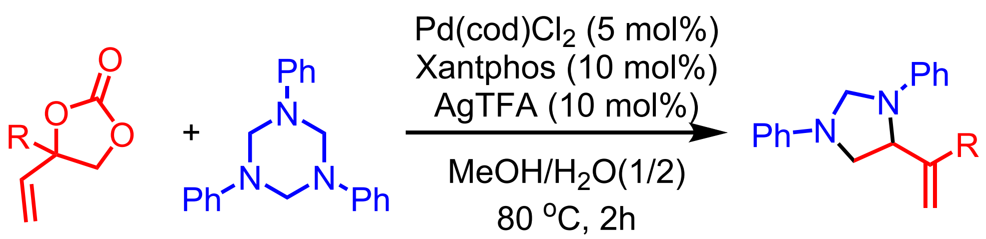


Entry	Catalyst (5 mol %)	Solvent	[Ag] (10 mol%)	T/°C	Time/h	Yield(%)[b] 3aa	4aa
1	$Pd(COD)Cl_2$	DCM	AgTFA	80	2	50	38
2	$Pd(OAc)_2$	DCM	AgTFA	80	2	16	13
3	$Pd(PPh_3)_4$	DCM	AgTFA	80	2	trace	10
4	$Pd(COD)Cl_2$	toluene	AgTFA	80	2	21	56
5	$Pd(COD)Cl_2$	H_2O	AgTFA	80	2	84	N.D.
6	$Pd(COD)Cl_2$	MeOH	AgTFA	80	2	20	28
7	$Pd(COD)Cl_2$	$DMSO/H_2O$(1/1)	AgTFA	80	2	55	N.D.
8	$Pd(COD)Cl_2$	DMF/H_2O (1/1)	AgTFA	80	2	67	N.D
9[c]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/1)	AgTFA	80	2	71	12
10[c]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (2/1)	AgTFA	80	2	89	N.D
11[c]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	80	2	99(85)	N.D.
12[d]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	10	74
13[e]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	3	81
14[f]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	trace	85(81)
15[d]	$Pd(COD)Cl_2$	DCM	AgTFA	60	1	13	64
16[e]	$Pd(COD)Cl_2$	DCM	AgTFA	60	1	8	66
17[f]	$Pd(COD)Cl_2$	DCM	AgTFA	60	1	15	81
18[f]	$[Pd(allyl)Cl]_2$	DCM	—	60	1	N.D.	N.D.
19	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	—	80	2	23%	N.D.
20[f]	—	DCM	AgTFA	60	1	N.D.	N.D.
21	—	$MeOH/H_2O$ (1/2)	AgTFA	80	2	N.D.	N.D.
22[f]	$Pd(TFA)_2$	DCM	AgTFA	60	1	8	84
23	$Pd(TFA)_2$	$MeOH/H_2O$ (1/2)	AgTFA	80	2	87	N.D.
24[f]	$Pd(TFA)_2$	DCM	AgOAc	60	1	12	73
25	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgOAc	80	2	30	N.D.

26[f]	$[Pd(allyl)Cl]_2$	DCM	AgOAc	60	1	N.D	N.D.
27[f]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	20	6	18	32
28[f]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	20	24	18	52
29[f]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	40	17	7	84
30[f]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	80	1	10	68
31	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	40	2	52	35
32	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	60	2	76	N.D.
33	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	100	2	63	N.D.
34[fg]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	7	79
35[fh]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	5	82
36[fi]	$[Pd(allyl)Cl]_2$	DCM	AgTFA	60	1	7	85
37[g]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	80	2	81	N.D.
38[h]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	80	2	84	N.D
39[i]	$Pd(COD)Cl_2$	$MeOH/H_2O$ (1/2)	AgTFA	80	2	95(83)	N.D

[a]Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol), Pd catalyst (5 mol %), Xantphos (10 mol %), AgTFA (10 mol %), Solvent (1mL). [b]Yields were determined by the ^1H NMR using CH_2Br_2 as the internal standard; isolated yield was given in parentheses. [c]Solvent (1 mL). [d] **1a** (0.1 mol), **2a** (0.05 mmol), Solvent (1.0 mL). [e] **1a** (0.1 mol), **2a** (0.045 mmol), Solvent (1.0 mL). [f] **1a** (0.1 mol), **2a** (0.06 mmol), Solvent (1.0 mL). [g] [Pd] 1 mol %, [h] [Pd] 2.5 mol %, [i] [Pd] 10 mol %.

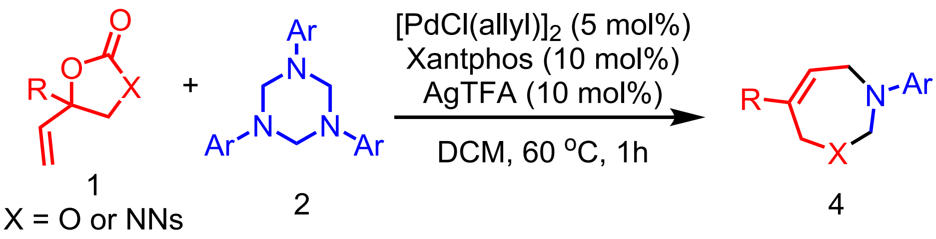
General Procedure for Pd (0)-Catalyzed [3 + 2] Cycloaddition



1 2 3

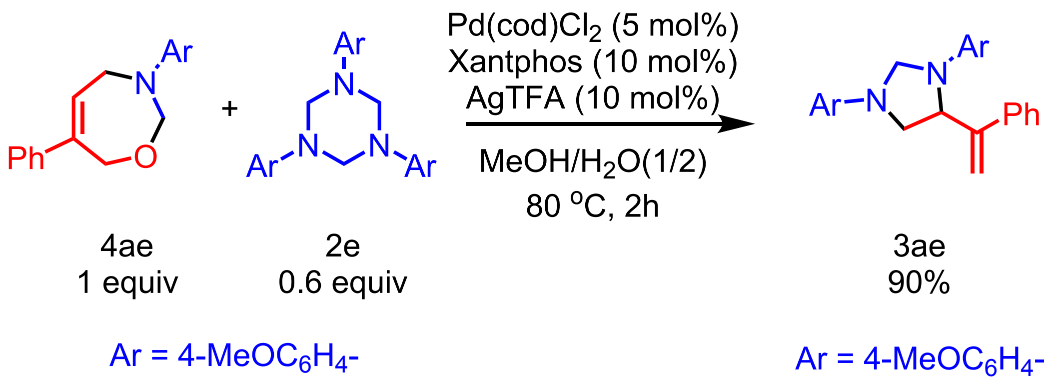
To a teflon-capped vial was charged with the respective vinylethylene carbonate (0.1 mmol, 1 eq.), triazine compounds (0.12 mmol, 1.2eq), xantphos (10 mol%), $Pd(cod)Cl_2$ (5 mol%), AgTFA (10 mol%), and $MeOH/H_2O$ (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by FCC to get the target product.

General Procedure for Pd (0)-Catalyzed [5 + 2] Cycloaddition

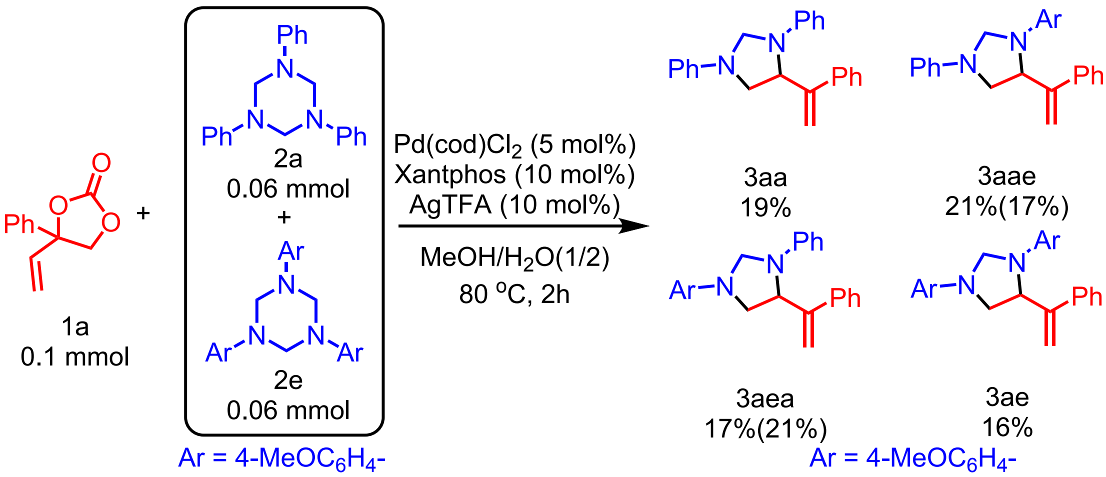


To a teflon-capped vial was charged with the respective vinylethylene carbonate (0.1 mmol, 1 eq.), the triazine compounds (0.12 mmol, 1.2eq), xantphos (10 mol%), $[Pd(allyl)Cl]_2$ (5 mol%), AgTFA (10 mol%), and DCM (1 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 60 °C with vigorous stirring for 1h. After that, the tube was cooled to r.t., then solvent was removed under vacuumin to give the residue. The crude residue was purified by FCC to get the target product.

Control experiments



To a teflon-capped vial was charged with the vinylethylene carbonate 4ae (0.1 mmol, 1 eq.), triazine compounds **2e** (0.06 mmol, 0.6 eq), xantphos (10 mol%), $Pd(cod)Cl_2$ (5 mol%), AgTFA (10 mol%), and $MeOH/H_2O$ (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =1:1) to afford product **3ae** (34.8 mg, 90%).



To a teflon-capped vial was charged with the vinylethylene carbonate **1a** (0.1 mmol, 1 eq.), triazine compounds **2a** (0.06 mmol, 0.6eq) and **2e** (0.06 mmol, 0.6eq), xantphos (10 mol%), Pd(cod)Cl_2 (5 mol%), AgTFA (10 mol%), and MeOH/H_2O (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =3:1) to afford product **3aa** (6.2mg, 19%), **3ae** (6.2mg, 16%), and the cross-cylcization products **3aae** and 3**aea** (7.5mg, 21% or 6.1mg, 17%).

the lower polar of 3aae and 3aea

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.45 – 7.34 (m, 3H), 7.32 – 7.26 (m, 2H), 6.93 – 6.88 (m, 2H), 6.83 (t, J = 7.3 Hz, 1H), 6.70 – 6.65 (m, 4H), 5.44 (s, 1H), 5.27 (s, 1H), 5.11 (d, J = 3.0 Hz, 1H), 4.93 (dd, J = 7.6, 3.4 Hz, 1H), 4.67 (d, J = 3.0 Hz, 1H), 3.80 (s, 3H), 3.76 (t, J = 8.2 Hz, 1H), 3.53 (dd, J = 8.6, 3.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.01, 146.46, 146.14, 139.74, 139.46, 129.29, 128.64, 127.92, 126.54, 118.00, 114.95, 113.65, 113.48, 112.91, 67.44, 61.28, 55.82, 53.41.

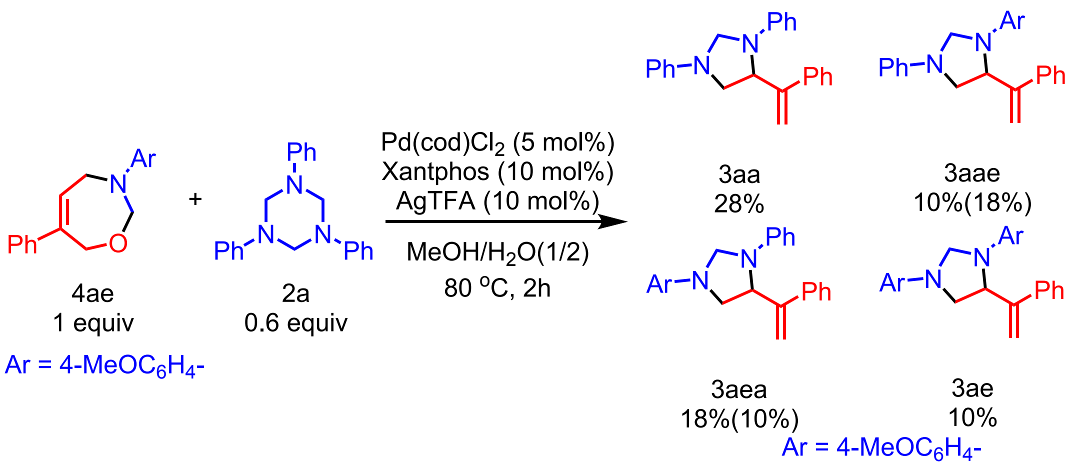
HRMS (EI) calcd. for $C_{24}H_{24}N_2O$ $[M]^+$: 356.1883, found: 356.1885

the bigger polar of 3aae and 3aea

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.46 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 6.92 – 6.85 (m, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.72 – 6.65 (m, 4H), 5.45 (s, 1H), 5.26 (s, 1H), 5.10 (d, *J* = 3.1 Hz, 1H), 4.98 (dd, *J* = 7.5, 2.2 Hz, 1H), 4.62 (d, *J* = 3.1 Hz, 1H), 3.79 (s, 3H), 3.63 (t, *J* = 8.1 Hz, 1H), 3.52 (dd, *J* = 8.5, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.70, 145.73, 145.03, 141.23, 139.45, 129.25, 128.67, 127.92, 126.51, 117.27, 114.91, 114.45, 113.59, 112.22, 67.59, 61.00, 55.79, 54.04.

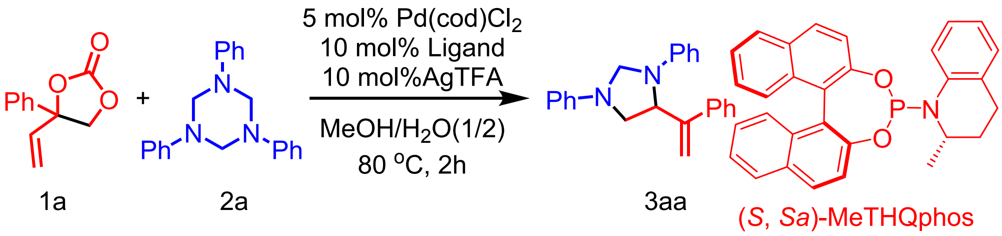
HRMS (EI) calcd. for $C_{24}H_{24}N_2O$ $[M]^+$: 356.1883, found: 356.1871



To a teflon-capped vial was charged with **4ae** (0.1 mmol, 1 eq.), triazine compounds **2a** (0.06 mmol, 0.6eq), xantphos (10 mol%), Pd(cod)Cl_2 (5 mol%), AgTFA (10 mol%), and MeOH/H_2O (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =3:1) to afford product **3aa** (9.3mg, 28%), **3ae** (3.7mg, 10%), and the cross-cylcization products **3aae** and 3**aea** (3.7mg, 10% or 6.6mg, 18%).

Preliminary asymmetric experiments

A preliminary asymmetric version of Pd-catalyzed formal migration [2+3] cycloaddition was developed by employing a commercially available chiral phosphoramidite ligand (S, Sa)-MeTHQphos, which provided 3aa with a moderate but promising enantiomeric excess of 54%.



20% yeild, 54% ee

HPLC conditions: 250 nm, flow rate: 0.3 ml/min, 100% MeCN, t_{minor} = 13.54 min, t_{major} = 14.50 min; 54% ee

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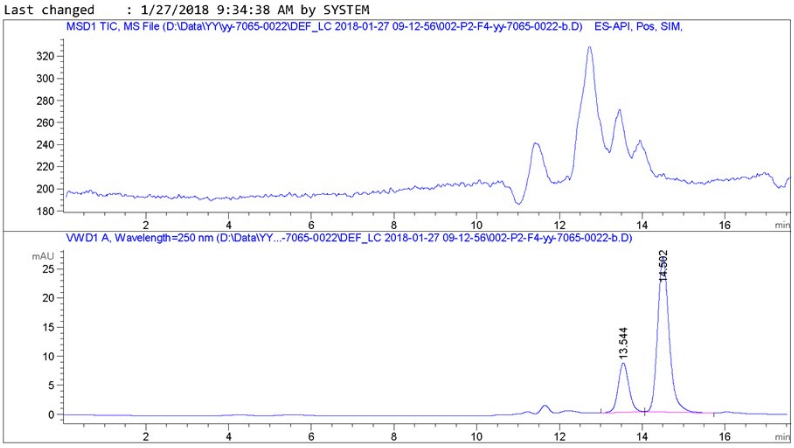


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                         Area Percent Report
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Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MSD1 TIC, MS File


Signal 2: VWD1 A, Wavelength=250 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.544 BB    0.2727  150.45573    8.49042  22.6535
   2  14.502 BB    0.2971  513.70624   26.51101  77.3465

Totals :                   664.16197   35.00143
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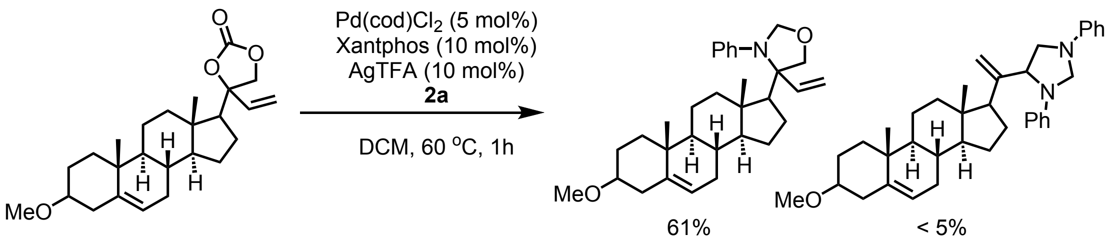
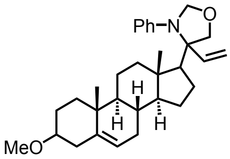
Synthetic Applications

Pregnenolone which can be used for many disease therapy, such as Alzheimer's disease, fibrocystic breast disease as well as relieving stress and improving immunity. From this view of point, we want to enrich its chemical space by incorporating our novel N-heterocyclic fragments into Pregnenolone analogue (Fig. 4). Under the aforementioned standard formal migration [5+2] conditions, we obtained a non-migration [2+3] cycloaddition product in good yield and only very trace desired product.



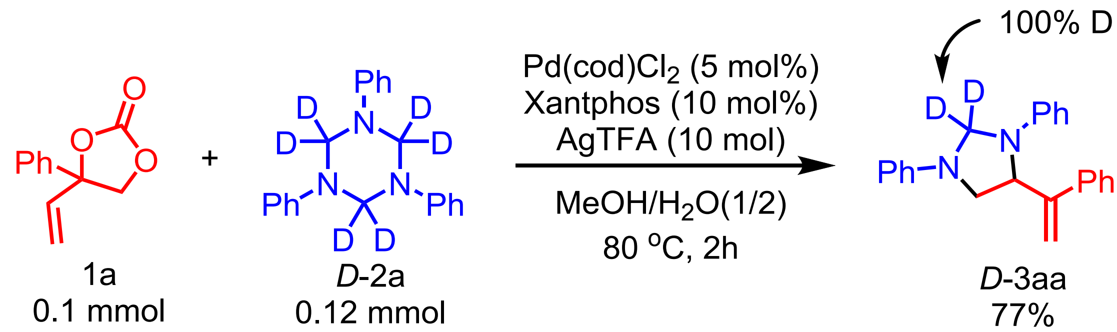


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 6.82 – 6.78 (m, 3H), 5.69 (t, J = 3.9 Hz, 1H), 5.35 – 5.33 (m, 1H), 5.12 (d, J = 9.4 Hz, 1H), 4.96 (d, J = 9.4 Hz, 1H), 4.13 – 3.98 (m, 4H), 3.34 (s, 3H), 3.08 – 3.00 (m, 1H), 2.41 – 2.34 (m, 1H), 2.18 – 2.10 (m, 1H), 2.01 – 1.87 (m, 2H), 1.86 – 1.79 (m, 1H), 1.79 – 1.71 (m, 1H), 1.70 – 0.97 (m, 12H), 0.95 (s, 3H), 0.94 – 0.86 (m, 2H), 0.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.01, 141.36, 140.95, 129.03, 124.53, 121.39, 118.48, 114.53, 82.78, 80.30, 70.62, 56.62, 56.19, 55.62, 50.23, 47.49, 43.57, 38.69, 38.33, 37.19, 36.93, 32.23, 31.79, 27.98, 24.86, 24.23, 20.97, 19.39, 12.69.

HRMS (ESI) calcd. for $C_{31}H_{44}NO_2^+$ $[M+H]^+$: 462.3367, found: 462.3362

Deuterium labelling experiments



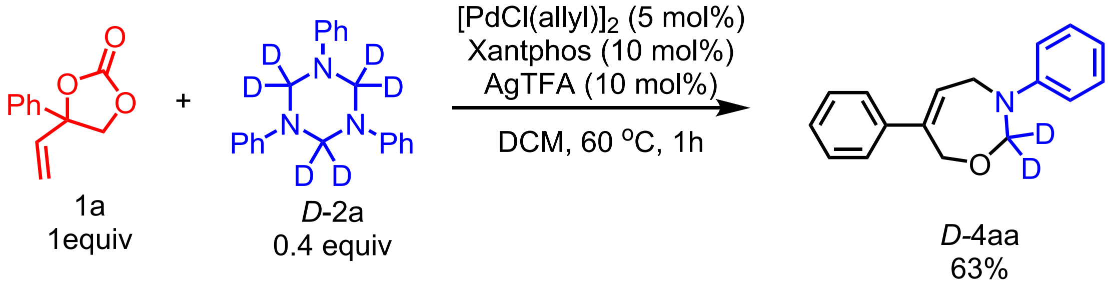
To a teflon-capped vial was charged with the vinylethylene carbonate **1a** (0.1 mmol, 1 eq.), triazine compounds ***D*-2a** (0.12 mmol, 0.12 eq), xantphos (10 mol%), $Pd(cod)Cl_2$ (5 mol%), AgTFA (10 mol%), and $MeOH/H_2O$ (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 ℃ with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =3:1) to afford product ***D*-3aa** (25.2mg, 77%).

1,3-diphenyl-4-(1-phenylvinyl)imidazolidine-2,2-*d*$_2$ (*D*-3aa)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.31 (m, 4H), 6.92 – 6.83 (m, 2H), 6.78 – 6.70 (m, 4H), 5.47 (s, 1H), 5.27 (s, 1H), 5.05 (dd, J = 7.6, 2.4 Hz, 1H), 3.76 (t, J = 8.2 Hz, 1H), 3.60 (dd, J = 8.6, 2.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.54, 145.80, 144.96, 139.41, 129.35, 129.32, 128.72, 127.99, 126.56, 118.19, 117.40, 113.55, 113.05, 112.32, 60.75, 53.19.

HRMS (EI) calcd. for $C_{23}H_{20}D_2N_2$ $[M]^+$: 328.1903, found: 328.1905



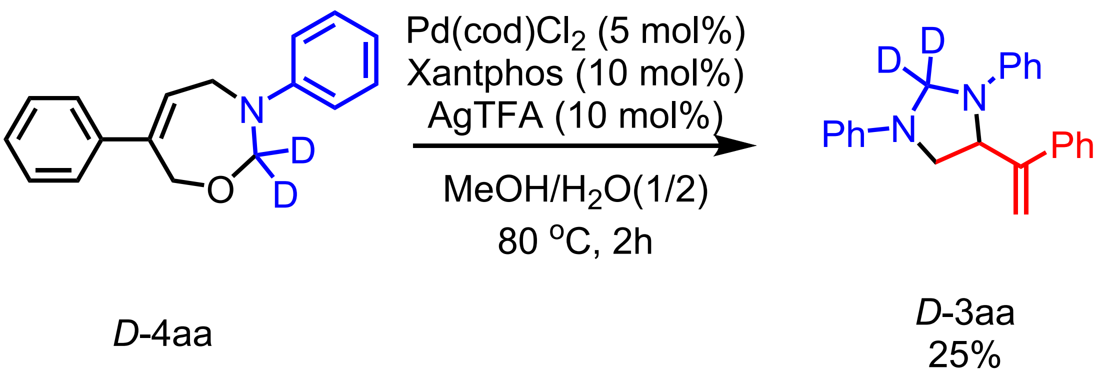
To a teflon-capped vial was charged with the vinylethylene carbonate **1a** (1 mmol, 1 eq.), the triazine compounds ***D*-2a** (0.4 mmol, 0.4eq), xantphos (10 mol%), $[PdCl(allyl)]_2$ (5 mol%), AgTFA (10 mol%), and DCM (10 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 60 °C with vigorous stirring for 1h. After that, the tube was cooled to r.t., then solvent was removed under vacuumin to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =1:1) to afford product ***D*-3aa** (150mg, 63%).

3,6-diphenyl-2,3,4,7-tetrahydro-1,3-oxazepine-2,2-*d*$_2$ (*D*-4aa)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 7H), 6.91 – 6.86 (m, 2H), 6.86 – 6.81 (m, 1H), 6.15 (t, *J* = 4.3 Hz, 1H), 4.52 (d, *J* = 1.2 Hz, 2H), 4.27 – 4.21 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.94, 141.65, 140.60, 129.23, 128.37, 127.79, 127.31, 126.18, 118.77, 114.36, 69.37, 47.39.

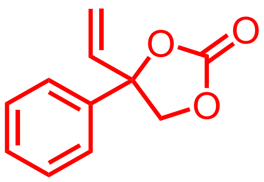
HRMS (EI) calcd. for $C_{17}H_{15}D_2NO$ $[M]^+$: 253.1430, found: 253.1431



To a teflon-capped vial was charged with ***D*-4aa** (0.1 mmol, 1 eq.), triazine compounds **2a** (0.06 mmol, 0.6eq), xantphos (10 mol%), Pd(cod)Cl_2 (5 mol%), AgTFA (10 mol%), and MeOH/H_2O (1/2) (2 mL) under an air atmosphere. The reaction mixture was stirred at r.t. for 1 min proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 2h. After that, the vial was cooled to r.t., diluted with ethyl acetate, washed with brine. The combined organic layers was dried over anhydrous Na_2SO_4, concentrated in vacuo to give the residue. The crude residue was purified by columnchromatography (petroleum ether/DCM =3:1) to afford product ***D*-3aa** (8.2mg, 25%)

Characterization data of 1 and 2

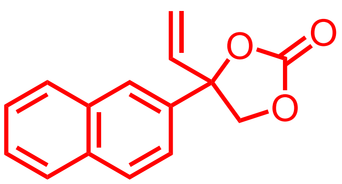
4-phenyl-4-vinyl-1,3-dioxolan-2-one (1a)



1a

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 – 7.34 (m, 5 H), 6.16 (dd, *J* = 17.20, 10.72 Hz, 1 H), 5.44 – 5.39 (m, 2 H), 4.65 (d, *J* = 8.48 Hz, 1 H), 4.57 (d, *J* = 8.44 Hz, 1 H)

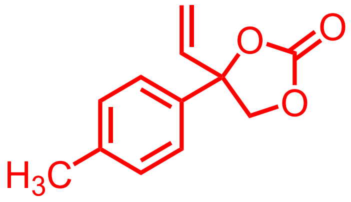
4-(naphthalen-2-yl)-4-vinyl-1,3-dioxolan-2-one (1b)



1b

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.85 (m, 4 H), 7.57 – 7.53 (m, 2 H), 7.41 –

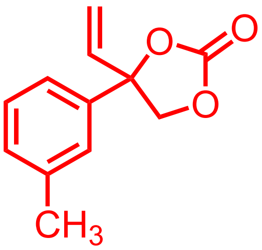
7.38 (m, 1 H), 6.25 (dd, J = 17.16, 10.68 Hz, 1 H), 5.49 - 5.45 (m, 2 H), 4.74 (d, J = 8.48 Hz, 1 H), 4.68 (d, J = 8.48 Hz, 1 H)



1c

4-(p-tolyl)-4-vinyl-1,3-dioxolan-2-one (1c)

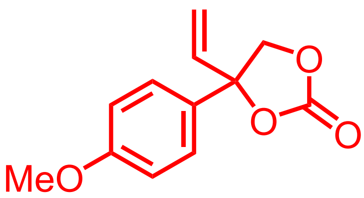
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.21 (m, 4 H), 6.14 (dd, J = 17.24, 10.72 Hz, 1 H), 5.43 – 5.39 (m, 2 H), 4.62 (d, J = 8.40 Hz, 1 H), 4.56 (d, J = 8.48 Hz, 1 H), 2.37 (s, 3 H)



1d

4-(m-tolyl)-4-vinyl-1,3-dioxolan-2-one (1d)

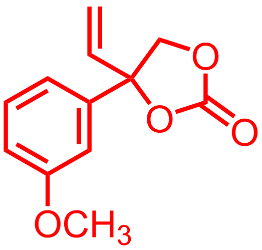
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.29 (m, 1 H), 7.20 – 7.12 (m, 3 H), 6.15 (dd, J = 17.20, 10.72 Hz, 1 H), 5.44 – 5.40 (m, 2 H), 4.64 (d, J = 8.44 Hz, 1 H), 4.56 (d, J = 8.44 Hz, 1 H), 2.38 (s, 3 H)



1e

4-(4-methoxyphenyl)-4-vinyl-1,3-dioxolan-2-one (1e)

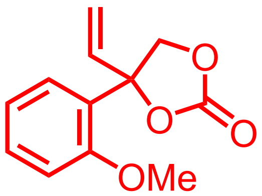
¹H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.27 (m, 2 H), 6.96 – 6.92 (m, 2 H), 6.14 (dd, *J* = 17.12, 10.76 Hz, 1 H), 5.43 – 5.40 (m, 2 H), 4.61 (d, *J* = 8.48 Hz, 1 H), 4.57 (d, *J* = 8.48 Hz, 1 H), 3.83 (s, 3 H)



1f

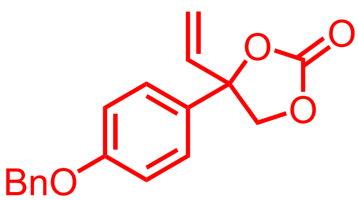
4-(3-methoxyphenyl)-4-vinyl-1,3-dioxolan-2-one (1f)

¹H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 1H), 6.97 – 6.87 (m, 3H), 6.15 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.44 (d, *J* = 9.7 Hz, 1H), 5.41 (d, *J* = 3.3 Hz, 1H), 4.66 (d, *J* = 8.5 Hz, 1H), 4.56 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 3H).



1g

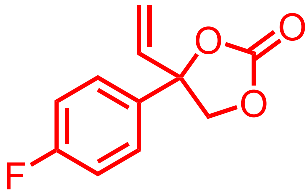
¹H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.25 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.42 (d, *J* = 17.1 Hz, 1H), 5.27 (d, *J* = 10.7 Hz, 1H), 4.76 (d, *J* = 8.9 Hz, 1H), 4.56 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 3H).



1h

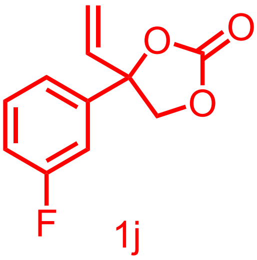
4-(4-(benzyloxy)phenyl)-4-vinyl-1,3-dioxolan-2-one (1h)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.28 (m, 7 H), 7.03 – 6.99 (m, 2 H), 6.14 (dd, J = 17.08, 10.76 Hz, 1 H), 5.42 – 5.41 (m, 2 H), 5.08 (s, 2 H), 4.60 (d, J = 8.44 Hz, 1 H), 4.56 (d, J = 8.48 Hz, 1 H)



1i

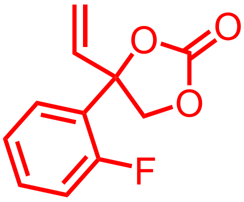
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.15 (t, J = 8.6 Hz, 2H), 6.16 (dd, J = 17.1, 10.7 Hz, 1H), 5.46 (s, 1H), 5.45 (d, J = 28.8 Hz, 1H), 4.66 (d, J = 8.5 Hz, 1H), 4.57 (d, J = 8.5 Hz, 1H).



1j

4-(3-fluorophenyl)-4-vinyl-1,3-dioxolan-2-one (1j)

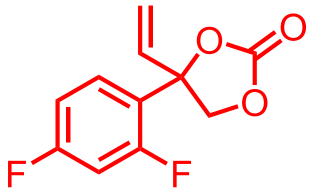
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.38 (m, 1 H), 7.14 – 7.06 (m, 3 H), 6.13 (dd, J = 17.12, 10.76 Hz, 1 H), 5.47 – 5.42 (m, 2 H), 4.65 (d, J = 8.48 Hz, 1 H), 4.55 (d, J = 8.52 Hz, 1 H)



1k

4-(2-fluorophenyl)-4-vinyl-1,3-dioxolan-2-one (1k)

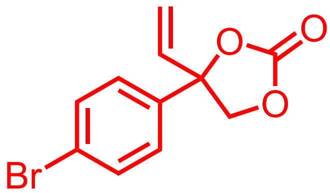
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (td, J = 7.7, 1.7 Hz, 1H), 7.41 (dddd, J = 8.2, 7.3, 5.4, 1.8 Hz, 1H), 7.26 (td, J = 7.6, 1.1 Hz, 1H), 7.14 (ddd, J = 11.1, 8.3, 1.0 Hz, 1H), 6.20 (ddd, J = 17.1, 10.7, 1.4 Hz, 1H), 5.50 – 5.40 (m, 1H), 5.39 (d, J = 10.7 Hz, 1H), 4.78 (dd, J = 8.8, 2.7 Hz, 1H), 4.63 (dd, J = 8.8, 1.7 Hz, 1H).



1l

4-(2,4-difluorophenyl)-4-vinyl-1,3-dioxolan-2-one (1l)

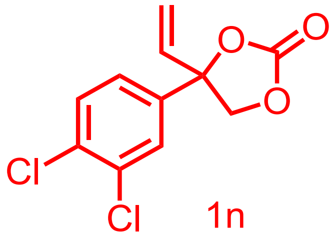
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (td, J = 8.7, 6.2 Hz, 1H), 6.99 (tdd, J = 8.8, 2.5, 1.0 Hz, 1H), 6.91 (ddd, J = 11.0, 8.4, 2.5 Hz, 1H), 6.17 (ddd, J = 17.1, 10.7, 1.3 Hz, 1H), 5.43 (dd, J = 17.1, 1.2 Hz, 1H), 5.41 (d, J = 1.2 Hz, 1H), 4.75 (dd, J = 8.8, 2.5 Hz, 1H), 4.60 (dd, J = 8.8, 1.7 Hz, 1H).



1m

4-(4-bromophenyl)-4-vinyl-1,3-dioxolan-2-one (1m)

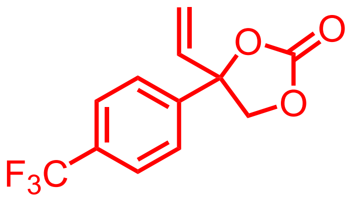
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 – 7.55 (m, 2 H), 7.25 – 7.22 (m, 2 H), 6.12 (dd, J = 17.16, 10.76 Hz, 1 H), 5.46 – 5.39 (m, 2 H), 4.65 (d, J = 8.52 Hz, 1 H), 4.53 (d, J = 8.52 Hz, 1 H)



1n

4-(3,4-dichlorophenyl)-4-vinyl-1,3-dioxolan-2-one (1n)

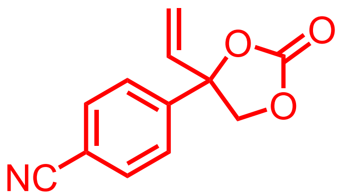
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.47 (m, 2 H), 7.22 – 7.19 (m, 1 H), 6.11 (dd, J = 17.12, 10.72 Hz, 1 H), 5.49 – 5.42 (m, 2 H), 4.65 (d, J = 8.60 Hz, 1 H), 4.52 (d, J = 8.56 Hz, 1 H)



1o

4-(4-(trifluoromethyl)phenyl)-4-vinyl-1,3-dioxolan-2-one (1o)

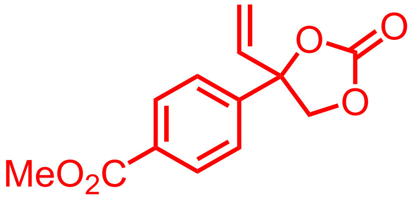
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.70 (m, 2 H), 7.51 – 7.49 (m, 2 H), 6.15 (dd, J = 17.20, 10.76 Hz, 1 H), 5.49 – 5.41 (m, 2 H), 4.70 (d, J = 8.52 Hz, 1 H), 4.56 (d, J = 8.56 Hz, 1 H)



1p

4-(4-isocyanophenyl)-4-vinyl-1,3-dioxolan-2-one (1p)

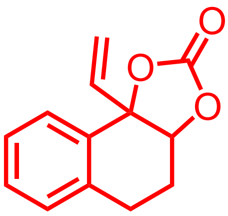
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.73 (m, 2 H), 7.51 – 7.48 (m, 2 H), 6.13 (dd, J = 17.12, 10.72 Hz, 1 H), 5.51 – 5.42 (m, 2 H), 4.70 (d, J = 8.60 Hz, 1 H), 4.54 (d, J = 8.56 Hz, 1 H)



1q

methyl 4-(2-oxo-4-vinyl-1,3-dioxolan-4-yl)benzoate (1q)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 8.09 (m, 2 H), 7.45 – 7.43 (m, 2 H), 6.15 (dd, J = 17.12, 10.72 Hz, 1 H), 5.46 (d, J = 10.76 Hz, 1 H), 5.43 (d, J = 17.16 Hz, 1 H), 4.69 (d, J = 8.52 Hz, 1 H), 4.56 (d, J = 8.48 Hz, 1 H), 3.94 (s, 3 H)

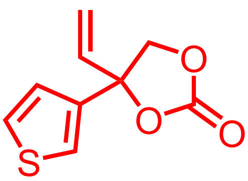


1r

9b-vinyl-3a,4,5,9b-tetrahydronaphtho[1,2-*d*][1,3]dioxol-2-one (1r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.21 (t, J = 8.0 Hz, 1H), 6.05 (dd, J = 17.0, 10.6 Hz, 1H), 5.46 (d, J = 10.6 Hz, 1H), 5.07 (d, J = 17.0 Hz, 1H), 4.60 (dd, J = 13.6, 5.3 Hz, 1H), 3.21 – 3.04 (m, 2H), 2.47 – 2.36 (m, 1H), 2.25 – 2.11 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.27, 134.70, 133.67, 132.81, 128.95, 128.70, 126.53, 123.51, 121.47, 86.65, 83.04, 25.54, 19.41.

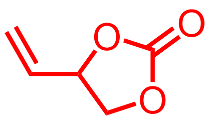


1s

4-(thiophen-3-yl)-4-vinyl-1,3-dioxolan-2-one (1s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 5.0, 3.0 Hz, 1H), 7.37 (dd, J = 2.9, 1.3 Hz, 1H), 7.08 (dd, J = 5.1, 1.2 Hz, 1H), 6.19 (dd, J = 17.2, 10.7 Hz, 1H), 5.47 (dd, J = 14.0, 3.2 Hz, 2H), 4.59 (q, J = 8.5 Hz, 2H).

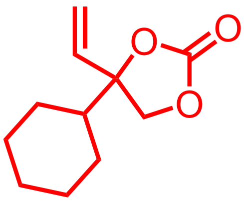
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.10, 139.17, 135.73, 127.78, 125.06, 123.13, 117.99, 83.79, 74.41.



1t

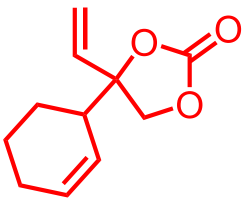
4-vinyl-1,3-dioxolan-2-one (1t)

Purchased from reagent company direct use.



1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.80 (m, 1H), 5.41 (dd, J = 23.7, 14.2 Hz, 2H), 4.34 (d, J = 8.4 Hz, 1H), 4.24 (d, J = 8.4 Hz, 1H), 1.92 – 1.78 (m, 3H), 1.77 – 1.65 (m, 3H), 1.34 – 1.00 (m, 5H).

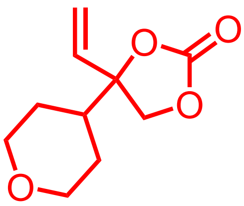


1v

4-(cyclohex-2-en-1-yl)-4-vinyl-1,3-dioxolan-2-one (1v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, J = 17.3, 10.8 Hz, 1H), 5.87 – 5.83 (m, 1H), 5.45 (d, J = 17.2 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 4.43 (d, J = 8.4 Hz, 1H), 4.34 (d, J = 8.4 Hz, 1H), 2.14 – 2.07 (m, 2H), 2.04 – 1.97 (m, 2H), 1.72 – 1.56 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.45, 135.66, 134.26, 125.86, 116.80, 86.66, 71.89, 24.95, 23.71, 22.25, 21.80.

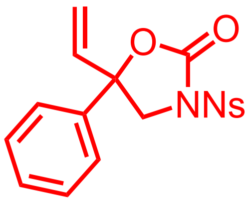


1w

4-(tetrahydro-2*H*-pyran-4-yl)-4-vinyl-1,3-dioxolan-2-one (1w)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (dd, J = 17.2, 11.0 Hz, 1H), 5.52 – 5.40 (m, 2H), 4.37 (d, J = 8.5 Hz, 1H), 4.26 (d, J = 8.5 Hz, 1H), 4.05 (dd, J = 11.4, 2.2 Hz, 2H), 3.43 – 3.33 (m, 2H), 1.98 (tt, J = 12.0, 3.5 Hz, 1H), 1.76 – 1.63 (m, 1H), 1.63 – 1.41 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.25, 134.06, 117.55, 86.24, 71.34, 67.39, 67.31, 42.65, 26.38, 26.24.

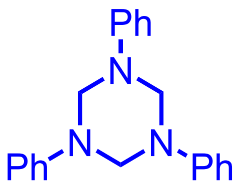


1x

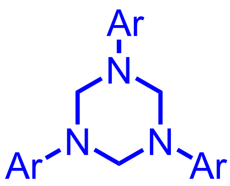
3-((4-nitrophenyl)sulfonyl)-5-phenyl-5-vinyloxazolidin-2-one (1x)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 – 8.35 (m, 2 H), 8.21 – 8.18 (m, 2 H), 7.41 –

7.36 (m, 3 H), 7.30-7.27 (m, 2 H), 6.08 (dd, J = 17.08, 10.72 Hz, 1 H), 5.38 – 5.33 (m, 2 H), 4.39 (d, J = 9.44 Hz, 1 H), 4.22 (d, J = 9.44 Hz, 1 H)



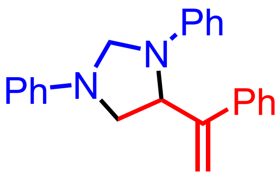
2a



2b, Ar = 4-FC_6H_4
2c, Ar = 4-ClC_6H_4
2d, Ar = 4-BrC_6H_4
2e, Ar = 4-$MeOC_6H_4$
2f, Ar = 4-$MeO_2CC_6H_4$
2g, Ar = PMB

Characterization Data for the Products 3

1,3-diphenyl-4-(1-phenylvinyl)imidazolidine (3aa)



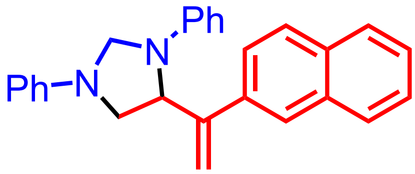
3aa
85%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.48 – 7.37 (m, 3H), 7.36 – 7.29 (m, 4H), 6.91 – 6.80 (m, 2H), 6.77 – 6.68 (m, 4H), 5.46 (s, 1H), 5.25 (s, 1H), 5.15 (d, J = 3.2 Hz, 1H), 5.04 (dd, J = 7.6, 2.2 Hz, 1H), 4.73 (d, J = 3.2 Hz, 1H), 3.74 (t, J = 8.2 Hz, 1H), 3.59 (dd, J = 8.7, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.48, 145.74, 144.87, 139.38, 129.34, 129.31, 128.71, 127.99, 126.54, 118.19, 117.39, 113.55, 113.05, 112.30, 66.68, 60.71, 53.16.

HRMS (ESI) calcd. for $C_{23}H_{22}N_2$ $[M+H]^+$: 327.1856, found: 327.1857

4-(1-(naphthalen-2-yl)vinyl)-1,3-diphenylimidazolidine



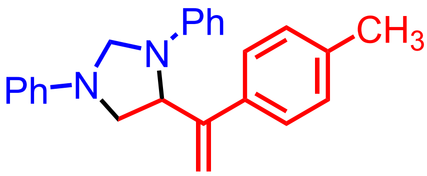
3ba
85%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.93 – 7.87 (m, 3H), 7.68 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.36 – 7.28 (m, 4H), 6.87 – 6.81 (m, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 5.59 (s, 1H), 5.34 (s, 1H), 5.19 (d, *J* = 2.1 Hz, 1H), 5.17 (d, *J* = 3.1 Hz, 1H), 4.75 (d, *J* = 3.2 Hz, 1H), 3.79 (t, *J* = 8.2 Hz, 1H), 3.64 (dd, *J* = 8.7, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.47, 145.58, 144.90, 136.64, 133.36, 132.98, 129.32, 128.36, 128.22, 127.66, 126.48, 126.24, 125.00, 124.90, 118.20, 117.43, 113.98, 113.05, 112.32, 66.70, 60.66, 53.29.

HRMS (ESI) calcd. for $C_{27}H_{24}N_2$ $[M+H]^+$: 377.2012, found: 377.2016

1,3-diphenyl-4-(1-(p-tolyl)vinyl)imidazolidine (3ca)



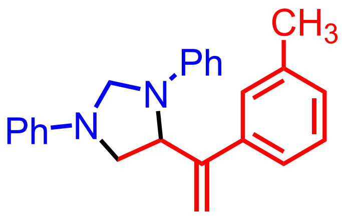
3ca
70%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.82 (m, 2H), 6.72 (dd, *J* = 7.8, 5.4 Hz, 4H), 5.44 (s, 1H), 5.22 (s, 1H), 5.15 (d, *J* = 3.2 Hz, 1H), 5.03 (dd, *J* = 7.6, 2.4 Hz, 1H), 4.74 (d, *J* = 3.2 Hz, 1H), 3.75 (t, *J* = 8.2 Hz, 1H), 3.59 (dd, *J* = 8.6, 2.8 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.52, 145.53, 144.94, 137.83, 136.45, 129.40, 129.33, 129.29, 126.38, 118.16, 117.36, 113.05, 112.70, 112.33, 66.70, 60.70, 53.24, 21.21.

HRMS (ESI) calcd. for $C_{24}H_{24}N_2$ $[M+H]^+$: 341.2012, found: 341.2016

1,3-diphenyl-4-(1-(m-tolyl)vinyl)imidazolidine (3da)



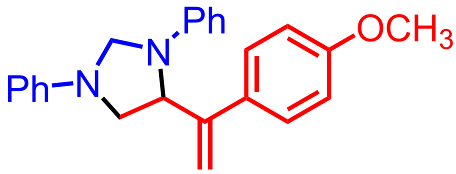
3da
82%

[1]H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 7H), 7.23 – 7.18 (m, 1H), 6.89 – 6.80 (m, 2H), 6.73 – 6.68 (m, 4H), 5.42 (s, 1H), 5.20 (s, 1H), 5.14 (d, J = 3.2 Hz, 1H), 5.02 (dd, J = 7.6, 2.2 Hz, 1H), 4.72 (d, J = 3.2 Hz, 1H), 3.72 (t, J = 8.2 Hz, 1H), 3.57 (dd, J = 8.7, 2.7 Hz, 1H), 2.44 (s, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 146.51, 145.78, 144.89, 139.41, 138.28, 129.30, 129.26, 128.72, 128.56, 127.28, 123.57, 118.13, 117.34, 113.24, 113.02, 112.29, 66.66, 60.68, 53.18, 21.58.

HRMS (ESI) calcd. for $C_{24}H_{24}N_2$ $[M+H]^-$: 339.2330, found: 329.2329

4-(1-(4-methoxyphenyl)vinyl)-1,3-diphenylimidazolidine (3ea)



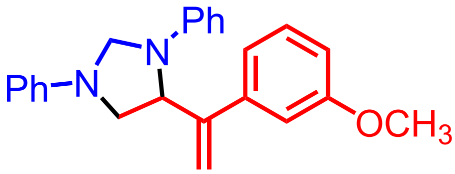
3ea
73%

[1]H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.34 – 7.27 (m, 4H), 6.99 – 6.94 (m, 2H), 6.87 – 6.80 (m, 2H), 6.70 (d, J = 8.0 Hz, 4H), 5.37 (s, 1H), 5.16 (s, 1H), 5.13 (d, J = 3.2 Hz, 1H), 5.00 (dd, J = 7.6, 2.5 Hz, 1H), 4.72 (d, J = 3.2 Hz, 1H), 3.88 (s, 3H), 3.74 (t, J = 8.2 Hz, 1H), 3.57 (dd, J = 8.6, 2.9 Hz, 1H).

[13]C NMR (100 MHz, $CDCl_3$) δ 159.45, 146.48, 145.12, 144.93, 131.72, 129.31, 129.26, 127.61, 118.13, 117.34, 114.06, 113.00, 112.29, 112.00, 66.68, 60.77, 55.35, 53.24.

HRMS (ESI) calcd. for $C_{24}H_{24}N_2O$ $[M+H]^+$: 357.1961, found: 357.1970

4-(1-(3-methoxyphenyl)vinyl)-1,3-diphenylimidazolidine (3fa)



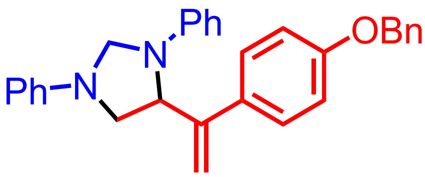
3fa
51%

[1]H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.13 – 7.08 (m, 1H), 7.07 – 7.04 (m, 1H), 6.96 – 6.90 (m, 1H), 6.88 – 6.79 (m, 2H), 6.74 – 6.65 (m, 4H), 5.44 (s, 1H), 5.23 (s, 1H), 5.12 (d, *J* = 3.2 Hz, 1H), 5.02 (dd, *J* = 7.6, 2.2 Hz, 1H), 4.71 (d, *J* = 3.2 Hz, 1H), 3.87 (s, 3H), 3.72 (t, *J* = 8.2 Hz, 1H), 3.58 (dd, *J* = 8.7, 2.7 Hz, 1H), 2.44 (s, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 159.77, 146.46, 145.66, 144.83, 140.87, 129.66, 129.31, 129.29, 118.93, 118.18, 117.38, 113.70, 113.04, 112.66, 112.26, 66.63, 60.71, 55.30, 53.12.

HRMS (ESI) calcd. for $C_{24}H_{24}N_2O$ $[M+H]^+$: 357.1961, found: 357.1964

4-(1-(4-(benzyloxy)phenyl)vinyl)-1,3-diphenylimidazolidine (3ha)



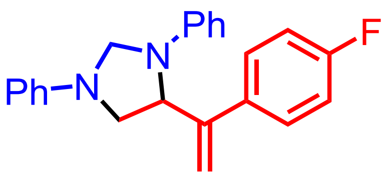
3ha
76%

[1]H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 6H), 7.42 – 7.36 (m, 1H), 7.34 – 7.29 (m, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.89 – 6.80 (m, 2H), 6.70 (d, *J* = 8.3 Hz, 4H), 5.38 (s, 1H), 5.17 (s, 1H), 5.15 (s, 2H), 5.13 (d, *J* = 3.3 Hz, 1H), 4.99 (dd, *J* = 7.5, 2.3 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 1H), 3.74 (t, *J* = 8.2 Hz, 1H), 3.58 (dd, *J* = 8.6, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.68, 146.48, 145.08, 144.93, 136.90, 131.96, 129.32, 129.27, 128.68, 128.09, 127.64, 127.51, 118.14, 117.35, 114.99, 113.02, 112.30, 112.08, 70.11, 66.69, 60.74, 53.25.

HRMS (EI) calcd. for $C_{30}H_{28}N_2O$ $[M]^+$: 432.2196, found: 432.2190

4-(1-(4-fluorophenyl)vinyl)-1,3-diphenylimidazolidine (3ia)



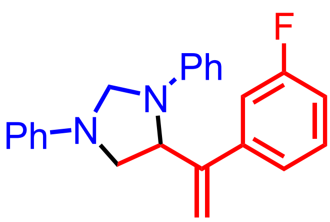
3ia
96%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.35 – 7.28 (m, 4H), 7.11 (t, J = 8.6 Hz, 2H), 6.90 – 6.82 (m, 2H), 6.73 – 6.67 (m, 4H), 5.39 (s, 1H), 5.24 (s, 1H), 5.10 (d, J = 3.2 Hz, 1H), 4.97 (dd, J = 7.6, 2.4 Hz, 1H), 4.71 (d, J = 3.2 Hz, 1H), 3.73 (t, J = 8.2 Hz, 1H), 3.55 (dd, J = 8.7, 2.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.58 (J_{C-F} = 247.3 Hz), 146.40, 145.13, 144.87, 135.41 (J_{C-F} = 3.2 Hz), 129.36, 129.33, 128.26 (J_{C-F} = 7.8 Hz), 118.28, 117.52, 115.57 (J_{C-F} = 21.3 Hz), 113.82, 113.04, 112.31, 66.70, 60.96, 53.08.

HRMS (EI) calcd. for $C_{23}H_{21}FN_2$ $[M]^+$: 344.1683, found: 344.1675

4-(1-(3-fluorophenyl)vinyl)-1,3-diphenylimidazolidine (3ja)



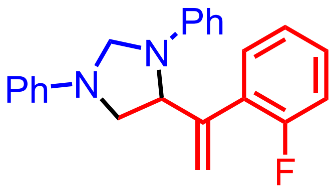
3ja
58%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (tt, J = 11.0, 5.5 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.25 – 7.20 (m, 1H), 7.12 – 7.06 (m, 1H), 6.90 – 6.82 (m, 2H), 6.75 – 6.66 (m, 4H), 5.48 (s, 1H), 5.30 (s, 1H), 5.14 (d, J = 3.2 Hz, 1H), 4.98 (dd, J = 7.6, 2.3 Hz, 1H), 4.72 (d, J = 3.2 Hz, 1H), 3.74 (t, J = 8.2 Hz, 1H), 3.57 (dd, J = 8.7, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.98 (J_{C-F} = 246.0 Hz), 146.39, 144.89, 144.77, 141.60 (J_{C-F} = 7.4 Hz), 130.23, 130.15, 129.35, 122.18 (J_{C-F} = 2.6 Hz), 118.33, 117.57, 114.93, 114.81 (J_{C-F} = 21.3 Hz), 113.59 (J_{C-F} = 22.1 Hz), 113.09, 112.30, 66.69, 60.66, 53.10.

HRMS (EI) calcd. for $C_{23}H_{21}FN_2$ $[M]^+$: 344.1683, found: 344.1677

4-(1-(2-fluorophenyl)vinyl)-1,3-diphenylimidazolidine (3ka)



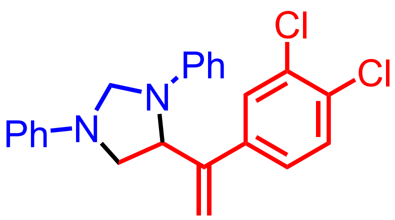
3ka
41%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 6H), 7.19 (t, J = 5.8 Hz, 1H), 7.15 (dd, J = 9.0, 6.7 Hz, 1H), 6.88 – 6.81 (m, 2H), 6.78 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 5.36 (s, 1H), 5.30 (s, 1H), 5.09 (d, J = 3.2 Hz, 1H), 5.06 – 4.99 (m, 1H), 4.69 (d, J = 3.2 Hz, 1H), 3.62 – 3.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.94 (J_{C-F} = 246.0 Hz), 146.58, 144.72, 143.13, 130.96, 130.91, 129.55 (J_{C-F} = 8.2 Hz), 129.32, 127.82 (J_{C-F} = 15.1 Hz), 124.48 (J_{C-F} = 3.2 Hz), 118.14, 117.28, 116.76, 115.88 (J_{C-F} = 22.9 Hz), 113.04, 112.31, 66.43, 60.72 (J_{C-F} = 3.8 Hz), 52.40.

HRMS (EI) calcd. for $C_{23}H_{21}FN_2$ $[M]^+$: 344.1683, found: 344.1674

4-(1-(3,4-dichlorophenyl)vinyl)-1,3-diphenylimidazolidine (3na)



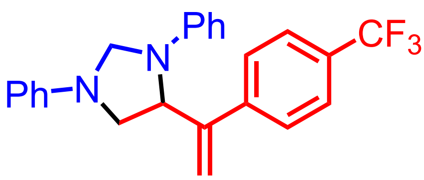
3na
63%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.1 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.36 – 7.30 (m, 5H), 6.90 – 6.83 (m, 2H), 6.74 – 6.66 (m, 4H), 5.46 (s, 1H), 5.32 (s, 1H), 5.11 (d, J = 3.2 Hz, 1H), 4.93 (dd, J = 7.6, 2.4 Hz, 1H), 4.70 (d, J = 3.2 Hz, 1H), 3.74 (t, J = 8.2 Hz, 1H), 3.53 (dd, J = 8.7, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.29, 144.70, 144.25, 139.36, 132.84, 132.02, 130.59, 129.38, 128.55, 125.93, 118.45, 117.73, 115.41, 113.11, 112.32, 66.72, 60.67, 53.05.

HRMS (EI) calcd. for $C_{23}H_{20}Cl_2N_2$ $[M]^+$: 394.0998, found: 394.0991

1,3-diphenyl-4-(1-(4-(trifluoromethyl)phenyl)vinyl)imidazolidine (3oa)



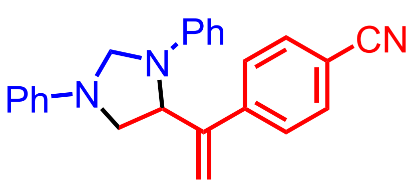
3oa
68%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.65 – 7.57 (m, 2H), 7.37 – 7.29 (m, 4H), 6.91 – 6.81 (m, 2H), 6.75 – 6.67 (m, 4H), 5.55 – 5.49 (m, 1H), 5.37 (s, 1H), 5.12 (d, J = 3.2 Hz, 1H), 5.01 (dd, J = 7.6, 2.3 Hz, 1H), 4.71 (d, J = 3.2 Hz, 1H), 3.75 (t, J = 8.2 Hz, 1H), 3.55 (dd, J = 8.7, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.32, 145.22, 144.76, 142.95, 129.98 (J_{C-F} = 32.6 Hz), 129.37, 126.95, 125.62 (J_{C-F} = 3.7 Hz), 124.13 (J_{C-F} = 272.2 Hz), 118.41, 117.68, 115.74, 113.09, 112.32, 66.72, 60.78, 53.06.

HRMS (EI) calcd. for $C_{24}H_{21}F_3N_2$ $[M]^+$: 394.1651, found: 394.1642

4-(1-(1,3-diphenylimidazolidin-4-yl)vinyl)benzonitrile (3pa)



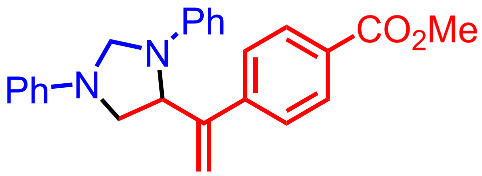
3pa
57%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.35 – 7.29 (m, 4H), 6.90 – 6.81 (m, 2H), 6.74 – 6.64 (m, 4H), 5.53 (s, 1H), 5.41 (s, 1H), 5.09 (d, J = 3.2 Hz, 1H), 4.98 (dd, J = 7.6, 2.4 Hz, 1H), 4.69 (d, J = 3.2 Hz, 1H), 3.75 (t, J = 8.2 Hz, 1H), 3.53 (dd, J = 8.8, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.20, 145.19, 144.64, 143.92, 132.43, 129.39, 127.32, 118.52, 117.80, 116.73, 113.09, 112.29, 66.70, 60.70, 53.08.

HRMS (ESI) calcd. for $C_{24}H_{21}N_3$ $[M+H]^+$: 352.1808, found: 352.1805

methyl 4-(1-(1,3-diphenylimidazolidin-4-yl)vinyl)benzoate (3qa)



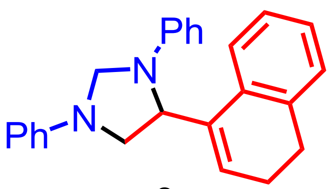
3qa
75%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.38 – 7.27 (m, 4H), 6.90 – 6.81 (m, 2H), 6.70 (dd, J = 8.3, 2.1 Hz, 4H), 5.54 (s, 1H), 5.35 (s, 1H), 5.13 (d, J = 3.2 Hz, 1H), 5.03 (dd, J = 7.5, 2.1 Hz, 1H), 4.71 (d, J = 3.2 Hz, 1H), 3.98 (s, 3H), 3.74 (t, J = 8.2 Hz, 1H), 3.55 (dd, J = 8.7, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.80, 146.35, 145.37, 144.75, 143.91, 130.21, 129.97, 129.56, 129.36, 126.55, 118.35, 117.60, 115.48, 113.08, 112.30, 66.68, 60.62, 53.11, 52.21.

HRMS (ESI) calcd. for $C_{25}H_{24}N_2O_2$ $[M+H]^+$: 385.1911, found: 385.1917

4-(3,4-dihydronaphthalen-1-yl)-1,3-diphenylimidazolidine (3ra)



3ra
63%

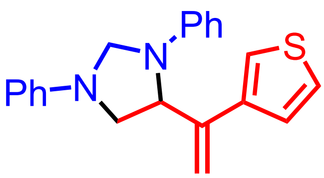
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 8H), 6.87 (t, J = 7.3 Hz, 1H), 6.82 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 6.02 (t, J = 4.4 Hz, 1H), 5.20 (d, J = 3.2 Hz, 1H), 5.12 – 5.06 (m, 1H), 4.73 (d, J = 3.2 Hz, 1H), 3.86 (t, J

= 8.1 Hz, 1H), 3.67 (dd, J = 8.5, 2.6 Hz, 1H), 2.80 (t, J = 8.0 Hz, 2H), 2.37 – 2.22 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.57, 145.02, 137.37, 133.92, 133.54, 129.34, 129.25, 128.16, 127.08, 126.56, 125.20, 121.89, 118.16, 117.19, 113.07, 112.32, 66.65, 58.30, 53.58, 28.13, 22.82.

HRMS (ESI) calcd. for $C_{25}H_{24}N_2$ $[M+H]^+$: 353.2012, found: 253.2010

1,3-diphenyl-4-(1-(thiophen-3-yl)vinyl)imidazolidine (3sa)



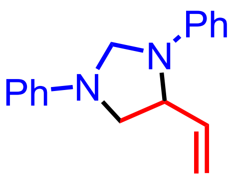
3sa
46%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 7H), 6.89 – 6.80 (m, 2H), 6.74 – 6.66 (m, 4H), 5.51 (s, 1H), 5.23 (s, 1H), 5.15 (d, J = 3.2 Hz, 1H), 4.96 (dd, J = 7.7, 2.7 Hz, 1H), 4.72 (d, J = 3.2 Hz, 1H), 3.82 (t, J = 8.2 Hz, 1H), 3.64 (dd, J = 8.6, 3.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.41, 144.88, 140.68, 140.04, 129.35, 129.27, 126.24, 126.03, 120.41, 118.24, 117.48, 113.06, 112.35, 111.98, 66.73, 60.72, 53.40.

HRMS (ESI) calcd. for $C_{21}H_{20}N_2S$ $[M+H]^+$: 333.1420, found: 333.1425

1,3-diphenyl-4-vinylimidazolidine (3ta)



3ta
40%

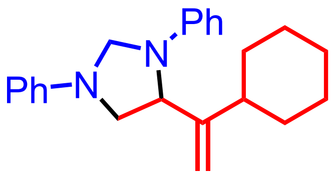
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 6.88 – 6.78 (m, 2H), 6.72 (dd, J = 7.9, 4.5 Hz, 4H), 5.93 (ddd, J = 17.1, 10.2, 6.8 Hz, 1H), 5.36 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.2 Hz, 1H), 4.96 (d, J = 3.3 Hz, 1H), 4.64 (d, J = 3.3 Hz, 1H), 4.55 (td,

J = 6.9, 3.4 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.53 (dd, J = 8.7, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.49, 145.44, 137.62, 129.34, 129.16, 118.04, 117.47, 116.71, 112.84, 112.79, 66.42, 59.91, 53.22

HRMS (EI) calcd. for $C_{17}H_{18}N_2$ $[M]^+$: 250.1465, found: 250.1456

4-(1-cyclohexylvinyl)-1,3-diphenylimidazolidine (3ua)



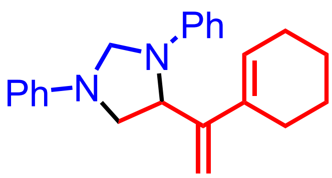
3ua
40%

^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H), 6.85 (t, J = 7.3 Hz, 1H), 6.79 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 7.9 Hz, 2H), 6.64 (d, J = 7.9 Hz, 2H), 5.06 (d, J = 3.3 Hz, 1H), 4.98 (s, 1H), 4.93 (s, 1H), 4.67 (d, J = 3.3 Hz, 1H), 4.48 (dd, J = 7.7, 3.2 Hz, 1H), 3.73 (t, J = 8.2 Hz, 1H), 3.51 (dd, J = 8.6, 3.3 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.89 – 1.70 (m, 4H), 1.40 – 1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.04, 146.51, 145.30, 129.32, 129.08, 117.98, 117.10, 112.91, 112.35, 108.96, 66.92, 61.97, 53.24, 41.31, 34.05, 32.95, 26.98, 26.87, 26.28.

HRMS (EI) calcd. for $C_{23}H_{28}N_2$ $[M]^+$: 332.2247, found: 332.2238

4-(1-(cyclohex-1-en-1-yl)vinyl)-1,3-diphenylimidazolidine (3va)



3va
40%

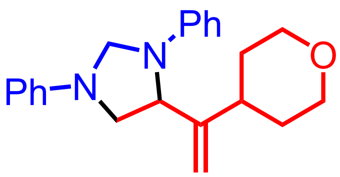
^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H), 6.84 (t, J = 7.3 Hz, 1H), 6.79 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 7.8 Hz, 2H), 6.58 (d, J = 7.9 Hz, 2H), 5.99 (t, J = 3.9 Hz, 1H), 5.18 – 5.06 (m, 2H), 4.97 (s, 1H), 4.87 (dd, J = 7.7, 2.2 Hz, 1H), 4.67 (d, J = 3.2

Hz, 1H), 3.73 (t, *J* = 8.1 Hz, 1H), 3.58 (dd, *J* = 8.5, 2.6 Hz, 1H), 2.41 – 2.17 (m, 4H), 1.83 – 1.73 (m, 2H), 1.73 – 1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.57, 145.20, 144.84, 135.09, 129.29, 129.17, 124.71, 117.98, 116.98, 112.96, 112.14, 109.10, 66.41, 58.70, 53.83, 26.47, 26.03, 22.87, 22.20.

HRMS (EI) calcd. for $C_{23}H_{26}N_2$ $[M]^+$: 330.2091, found: 330.2084

1,3-diphenyl-4-(1-(tetrahydro-2*H*-pyran-4-yl)vinyl)imidazolidine (3wa)



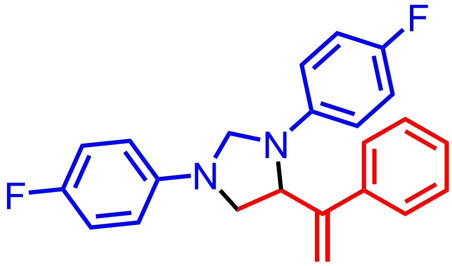
3wa
26%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 2H), 5.13 (s, 1H), 5.08 (d, *J* = 3.3 Hz, 1H), 5.02 (s, 1H), 4.65 (d, *J* = 3.3 Hz, 1H), 4.52 (dd, *J* = 7.8, 3.4 Hz, 1H), 4.08 – 3.97 (m, 2H), 3.75 (t, *J* = 8.3 Hz, 1H), 3.54 – 3.38 (m, 3H), 2.26 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.75 – 1.64 (m, 2H), 1.61 – 1.54 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.98, 146.35, 145.37, 129.39, 129.19, 118.21, 117.42, 112.98, 112.40, 110.57, 68.40, 68.37, 67.10, 62.26, 53.35, 37.87, 33.55, 32.75.

HRMS (ESI) calcd. for $C_{22}H_{26}N_2O$ $[M+H]^+$: 335.2118, found: 335.2122

1,3-bis(4-fluorophenyl)-4-(1-phenylvinyl)imidazolidine (3ab)



3ab
64%

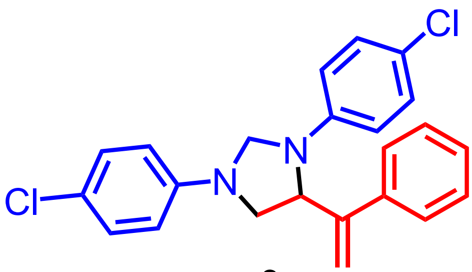
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.48 – 7.36 (m, 3H), 7.07 –

6.96 (m, 4H), 6.65 – 6.56 (m, 4H), 5.46 (s, 1H), 5.25 (s, 1H), 5.05 (d, J = 2.9 Hz, 1H), 4.94 (dd, J = 7.6, 2.9 Hz, 1H), 4.62 (d, J = 2.9 Hz, 1H), 3.71 (t, J = 8.1 Hz, 1H), 3.50 (dd, J = 8.5, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 156.34 (J_{C-F} = 236.8 Hz), 155.86 (J_{C-F} = 234.4 Hz), 145.68, 143.08, 141.55, 139.20, 128.72, 128.07, 126.48, 115.80 (J_{C-F} = 22.3 Hz), 115.77 (J_{C-F} = 22.3 Hz), 114.00, 113.95 (J_{C-F} = 7.4 Hz), 113.69, 113.03 (J_{C-F} = 7.3 Hz), 67.78, 61.35, 53.98.

HRMS (EI) calcd. for $C_{23}H_{20}F_2N_2$ [M]$^+$: 362.1589, found: 362.1592

1,3-bis(4-chlorophenyl)-4-(1-phenylvinyl)imidazolidine (3ac)



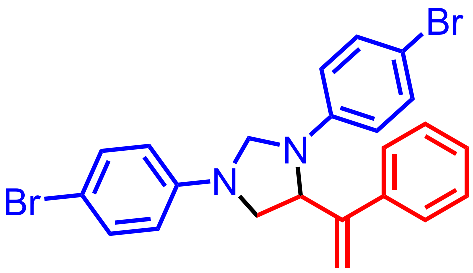
3ac
73%

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.34 (m, 5H), 7.27 – 7.19 (m, 4H), 6.65 – 6.56 (m, 4H), 5.44 (s, 1H), 5.17 (s, 1H), 5.02 (d, J = 3.2 Hz, 1H), 4.98 (dd, J = 7.6, 2.5 Hz, 1H), 4.64 (d, J = 3.2 Hz, 1H), 3.73 (t, J = 8.2 Hz, 1H), 3.52 (dd, J = 8.7, 2.9 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 145.37, 144.81, 143.28, 138.98, 129.16, 129.14, 128.75, 128.14, 126.46, 123.28, 122.54, 114.07, 113.68, 113.44, 66.75, 60.86, 53.33.

HRMS (EI) calcd. for $C_{23}H_{20}Cl_2N_2$ [M]$^+$: 394.0998, found: 394.0983

1,3-bis(4-bromophenyl)-4-(1-phenylvinyl)imidazolidine (3ad)



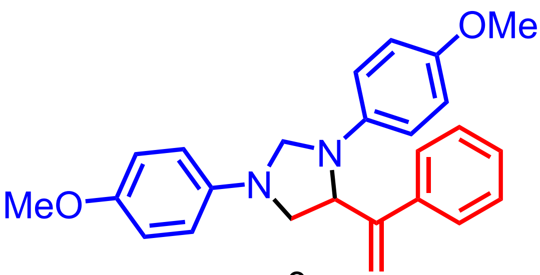
3ad
52%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 9H), 6.58 – 6.50 (m, 4H), 5.44 (s, 1H), 5.16 (s, 1H), 5.01 (d, J = 3.2 Hz, 1H), 4.98 (dd, J = 7.6, 2.5 Hz, 1H), 4.63 (d, J = 3.2 Hz, 1H), 3.72 (t, J = 8.2 Hz, 1H), 3.52 (dd, J = 8.7, 2.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.25, 145.16, 143.61, 138.92, 132.04, 132.01, 128.77, 128.17, 126.46, 114.54, 113.95, 113.69, 110.41, 109.66, 66.54, 60.74, 53.20.

HRMS (EI) calcd. for $C_{23}H_{20}Br_2N_2$ $[M]^+$: 481.9988, found: 481.9968

1,3-bis(4-methoxyphenyl)-4-(1-phenylvinyl)imidazolidine (3ae)



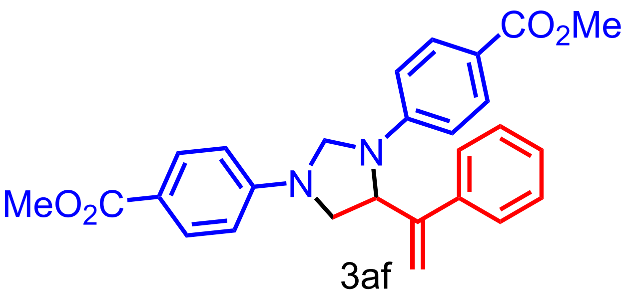
3ae
62%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.45 – 7.34 (m, 3H), 6.93 – 6.86 (m, 4H), 6.69 – 6.63 (m, 4H), 5.45 (s, 1H), 5.31 (s, 1H), 5.07 (d, J = 2.9 Hz, 1H), 4.89 (dd, J = 7.5, 3.2 Hz, 1H), 4.58 (d, J = 2.9 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.66 (t, J = 8.1 Hz, 1H), 3.47 (dd, J = 8.5, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.61, 151.94, 146.18, 141.28, 139.94, 139.55, 128.62, 127.87, 126.52, 114.96, 114.91, 114.34, 113.66, 113.34, 68.34, 61.57, 55.84, 55.79, 54.31.

HRMS (ESI) calcd. for $C_{25}H_{26}N_2O_2$ $[M+H]^+$: 387.2067, found: 387.2078

dimethyl 4,4'-(4-(1-phenylvinyl)imidazolidine-1,3-diyl)dibenzoate (3af)



3af
68%

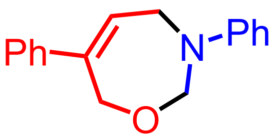
^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, J = 8.1 Hz, 4H), 7.49 – 7.35 (m, 5H), 6.65 (dd, J = 19.4, 8.7 Hz, 4H), 5.43 (s, 1H), 5.16 (d, J = 7.1 Hz, 1H), 5.12 (d, J = 3.9 Hz, 1H), 5.09 (s, 1H), 4.87 (d, J = 3.9 Hz, 1H), 3.89 (s, 6H), 3.85 (t, J = 8.3 Hz, 1H), 3.67 (dd, J = 9.0, 1.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.19, 167.14, 149.01, 147.59, 144.94, 138.63, 131.46, 128.84, 128.31, 126.47, 119.43, 119.12, 113.71, 111.77, 111.54, 65.45, 60.28, 52.43, 51.68.

HRMS (ESI) calcd. for $C_{27}H_{26}N_2O_4$ $[M+H]^+$: 443.1965, found: 443.1959

Characterization Data for the Products 4

3,6-diphenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4aa)



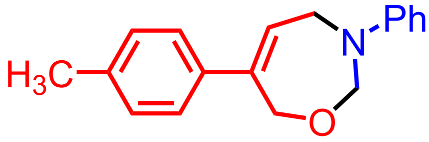
4aa
81%

^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 7H), 6.88 (d, J = 8.0 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.15 (t, J = 4.3 Hz, 1H), 5.17 (s, 2H), 4.52 (d, J = 1.1 Hz, 2H), 4.24 (d, J = 4.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.94, 141.60, 140.57, 129.26, 128.40, 127.81, 127.34, 126.20, 118.79, 114.38, 82.93, 69.45, 47.41.

HRMS (EI) calcd. for $C_{17}H_{17}NO$ $[M]^+$: 251.1305, found: 251.1301

3-phenyl-6-(p-tolyl)-2,3,4,7-tetrahydro-1,3-oxazepine (4ca)



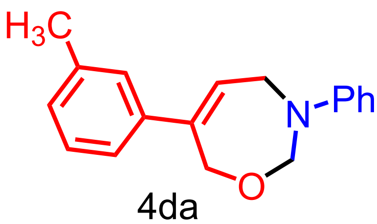
4ca
62%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.19 – 7.11 (m, 4H), 6.88 (d, J = 8.1 Hz, 2H), 6.84 (t, J = 7.5 Hz, 1H), 6.13 (t, J = 4.3 Hz, 1H), 5.17 (s, 2H), 4.51 (d, J = 0.8 Hz, 2H), 4.23 (d, J = 4.2 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.96, 141.38, 137.63, 137.10, 129.21, 129.05, 126.96, 126.04, 118.71, 114.37, 82.92, 69.50, 47.37, 21.09.

HRMS (ESI) calcd. for $C_{18}H_{19}NO$ $[M+H]^+$: 266.1539, found: 266.1538

3-phenyl-6-(m-tolyl)-2,3,4,7-tetrahydro-1,3-oxazepine (4da)



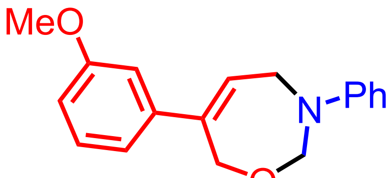
4da
62%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.11 – 7.06 (m, 3H), 6.89 (d, J = 8.2 Hz, 2H), 6.85 (t, J = 7.4 Hz, 1H), 6.15 (t, J = 4.3 Hz, 1H), 5.17 (s, 2H), 4.52 (d, J = 0.8 Hz, 2H), 4.24 (d, J = 4.2 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.95, 141.63, 140.55, 137.97, 129.24, 128.28, 128.07, 127.54, 126.92, 123.25, 118.74, 114.38, 82.92, 69.49, 47.39, 21.47.

HRMS (ESI) calcd. for $C_{18}H_{19}NO$ $[M+H]^+$: 266.1539, found: 266.1539

6-(3-methoxyphenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4fa)



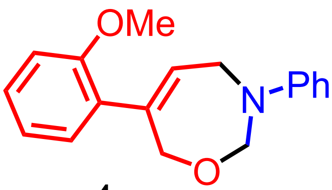
4fa
75%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 3H), 6.90 – 6.77 (m, 6H), 6.17 (t, *J* = 4.3 Hz, 1H), 5.16 (s, 2H), 4.51 (d, *J* = 0.9 Hz, 2H), 4.23 (d, *J* = 4.2 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.52, 147.92, 142.05, 141.47, 129.36, 129.24, 127.92, 118.79, 118.69, 114.38, 112.58, 112.08, 82.91, 69.41, 55.26, 47.39.

HRMS (ESI) calcd. for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1489, found: 282.1496

6-(2-methoxyphenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ga)



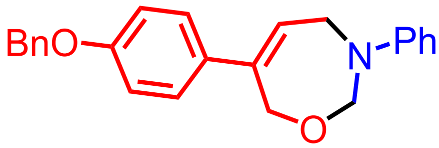
4ga
77%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 3H), 7.11 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.88 – 6.83 (m, 2H), 5.97 (t, *J* = 4.2 Hz, 1H), 5.17 (s, 2H), 4.40 (d, *J* = 0.9 Hz, 2H), 4.23 (d, *J* = 4.1 Hz, 2H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.59, 148.19, 141.56, 130.66, 129.94, 129.11, 128.91, 128.71, 120.62, 118.70, 114.67, 110.79, 83.07, 69.51, 55.47, 47.83.

HRMS (ESI) calcd. for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1489, found: 282.1486

6-(4-(benzyloxy)phenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ha)



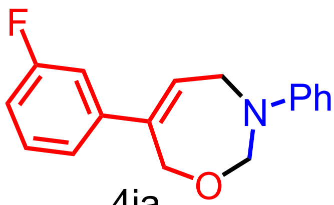
4ha
85%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 5H), 7.30 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 6.95 – 6.90 (m, 2H), 6.91 – 6.80 (m, 3H), 6.08 (t, J = 4.2 Hz, 1H), 5.16 (s, 2H), 5.07 (s, 2H), 4.49 (d, J = 4.2 Hz, 2H), 4.22 (d, J = 4.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.17, 147.93, 140.98, 136.90, 133.24, 129.22, 128.64, 128.03, 127.47, 127.33, 126.36, 118.69, 114.67, 114.34, 82.92, 70.02, 69.53, 47.30.

HRMS (ESI) calcd. for $C_{24}H_{23}NO_2$ $[M+H]^+$: 358.1802, found: 358.1806

6-(3-fluorophenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ja)



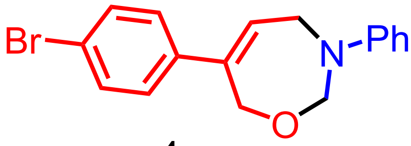
4ja
63%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 3H), 7.06 – 7.01 (m, 1H), 7.00 – 6.93 (m, 2H), 6.91 – 6.82 (m, 3H), 6.19 (t, J = 4.3 Hz, 1H), 5.16 (s, 2H), 4.49 (d, J = 1.1 Hz, 2H), 4.24 (d, J = 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.74 (J_{C-F} = 245.6 Hz), 147.81, 142.73 (J_{C-F} = 7.4 Hz), 140.61, 129.83 (J_{C-F} = 8.4 Hz), 129.28, 128.90, 121.76 (J_{C-F} = 2.6 Hz), 118.90, 114.32, 114.12 (J_{C-F} = 21.2 Hz), 113.25 (J_{C-F} = 21.9 Hz), 82.91, 69.11, 47.34.

HRMS (ESI) calcd. for $C_{17}H_{16}FNO$ $[M+H]^+$: 270.1289, found: 270.1290

6-(4-bromophenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ma)



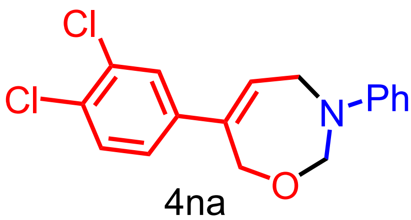
4ma
62%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.30 – 7.24 (m, 2H), 7.15 – 7.09 (m, 2H), 6.89 – 6.82 (m, 3H), 6.15 (t, *J* = 4.3 Hz, 1H), 5.16 (s, 2H), 4.47 (d, *J* = 1.2 Hz, 2H), 4.22 (d, *J* = 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.81, 140.64, 139.42, 131.47, 129.28, 128.51, 127.80, 121.28, 118.89, 114.33, 82.93, 69.13, 47.39.

HRMS (ESI) calcd. for $C_{17}H_{16}BrNO$ $[M+H]^+$: 330.0488, found: 330.0483

6-(3,4-dichlorophenyl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4na)



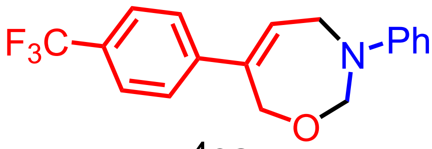
4na
66%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 2H), 7.08 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.90 – 6.83 (m, 3H), 6.18 (t, *J* = 4.3 Hz, 1H), 5.15 (s, 2H), 4.45 (d, *J* = 0.9 Hz, 2H), 4.23 (d, *J* = 4.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.70, 140.48, 139.66, 132.43, 131.25, 130.27, 129.62, 129.33, 128.06, 125.43, 119.00, 114.30, 82.92, 68.88, 47.36.

HRMS (ESI) calcd. for $C_{17}H_{15}Cl_2NO$ $[M+H]^+$: 320.0603, found: 320.0612

3-phenyl-6-(4-(trifluoromethyl)phenyl)-2,3,4,7-tetrahydro-1,3-oxazepine (4oa)



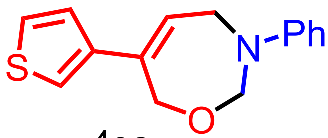
4oa
61%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.31 – 7.25 (m, 2H), 6.90 – 6.83 (m, 3H), 6.24 (t, J = 4.3 Hz, 1H), 5.18 (s, 2H), 4.51 (d, J = 1.3 Hz, 2H), 4.26 (d, J = 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.78, 144.07, 140.64, 129.96, 129.48, 129.31, 126.41, 125.34 ($J_{C\text{-}F}$ = 3.7 Hz), 124.13 ($J_{C\text{-}F}$ = 271.3 Hz), 119.00, 114.34, 82.94, 68.99, 47.47.

HRMS (ESI) calcd. for $C_{18}H_{16}F_3NO$ $[M+H]^+$: 320.1257, found: 320.1256

3-phenyl-6-(thiophen-3-yl)-2,3,4,7-tetrahydro-1,3-oxazepine (4sa)



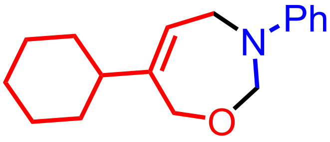
4sa
79%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.16 (dd, J = 5.1, 1.4 Hz, 1H), 7.05 (dd, J = 2.9, 1.3 Hz, 1H), 6.88 – 6.81 (m, 3H), 6.31 – 6.28 (m, 1H), 5.15 (s, 2H), 4.52 (dd, J = 2.6, 1.4 Hz, 2H), 4.27 – 4.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.82, 140.89, 136.21, 129.24, 126.17, 125.74, 125.72, 119.62, 118.73, 114.32, 82.89, 68.98, 47.03.

HRMS (ESI) calcd. for $C_{15}H_{15}NOS$ $[M+H]^+$: 258.0959, found: 258.0955

6-cyclohexyl-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ua)



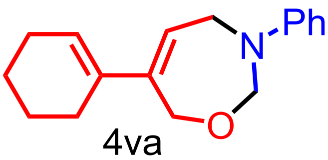
4ua
37%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.86 – 6.79 (m, 3H), 5.61 (t, *J* = 3.9 Hz, 1H), 5.06 (s, 2H), 4.08 (s, 2H), 4.06 (d, *J* = 4.1 Hz, 2H), 1.84 – 1.55 (m, 6H), 1.32 – 1.02 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.13, 146.49, 129.04, 121.52, 118.48, 114.46, 82.72, 68.82, 47.35, 43.98, 31.91, 26.55, 26.20.

HRMS (ESI) calcd. for $C_{17}H_{23}NO$ $[M+H]^+$: 258.1852, found: 258.1854

6-(cyclohex-1-en-1-yl)-3-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4va)



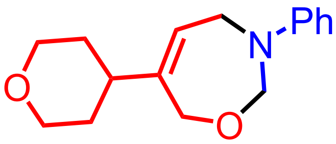
4va
33%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 6.84 – 6.77 (m, 3H), 5.91 (t, *J* = 4.4 Hz, 1H), 5.61 (t, *J* = 3.9 Hz, 1H), 5.06 (s, 2H), 4.35 (s, 2H), 4.13 (d, *J* = 4.4 Hz, 2H), 2.23 – 2.05 (m, 4H), 1.71 – 1.51 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.93, 141.25, 135.12, 129.15, 123.59, 123.04, 118.33, 114.12, 82.68, 67.57, 46.72, 26.39, 25.73, 22.87, 22.04.

HRMS (ESI) calcd. for $C_{17}H_{21}NO$ $[M+H]^+$: 256.1696, found: 256.1698

3-phenyl-6-(tetrahydro-2*H*-pyran-4-yl)-2,3,4,7-tetrahydro-1,3-oxazepine (4wa)



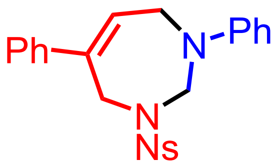
4wa
40%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 6.86 – 6.80 (m, 3H), 5.69 – 5.64 (m, 1H), 5.07 (s, 2H), 4.10 – 4.06 (m, 4H), 4.02 – 3.95 (m, 2H), 3.38 (td, *J* = 11.5, 2.6 Hz, 2H), 2.04 (dt, *J* = 11.2, 5.8 Hz, 1H), 1.55 – 1.43 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.95, 144.61, 129.11, 122.71, 118.65, 114.41, 82.78, 68.42, 68.09, 47.27, 40.91, 31.53.

HRMS (ESI) calcd. for $C_{16}H_{21}NO_2$ $[M+H]^+$: 260.1645, found: 260.1645

3-((4-nitrophenyl)sulfonyl)-1,5-diphenyl-2,3,4,7-tetrahydro-1*H*-1,3-diazepine (4xa)



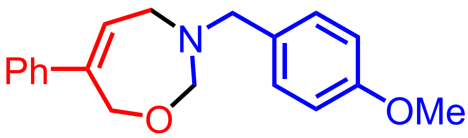
4xa
41%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 6.92 – 6.81 (m, 3H), 5.98 (t, *J* = 4.3 Hz, 1H), 5.23 (s, 2H), 4.39 (s, 2H), 4.02 (d, *J* = 4.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.83, 146.95, 145.64, 140.62, 138.77, 129.53, 128.66, 128.23, 127.97, 127.92, 125.92, 123.97, 119.71, 114.29, 65.84, 49.09, 47.77.

HRMS (ESI) calcd. for $C_{23}H_{21}N_3O_4S$ $[M+H]^+$: 436.1326, found: 436.1335

3-(4-methoxybenzyl)-6-phenyl-2,3,4,7-tetrahydro-1,3-oxazepine (4ag)



4ag
40%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 7H), 6.94 – 6.86 (m, 2H), 6.08 – 5.92 (m, 1H), 4.76 (s, 2H), 4.74 (s, 2H), 3.93 (s, 2H), 3.83 (s, 3H), 3.62 (d, *J* = 5.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.79, 145.14, 141.31, 130.91, 130.11, 129.42, 128.42, 127.27, 126.19, 113.74, 90.15, 72.77, 55.28, 54.28, 50.03.

References

[1] J. Chen, D. Liu, N. Butt, C. Li, D. Fan, Y. Liu, W. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 11632.

[2] W. S. Guo, L. Martinez-Rodriguez, E. Martin, E. C. Escudero-Adan, A. W. Kleij, *Angew. Chem. Int. Ed.* **2016**, *55*, 11037.

[3] K. Ohmatsu, N. Imagawa, T. Ooi, *Nature Chem.* **2014**, *6*, 47.

[4] Zhu, C., Xu, G., Sun, J. *Angew. Chem. Int. Ed.* **2016** *55*, 11867.

X-ray molecular structure and Crystallographic Data of 3ac:

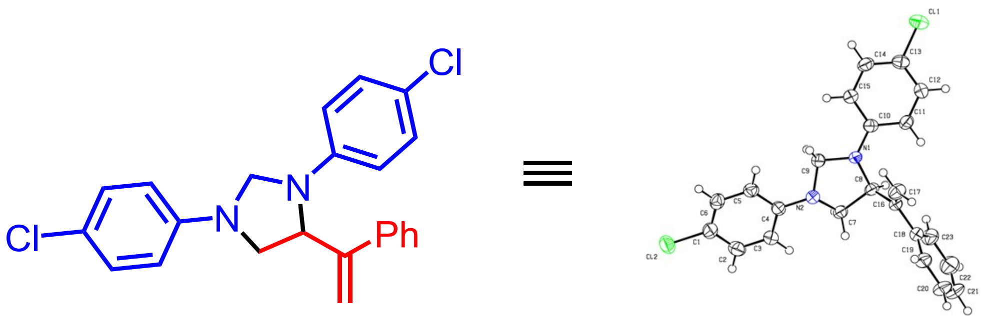


Table S3 Crystal data and structure refinement for 3ac.

Identification code	3ac
Empirical formula	$C_{23}H_{20}Cl_2N_2$
Formula weight	395.31
Temperature/K	173
Crystal system	orthorhombic
Space group	Pbca
a/Å	5.8417(2)
b/Å	26.8280(9)
c/Å	28.4867(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4464.5(3)
Z	8
ρ_{calc}g/cm^3	1.176
μ/mm^{-1}	2.671
F(000)	1648
Crystal size/mm^3	0.12 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.206 to 127.99
Index ranges	$-6 \leq h \leq 4$, $-30 \leq k \leq 29$, $-32 \leq l \leq 33$
Reflections collected	27104
Independent reflections	3698 [R_{int} = 0.1037, R_{sigma} = 0.0538]
Data/restraints/parameters	3698/0/244
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0668, wR_2 = 0.1439
Final R indexes [all data]	R_1 = 0.0917, wR_2 = 0.1557
Largest diff. peak/hole / e Å^{-3}	0.23/-0.29

Table S4 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 3ac. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	-2136.3(19)	8640.4(4)	2880.1(4)	48.9(3)
Cl2	12755(2)	6597.0(4)	5706.4(4)	52.1(3)
N2	6356(5)	6649.2(11)	4088(1)	32.2(7)
N1	3781(6)	7024.0(11)	3609.1(10)	34.0(8)
C10	2393(6)	7400.9(13)	3431.9(12)	30.2(8)
C16	3491(6)	6202.7(13)	3206.1(12)	27.4(8)
C18	2514(7)	5690.1(14)	3198.7(13)	33.1(9)
C15	2926(7)	7896.4(14)	3517.0(13)	36.2(9)
C9	5571(7)	7138.9(13)	3935.7(12)	31.3(9)
C11	464(7)	7294.2(14)	3156.0(13)	34.9(9)
C7	4406(7)	6313.8(13)	4069.9(13)	32.7(9)
C8	3046(7)	6505.5(12)	3645.3(12)	30.2(8)
C5	9455(7)	7011.8(14)	4540.7(13)	35.0(9)
C12	-903(7)	7672.3(15)	2983.7(13)	36.6(9)
C4	7833(7)	6635.7(14)	4476.6(12)	31.9(8)
C13	-386(7)	8161.8(14)	3085.9(13)	36.3(9)
C14	1522(7)	8276.8(14)	3346.0(14)	38.8(10)
C6	10955(7)	6998.0(15)	4914.8(13)	37.4(9)
C3	7748(7)	6249.3(15)	4802.4(14)	41.4(10)
C2	9244(8)	6239.3(16)	5177.7(15)	45.5(11)
C17	4729(7)	6385.1(15)	2856.9(14)	41.4(10)
C19	3698(8)	5302.2(15)	2983.8(14)	44.5(11)
C23	406(7)	5582.0(16)	3398.2(16)	44.7(10)
C1	10850(7)	6612.0(15)	5235.2(14)	39.6(10)
C20	2841(10)	4825.9(16)	2973.7(18)	61.8(14)
C22	-470(9)	5096.5(18)	3387(2)	65.4(15)
C21	788(11)	4720.7(17)	3180(2)	68.7(16)

Table S5 Anisotropic Displacement Parameters (Å²×10³) for 3ac. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	50.5(6)	39.0(5)	57.3(6)	5.7(5)	-2.8(5)	13.7(5)
Cl2	54.9(7)	58.1(7)	43.3(6)	-10.4(5)	-16.2(5)	16.1(6)
N2	34.8(17)	28.0(16)	33.9(17)	-0.4(14)	-4.7(14)	-0.9(14)
N1	47(2)	21.0(15)	33.9(17)	-1.8(13)	-12.9(15)	1.5(14)
C10	36(2)	27.1(19)	27.6(19)	0.7(15)	2.1(16)	2.4(16)

C16	31.2(19)	22.2(18)	28.9(19)	-1.9(15)	-1.4(16)	-0.6(15)
C18	37(2)	28.7(19)	34(2)	-1.3(16)	-6.1(18)	-0.5(17)
C15	38(2)	29(2)	41(2)	0.2(17)	-5.3(19)	-1.3(18)
C9	38(2)	27.9(19)	28.5(19)	-0.6(15)	-3.7(17)	0.6(17)
C11	43(2)	29(2)	33(2)	-3.8(16)	-3.8(19)	-4.0(18)
C7	42(2)	25.2(19)	31(2)	-1.7(16)	-2.3(17)	-0.5(17)
C8	34(2)	22.3(18)	34(2)	-1.2(15)	-0.2(16)	-2.6(16)
C5	39(2)	31(2)	35(2)	-2.2(16)	0.2(18)	3.3(18)
C12	36(2)	38(2)	36(2)	-0.3(17)	-7.0(18)	1.2(18)
C4	35(2)	32(2)	27.9(18)	-5.1(15)	-1.9(17)	7.0(17)
C13	40(2)	33(2)	36(2)	2.1(17)	7.2(19)	7.1(18)
C14	48(3)	26(2)	43(2)	-4.1(17)	0(2)	-0.1(18)
C6	36(2)	39(2)	37(2)	-10.2(18)	-0.5(18)	2.1(18)
C3	48(3)	32(2)	45(2)	4.5(18)	-13(2)	-1.4(19)
C2	54(3)	39(2)	43(2)	5.3(19)	-6(2)	7(2)
C17	49(2)	37(2)	39(2)	-1.7(18)	7(2)	-5(2)
C19	55(3)	34(2)	45(2)	-7.5(19)	-6(2)	7(2)
C23	36(2)	39(2)	59(3)	2(2)	0(2)	-8.9(19)
C1	45(2)	40(2)	35(2)	-14.3(18)	-4.0(18)	10(2)
C20	90(4)	28(2)	68(3)	-13(2)	-19(3)	7(3)
C22	55(3)	50(3)	91(4)	14(3)	-12(3)	-19(3)
C21	90(4)	26(2)	90(4)	1(3)	-28(4)	-18(3)

Table S6 Bond Lengths for 3ac.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C13	1.743(4)	C15	C14	1.397(5)
Cl2	C1	1.744(4)	C11	C12	1.381(5)
N2	C9	1.458(4)	C7	C8	1.536(5)
N2	C7	1.453(5)	C5	C4	1.396(5)
N2	C4	1.404(5)	C5	C6	1.380(5)
N1	C10	1.391(5)	C12	C13	1.379(5)
N1	C9	1.433(5)	C4	C3	1.392(5)
N1	C8	1.460(4)	C13	C14	1.374(6)
C10	C15	1.387(5)	C6	C1	1.382(6)
C10	C11	1.403(5)	C3	C2	1.381(6)
C16	C18	1.489(5)	C2	C1	1.381(6)
C16	C8	1.514(5)	C19	C20	1.373(6)
C16	C17	1.324(5)	C23	C22	1.400(6)
C18	C19	1.391(5)	C20	C21	1.365(8)
C18	C23	1.387(6)	C22	C21	1.380(7)

Table S7 Bond Angles for 3ac.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N2	C9	107.5(3)	C16	C8	C7	112.5(3)
C4	N2	C9	116.8(3)	C6	C5	C4	120.8(4)
C4	N2	C7	119.6(3)	C13	C12	C11	119.9(4)
C10	N1	C9	120.3(3)	C5	C4	N2	120.1(3)
C10	N1	C8	123.1(3)	C3	C4	N2	121.5(3)
C9	N1	C8	112.0(3)	C3	C4	C5	118.4(4)
N1	C10	C11	121.5(3)	C12	C13	Cl1	120.1(3)
C15	C10	N1	120.2(3)	C14	C13	Cl1	119.5(3)
C15	C10	C11	118.3(3)	C14	C13	C12	120.4(4)
C18	C16	C8	116.2(3)	C13	C14	C15	120.0(4)
C17	C16	C18	122.7(3)	C5	C6	C1	120.1(4)
C17	C16	C8	121.1(3)	C2	C3	C4	120.5(4)
C19	C18	C16	120.4(4)	C1	C2	C3	120.5(4)
C23	C18	C16	121.9(4)	C20	C19	C18	121.6(5)
C23	C18	C19	117.7(4)	C18	C23	C22	120.7(4)
C10	C15	C14	120.5(4)	C6	C1	Cl2	119.8(3)
N1	C9	N2	103.2(3)	C2	C1	Cl2	120.5(3)
C12	C11	C10	120.9(4)	C2	C1	C6	119.6(4)
N2	C7	C8	103.1(3)	C21	C20	C19	120.3(5)
N1	C8	C16	113.7(3)	C21	C22	C23	119.6(5)
N1	C8	C7	102.9(3)	C20	C21	C22	120.1(4)

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ac.

Atom	*x*	*y*	*z*	U(eq)
H15	4256	7978	3693	43
H9A	4979	7335	4204	38
H9B	6820	7327	3782	38
H11	94	6957	3087	42
H7A	3487	6335	4361	39
H7B	4903	5965	4022	39
H8	1374	6495	3720	36
H5	9528	7281	4324	42
H12	-2197	7595	2795	44
H14	1888	8615	3410	47
H6	12061	7255	4952	45
H3	6651	5991	4766	50
H2	9168	5974	5398	55
H17A	5026	6187	2587	50
H17B	5321	6714	2876	50

H19	5134	5369	2841	53
H23	-451	5840	3544	54
H20	3680	4568	2823	74
H22	-1924	5026	3521	79
H21	224	4389	3181	82

Experimental

Single crystals of C23H20Cl2N2 [3ac] were []. A suitable crystal was selected and [] on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 173.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

[1]. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2]. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[3]. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [3ac]

Crystal Data for $C_{23}H_{20}Cl_2N_2$ (M =395.31 g/mol): orthorhombic, space group Pbca (no. 61), a = 5.8417(2) Å, b = 26.8280(9) Å, c = 28.4867(11) Å, V = 4464.5(3) Å^3, Z = 8, T = 173.0 K, μ(CuKα) = 2.671 mm^{-1}, $Dcalc$ = 1.176 g/cm^3, 27104 reflections measured (6.206° ≤ 2Θ ≤ 127.99°), 3698 unique (R_{int} = 0.1037, R_{sigma} = 0.0538) which were used in all calculations. The final R_1 was 0.0668 (I > 2σ(I)) and wR_2 was 0.1557 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2.a Ternary CH refined with riding coordinates:

C8(H8)

2.b Secondary CH2 refined with riding coordinates:

C9(H9A,H9B), C7(H7A,H7B)

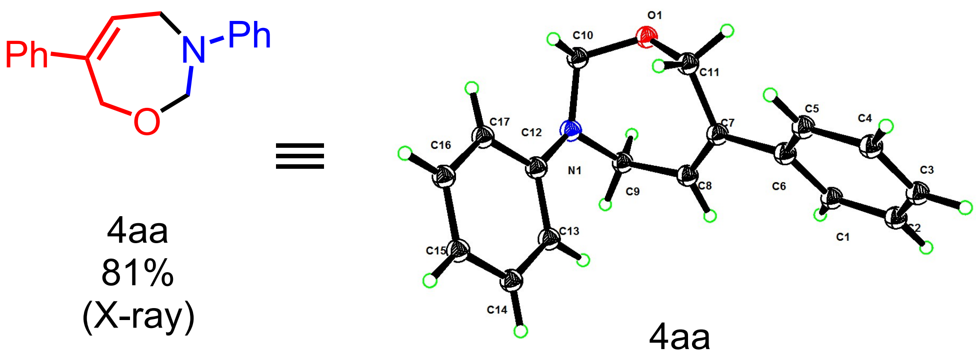
2.c Aromatic/amide H refined with riding coordinates:

C15(H15), C11(H11), C5(H5), C12(H12), C14(H14), C6(H6), C3(H3), C2(H2), C19(H19), C23(H23), C20(H20), C22(H22), C21(H21)

2.d X=CH2 refined with riding coordinates:

C17(H17A,H17B)

X-ray molecular structure and Crystallographic Data of 4aa:



4aa
81%
(X-ray)

4aa

Table S15 Crystal data and structure refinement for 4aa.

Identification code	4aa
Empirical formula	$C_{17}H_{17}NO$
Formula weight	251.31
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.587(6)
b/Å	6.230(3)
c/Å	15.598(7)
α/°	90
β/°	92.110(11)

γ/°	90
Volume/Å^3	1319.4(10)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.078
F(000)	536
Crystal size/mm^3	0.19 × 0.15 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.904 to 54.686
Index ranges	-17 ≤ h ≤ 17, -7 ≤ k ≤ 7, -20 ≤ l ≤ 20
Reflections collected	9583
Independent reflections	2927 [R_{int} = 0.0972, R_{sigma} = 0.1127]
Data/restraints/parameters	2927/202/181
Goodness-of-fit on F^2	0.942
Final R indexes [I>=2σ (I)]	R_1 = 0.0556, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.1533, wR_2 = 0.1279
Largest diff. peak/hole / e Å^{-3}	0.16/-0.20

Table S16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	6365.2(14)	6395(3)	8289.4(13)	35.5(5)
O1	5562.8(15)	8574(3)	9305.9(14)	44.2(6)
C12	6285.3(16)	6351(4)	7391.2(16)	32.8(6)
C6	3184.0(18)	5729(4)	8705.7(15)	35.1(6)
C7	4273.2(18)	6052(4)	8780.9(15)	32.3(6)
C8	4899.3(18)	4409(4)	8760.1(15)	38.2(7)
C9	6004.6(18)	4587(4)	8779.3(17)	41.2(7)
C1	2741.8(19)	3837(4)	8976.2(16)	42.9(7)
C13	5939.6(17)	4532(4)	6946.8(17)	41.6(7)
C5	2577.6(19)	7312(4)	8336.1(17)	45.0(7)
C17	6590.1(18)	8086(4)	6895.1(18)	44.0(7)
C11	4624.4(19)	8337(4)	8886.4(19)	48.6(7)
C16	6527.3(19)	8009(5)	6013.9(19)	52.5(8)
C10	6367.3(19)	8399(4)	8755.4(18)	49.8(7)
C2	1734(2)	3561(5)	8885.0(17)	53.6(8)
C3	1144(2)	5151(5)	8521.6(18)	56.5(8)
C15	6175(2)	6212(6)	5588.5(19)	58.7(8)
C4	1569.1(19)	7021(5)	8253.3(18)	53.2(8)
C14	5894(2)	4472(5)	6058.0(19)	56.1(8)
O0AA	5390(7)	9326(18)	8555(9)	54(3)

Table S17 Anisotropic Displacement Parameters (Å^2×10^3) for 4aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	39.7(12)	27.2(11)	39.8(12)	0.3(10)	2.3(10)	-4(1)
O1	46.1(13)	40.5(13)	46.0(14)	-14.2(12)	1.0(11)	-3.9(11)
C12	25.5(13)	32.5(14)	40.6(15)	1.6(13)	2.1(11)	4.8(12)
C6	42.2(15)	33.8(15)	29.8(14)	-0.8(12)	7.1(12)	0.1(12)
C7	39.2(14)	30.2(14)	27.7(14)	-1.5(12)	1.9(11)	-0.8(12)
C8	42.5(16)	28.2(14)	44.0(16)	2.9(13)	3.5(13)	-1.9(13)
C9	45.7(17)	34.9(15)	43.0(16)	3.1(13)	2.5(13)	4.5(13)
C1	48.9(17)	39.1(16)	41.0(16)	-1.3(13)	7.3(13)	-6.2(14)
C13	37.2(16)	42.6(16)	45.0(17)	0.0(14)	0.2(13)	-4.2(13)
C5	40.4(16)	51.9(18)	42.9(17)	3.1(14)	2.4(14)	6.0(14)
C17	36.7(15)	44.3(17)	51.2(18)	10.3(15)	3.0(13)	-1.8(14)
C11	45.9(17)	33.2(16)	66(2)	-5.8(15)	-6.9(15)	5.5(14)
C16	41.8(17)	61(2)	55.0(19)	19.8(17)	3.2(15)	-4.2(15)
C10	46.8(17)	43.0(17)	60.2(19)	-11.7(16)	10.5(15)	-6.2(15)
C2	56.7(19)	55.5(19)	49.4(18)	-6.7(16)	14.3(16)	-18.2(17)
C3	37.8(18)	82(2)	49.3(19)	-10.5(18)	4.1(15)	-4.3(17)
C15	45.5(18)	89(2)	41.2(17)	8.5(18)	-2.4(14)	2.0(18)
C4	41.2(17)	69(2)	49.5(19)	-0.5(16)	3.0(15)	6.7(16)
C14	52.4(19)	67(2)	48.6(18)	-9.7(17)	-2.4(15)	-10.1(16)
O0AA	46(6)	35(6)	82(9)	2(7)	9(6)	-2(5)

Table S18 Bond Lengths for 4aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C12	1.401(3)	C8	C9	1.505(3)
N1	C9	1.456(3)	C1	C2	1.383(4)
N1	C10	1.445(3)	C13	C14	1.386(4)
O1	C11	1.419(3)	C5	C4	1.383(3)
O1	C10	1.419(3)	C17	C16	1.375(4)
C12	C13	1.401(3)	C11	O0AA	1.330(10)
C12	C17	1.400(3)	C16	C15	1.378(4)
C6	C7	1.494(3)	C10	O0AA	1.471(10)
C6	C1	1.395(3)	C2	C3	1.382(4)
C6	C5	1.396(3)	C3	C4	1.372(4)
C7	C8	1.332(3)	C15	C14	1.370(4)
C7	C11	1.509(3)			

Table S19 Bond Angles for 4aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

C12	N1	C9	119.6(2)	C2	C1	C6	120.7(3)
C12	N1	C10	121.2(2)	C14	C13	C12	121.2(3)
C10	N1	C9	113.5(2)	C4	C5	C6	120.9(3)
C10	O1	C11	114.3(2)	C16	C17	C12	121.1(3)
C13	C12	N1	121.5(2)	O1	C11	C7	115.1(2)
C17	C12	N1	121.6(2)	O0AA	C11	C7	130.0(6)
C17	C12	C13	116.8(2)	C17	C16	C15	121.2(3)
C1	C6	C7	121.8(2)	N1	C10	O0AA	104.3(5)
C1	C6	C5	117.9(2)	O1	C10	N1	112.6(2)
C5	C6	C7	120.3(2)	C3	C2	C1	120.7(3)
C6	C7	C11	116.4(2)	C4	C3	C2	119.3(3)
C8	C7	C6	121.7(2)	C14	C15	C16	118.9(3)
C8	C7	C11	121.9(2)	C3	C4	C5	120.6(3)
C7	C8	C9	125.5(2)	C15	C14	C13	120.7(3)
N1	C9	C8	113.7(2)	C11	O0AA	C10	116.7(8)

Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4aa.

Atom	*x*	*y*	*z*	U(eq)
H8	4625	3007	8731	46
H9A	6247	4730	9383	49
H9B	6282	3245	8549	49
H1	3137	2727	9226	51
H13	5732	3316	7260	50
H5	2861	8606	8139	54
H17	6845	9336	7172	53
H11A	4646	9005	8311	58
H11B	4135	9140	9215	58
H11C	4048	9228	8711	58
H11D	4715	8539	9514	58
H16	6730	9215	5693	63
H10A	6991	8523	9101	60
H10B	6341	9603	8341	60
H10C	6895	9359	8561	60
H10D	6464	8149	9380	60
H2	1443	2266	9074	64
H3	452	4951	8458	68
H15	6128	6180	4979	70
H4	1167	8125	8008	64
H14	5666	3212	5771	67

Table S21 Atomic Occupancy for 4aa.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O1	0.85	H11A	0.85	H11B	0.85
H11C	0.15	H11D	0.15	H10A	0.85
H10B	0.85	H10C	0.15	H10D	0.15
O0AA	0.15				

Experimental

Single crystals of $C_{17}H_{17}NO$ **[4aa]** were **[]**. A suitable crystal was selected and **[]** on a **'Bruker APEX-II CCD'** diffractometer. The crystal was kept at 173 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [4aa]

Crystal Data for $C_{17}H_{17}NO$ (M =251.31 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 13.587(6) Å, b = 6.230(3) Å, c = 15.598(7) Å, β = 92.110(11)°, V = 1319.4(10) Å^3, Z = 4, T = 173 K, μ(MoKα) = 0.078 mm^{-1}, $Dcalc$ = 1.265 g/cm^3, 9583 reflections measured (3.904° ≤ 2Θ ≤ 54.686°), 2927 unique (R_{int} = 0.0972, R_{sigma} = 0.1127) which were used in all calculations. The final R_1 was 0.0556 (I > 2σ(I)) and wR_2 was 0.1279 (all data).

Refinement model description

Number of restraints - 202, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups

2. Restrained distances

O0AA-C11 ≈ O1-C11 ≈ O1-C10 ≈ O0AA-C10

with sigma of 0.02

3. Rigid bond restraints

All non-hydrogen atoms

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

4. Uiso/Uaniso restraints and constraints

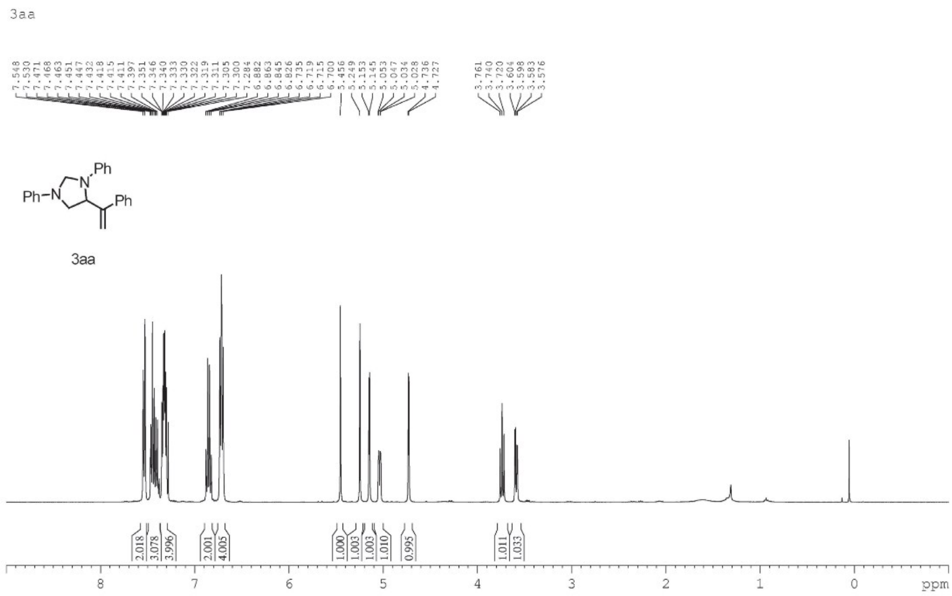
All non-hydrogen atoms have similar U: within 2A with sigma of 0.04 and sigma

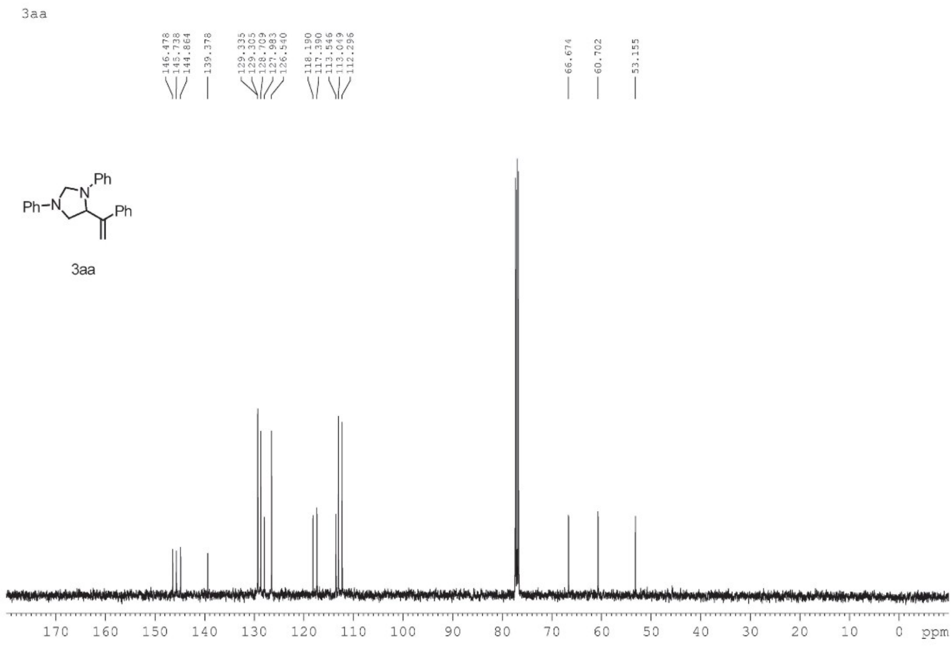
for terminal atoms of 0.08

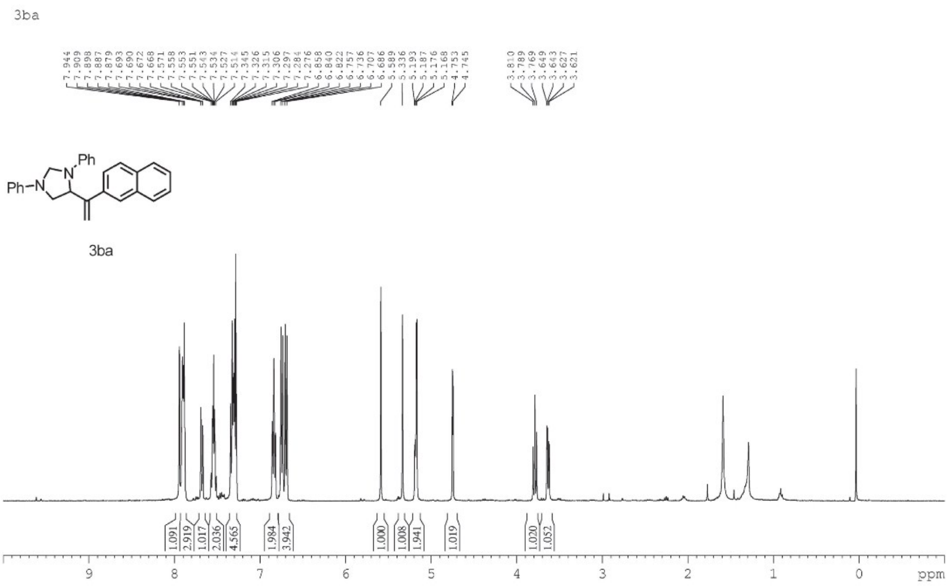
5. Others

Fixed Sof: O1(0.85) H11A(0.85) H11B(0.85) H11C(0.15) H11D(0.15)

H10A(0.85)
H10B(0.85) H10C(0.15) H10D(0.15) O0AA(0.15)
6.a Secondary CH2 refined with riding coordinates:
C9(H9A,H9B), C11(H11A,H11B), C11(H11C,H11D), C10(H10A,H10B), C10(H10C,H10D)
6.b Aromatic/amide H refined with riding coordinates:
C8(H8), C1(H1), C13(H13), C5(H5), C17(H17), C16(H16), C2(H2), C3(H3),
C15(H15), C4(H4), C14(H14)



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3.810 3.789 3.769 3.649 3.643 3.627 3.621
Ph
Ph
N
N
3ba
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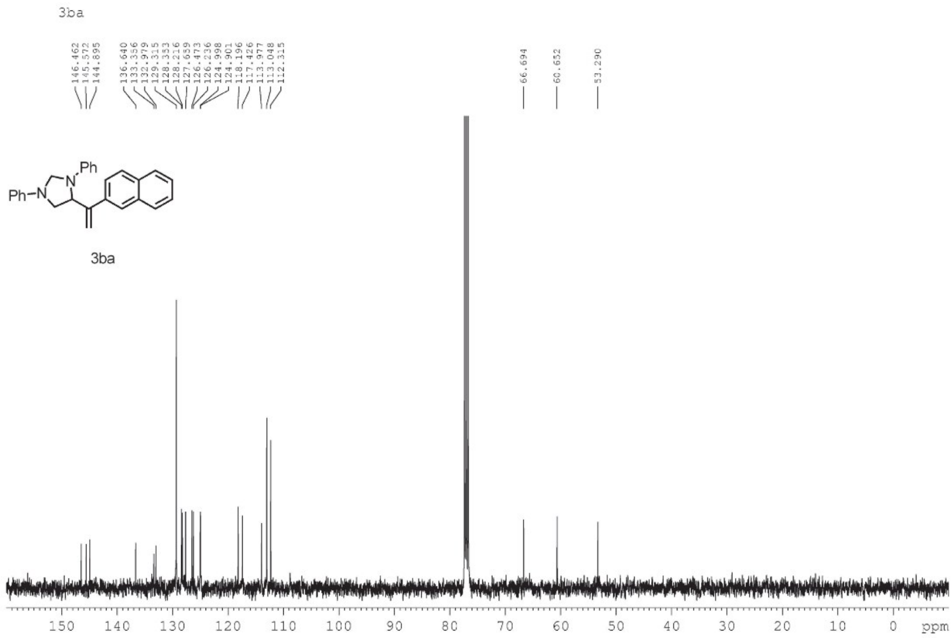
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136.640 133.356 132.979 129.315 128.353 128.216 127.659 126.473 126.236 124.998 124.901 118.196 117.426 113.977 113.048 112.315
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60.652
53.290
Ph
Ph
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N
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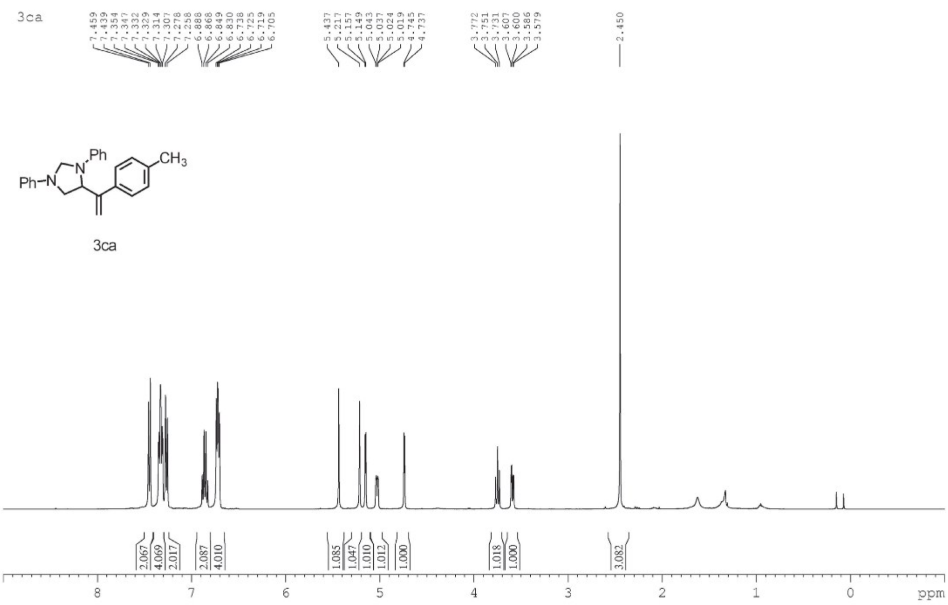
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6.738
6.725
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3.751
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Ph
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1.085
1.047
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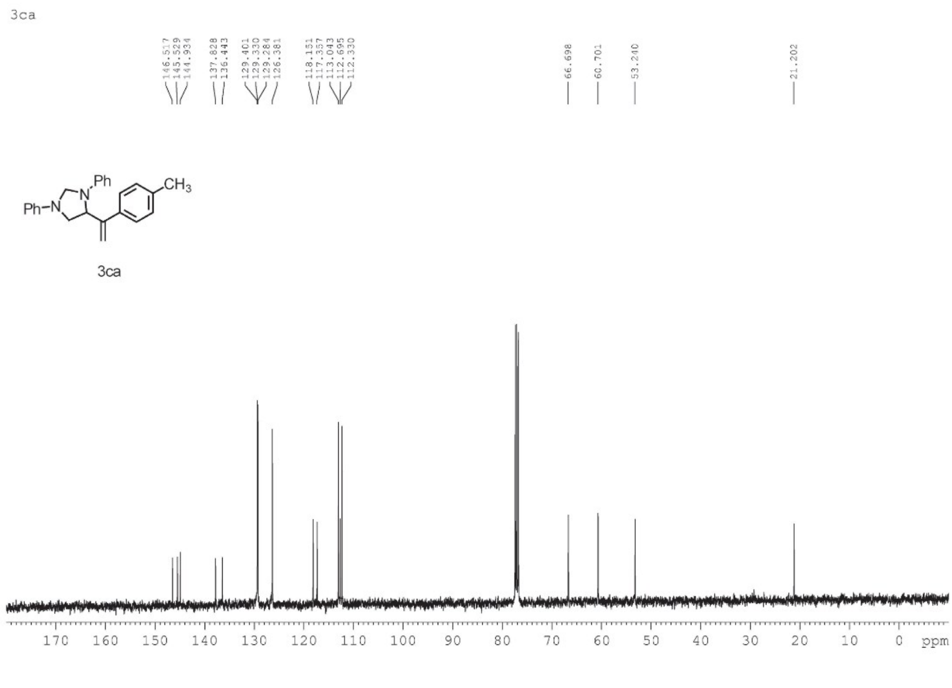
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113.043
112.695
112.330
66.698
60.701
53.240
21.202
Ph
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Ph
N
CH3
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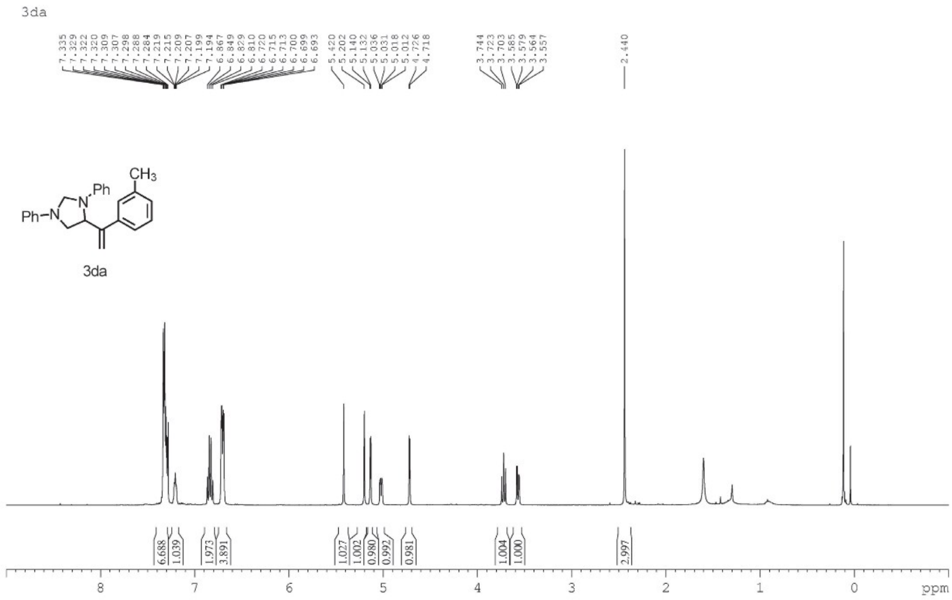

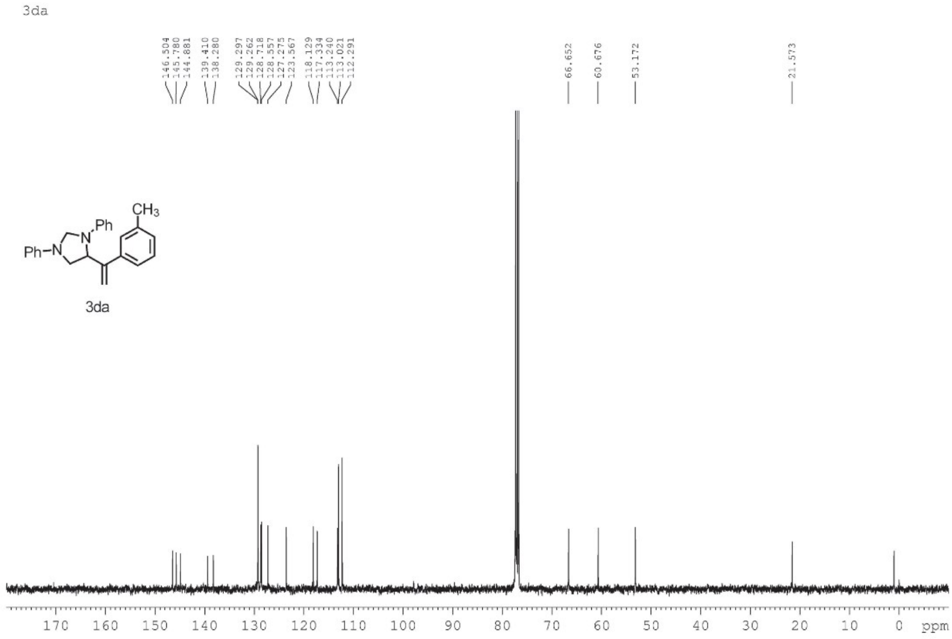

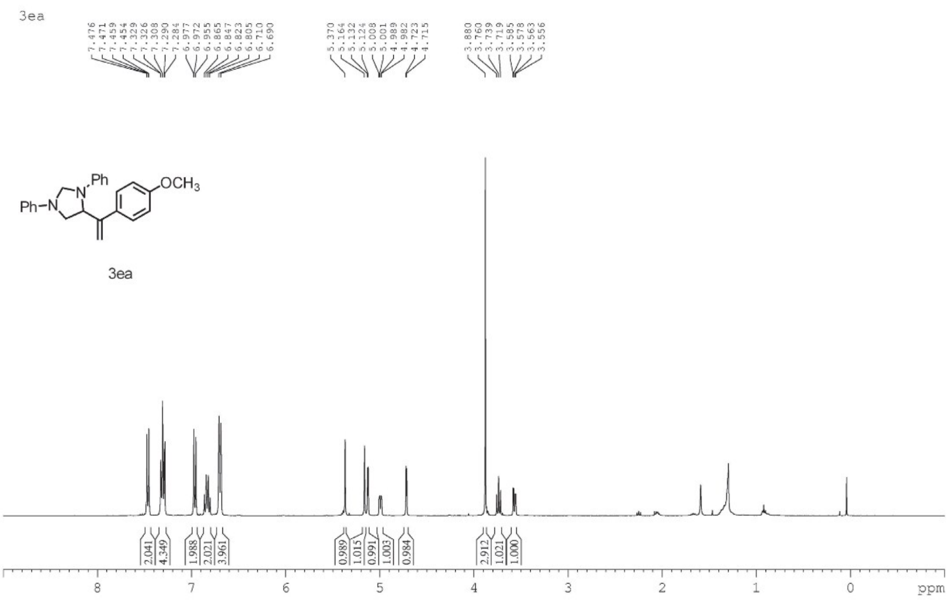
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6.865
6.847
6.823
6.805
6.710
6.690
5.370
5.164
5.132
5.126
5.008
5.001
4.989
4.982
4.723
4.715
3.880
3.760
3.739
3.719
3.585
3.578
3.563
3.556
Ph
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Ph
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OCH3
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0.989
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3
2
1
0
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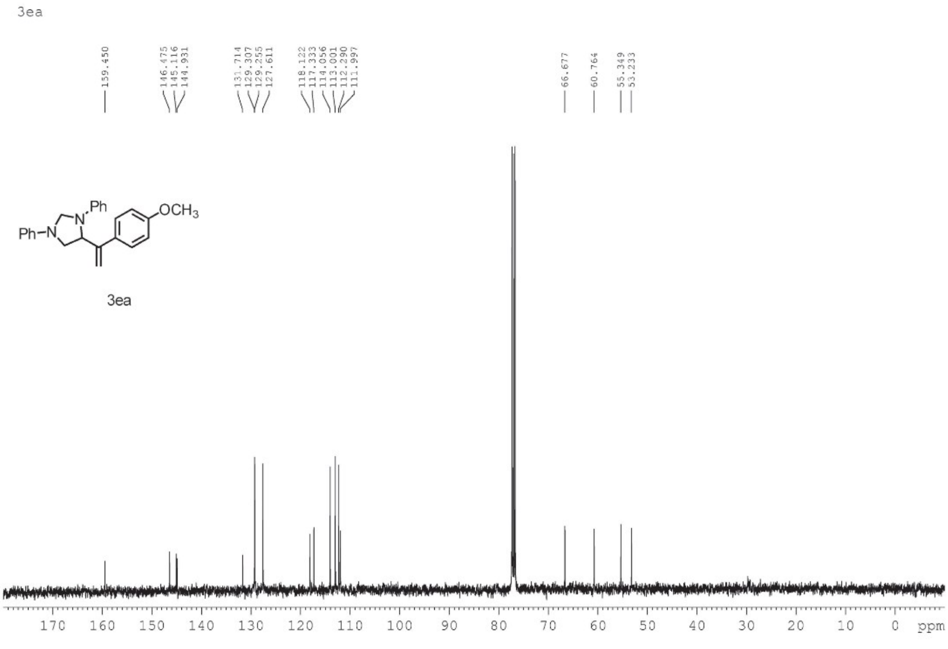
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113.001
112.290
111.997
66.677
60.764
55.349
53.233
Ph
N
Ph
N
OCH3
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60
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20
10
0
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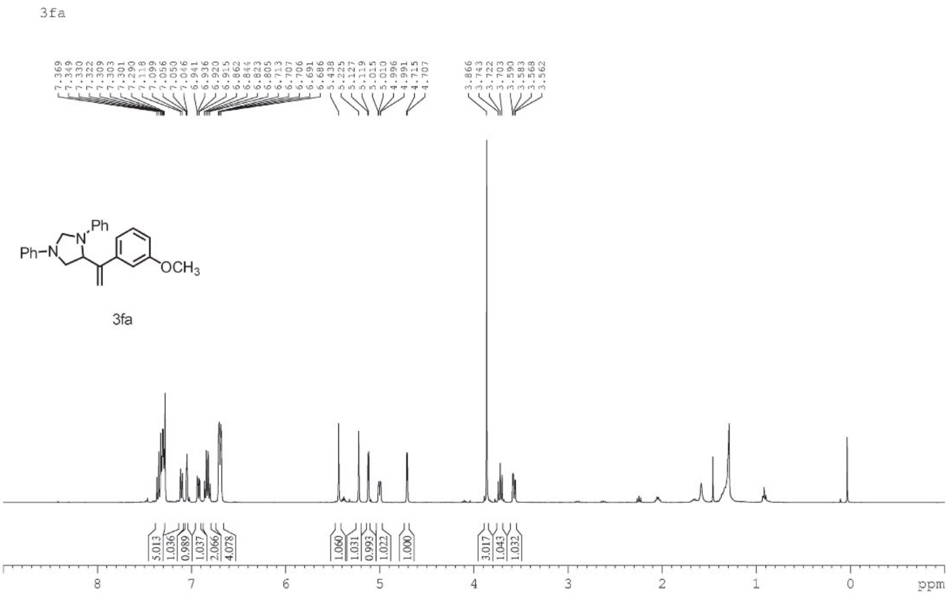

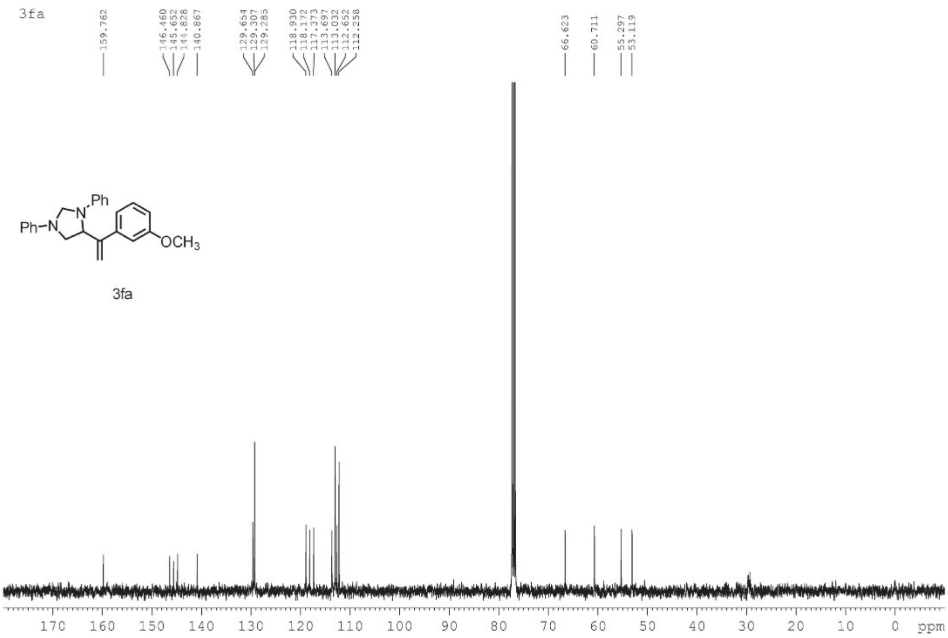

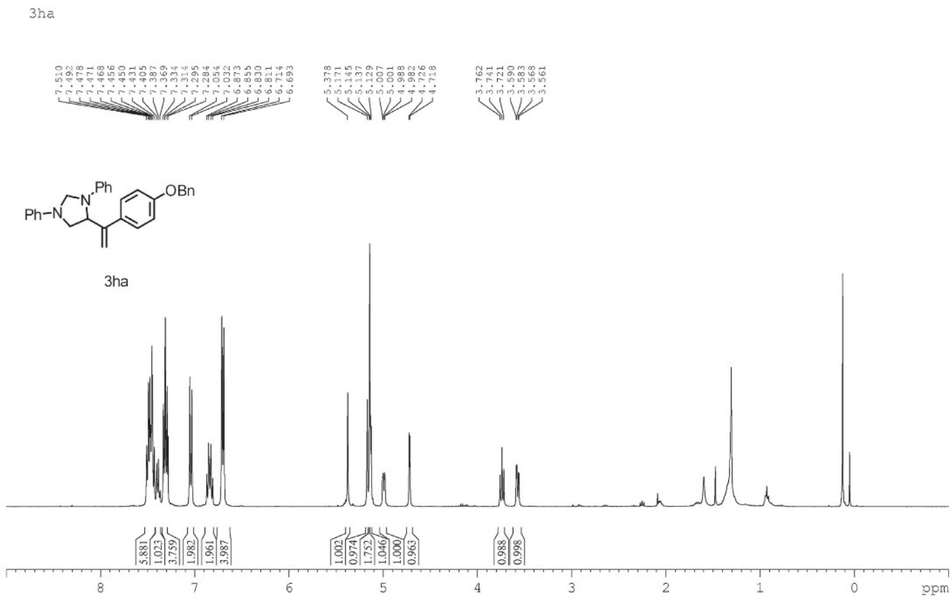
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5.378 5.171 5.145 5.137 5.129 5.007 5.001 4.988 4.982 4.726 4.718
3.762 3.741 3.721 3.590 3.583 3.568 3.561
Ph
OBn
Ph
N
N
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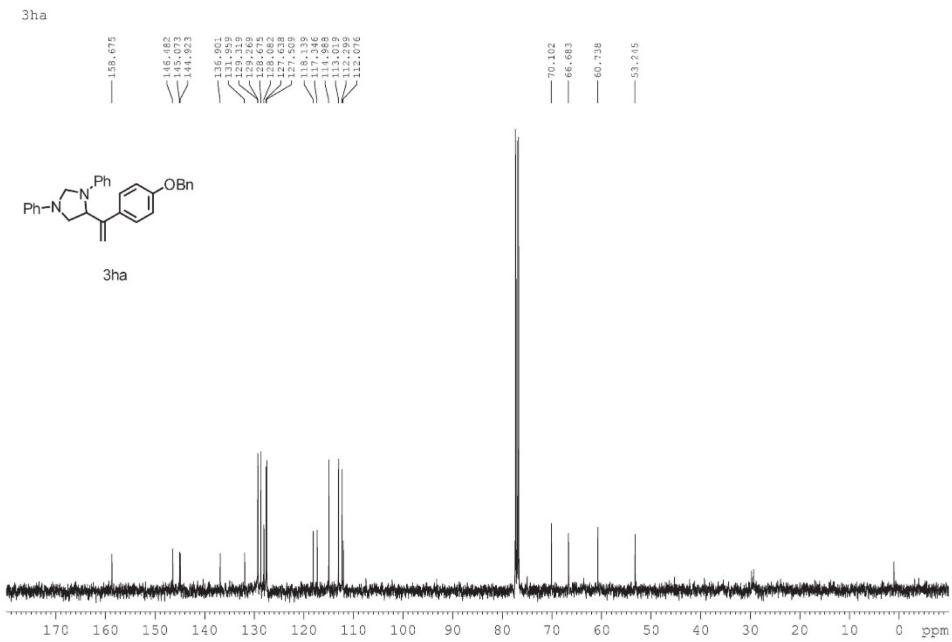
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Ph
OBn
Ph
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N
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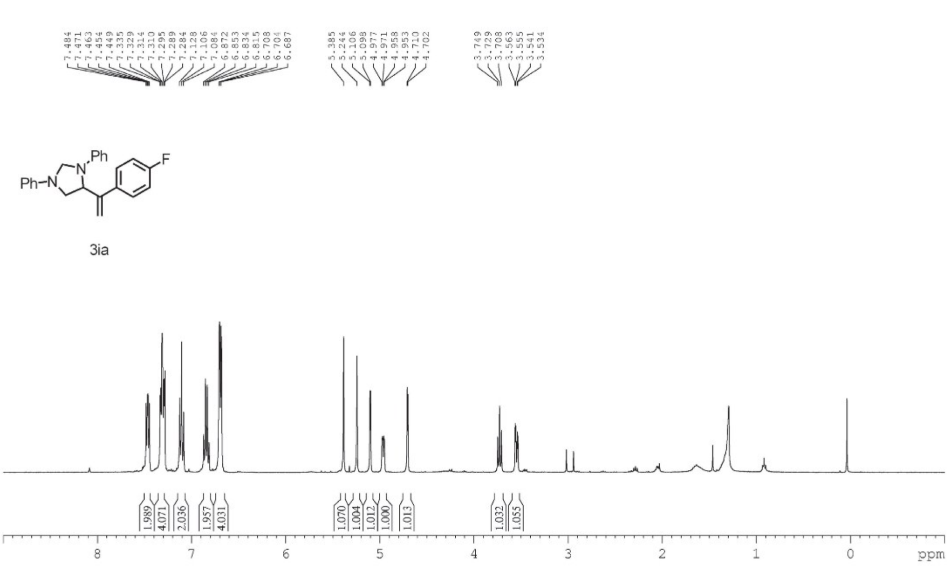
3ia



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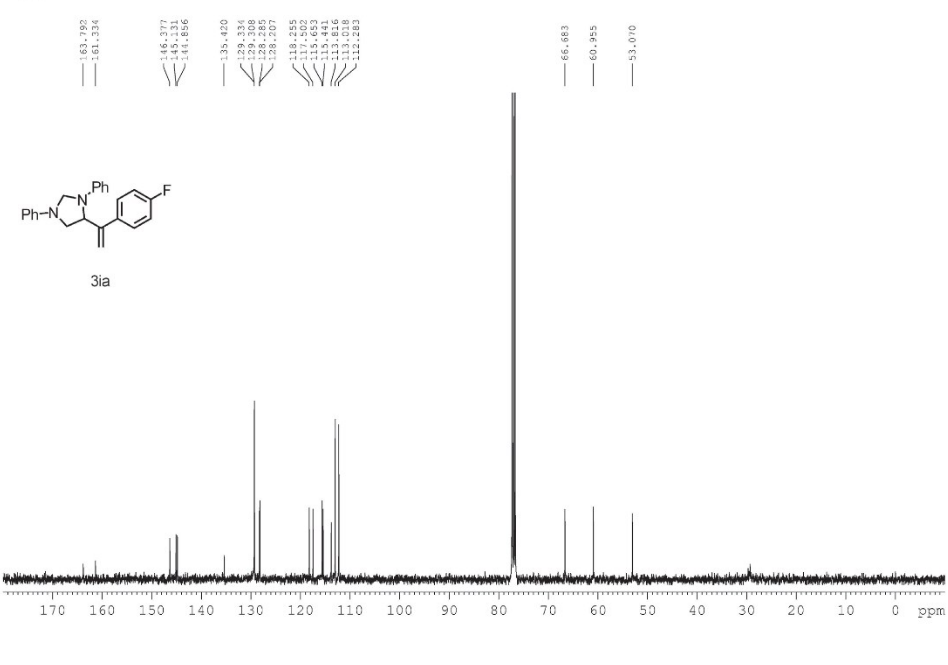

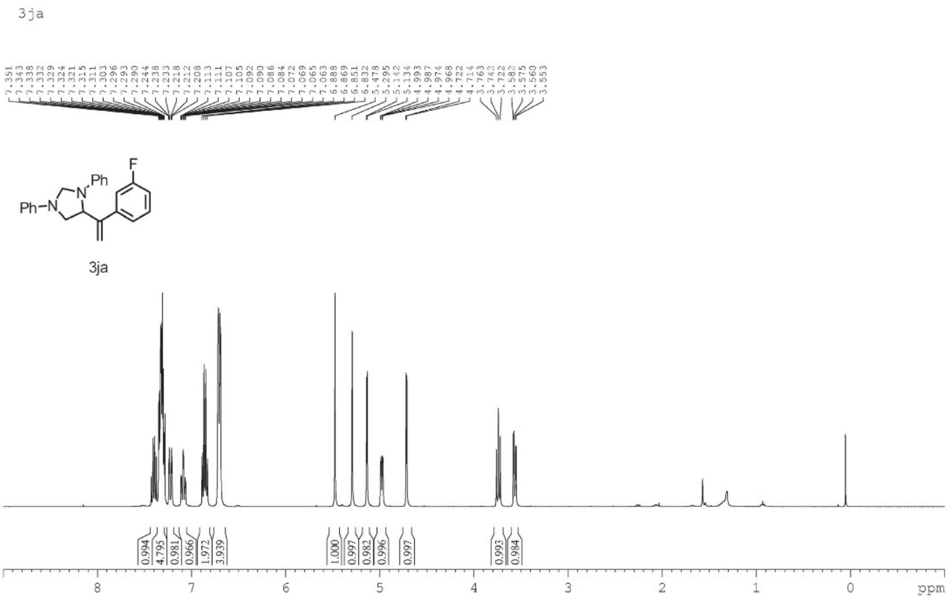
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Ph
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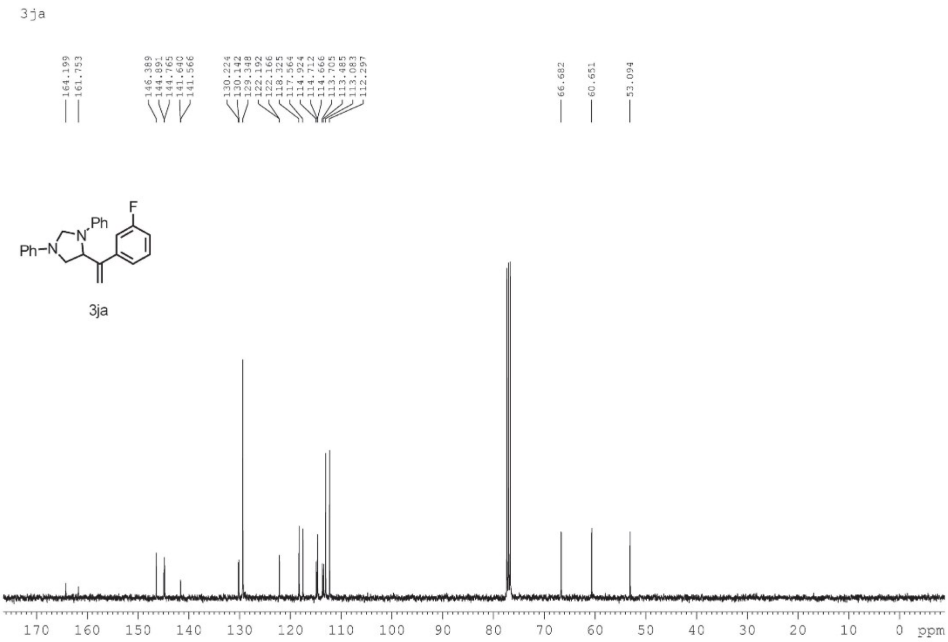
N
F
3ja
ppm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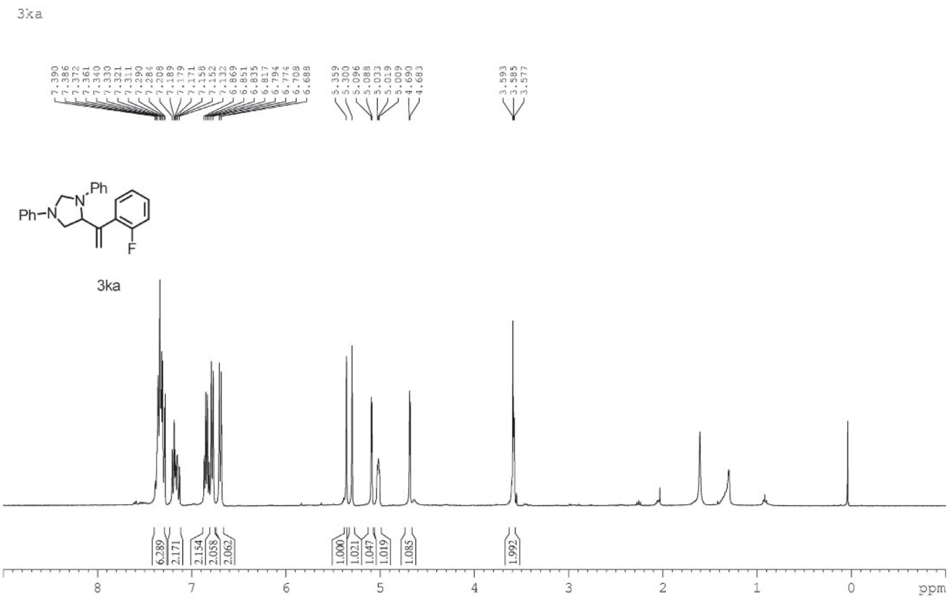
F
3ja
ppm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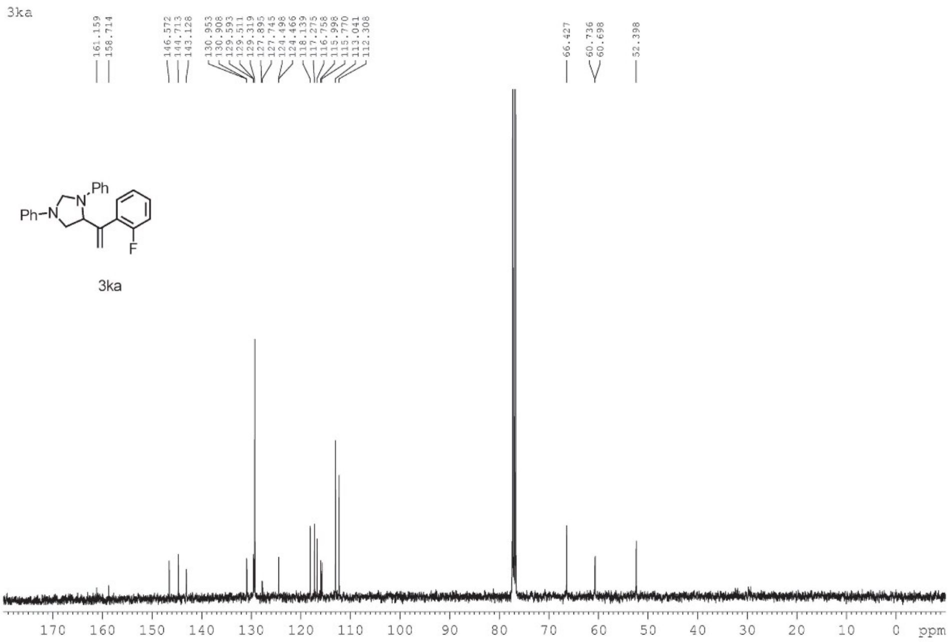
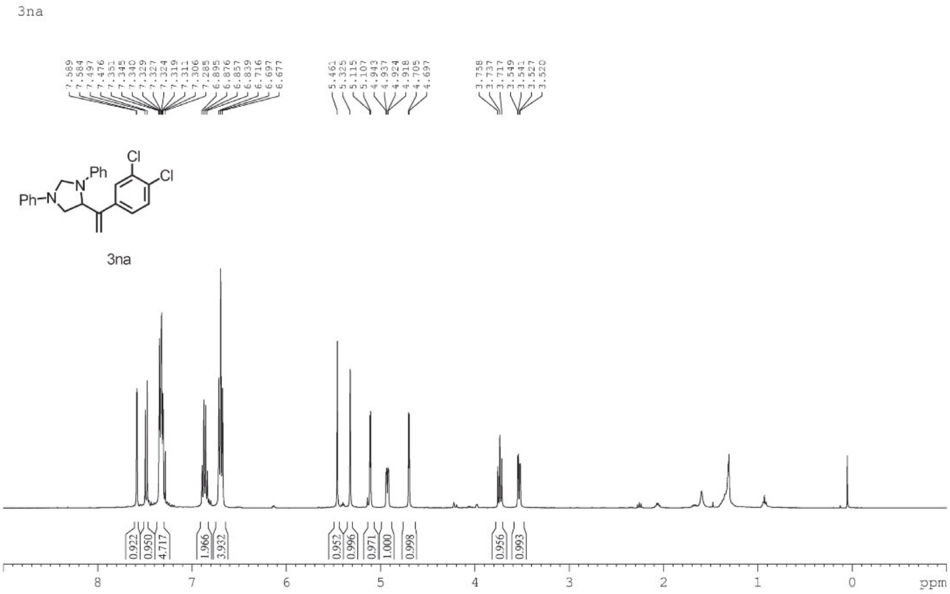
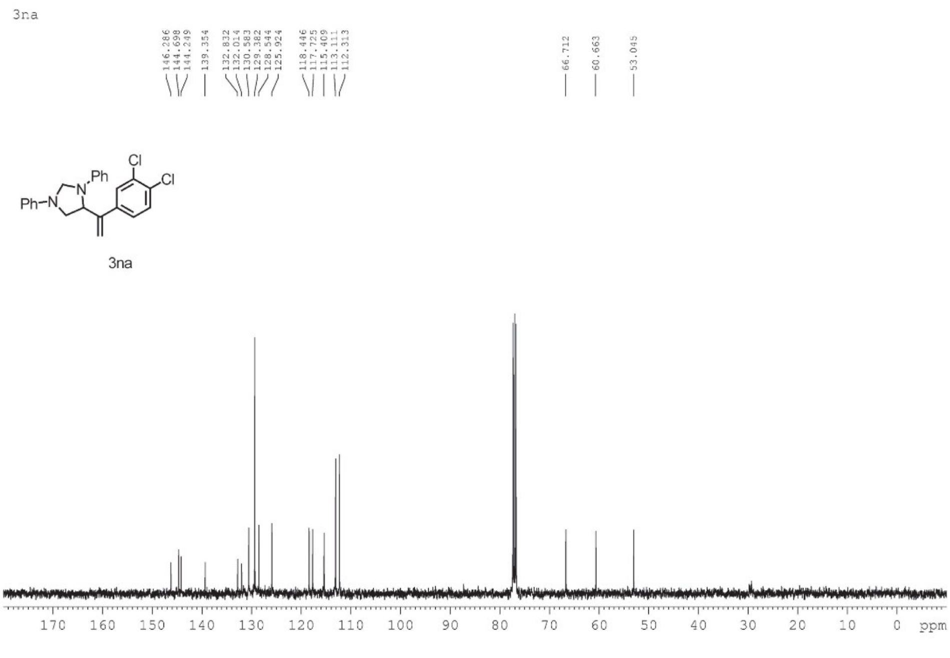
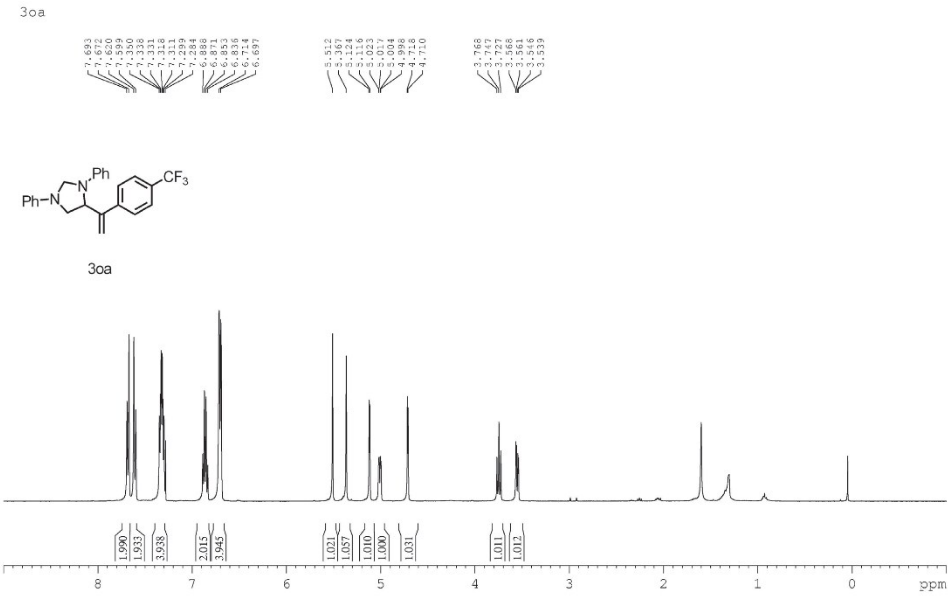
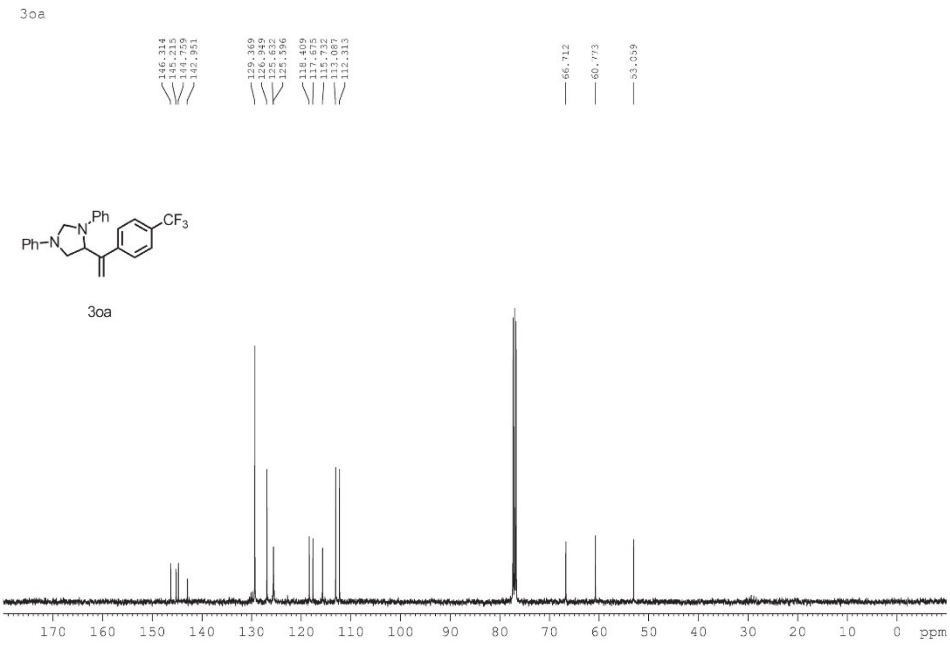
3.593 3.585 3.577
Ph
N
Ph
N
F
3ka
6.289 2.171 2.154 2.058 2.062 1.000 1.021 1.047 1.019 1.085 1.992
8 7 6 5 4 3 2 1 0 ppm

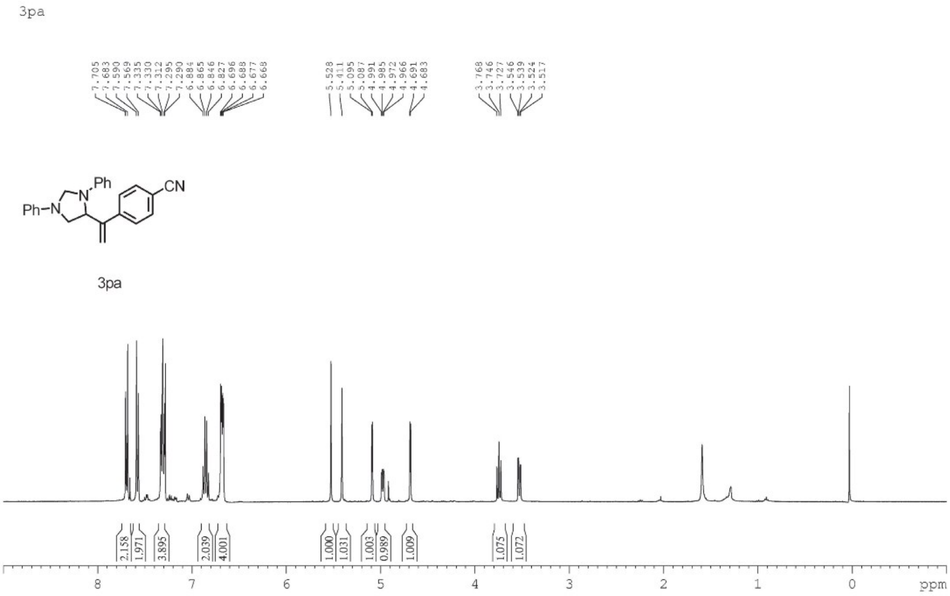

3ka
161.159 158.714
146.572 144.713 143.128
130.953 130.908 129.593 129.511 129.319 127.895 127.745 124.498 124.466 118.139 117.275 116.758 115.998 115.770 113.041 112.308
66.427
60.736 60.698
52.398
Ph
N
Ph
N
F
3ka
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

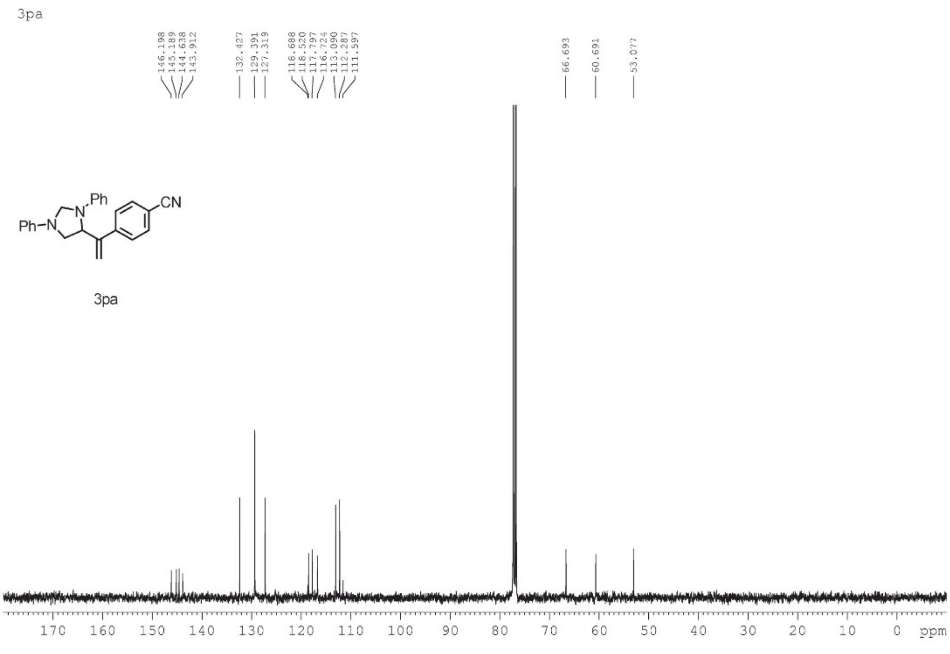

3na
7.589
7.584
7.497
7.476
7.351
7.345
7.340
7.329
7.327
7.324
7.319
7.311
7.306
7.285
6.895
6.876
6.857
6.839
6.716
6.697
6.677
5.461
5.325
5.115
5.107
4.943
4.937
4.924
4.918
4.705
4.697
3.758
3.737
3.717
3.549
3.541
3.527
3.520
Cl
Cl
Ph
N
Ph
N
3na
0.922
0.950
4.717
1.966
3.932
0.952
0.996
0.971
1.000
0.998
0.956
0.993
8
7
6
5
4
3
2
1
0
ppm

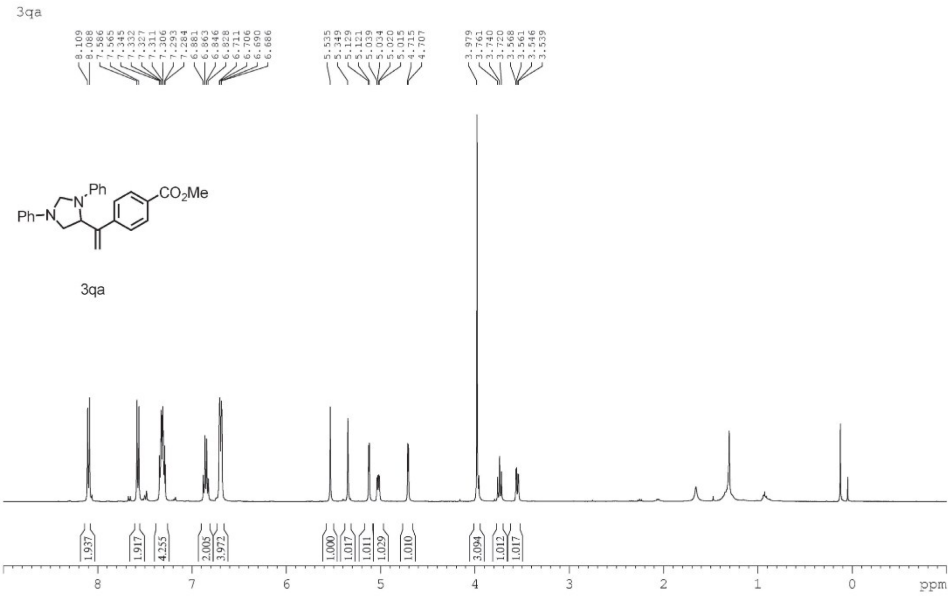

3na
146.286
144.698
144.249
139.354
132.832
132.014
130.583
129.382
128.544
125.924
118.446
117.725
115.409
113.111
112.313
66.712
60.663
53.045
Cl
Cl
Ph
N
Ph
N
3na
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

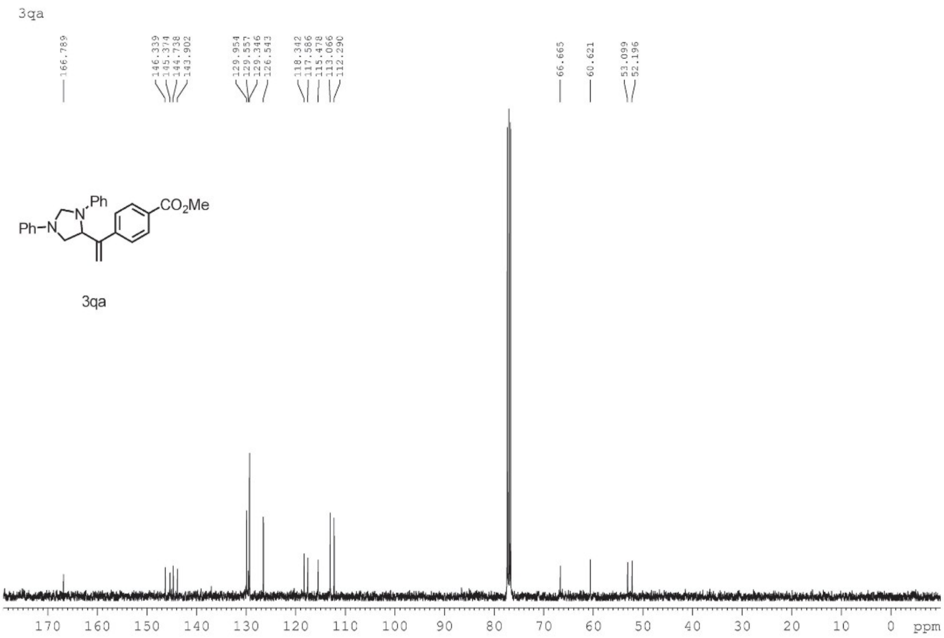

3oa
7.693 7.672 7.620 7.599 7.350 7.338 7.331 7.318 7.311 7.299 7.284 6.888 6.871 6.853 6.836 6.714 6.697
5.512 5.367 5.124 5.116 5.023 5.017 5.004 4.998 4.718 4.710
3.768 3.747 3.727 3.568 3.561 3.546 3.539
Ph
CF3
Ph–N
N
3oa
1.990 1.933 3.938 2.015 3.945 1.021 1.057 1.010 1.000 1.031 1.011 1.012
8 7 6 5 4 3 2 1 0 ppm

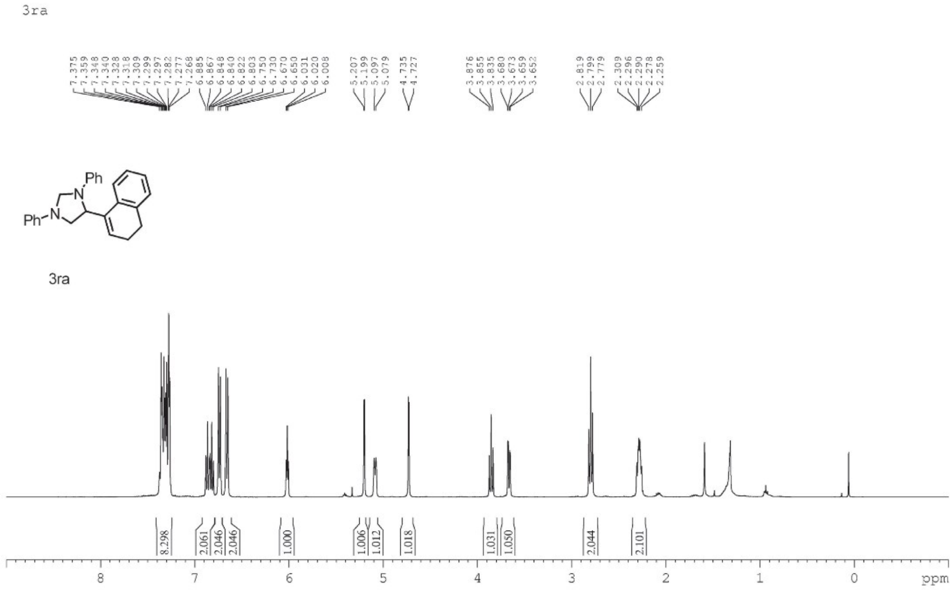

3oa
146.314 145.215 144.759 142.951
129.369 126.949 125.632 125.596
118.409 117.675 115.732 113.087 112.313
66.712
60.773
53.059
Ph
CF3
Ph–N
N
3oa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

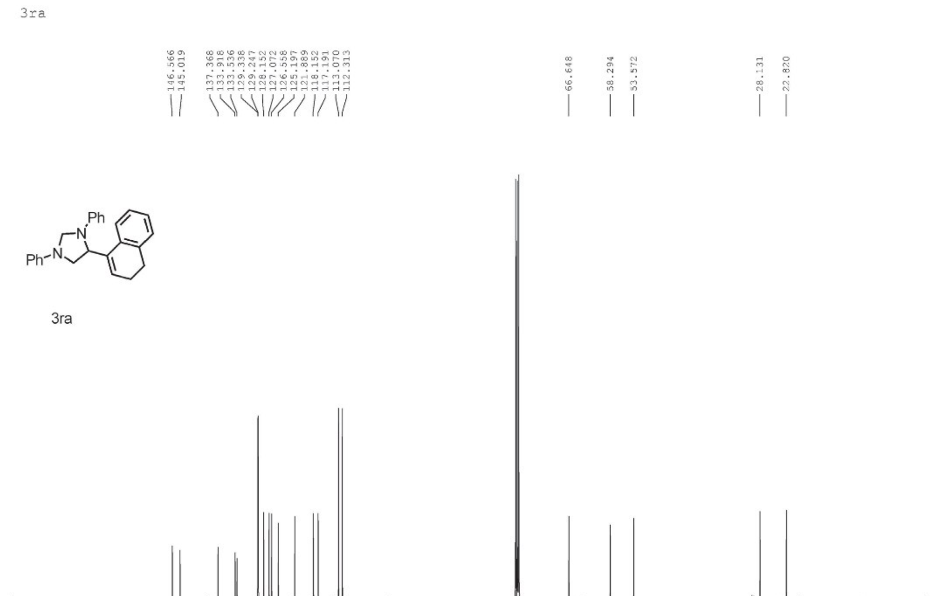

3pa
7.705
7.683
7.593
7.569
7.335
7.330
7.312
7.295
7.290
6.884
6.865
6.846
6.827
6.696
6.688
6.677
6.668
5.528
5.411
5.095
5.087
4.991
4.985
4.972
4.966
4.691
4.683
3.768
3.746
3.727
3.546
3.539
3.524
3.517
Ph
N
CN
Ph
N
3pa
2.158
1.971
3.895
2.039
4.001
1.000
1.031
1.003
0.989
1.009
1.075
1.072
8
7
6
5
4
3
2
1
0
ppm

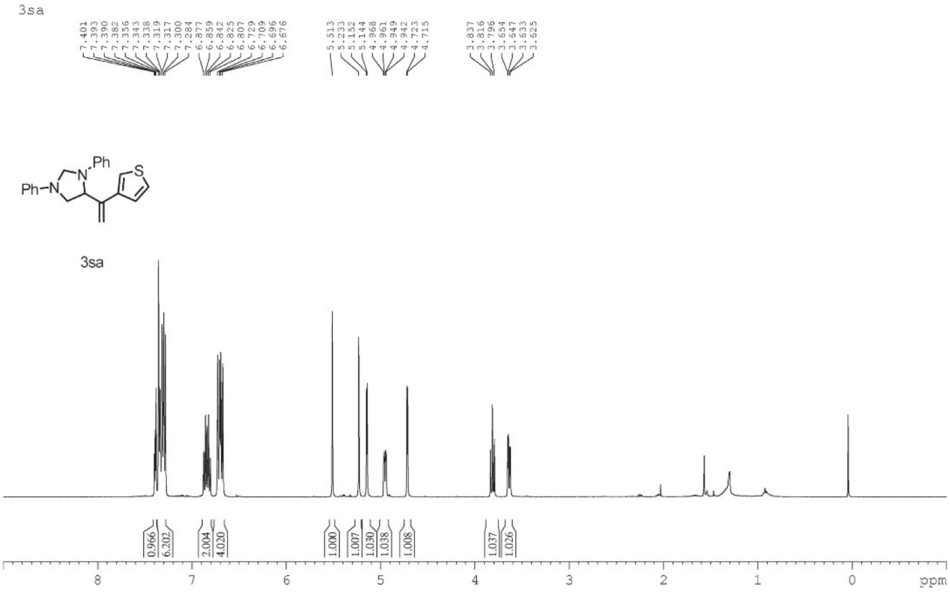

3pa
146.198
145.189
144.638
143.912
132.427
129.391
127.319
118.688
118.520
117.797
116.724
113.090
112.287
111.597
66.693
60.691
53.077
Ph
N
CN
Ph
N
3pa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

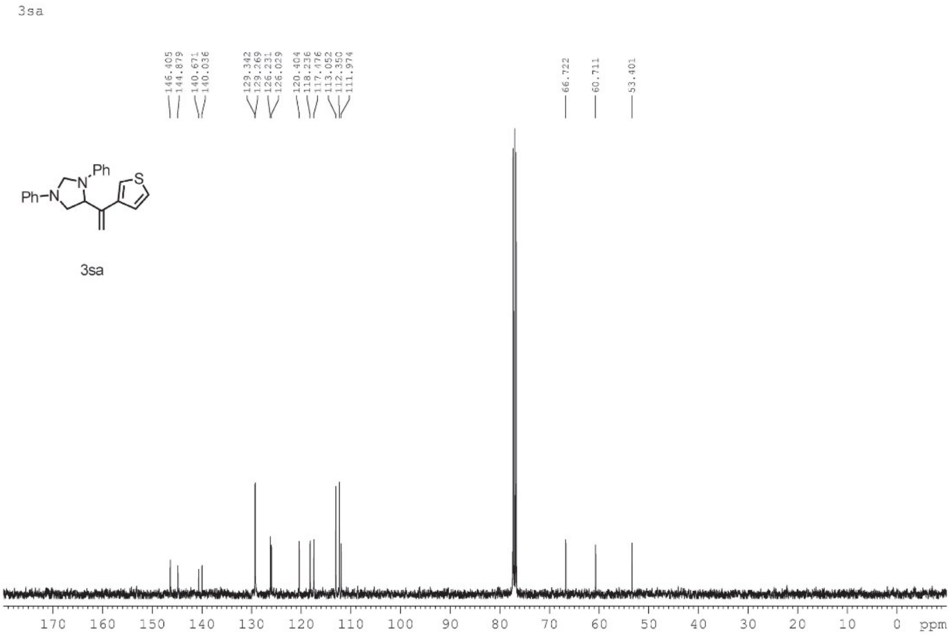

3qa
8.109
8.088
7.586
7.565
7.345
7.332
7.327
7.311
7.306
7.293
7.284
6.881
6.863
6.846
6.828
6.711
6.706
6.690
6.686
5.535
5.349
5.129
5.121
5.039
5.034
5.020
5.015
4.715
4.707
3.979
3.761
3.740
3.720
3.568
3.561
3.546
3.539
Ph
CO_2Me
Ph
N
N
3qa
1.937
1.917
4.255
2.005
3.972
1.000
1.017
1.011
1.029
1.010
3.094
1.012
1.017
8
7
6
5
4
3
2
1
0
ppm

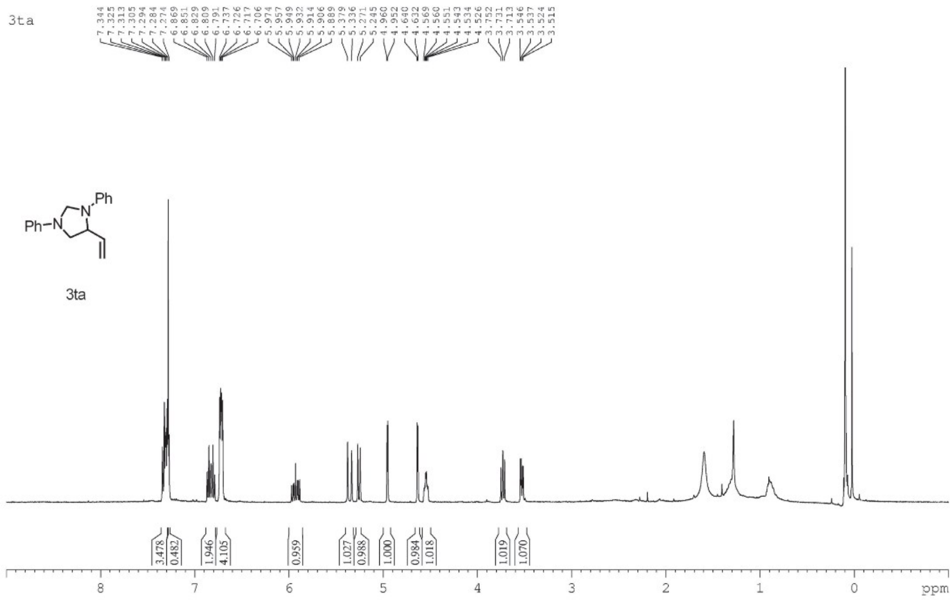

3qa
166.789
146.339
145.374
144.738
143.902
129.954
129.557
129.346
126.543
118.342
117.586
115.478
113.066
112.290
66.665
60.621
53.099
52.196
Ph
CO_2Me
Ph
N
N
3qa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

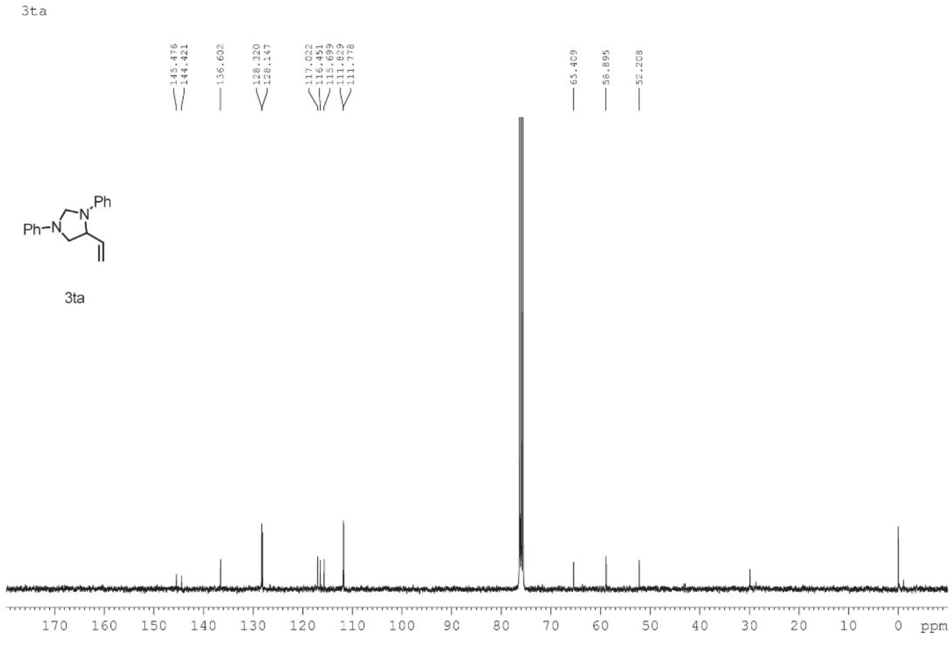

3ra
Ph
N
Ph
N
3ra
8.298
2.061
2.046
2.046
1.000
1.006
1.012
1.018
1.031
1.050
2.044
2.101
ppm

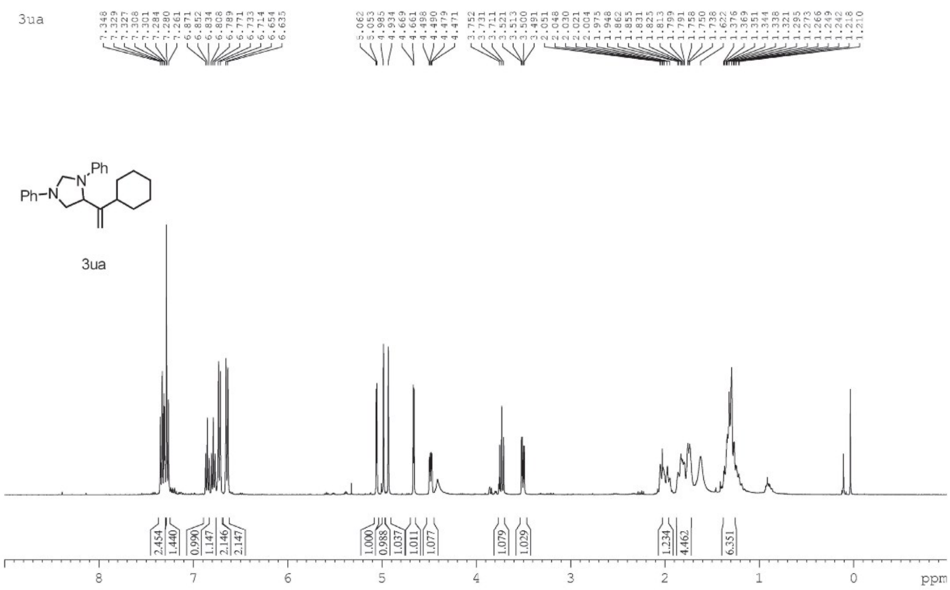

3ra
146.566
145.019
137.368
133.918
133.536
129.338
129.247
128.152
127.072
126.558
125.197
121.889
118.152
117.191
113.070
112.313
66.648
58.294
53.572
28.131
22.820
Ph
N
Ph
N
3ra
ppm

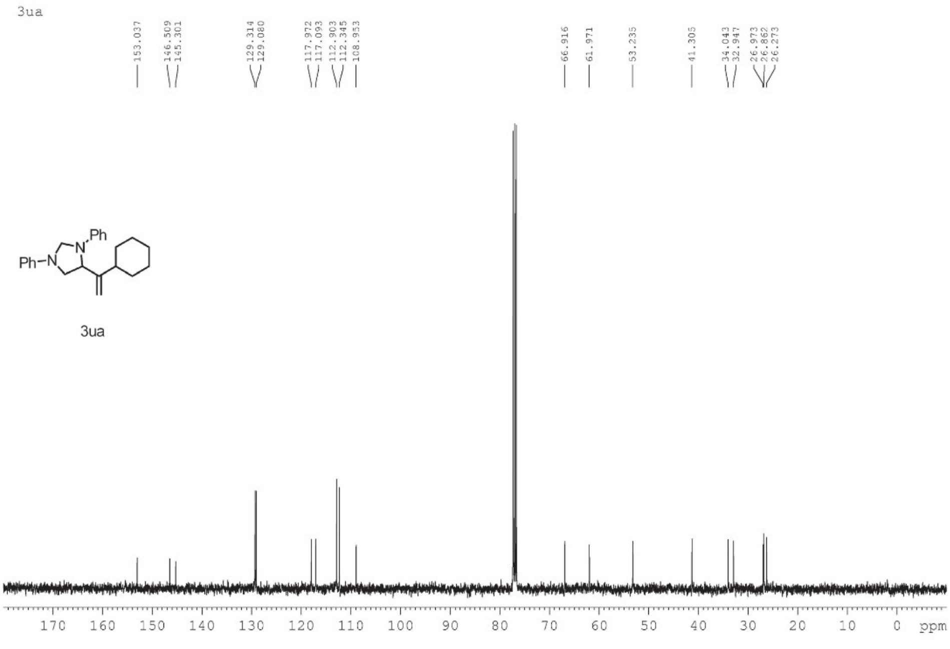

3sa
7.401
7.393
7.390
7.382
7.356
7.343
7.338
7.319
7.317
7.300
7.284
6.877
6.859
6.842
6.825
6.807
6.729
6.709
6.696
6.676
5.513
5.233
5.152
5.144
4.968
4.961
4.949
4.942
4.723
4.715
3.837
3.816
3.796
3.654
3.647
3.633
3.625
Ph
N
Ph
N
S
3sa
0.966
6.202
2.004
4.020
1.000
1.007
1.030
1.038
1.008
1.037
1.026
8
7
6
5
4
3
2
1
0
ppm

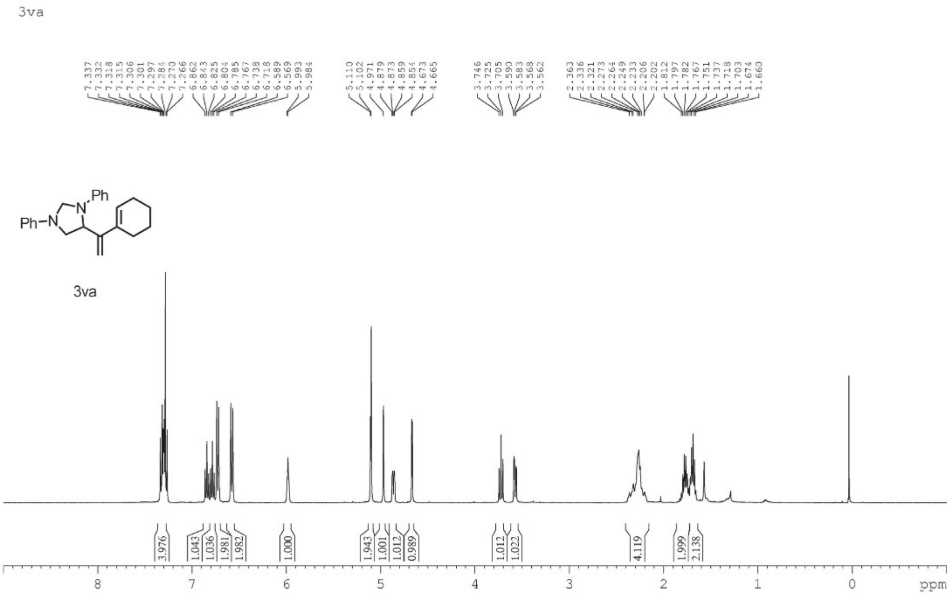

3sa
146.405
144.879
140.671
140.036
129.342
129.269
126.231
126.029
120.404
118.236
117.476
113.052
112.350
111.974
66.722
60.711
53.401
Ph
N
Ph
N
S
3sa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

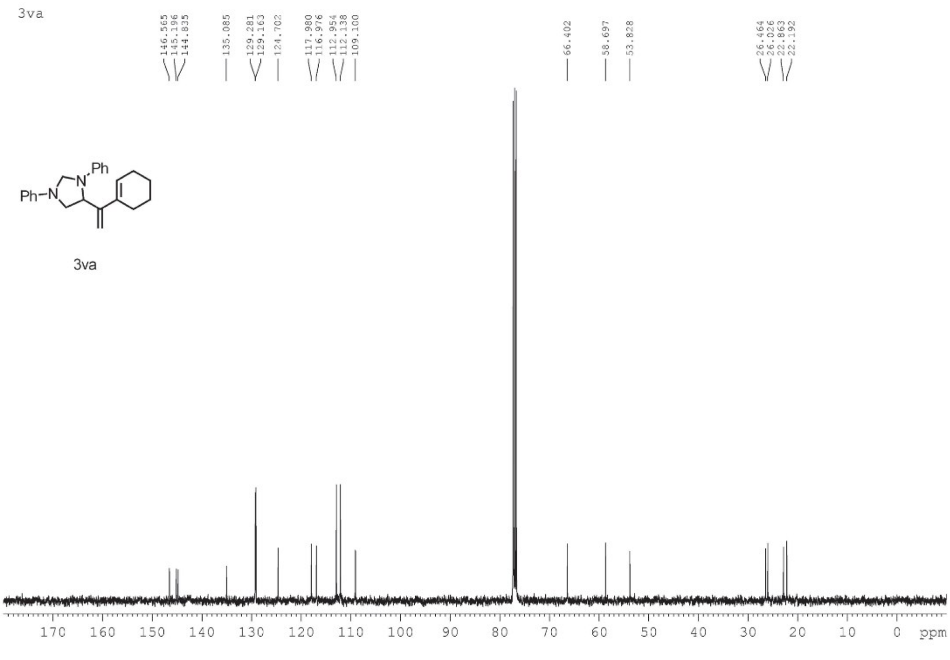

3ta
7.344 7.325 7.313 7.305 7.294 7.284 7.274 6.869 6.851 6.829 6.809 6.791 6.737 6.726 6.717 6.706 5.974 5.957 5.949 5.932 5.914 5.906 5.889 5.379 5.336 5.271 5.245 4.960 4.952 4.640 4.632 4.569 4.560 4.551 4.543 4.534 4.526 3.752 3.731 3.713 3.546 3.537 3.524 3.515
Ph
Ph
N
N
3ta
3.478 0.482 1.946 4.105 0.959 1.027 0.988 1.000 0.984 1.018 1.019 1.070
8 7 6 5 4 3 2 1 0 ppm


3ta
145.476 144.421 136.602 128.320 128.147 117.022 116.451 115.899 111.829 111.778 65.409 58.895 52.208
Ph
Ph
N
N
3ta
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

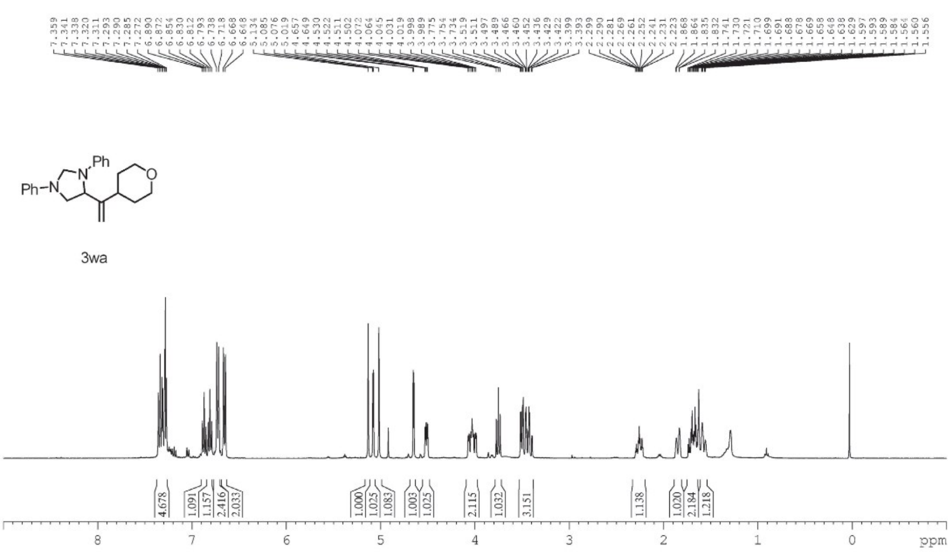

3ua
3ua
Ph
Ph
N
N
8
7
6
5
4
3
2
1
0
ppm


3ua
153.037
146.509
145.301
129.314
129.080
117.972
117.093
112.903
112.345
108.953
66.916
61.971
53.235
41.305
34.043
32.947
26.973
26.862
26.273
3ua
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3va
7.337 7.332 7.318 7.315 7.306 7.301 7.297 7.286 7.270 7.266 6.862 6.843 6.825 6.804 6.785 6.767 6.738 6.718 6.589 6.569 5.993 5.984
5.110 5.102 4.971 4.879 4.873 4.859 4.854 4.673 4.665
3.746 3.725 3.705 3.590 3.583 3.568 3.562
2.363 2.336 2.321 2.273 2.264 2.249 2.233 2.206 2.202 1.812 1.797 1.782 1.767 1.751 1.737 1.718 1.703 1.674 1.660
Ph
Ph
N
N
3va
3.976 1.043 1.036 1.981 1.982 1.000 1.943 1.001 1.012 0.989 1.012 1.022 4.119 1.999 2.138
8 7 6 5 4 3 2 1 0 ppm


3va
146.565 145.196 144.835 135.085 129.281 129.163 124.702 117.980 116.976 112.954 112.138 109.100
66.402 58.697 53.828
26.464 26.026 22.863 22.192
Ph
Ph
N
N
3va
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3wa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7.341
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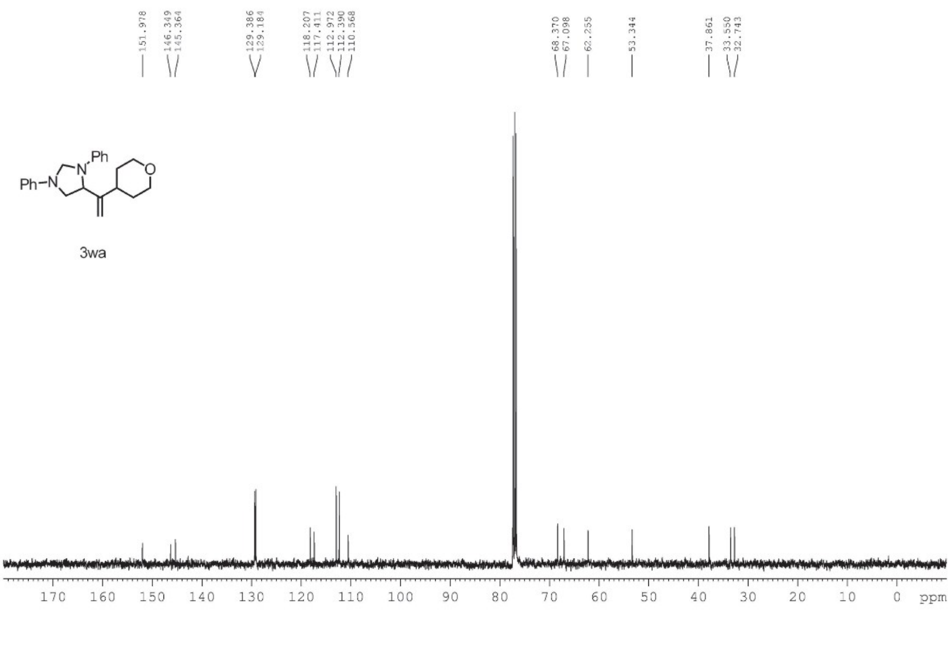
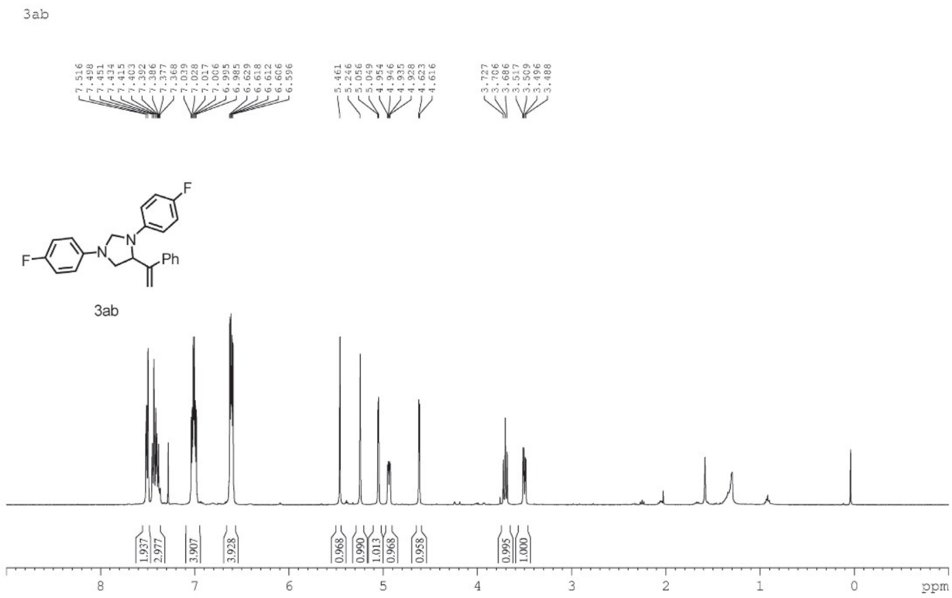
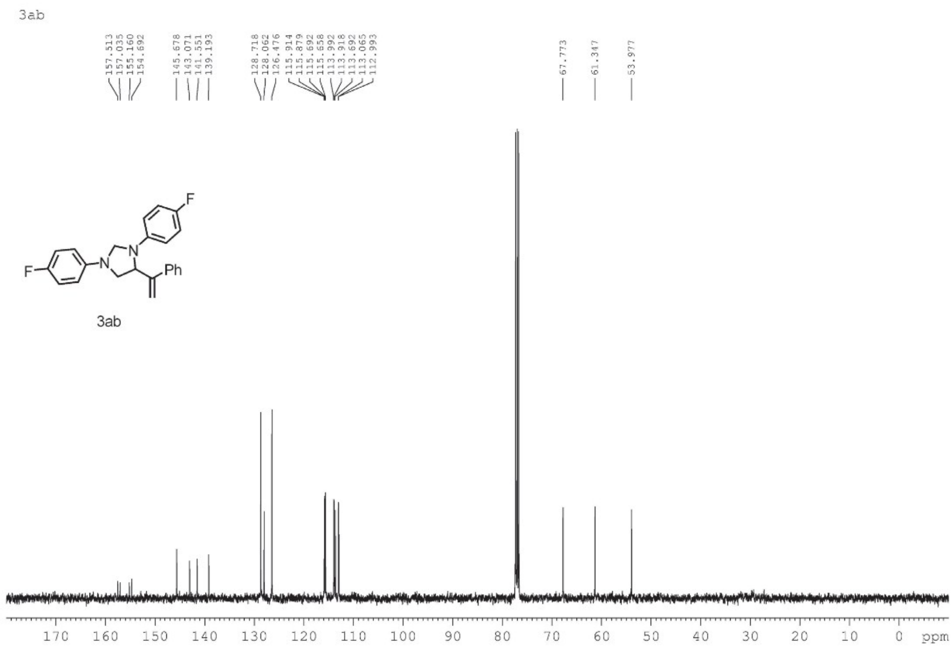
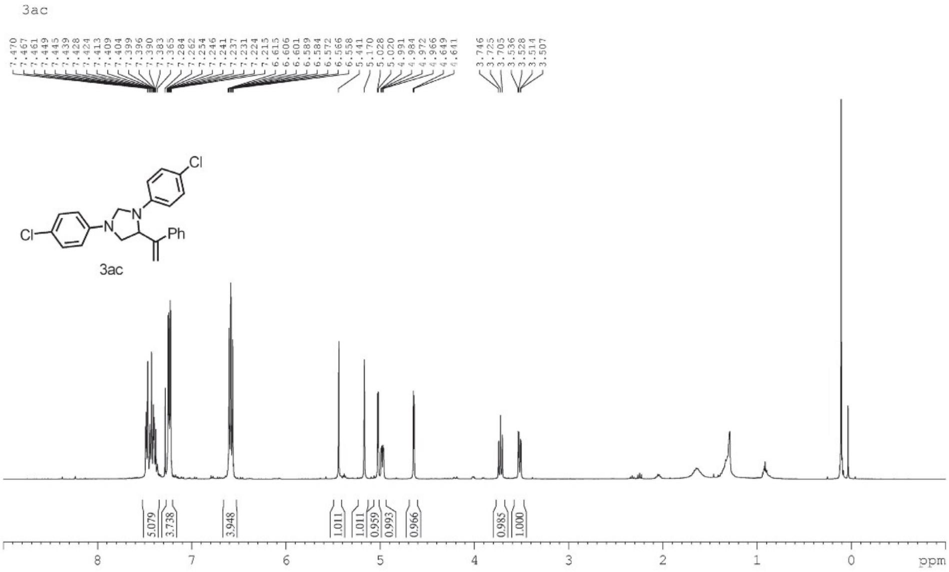
7.320
7.311
7.293
7.290
7.285
7.272
6.890
6.872
6.854
6.830
6.812
6.793
6.738
6.718
6.668
6.648
5.134
5.085
5.076
5.019
4.657
4.649
4.530
4.522
4.511
4.502
4.072
4.064
4.045
4.031
4.019
3.998
3.989
3.775
3.754
3.734
3.519
3.511
3.497
3.489
3.466
3.460
3.452
3.436
3.429
3.422
3.399
3.393
2.299
2.290
2.281
2.269
2.261
2.252
2.241
2.231
2.223
1.868
1.864
1.835
1.832
1.741
1.730
1.721
1.710
1.699
1.691
1.688
1.678
1.669
1.658
1.648
1.638
1.629
1.597
1.593
1.589
1.584
1.564
1.560
1.556
Ph
Ph–N
N
O
3wa
4.678
1.091
1.157
2.416
2.033
1.000
1.025
1.083
1.003
1.025
2.115
1.032
3.151
1.138
1.020
2.184
1.218
8
7
6
5
4
3
2
1
0
ppm

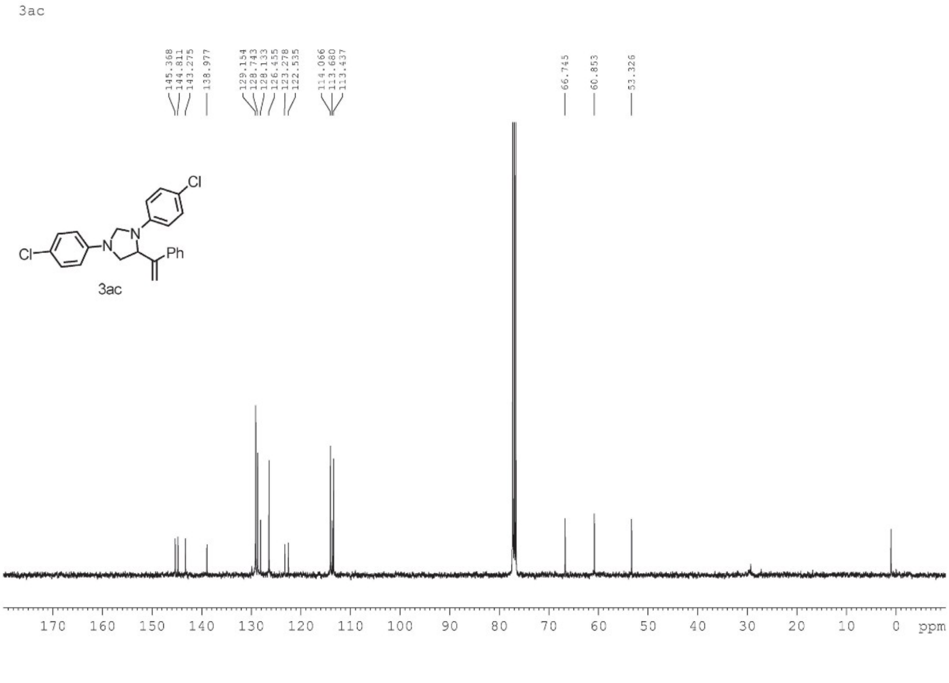
3wa


151.978
146.349
145.364
129.386
129.184
118.207
117.411
112.972
112.390
110.568
68.370
67.098
62.255
53.344
37.861
33.550
32.743
Ph
Ph–N
N
O
3wa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

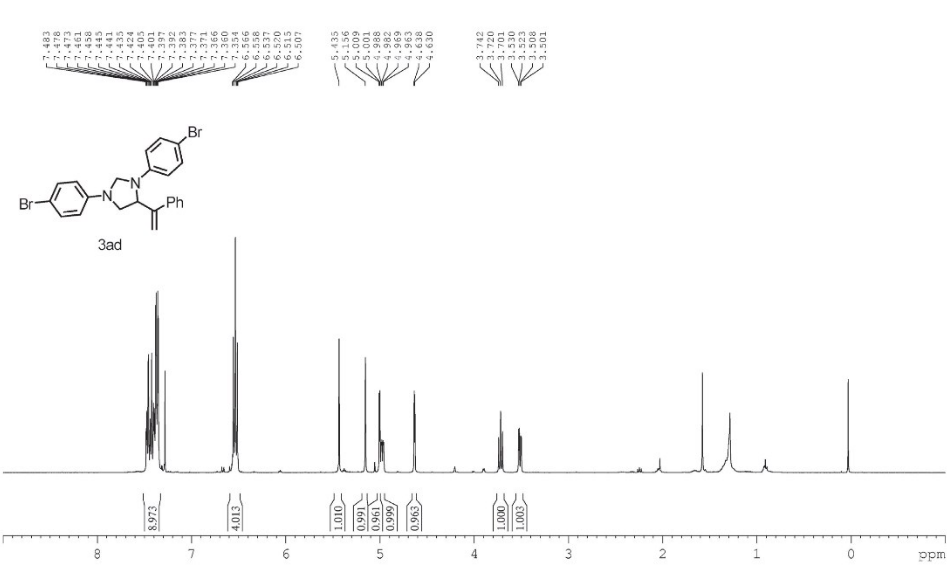

3ab
7.516
7.498
7.451
7.434
7.415
7.403
7.392
7.386
7.377
7.368
7.039
7.028
7.017
7.006
6.995
6.985
6.629
6.618
6.612
6.606
6.596
5.461
5.246
5.056
5.049
4.954
4.946
4.935
4.928
4.623
4.616
3.727
3.706
3.686
3.517
3.509
3.496
3.488
F
N
N
F
Ph
3ab
1.937
2.977
3.907
3.928
0.968
0.990
1.013
0.968
0.958
0.995
1.000
8
7
6
5
4
3
2
1
0
ppm


3ab
157.513
157.035
155.160
154.892
145.678
143.071
141.551
139.193
128.718
128.062
126.476
115.914
115.879
115.692
115.658
113.992
113.918
113.092
113.065
112.993
67.773
61.347
53.977
F
N
N
F
Ph
3ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

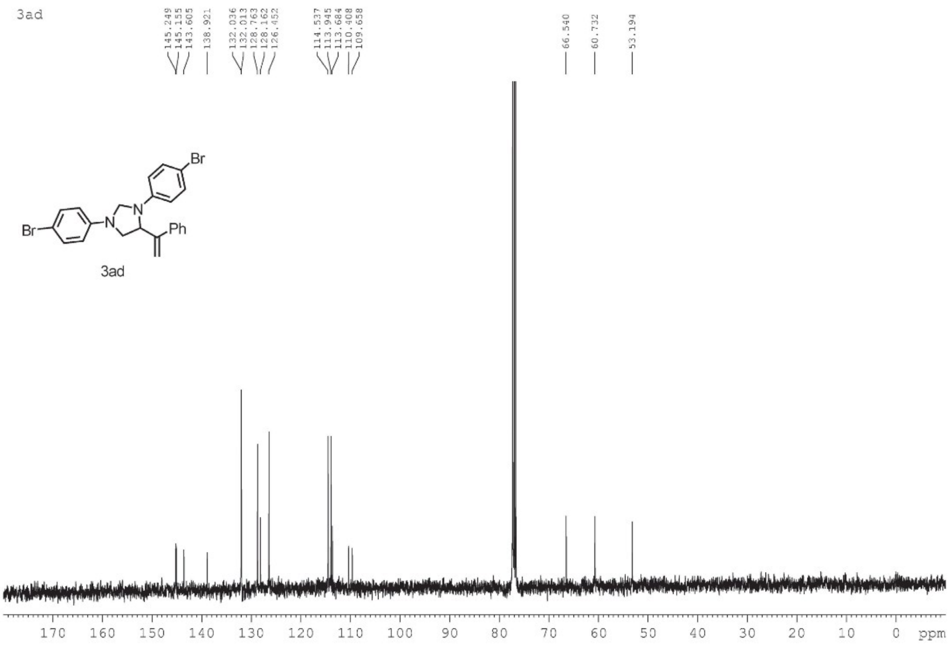

3ac
7.470 7.461 7.449 7.445 7.439 7.428 7.424 7.413 7.409 7.404 7.399 7.396 7.390 7.383 7.365 7.284 7.262 7.254 7.246 7.241 7.237 7.231 7.224 7.215 6.615 6.606 6.601 6.589 6.584 6.572 6.566 6.558 5.441 5.170 5.028 5.020 4.991 4.984 4.972 4.966 4.649 4.611 3.746 3.725 3.705 3.536 3.528 3.514 3.507
Cl
N
N
Ph
Cl
3ac
5.079 3.738 3.948 1.011 1.011 0.959 0.993 0.966 0.985 1.000
ppm

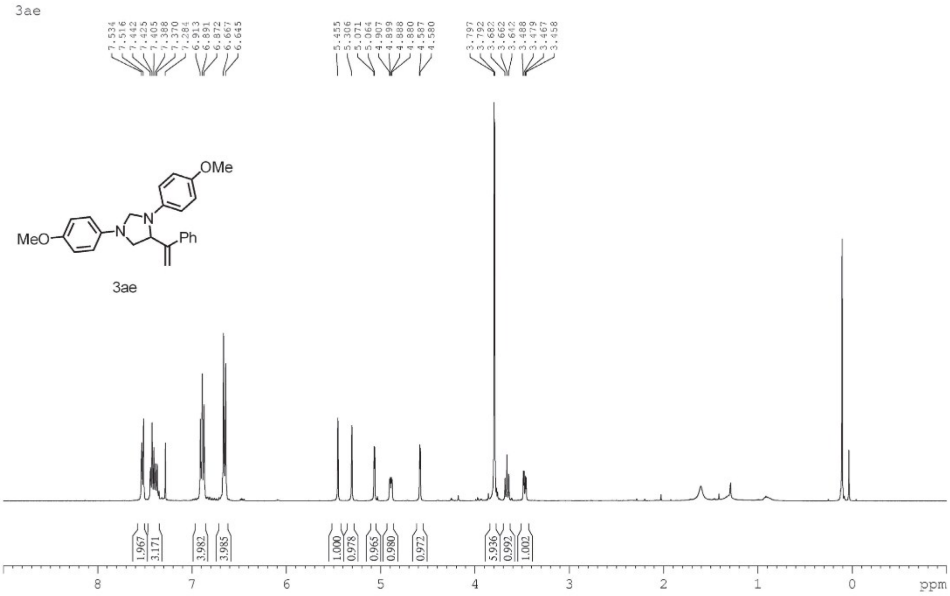

3ac
145.368 144.811 143.275 138.977 129.154 128.743 128.133 126.455 123.278 122.535 114.066 113.680 113.437 66.745 60.853 53.326
Cl
N
N
Ph
Cl
3ac
ppm

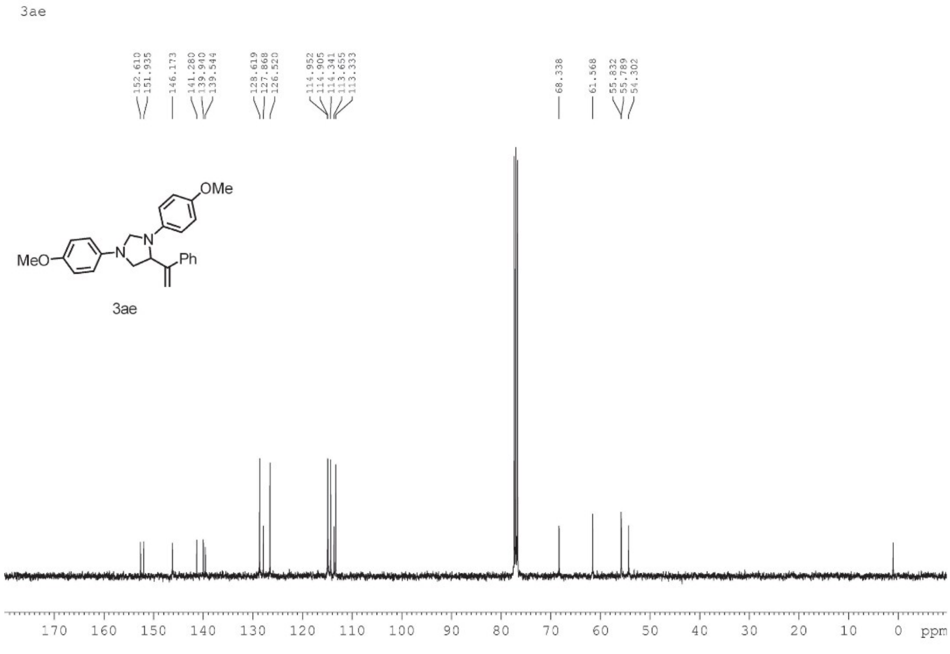
3ad

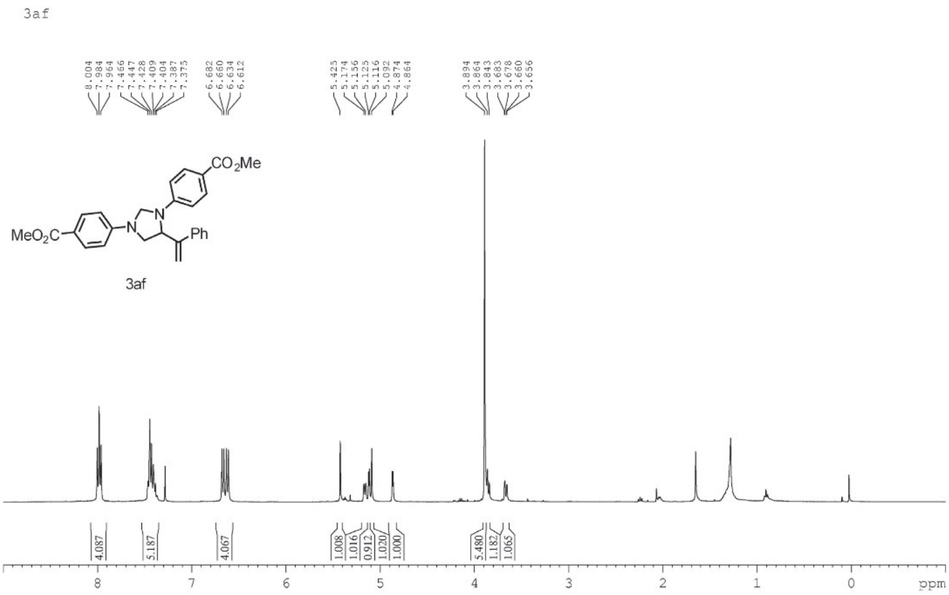


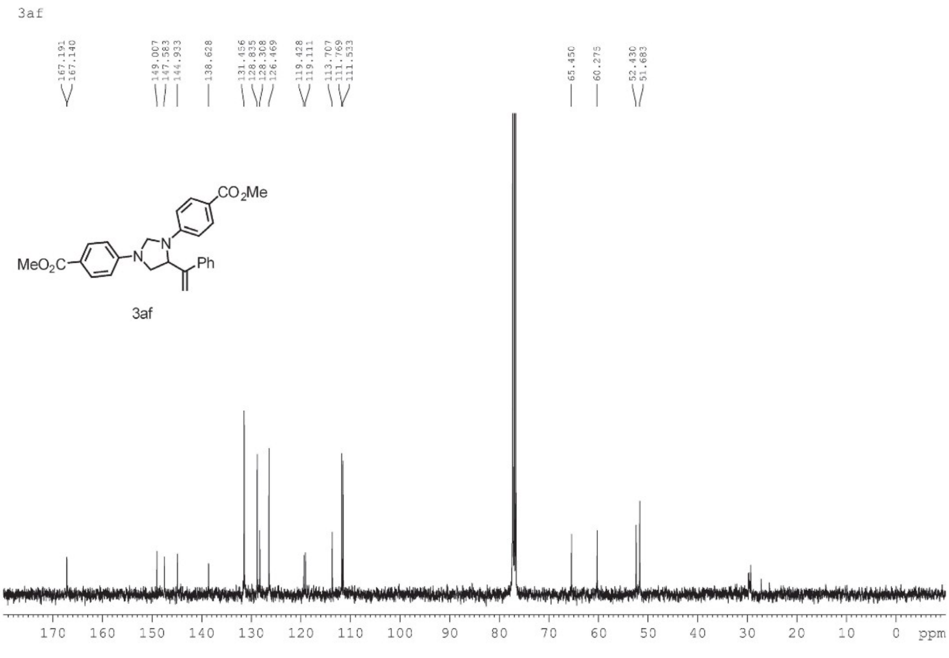
3ad




3ae
7.534 7.516 7.442 7.425 7.405 7.388 7.370 7.284 6.913 6.891 6.872 6.667 6.645
5.455 5.306 5.071 5.064 4.907 4.899 4.888 4.880 4.587 4.580
3.797 3.792 3.682 3.662 3.642 3.488 3.479 3.467 3.458
OMe
MeO
N
N
Ph
3ae
1.967 3.171 3.982 3.985 1.000 0.978 0.965 0.980 0.972 5.936 0.992 1.002
8 7 6 5 4 3 2 1 0 ppm

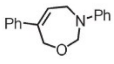

3ae
152.610 151.935 146.173 141.280 139.940 139.544 128.619 127.868 126.520 114.952 114.905 114.341 113.655 113.333 68.338 61.568 55.832 55.789 54.302
OMe
MeO
N
N
Ph
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3af
CO2Me
MeO2C
N
N
Ph
3af
ppm

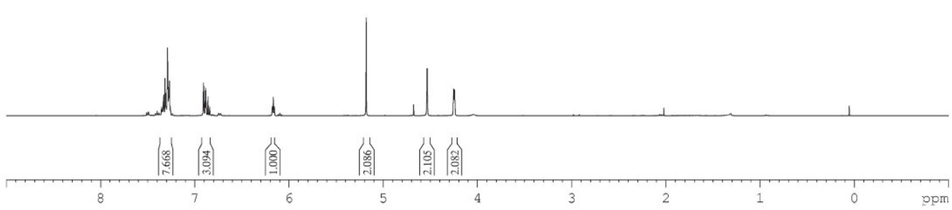

3af
CO2Me
MeO2C
N
N
Ph
3af
ppm

-9007-0096-p2 CDCl3

7.356 7.352 7.338 7.337 7.334 7.330 7.317 7.309 7.304 7.294 7.291 7.284 7.279 7.277 7.275 7.271 7.269 7.261 6.910 6.908 6.903 6.891 6.888 6.886 6.882 6.879 6.863 6.861 6.845 6.843 6.179 6.171 6.168 6.166 6.157 5.182 4.537 4.534 4.254 4.244

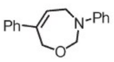


4aa



4aa

147.940 141.598 140.565 129.253 128.993 127.802 127.338 126.192 118.784 114.381 82.930 69.447 47.407



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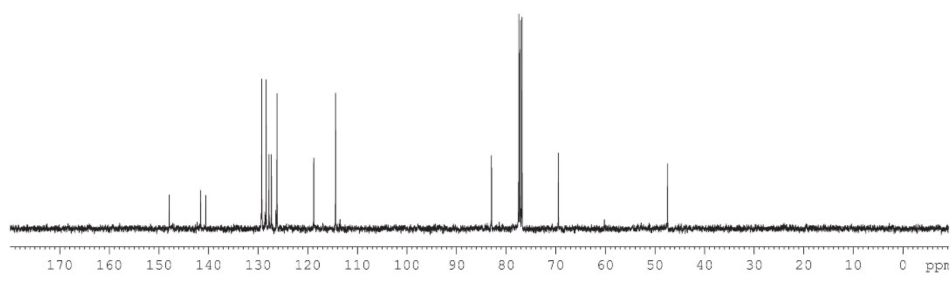
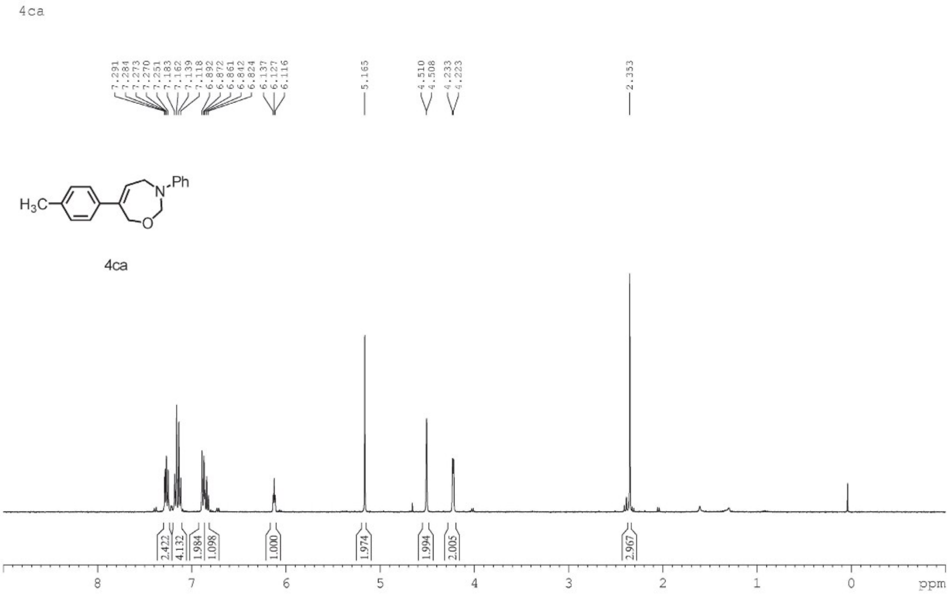
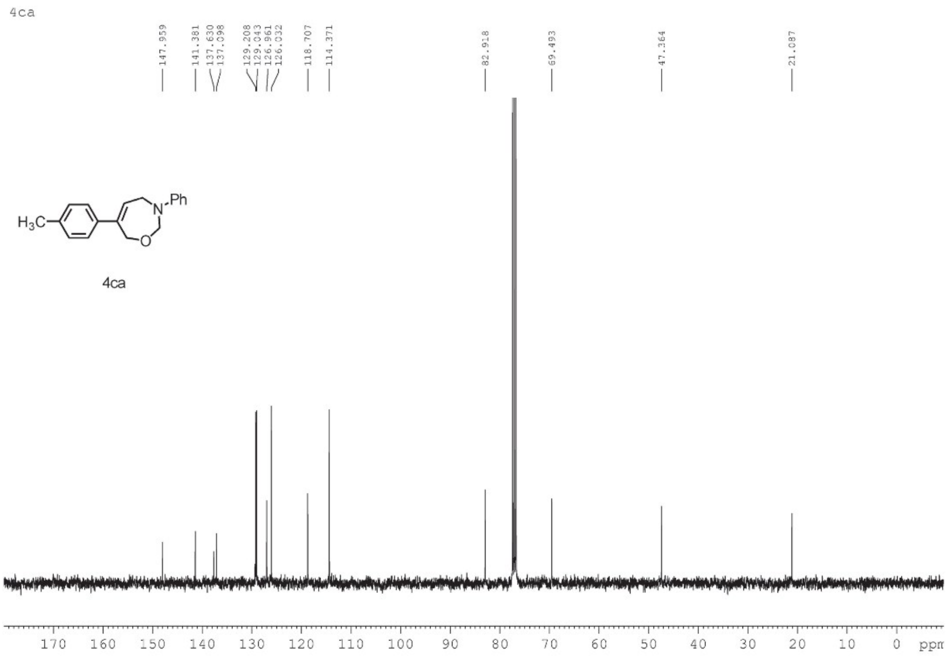
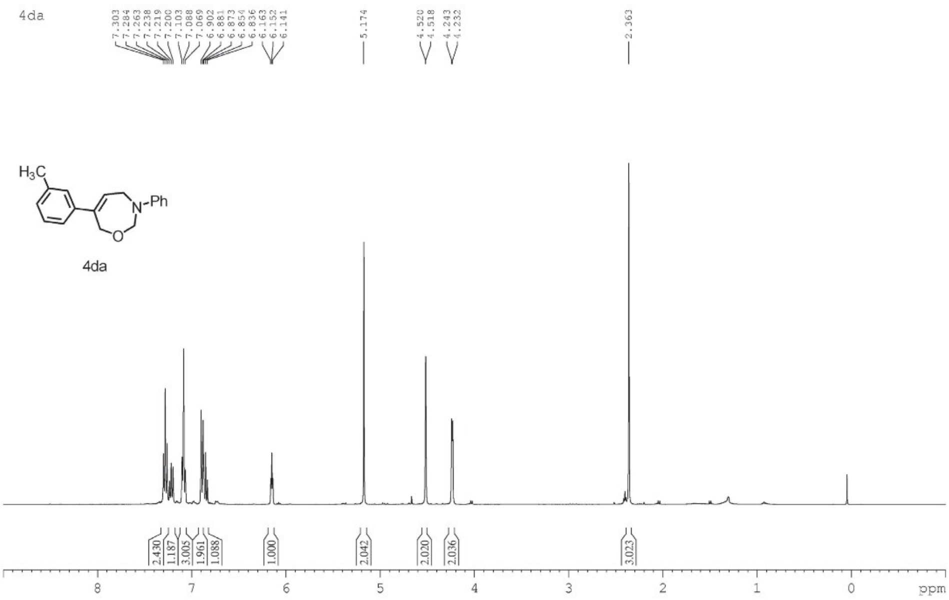
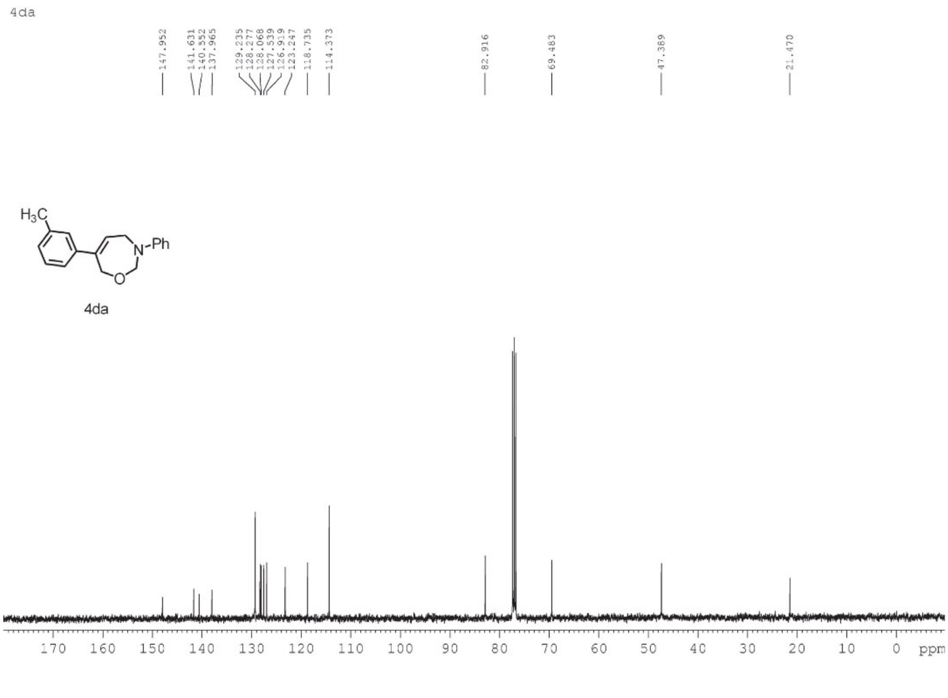



4ca
7.291
7.284
7.273
7.270
7.251
7.183
7.162
7.139
7.118
6.892
6.872
6.861
6.842
6.824
6.137
6.127
6.116
5.165
4.510
4.508
4.233
4.223
2.353
H3C
N
Ph
O
4ca
2.422
4.132
1.984
1.098
1.000
1.974
1.994
2.005
2.967
8
7
6
5
4
3
2
1
0
ppm


4ca
147.959
141.381
137.630
137.398
129.208
129.043
126.961
126.032
118.707
114.371
82.918
69.493
47.364
21.087
H3C
N
Ph
O
4ca
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


4da
7.303
7.284
7.263
7.238
7.219
7.200
7.103
7.088
7.069
6.902
6.881
6.873
6.854
6.836
6.163
6.152
6.141
5.174
4.520
4.518
4.243
4.232
2.363
H_3C
N
Ph
O
4da
2.430
1.187
3.005
1.961
1.088
1.000
2.042
2.020
2.036
3.023
8
7
6
5
4
3
2
1
0
ppm


4da
147.952
141.631
140.552
137.965
129.235
128.277
128.068
127.539
126.939
123.247
118.735
114.373
82.916
69.483
47.389
21.470
H_3C
N
Ph
O
4da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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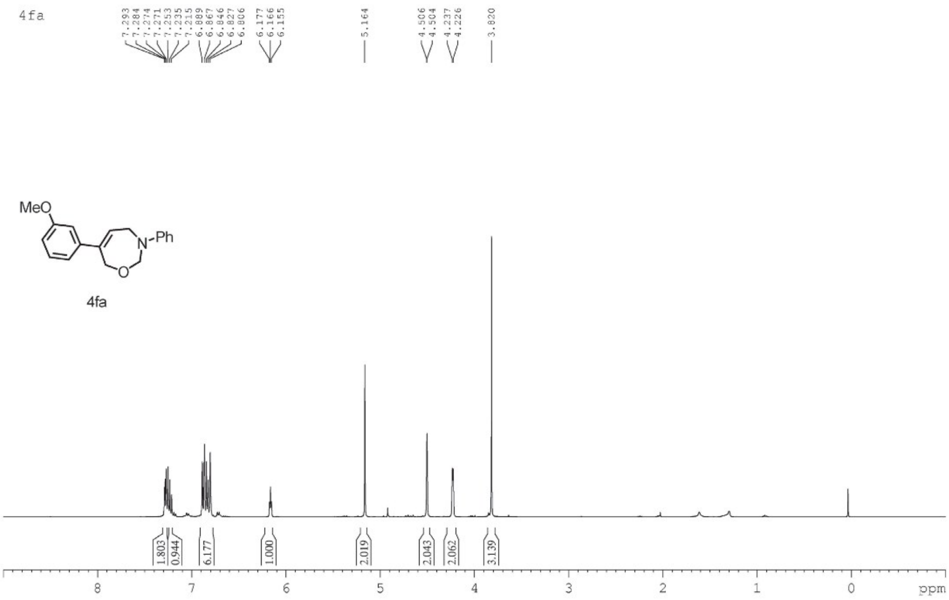
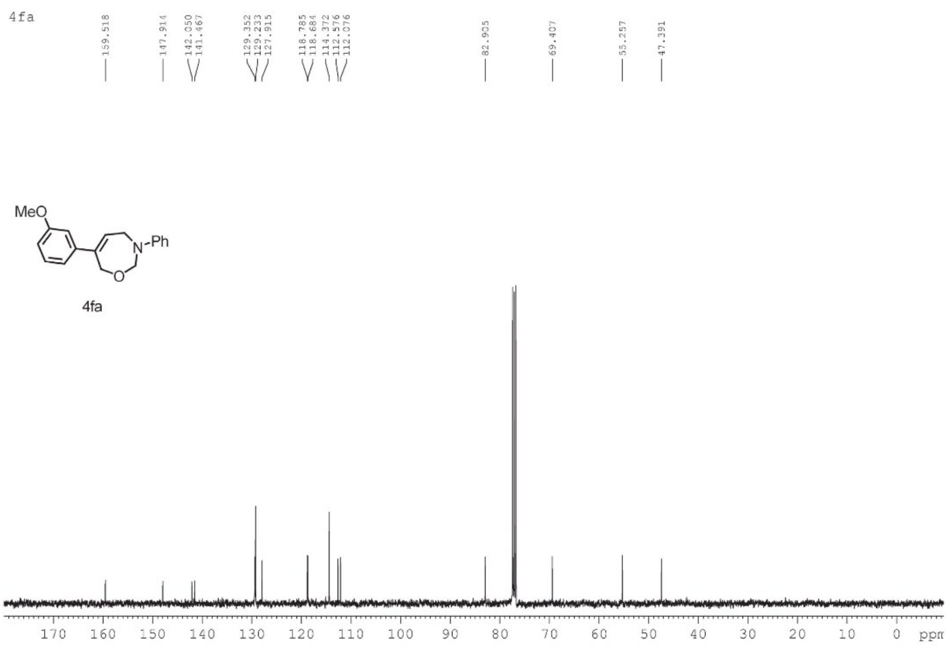
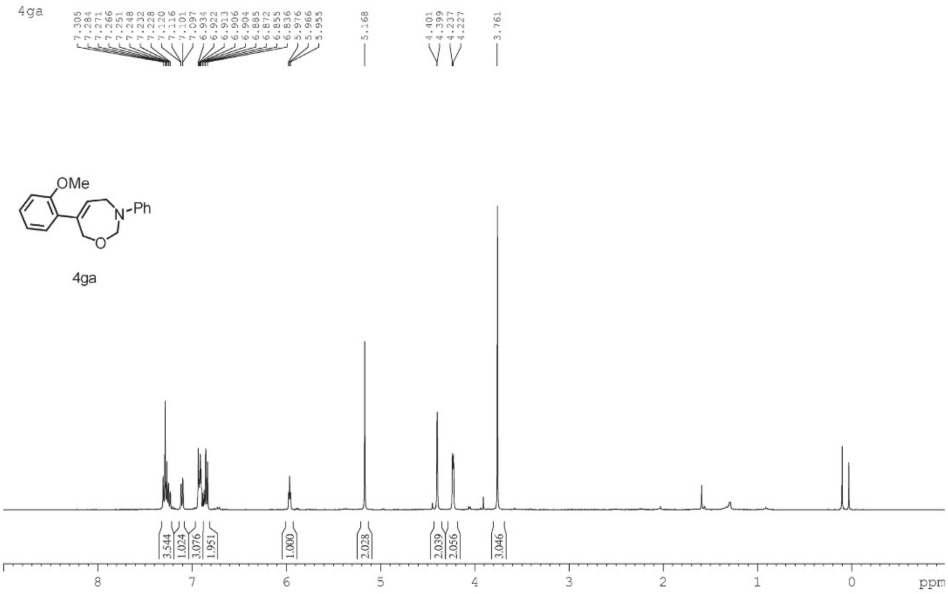
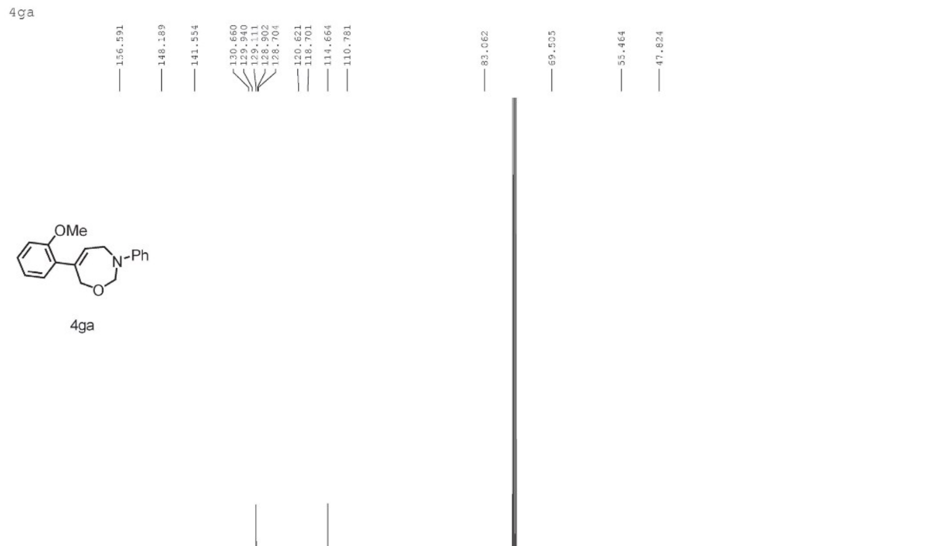
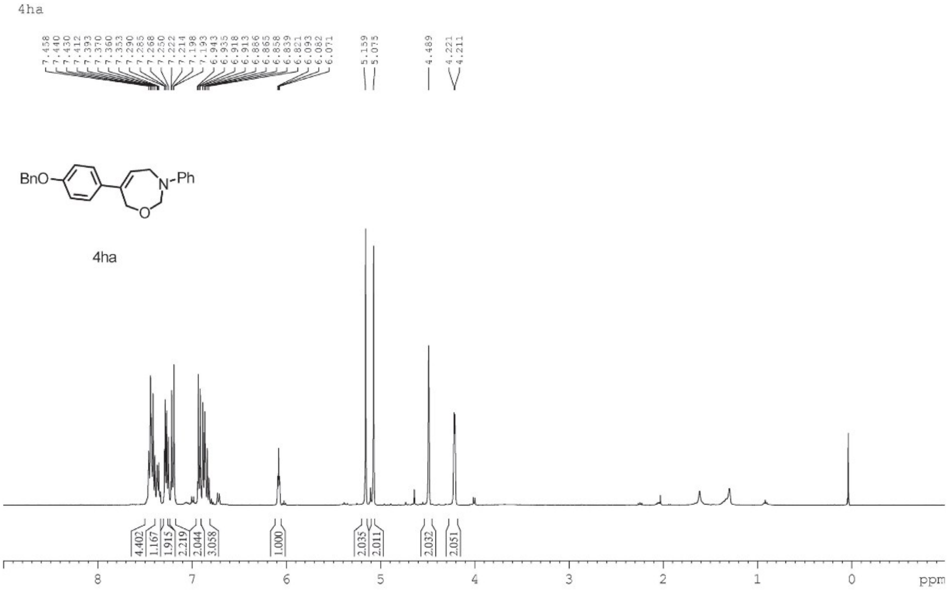
ppm

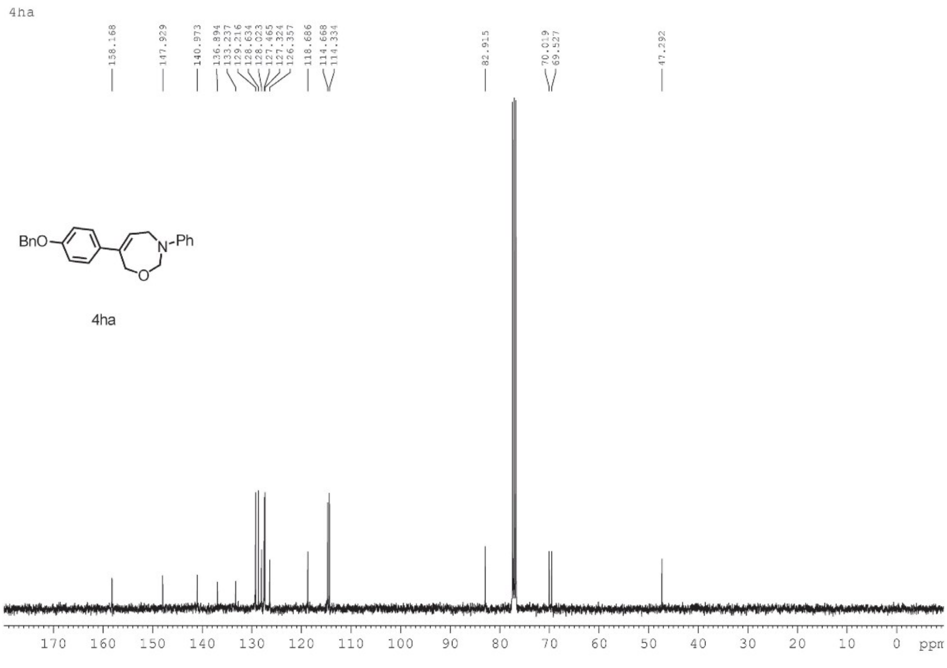

4fa
7.293
7.284
7.274
7.271
7.253
7.235
7.215
6.889
6.867
6.846
6.827
6.806
6.177
6.166
6.155
5.164
4.506
4.504
4.237
4.226
3.820
MeO
N
Ph
O
4fa
1.803
0.944
6.177
1.000
2.019
2.043
2.062
3.139
8
7
6
5
4
3
2
1
0
ppm

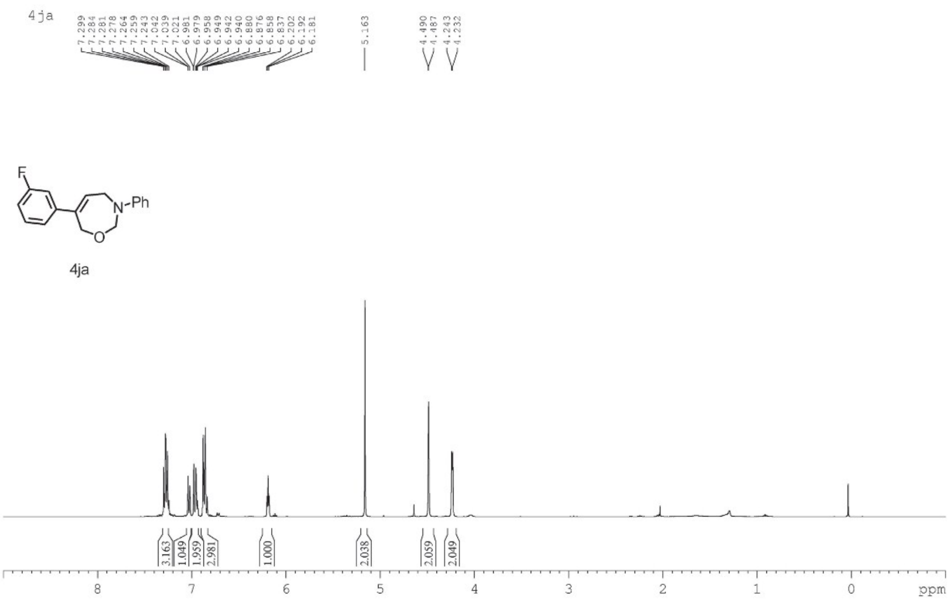

4fa
159.518
147.914
142.050
141.467
129.352
129.233
127.915
118.785
118.684
114.372
112.576
112.076
82.925
69.407
55.257
47.391
MeO
N
Ph
O
4fa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

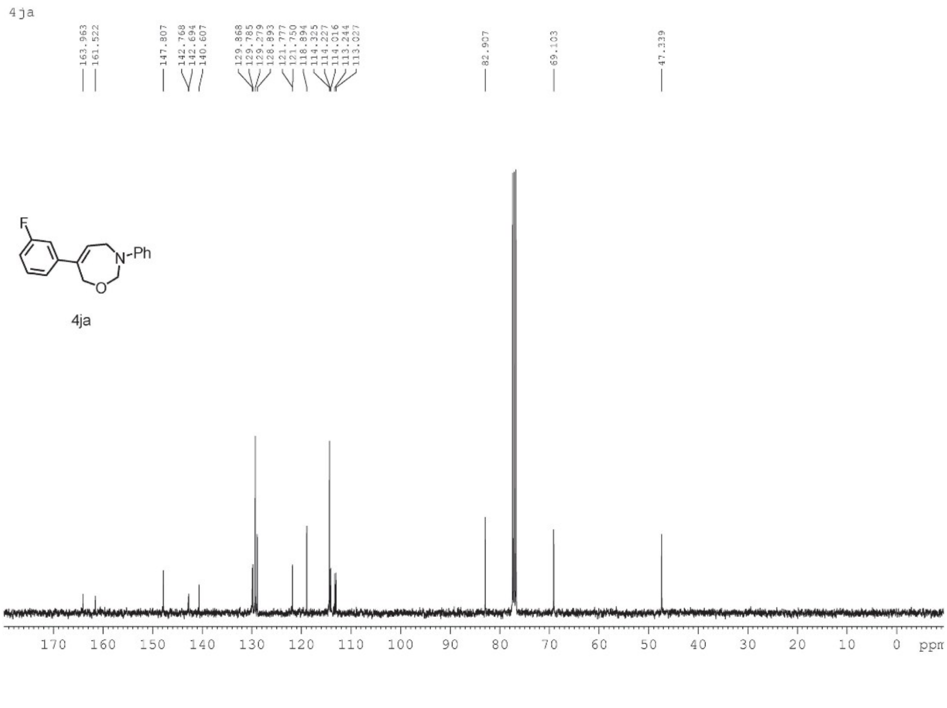

4ga
7.305
7.284
7.271
7.266
7.251
7.248
7.232
7.228
7.120
7.116
7.101
7.097
6.934
6.922
6.913
6.906
6.904
6.885
6.872
6.855
6.836
5.976
5.966
5.955
5.168
4.401
4.399
4.237
4.227
3.761
OMe
N
Ph
O
4ga
3.544
1.024
3.076
1.951
1.000
2.028
2.039
2.056
3.046
8
7
6
5
4
3
2
1
0
ppm

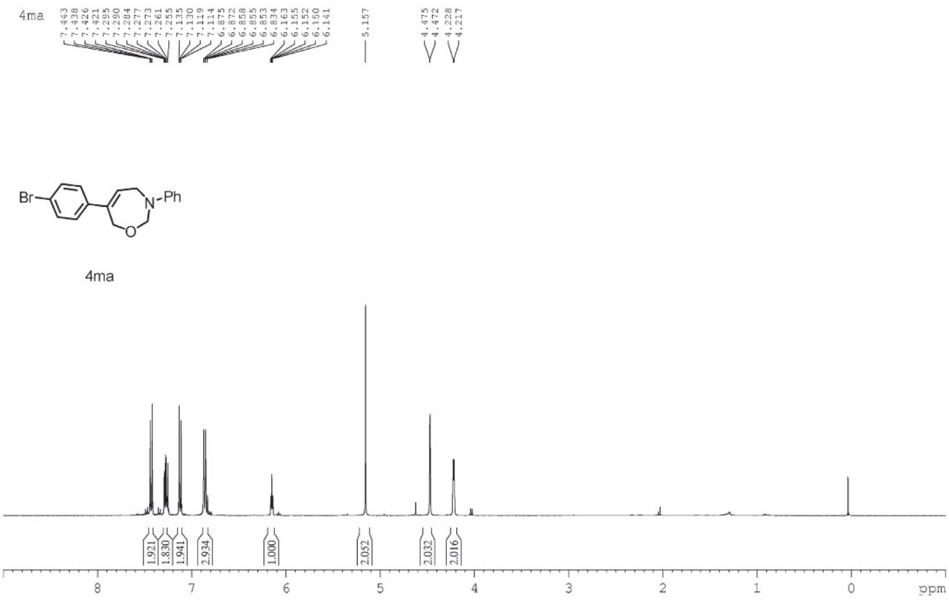

4ga
156.591
148.189
141.554
130.660
129.940
129.111
128.902
128.704
120.621
118.701
114.664
110.781
83.062
69.535
55.464
47.824
OMe
N
Ph
O
4ga
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

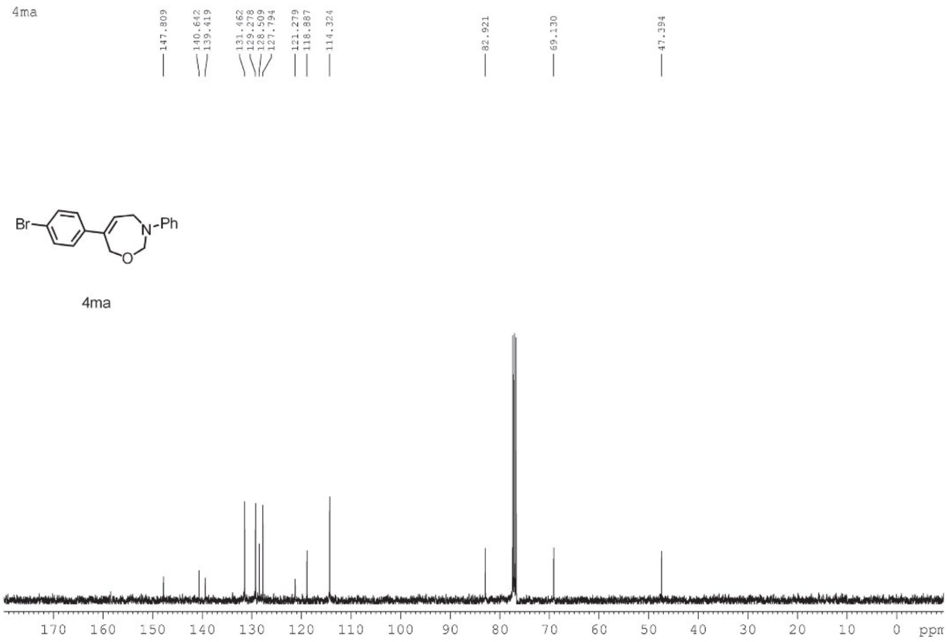

4ha
BnO
N-Ph
O
4ha
ppm

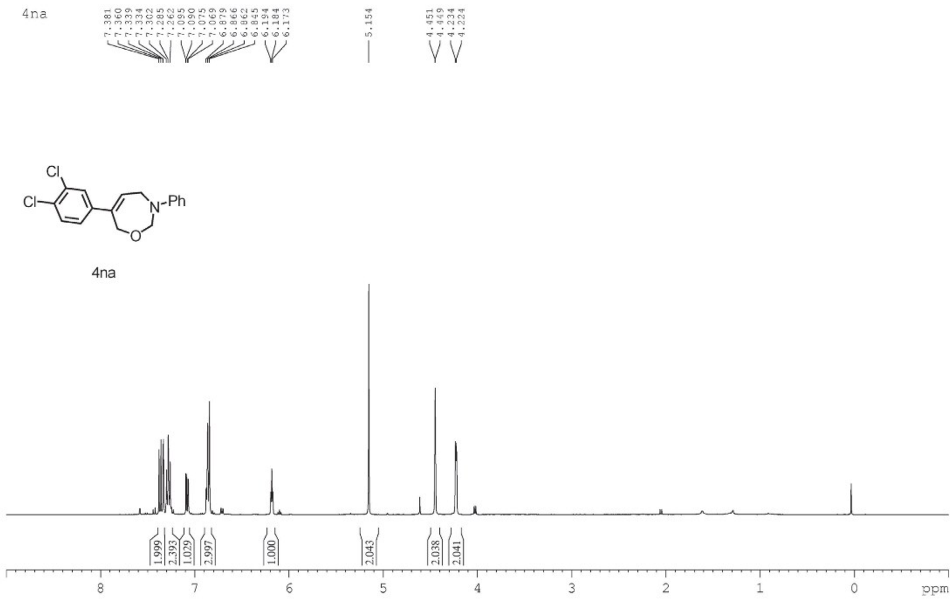

4ha
158.168
147.929
140.973
82.915
47.292
BnO
N-Ph
O
4ha
ppm


4ja
7.299 7.284 7.281 7.278 7.264 7.259 7.243 7.042 7.039 7.021 6.981 6.979 6.958 6.949 6.942 6.940 6.880 6.876 6.858 6.857 6.202 6.192 6.181
5.163
4.490 4.487 4.243 4.232
F
N-Ph
O
4ja
3.163 1.049 1.959 2.981 1.000 2.038 2.059 2.049
8 7 6 5 4 3 2 1 0 ppm


4ja
163.963 161.522
147.807 142.768 142.694 140.607
129.868 129.785 129.279 128.893 121.777 121.750 118.894 114.325 114.227 114.016 113.244 113.027
82.927
69.103
47.339
F
N-Ph
O
4ja
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


4ma
7.443
7.438
7.426
7.421
7.295
7.290
7.284
7.277
7.273
7.261
7.255
7.135
7.130
7.119
7.114
6.875
6.872
6.858
6.855
6.853
6.834
6.163
6.155
6.152
6.150
6.141
5.157
4.475
4.472
4.228
4.217
Br
N
Ph
O
4ma
1.921
1.830
1.941
2.934
1.000
2.052
2.032
2.016
8
7
6
5
4
3
2
1
0
ppm


4ma
147.809
140.642
139.419
131.462
129.278
128.509
127.794
121.279
118.387
114.324
82.921
69.130
47.394
Br
N
Ph
O
4ma
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.360
7.339
7.334
7.302
7.285
7.262
7.095
7.090
7.075
7.069
6.879
6.866
6.862
6.845
6.194
6.184
6.173
5.154
4.451
4.449
4.234
4.224
Cl
Cl
N
Ph
O
4na
1.999
2.393
1.029
2.997
1.000
2.043
2.038
2.041
8
7
6
5
4
3
2
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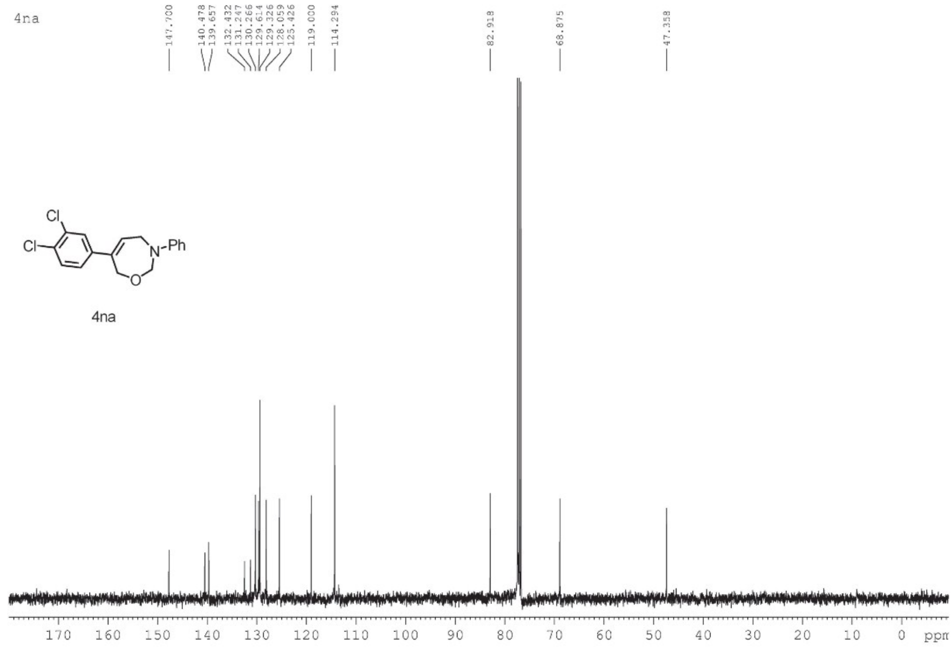
0
ppm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131.247
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129.614
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128.059
125.426
119.000
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68.875
47.358
Cl
Cl
N
Ph
O
4na
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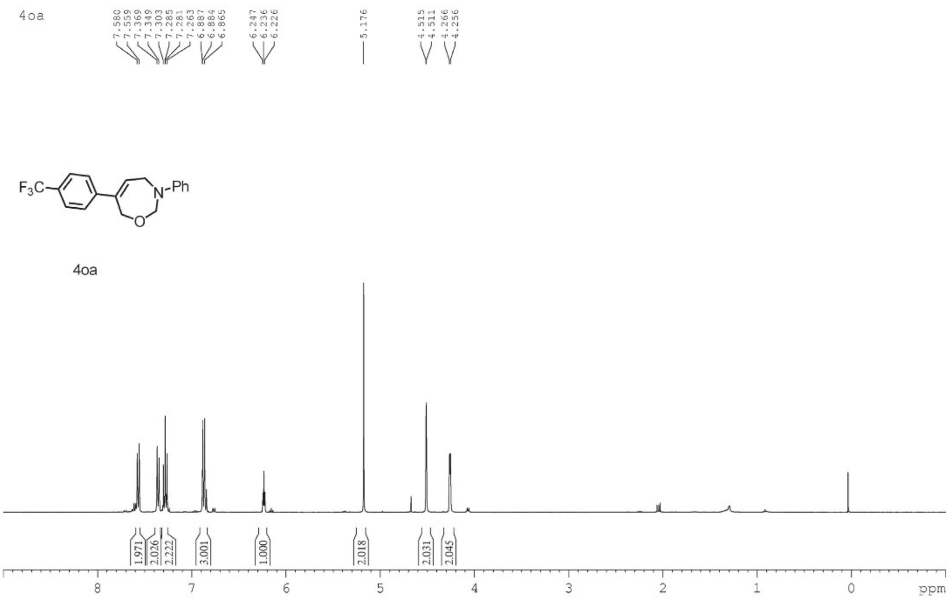
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.303
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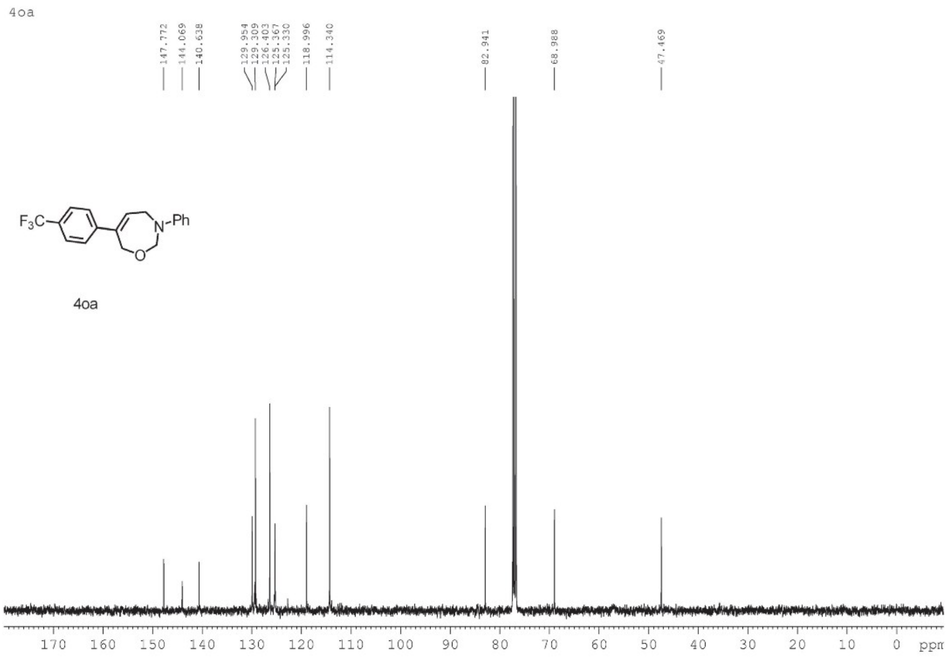
7.281
7.263
6.887
6.884
6.865
6.247
6.236
6.226
5.176
4.515
4.511
4.266
4.256
F3C
N
Ph
O
4oa
1.971
2.026
2.222
3.001
1.000
2.018
2.031
2.045
8
7
6
5
4
3
2
1
0
ppm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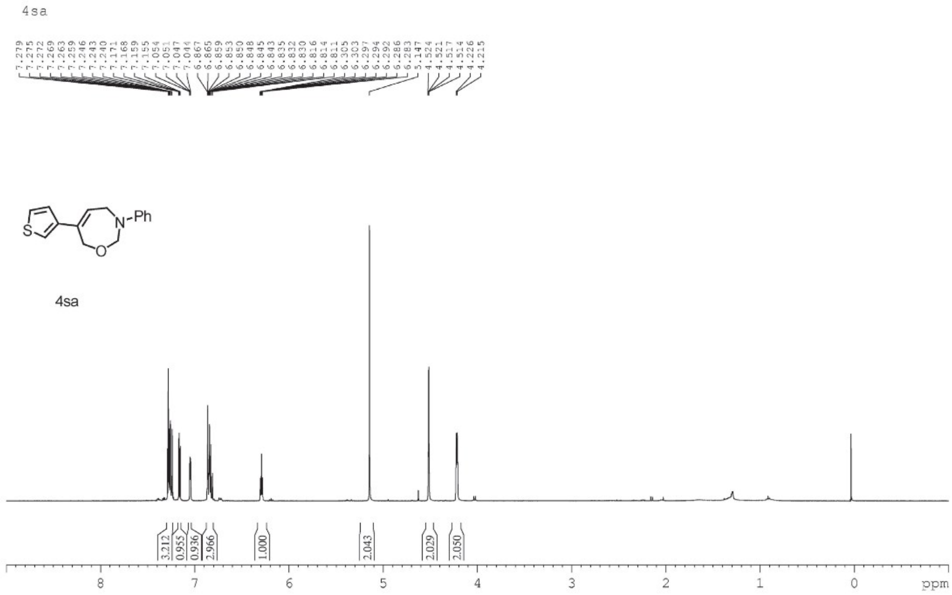
129.954
129.309
126.403
125.367
125.330
118.996
114.340
82.941
68.988
47.469
F3C
N
Ph
O
4oa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.269
7.263
7.259
7.246
7.243
7.240
7.171
7.168
7.159
7.155
7.054
7.051
7.047
7.044
6.867
6.865
6.859
6.853
6.850
6.848
6.845
6.843
6.835
6.832
6.830
6.826
6.814
6.811
6.305
6.303
6.297
6.294
6.292
6.286
6.283
5.147
4.524
4.521
4.517
4.514
4.226
4.215
N
Ph
S
O
4sa
3.212
0.955
0.936
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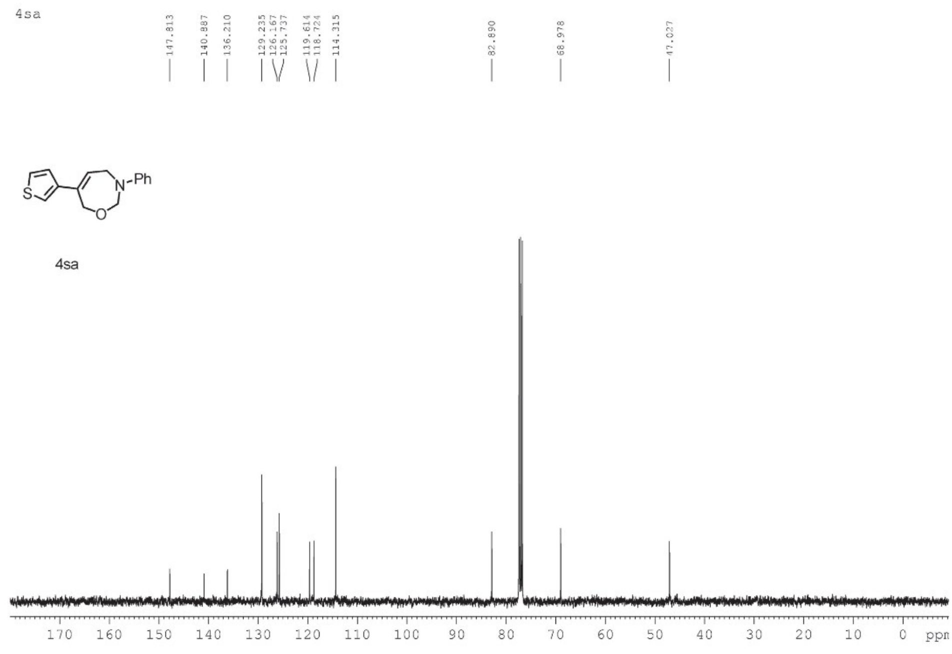
1.000
2.043
2.029
2.050
8
7
6
5
4
3
2
1
0
ppm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126.167
125.737
119.614
118.724
114.315
82.890
68.978
47.027
N
Ph
S
O
4sa
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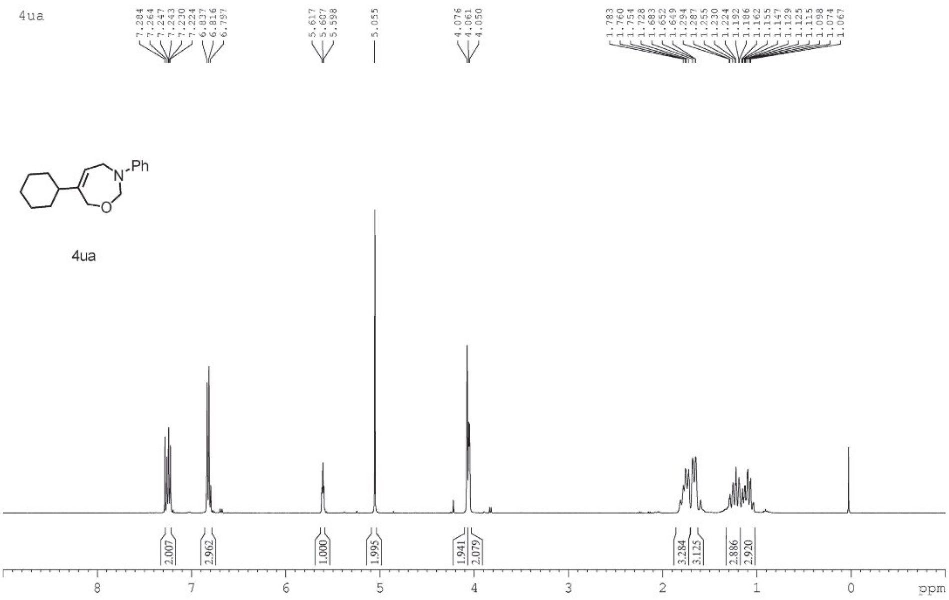
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


4ua
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7.247
7.243
7.230
7.224
6.837
6.816
6.797
5.617
5.607
5.598
5.055
4.076
4.061
4.050
Ph
N
O
4ua
2.007
2.962
1.000
1.995
1.941
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3.125
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2.920
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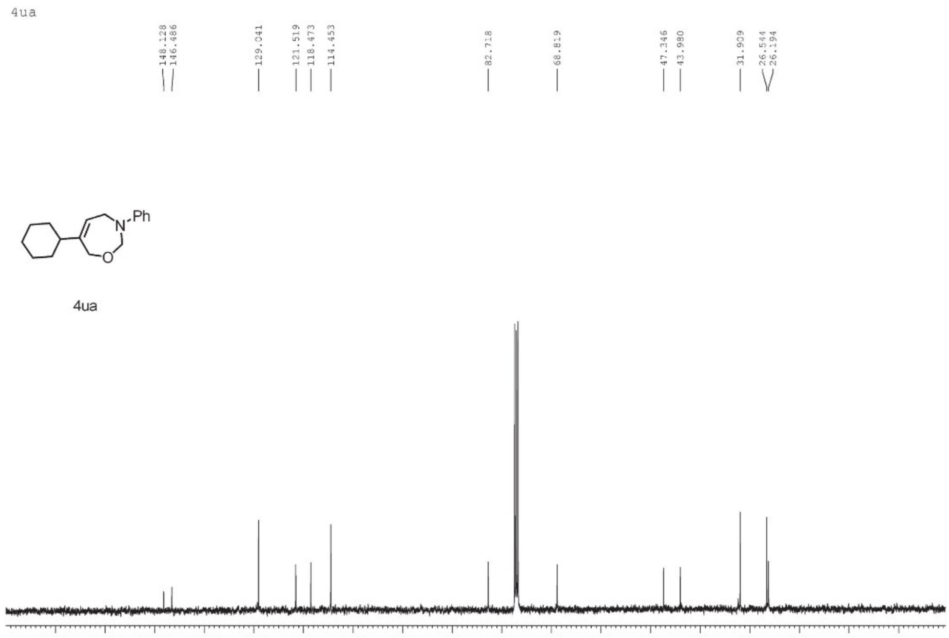
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121.519
118.473
114.453
82.718
68.819
47.346
43.980
31.959
26.544
26.194
Ph
N
O
4ua
170
160
150
140
130
120
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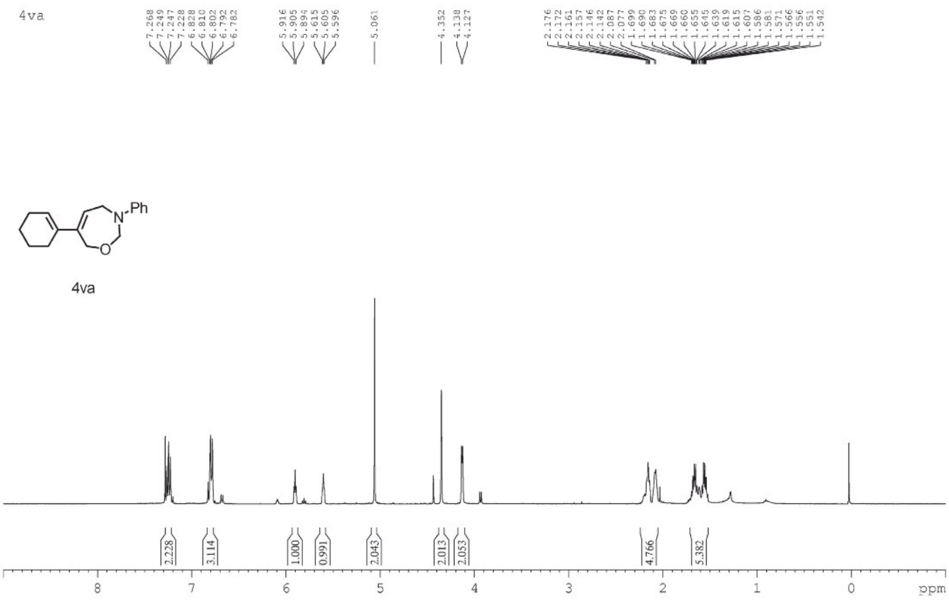
100
90
80
70
60
50
40
30
20
10
0
ppm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7.247
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6.828
6.810
6.802
6.792
6.782
5.916
5.905
5.894
5.615
5.605
5.596
5.061
4.352
4.138
4.127
2.176
2.172
2.161
2.157
2.146
2.142
2.087
2.077
1.699
1.690
1.683
1.675
1.669
1.660
1.655
1.645
1.639
1.619
1.615
1.607
1.586
1.581
1.571
1.566
1.556
1.551
1.542
N
Ph
O
4va
2.228
3.114
1.000
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2.043
2.013
2.053
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8
7
6
5
4
3
2
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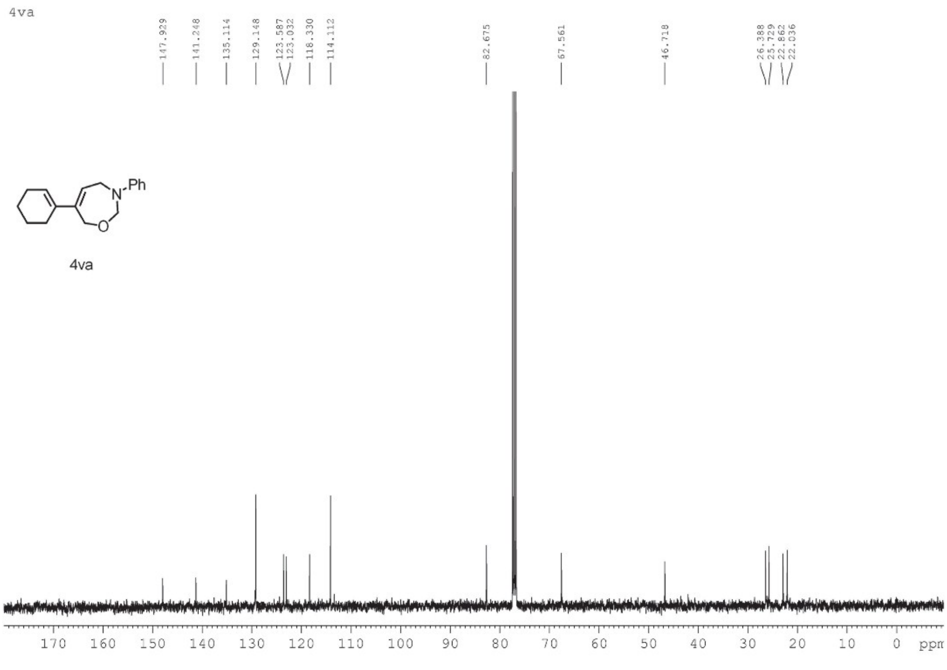
ppm


4va
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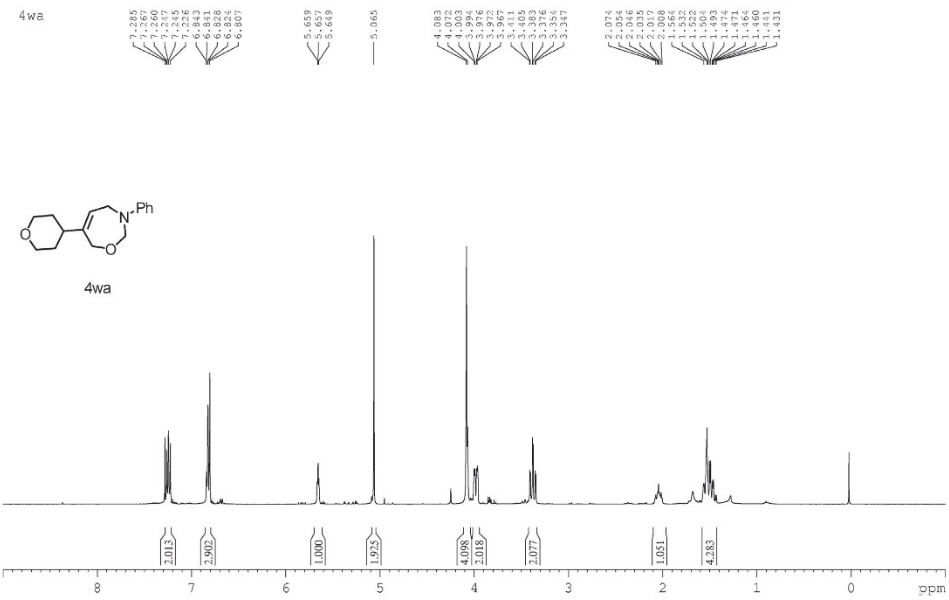
129.148
123.587
123.032
118.330
114.112
82.675
67.561
46.718
26.388
25.729
22.862
22.036
N
Ph
O
4va
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


4wa
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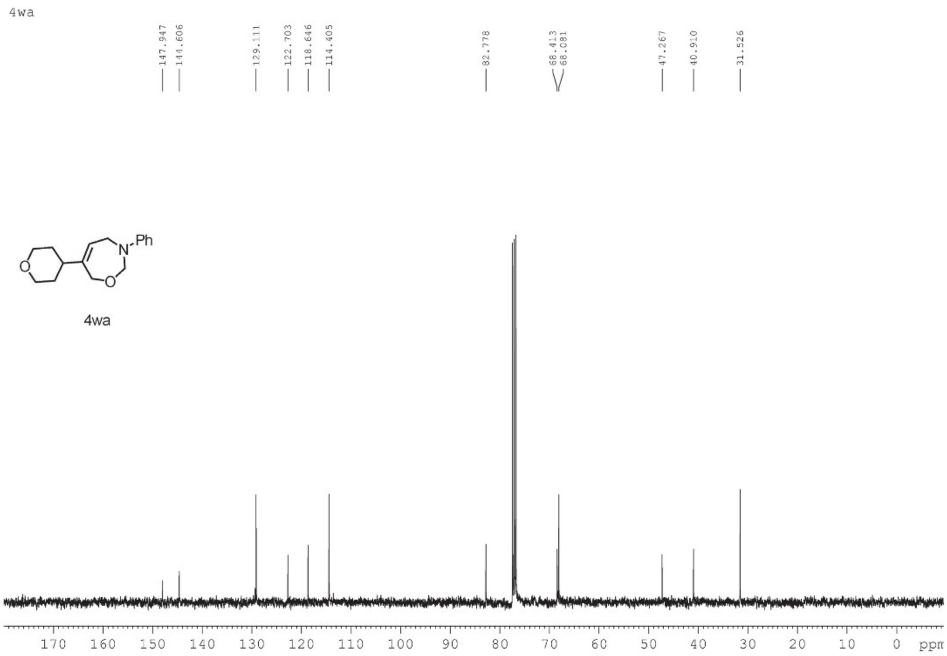
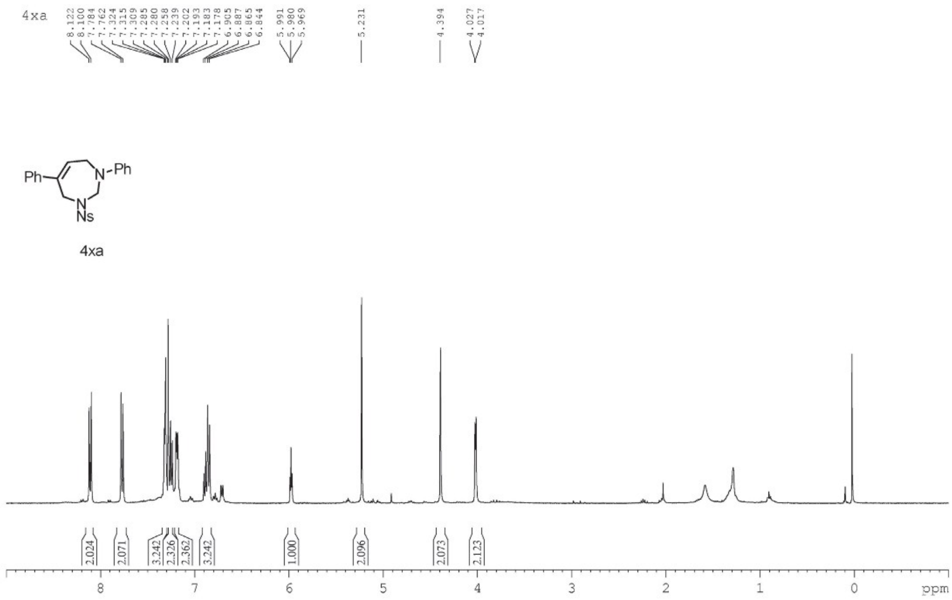
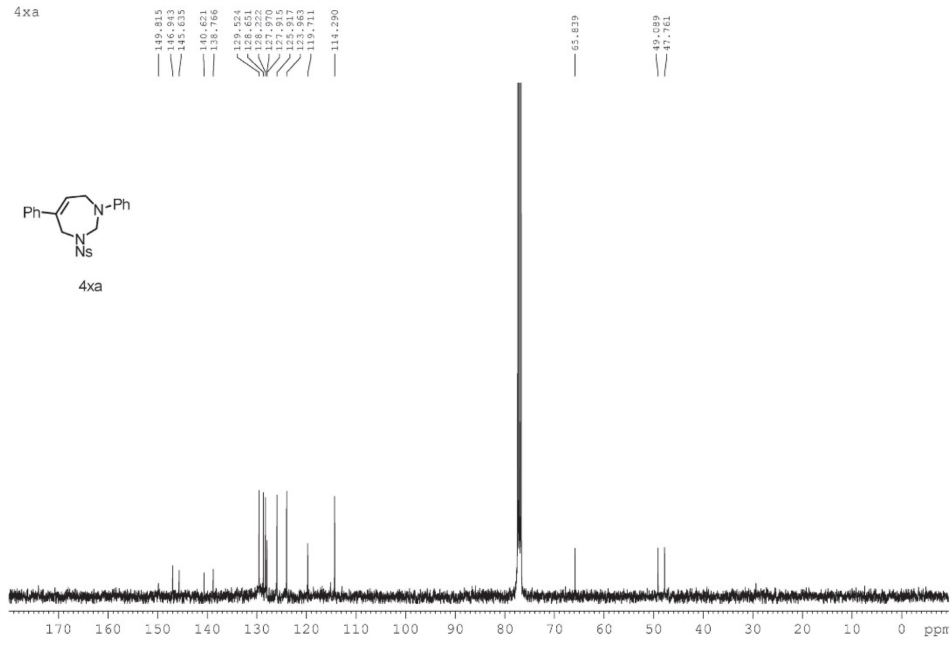
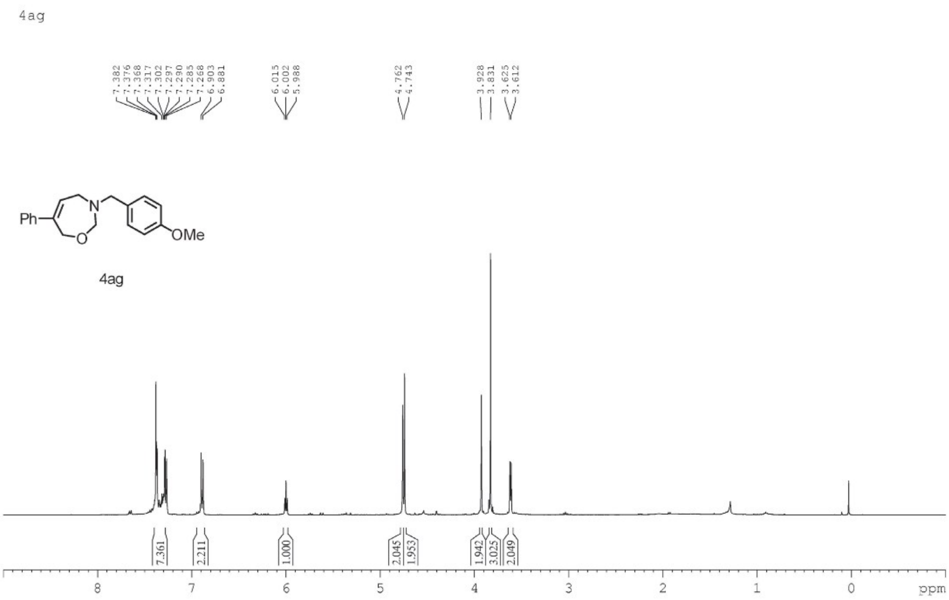
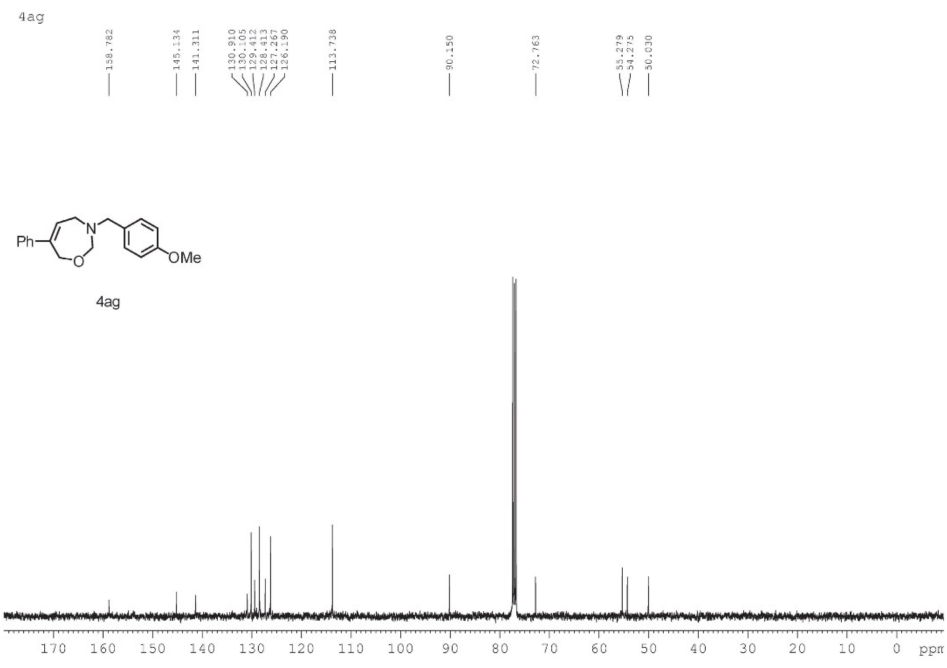
5.659 5.657 5.649
5.065
4.083 4.072 4.003 3.994 3.976 3.972 3.967 3.411 3.405 3.383 3.376 3.354 3.347
2.074 2.054 2.046 2.035 2.017 2.008 1.564 1.532 1.522 1.504 1.493 1.474 1.471 1.464 1.460 1.441 1.431
N
Ph
O
O
4wa
2.013 2.902 1.000 1.925 4.098 2.018 2.077 1.051 4.283
8 7 6 5 4 3 2 1 0 ppm

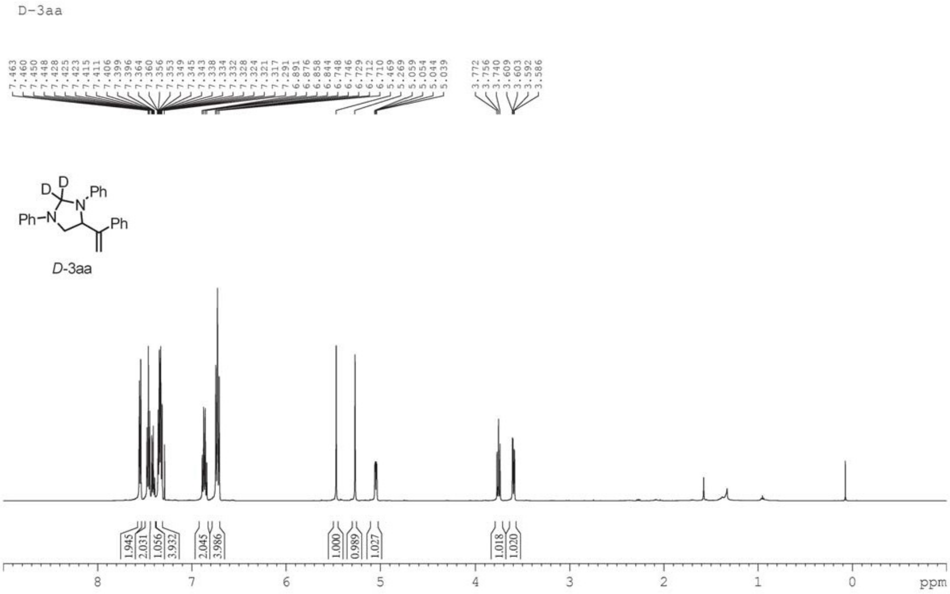

4wa
147.947 144.606 129.111 122.703 118.646 114.405 82.778 68.413 68.081 47.267 40.910 31.526
N
Ph
O
O
4wa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

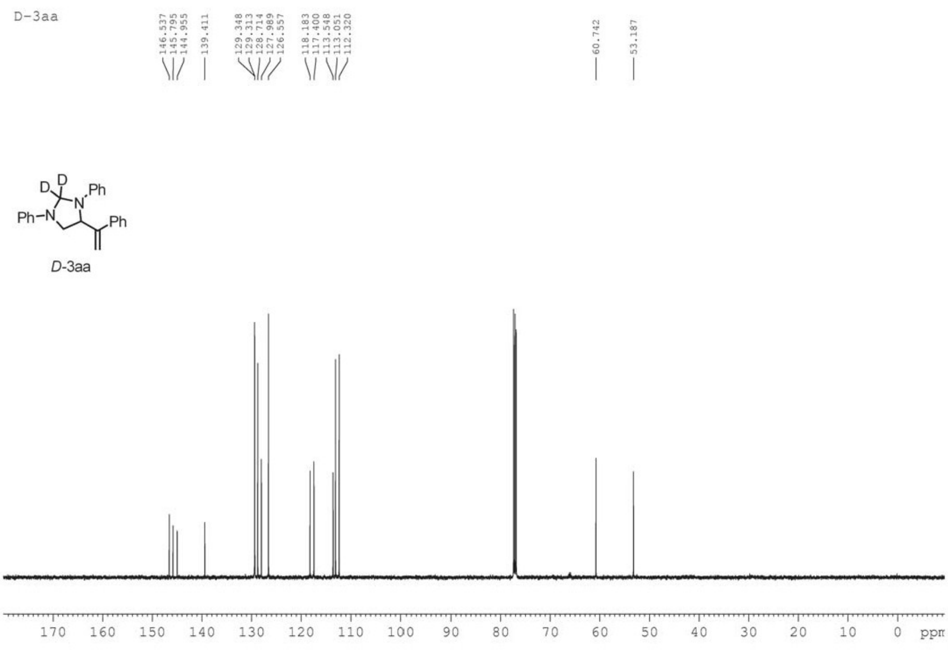

4xa
8.122
8.100
7.784
7.762
7.324
7.315
7.309
7.285
7.280
7.258
7.239
7.202
7.193
7.183
7.178
6.905
6.887
6.865
6.844
5.991
5.980
5.969
5.231
4.394
4.027
4.017
Ph
N
Ph
N
Ns
4xa
2.024
2.071
3.242
2.326
2.362
3.242
1.000
2.096
2.073
2.123
8
7
6
5
4
3
2
1
0
ppm

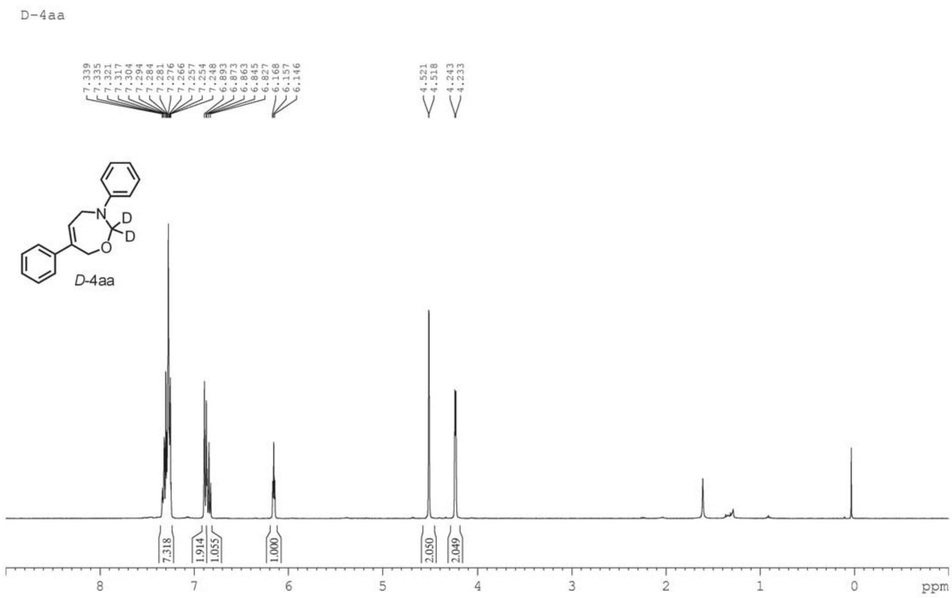

4xa
149.815
146.943
145.635
140.621
138.766
129.524
128.651
128.222
127.970
127.915
125.917
123.963
119.711
114.290
65.839
49.089
47.761
Ph
N
Ph
N
Ns
4xa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

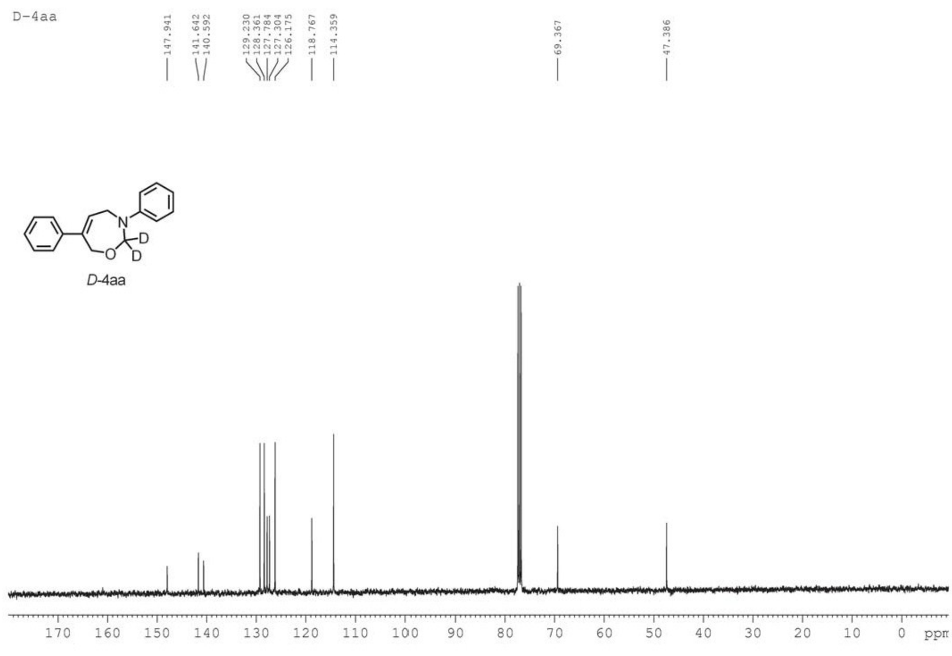

4ag
7.382
7.376
7.368
7.317
7.302
7.297
7.290
7.285
7.268
6.903
6.881
6.015
6.002
5.988
4.762
4.743
3.928
3.831
3.625
3.612
Ph
N
O
OMe
4ag
7.361
2.211
1.000
2.045
1.953
1.942
3.025
2.049
8
7
6
5
4
3
2
1
0
ppm


4ag
158.782
145.134
141.311
130.910
130.105
129.412
128.413
127.267
126.190
113.738
90.150
72.763
55.279
54.275
50.030
Ph
N
O
OMe
4ag
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

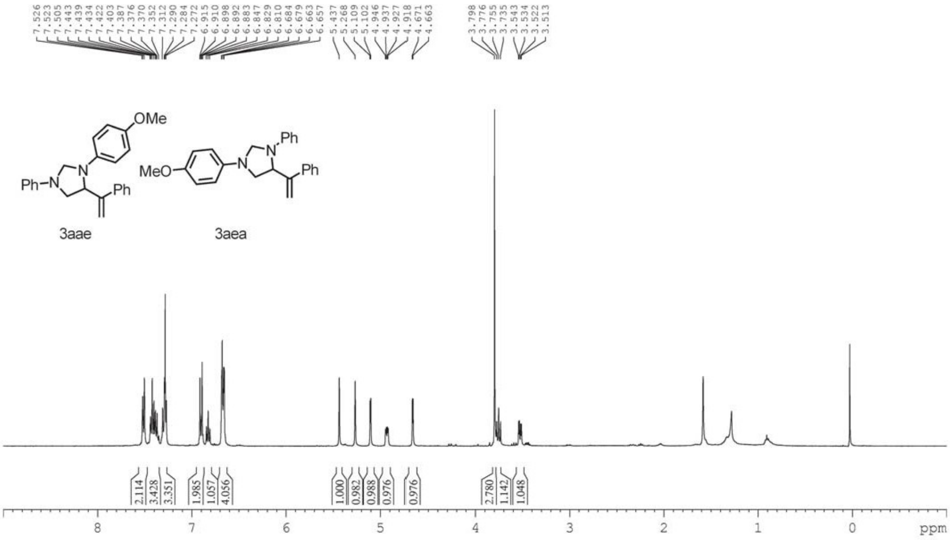

D-3aa
7.463 7.460 7.448 7.428 7.425 7.423 7.415 7.411 7.406 7.399 7.396 7.364 7.360 7.356 7.353 7.349 7.345 7.343 7.338 7.334 7.332 7.328 7.324 7.321 7.317 6.891 6.876 6.858 6.844 6.748 6.746 6.729 6.712 6.710 5.469 5.269 5.059 5.054 5.044 5.039
3.772 3.756 3.740 3.609 3.603 3.592 3.586
D D
Ph
Ph
N
N
Ph
D-3aa
1.945 2.031 1.056 3.932 2.045 3.986 1.000 0.989 1.027 1.018 1.020
8 7 6 5 4 3 2 1 0 ppm


D-3aa
146.537 145.795 144.955 139.411 129.348 129.313 128.714 127.989 126.557 118.183 117.400 113.548 113.051 112.320
60.742
53.187
D D
Ph
Ph
N
N
Ph
D-3aa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

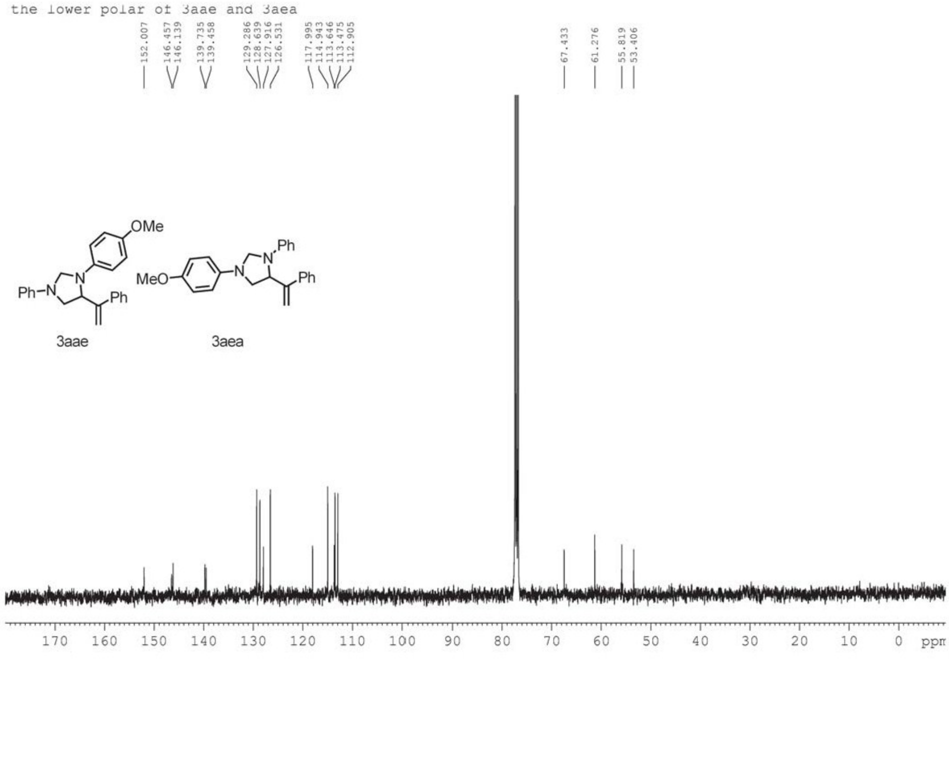

D-4aa
7.339
7.335
7.321
7.317
7.304
7.294
7.284
7.281
7.276
7.266
7.257
7.254
7.248
6.893
6.873
6.863
6.845
6.827
6.168
6.157
6.146
4.521
4.518
4.243
4.233
N
D
D
O
D-4aa
7.318
1.914
1.055
1.000
2.050
2.049
8
7
6
5
4
3
2
1
0
ppm


D-4aa
147.941
141.642
140.592
129.230
128.361
127.784
127.304
126.175
118.767
114.359
69.367
47.386
N
D
O
D
D-4aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

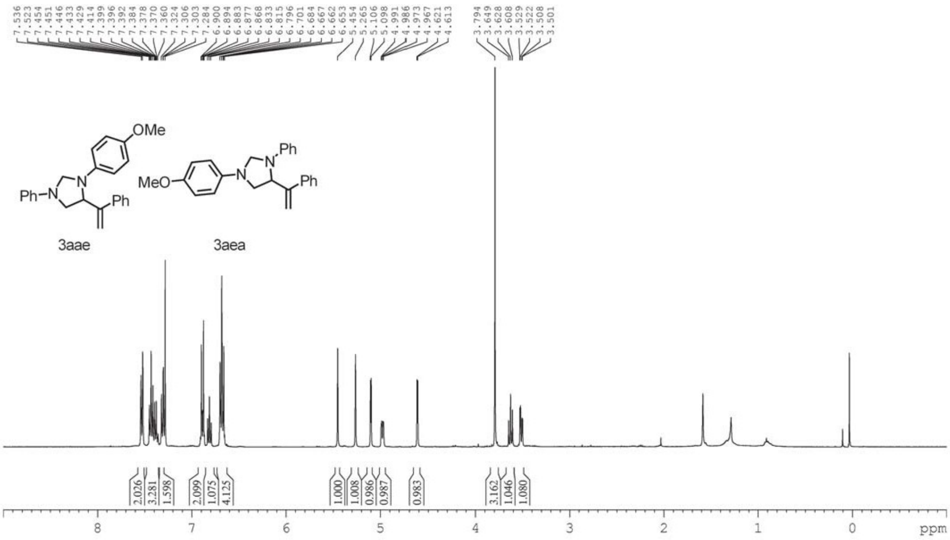
the lower polar of 3aae and 3aea



the lower polar of 3aae and 3aea



the bigger polar of 3aae and 3aea



the bigger polar of 3aae and 3aea