Supporting Information

Electrocatalytic aziridination of alkenes mediated by *n*-Bu_4NI: a radical pathway

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Contents

1) Table S1. Optimization of conditions

Entry	Cell [a]	Anode/ cathode	electrolyte	Catalyst (%)	Base (eq.)	J [b]	Charge (F/mol)	Yield [c] (%)
1	D	Pt/Fe	Et_3N/HOAc/ CH_3CN	Bu_4NI (20)	K_2CO_3 (1)	4	3	trace
2	D	Pt/Fe	Et_3N/HOAc/ CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	trace
3	D	GC/Fe	Et_3N/HOAc/ CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	32
4	U. D	GC/Fe	Et_3N/HOAc/ CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	55
5	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	67
6	D	C/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	56
7	U. D	GC/Fe	CF_3CH_2OH	Bu_4NI (20)	K_2CO_3 (1)	4	3	51
8	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Et_4NI (20)	K_2CO_3 (1)	4	3	51
9	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	NaI (20)	K_2CO_3 (1)	4	3	48
10	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NBr (20)	K_2CO_3 (1)	4	3	36
11	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	NaBr (20)	K_2CO_3 (1)	4	3	27
12	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NCl (20)	K_2CO_3 (1)	4	3	Trace

13	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (1)	4	3	65
14	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (5)	K_2CO_3 (1)	4	3	46
15	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (0)	K_2CO_3 (1)	4	3	Trace
16	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (3)	4	3	23
17	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	Lutidine (1)	4	3	21
18	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	NaOAc (1)	4	3	Trace
19	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	----	4	3	12
20	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (1)	8	3	48
21	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (1)	12	3	28
22	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (1)	4	2.5	61
23	U. D	GC/Fe	$LiClO_4$/ CF_3CH_2OH	Bu_4NI (10)	K_2CO_3 (1)	4	3.5	63

[a] D: divided cell; U. D: undivided cell.

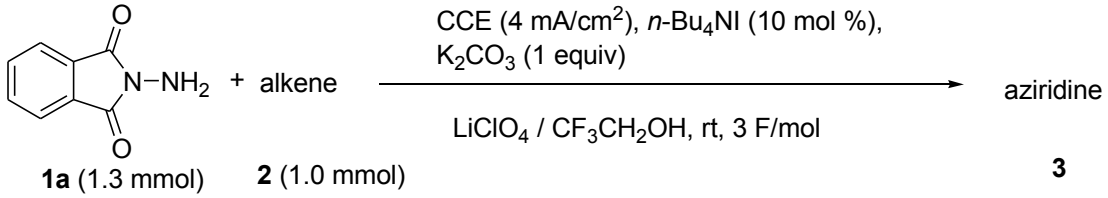
[b] J: current density (mA/cm^2)

[c] Isolated yield.

2) Instruments and reagents

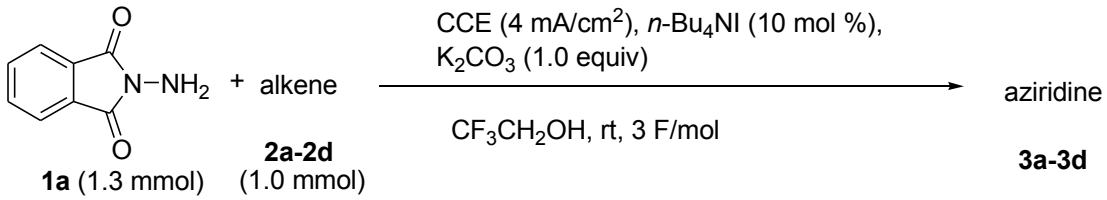
All melting points were measured with a XT4A Electrothermal melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with an AV 400 M Bruker spectrometer (400 MHz ^{1}H frequency and 100 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). Starting *N*-aminophthalimide was synthesized according to a known procedure.[1] Other alkene starting materials and solvents were obtained from Beijing Chemicals Co. and used without further purification. Reactions were monitored by thin-layer chromatography and products were isolated following column chromatography (petroleum ether/ethyl acetate), performed on silica gel (400-500 mesh).

3) Typical procedure for the synthesis of aziridines 3a-3l by constant current electrolysis (CCE) in the presence of supporting electrolyte



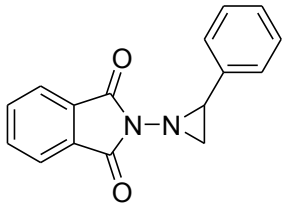
A 50 mL beaker-type cell was equipped with a GC cathode and a Fe plate anode which were connected to a DC regulated power supply. To the cell was added *N*-aminophthalimide **1a** (1.3 mmol), alkene **2** (1 mmol), K_2CO_3 (1 mmol), *n*-Bu_4NI (0.1 mmol) and $LiClO_4$ (0.5 mmol) dissolved in 10 mL of CF_3CH_2OH. The mixture was electrolyzed using constant current conditions (~4 mA/cm^2) at room temperature while stirring. The electrolysis was terminated when 3 F/mol of charge had been consumed. After the electrolysis, the solvent, CF_3CH_2OH, was removed under reduced pressure; extraction was carried out using CH_2Cl_2 (3×15 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, and dried over $MgSO_4$. Purified product was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

4) Typical procedure for the synthesis of aziridines 3a-3d by constant current electrolysis (CCE) in the absence of supporting electrolyte

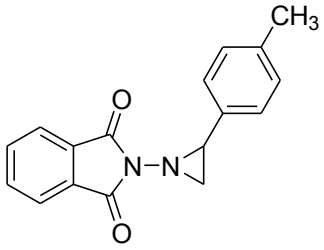


The procedure is identical to that in the presence of conduting salt, but $LiClO_4$ was not added. In these cases, the cell voltage increased to 15-25 V from 7-12 when 0.1 M $LiClO_4$ was present.

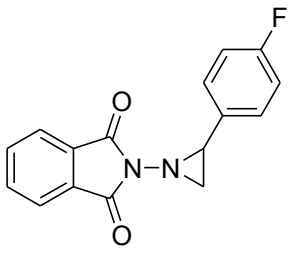
5) Characterization Data (references have been provided for known structures).



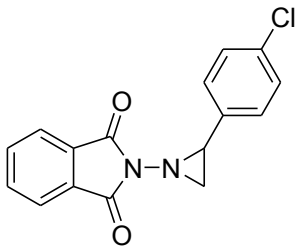
***N*-(Aminophthalimide)-2-phenylaziridine (3a).**[2] Isolated as a colorless solid (171 mg, 0.65 mmol, 65% yield); M.P.: 149-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.73-7.71 (m, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 3.64 (dd, *J* = 7.6 Hz, 6.0 Hz, 1H), 2.92 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 2.82 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H).



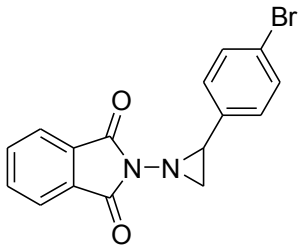
***N*-(Aminophthalimide)-2-*p*-methyl-phenylaziridine (3b).**[2] Isolated as a white solid (197 mg, 0.71 mmol, 71% yield); M.P.: 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.73-7.70 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.61-3.58 (m, 1H), 2.89 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 2.81 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H), 2.38 (s, 3H).



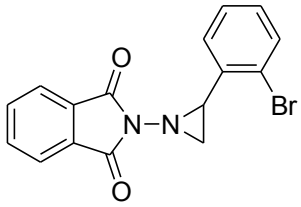
***N*-(Aminophthalimide)-2-*p*-fluoro-phenylaziridine (3c).**[2] Isolated as a colorless solid (178 mg, 0.63 mmol, 63% yield); M.P.: 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.81(m, 2H), 7.75-7.71 (m, 2H), 7.49-7.45 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 2H), 3.62-3.59 (m, 1H), 2.91 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 2.79 (dd, *J* = 5.6 Hz, 2.4 Hz, 1H).



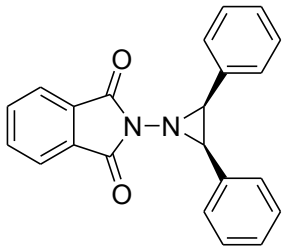
***N*-(Aminophthalimide)-2-*p*-chloro-phenylaziridine (3d).**[2] Isolated as a white solid (194 mg, 0.65 mmol, 65% yield); M.P.: 151-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.75-7.71 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.59 (dd, *J* = 7.6 Hz, 6.0 Hz, 1H), 2.93 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 2.77 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H).



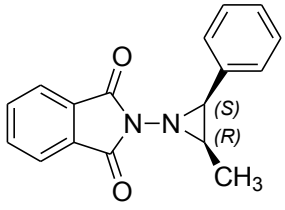
***N*-(Aminophthalimide)-2-*p*-bromo-phenylaziridine (3e).**[2] Isolated as a white solid (233 mg, 0.68 mmol, 68% yield); M.P.: 142-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.81 (m, 2H), 7.74-7.71 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 3.58 (dd, *J* = 7.6 Hz, 5.6 Hz, 1H), 2.93 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 2.77 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H).



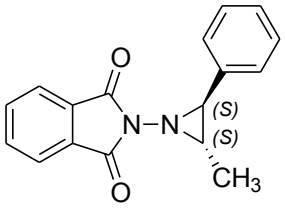
***N*-(Aminophthalimide)-2-*o*-bromo-phenylaziridine (3f).**[2] Isolated as a yellow solid (195 mg, 0.57 mmol, 57% yield); M.P.: 143-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.71 (m, 4H), 7.62-7.57 (m, 2H), 7.35 (t, *J* = 7.2 Hz,, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 3.81 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 3.07 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 2.57 (dd, *J* = 5.6 Hz, 2.0 Hz, 1H).



***Cis*-2,3-Diphenyl-1-phthalimidoaziridine (3g).**[3] Isolated as a yellow solid (231 mg, 0.68 mmol, 68% yield); M.P.: 136-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.58 (m, 8H), 7.46-7.28 (m, 6H), 4.96 (d, *J* = 6.0 Hz, 1H), 4.00 (d, *J* = 6.0 Hz, 1H).

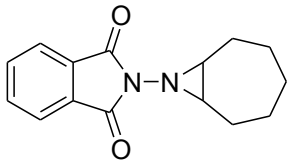


Cis-

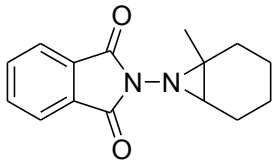


Trans-

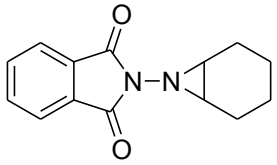
***N*-(Aminophthalimide)-2-methyl-3-phenylaziridine (*cis* : *trans* = 2:1) (3h).**[2] Isolated as a yellow solid (172 mg, 0.62 mmol, 62% yield); M.P.: 91-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 4H), 7.62-7.59 (m, 4H), 7.46-7.44 (m, 3H), 7.41-7.31 (m, 8H), 7.26-7.21 (m, 6H), 4.02-3.97 (m, 1H), 3.75 (d, *J* = 5.6 Hz, 2H), 3.53 (d, *J* = 5.6 Hz, 1H), 2.30-2.94 (m, 2H), 1.61 (d, *J* = 6.0 Hz, 3H), 1.51 (d, *J* = 6.0 Hz, 6H).



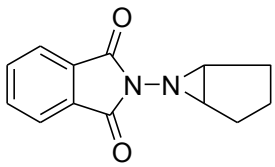
***N*-(Aminophthalimide)-8-azabicyclo[5.1.0]octane (3i).**[2] Isolated as a yellow oil (59 mg, 0.23 mmol, 23% yield, at room temperature); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.74 (m, 2H), 7.69-7.66 (m, 2H), 2.73-2.67 (m, 2H), 2.22-2.17 (m, 2H), 2.07-1.02 (m, 2H), 1.69-1.39 (m, 6H).



***N*-(Aminophthalimide)-1-methyl-7-azabicyclo[4.1.0]heptane (3j).**[2] Isolated as a yellow oil (69 mg, 0.27 mmol, 27% yield, at room temperature); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.75 (m, 2H), 7.70-7.67 (m, 2H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.29-2.15 (m, 2H), 2.08-1.99 (m, 1H), 1.79-1.72 (m, 1H), 1.51-1.42 (m, 3H), 1.36-1.24 (m, 4H).



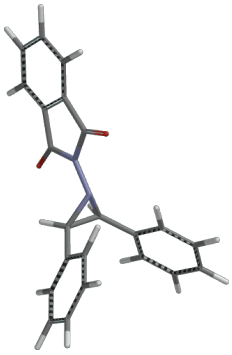
***N*-(Aminophthalimide)-7-azabicyclo[4.1.0]heptane (3k).**[2] Isolated as a colorless solid (58 mg, 0.24 mmol, 24% yield, at 0 °C); M.P.: 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.74(m, 2H), 7.69-7.66 (m, 2H), 2.78-2.73 (m, 2H), 2.31-2.24 (m, 2H), 2.01-1.96 (m, 2H), 1.49-1.41 (m, 2H), 1.35-1.30 (m, 2H).



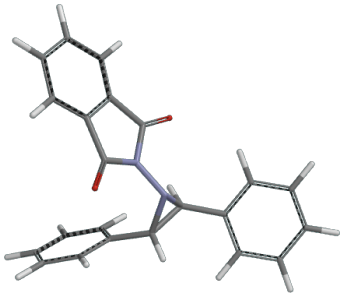
***N*-(Aminophthalimide)-6-azabicyclo[3.1.0]hexane (3l).**[2] Isolated as a light yellow solid (66 mg, 0.29 mmol, 29% yield, at 0 °C); M.P.: 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.75 (m, 2H), 7.70-7.66 (m, 2H), 3.18 (s, 2H), 2.35 (dd, J = 13.6 Hz, 8.4 Hz, 2H), 1.84-1.76 (m, 2H), 1.69-1.58 (m, 1H), 1.48-1.38 (m, 1H).

6）DFT calculation of *cis*- and *trans*- **3g**

A density functional calculation was performed in an effort to evaluate the relative energy of the cis and trans disubstituted aziridines **3g**. The B3LYP method was employed using a 6-31G(d) basis set and the Spartan 08 software package. The energy difference (vacuum) turned out to be 2.33 kcal/mol, with the *cis*-form being of lower energy. We conclude that the vicinal interaction between two Ph units is less than that of Ph with Pht. This preference is reflected experimentally as well, with only **3g** being isolated in the aziridination reaction with cis- and with trans-stilbene.



cis-**3g**



trans-**3g**

7) References

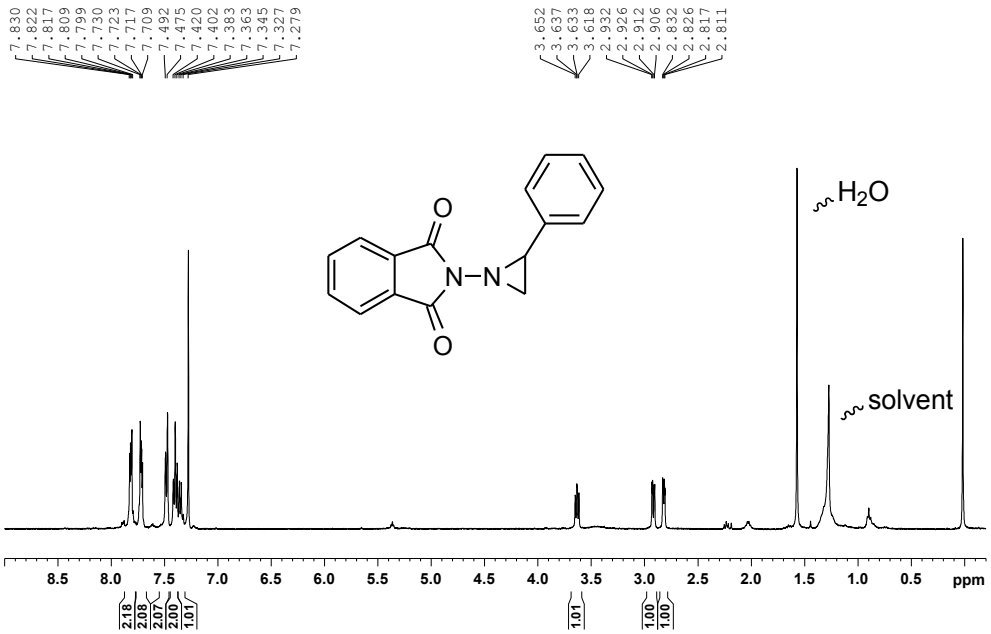
[1] Drew, H. D. K.; Hatt, H. H. *J. Chem. Soc.* **1937**, 16.

[2] Akira Y.; Kyle R. M.; C.-J. Zhu,; Victor N. N.; and Viktor V. Z.; *Angew. Chem. Int. Ed.* **2012**, *51*, 8059.

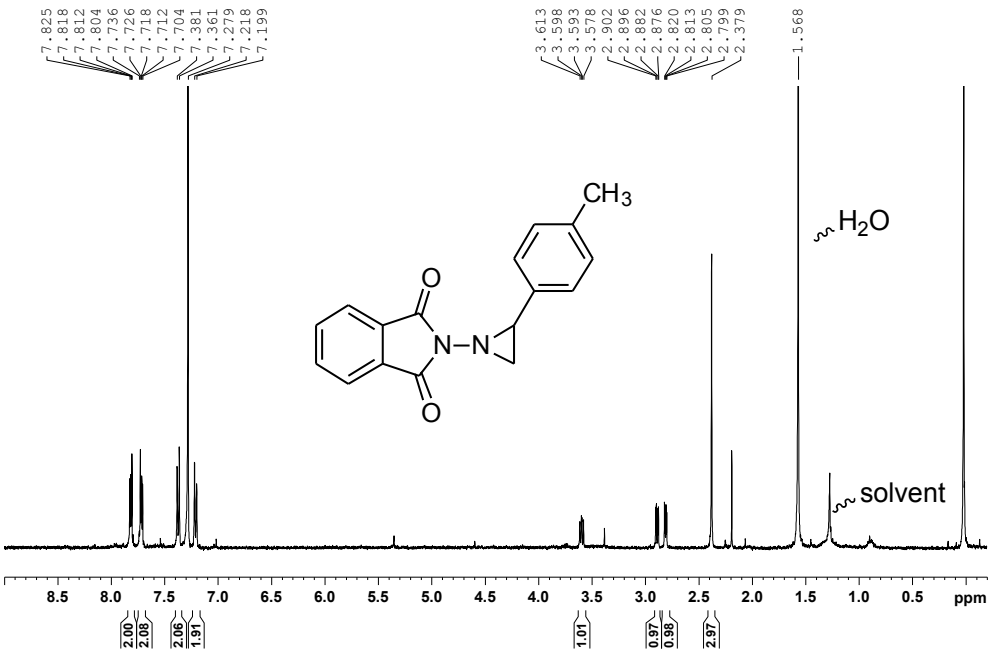
[3] Krasnova, L. B.; Hili, R. M.; Chernoloz, O. V.; Yudin A. K. *ARKIVOC* **2005**, (iv), 26.

8) ^{1}H NMR spectra of products

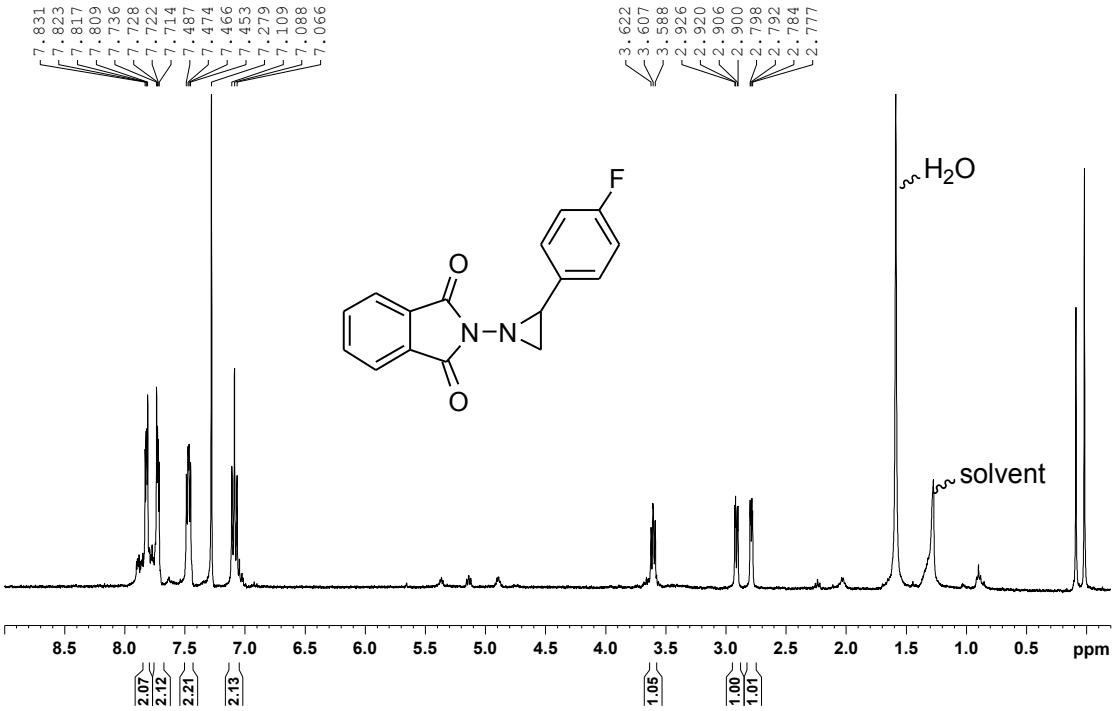
^{1}H NMR of **3a**:



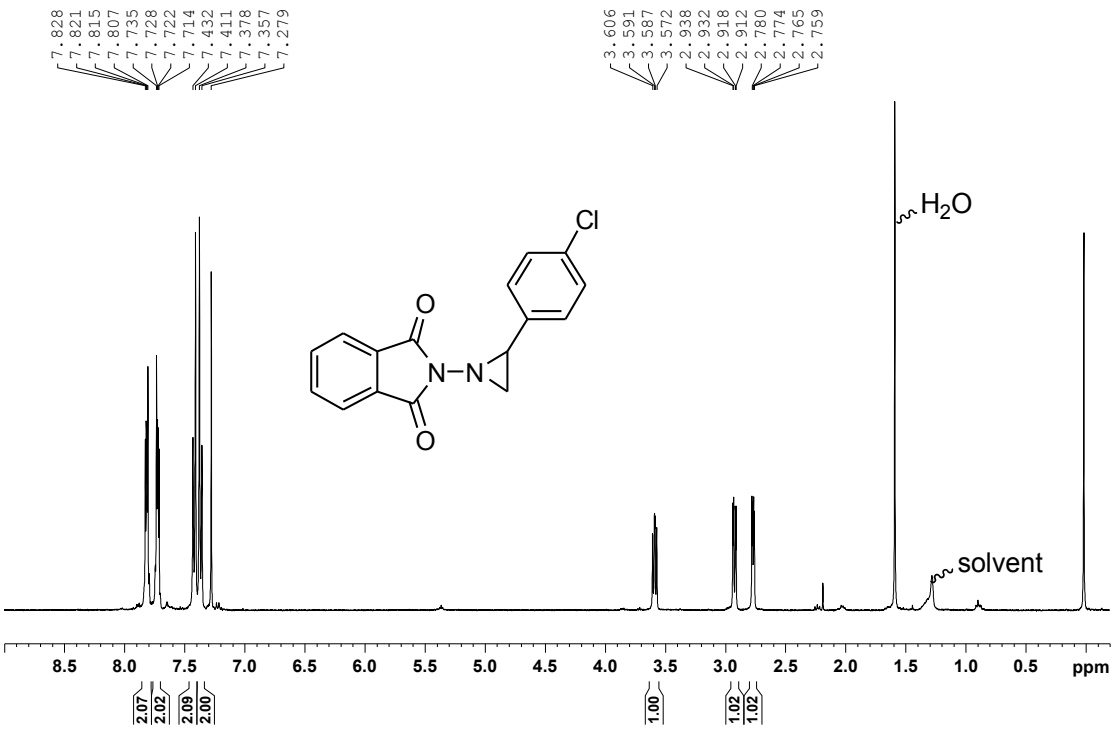
^{1}H NMR of **3b**:



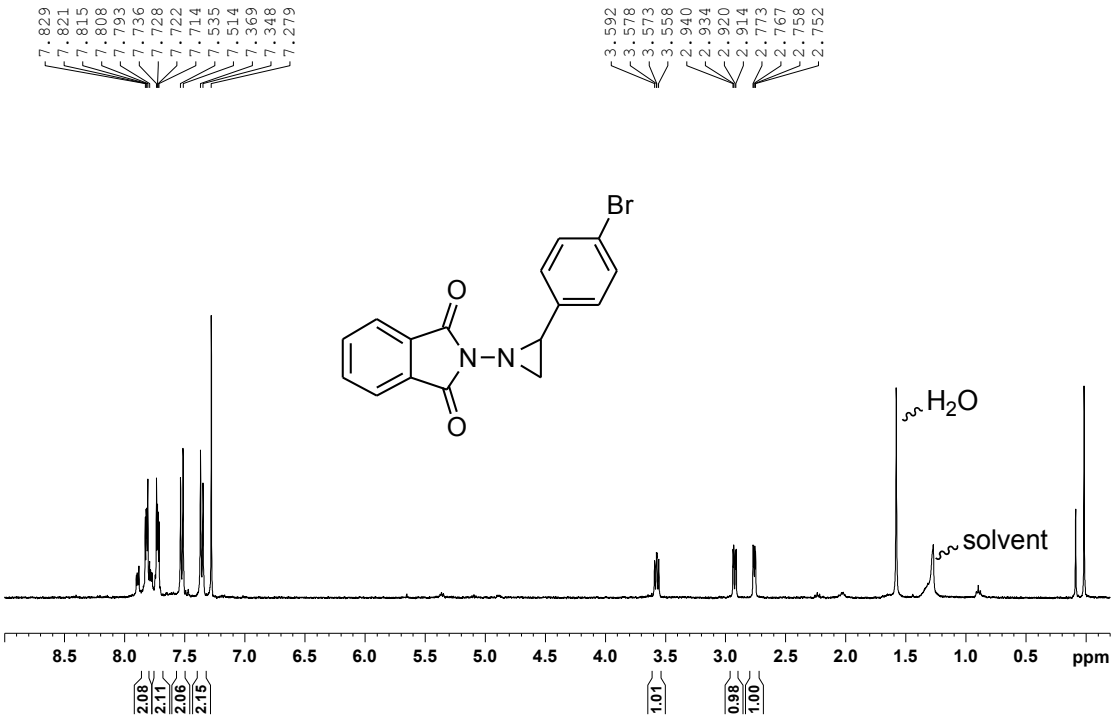
^{1}H NMR of **3c**:



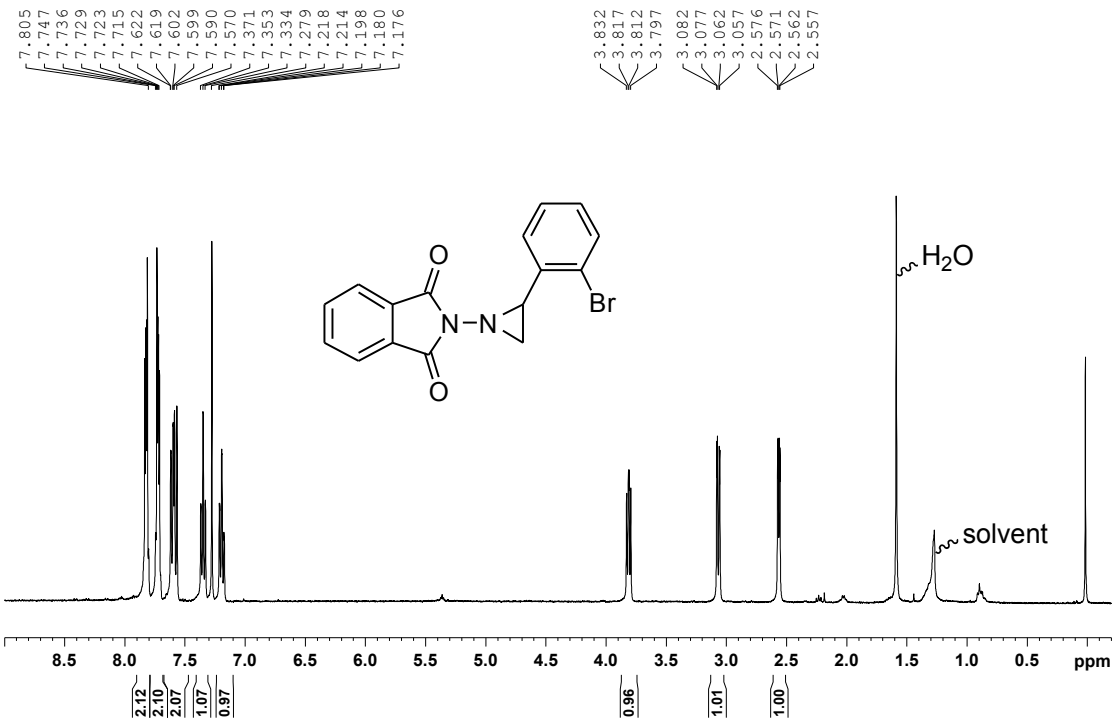
^{1}H NMR of **3d**:



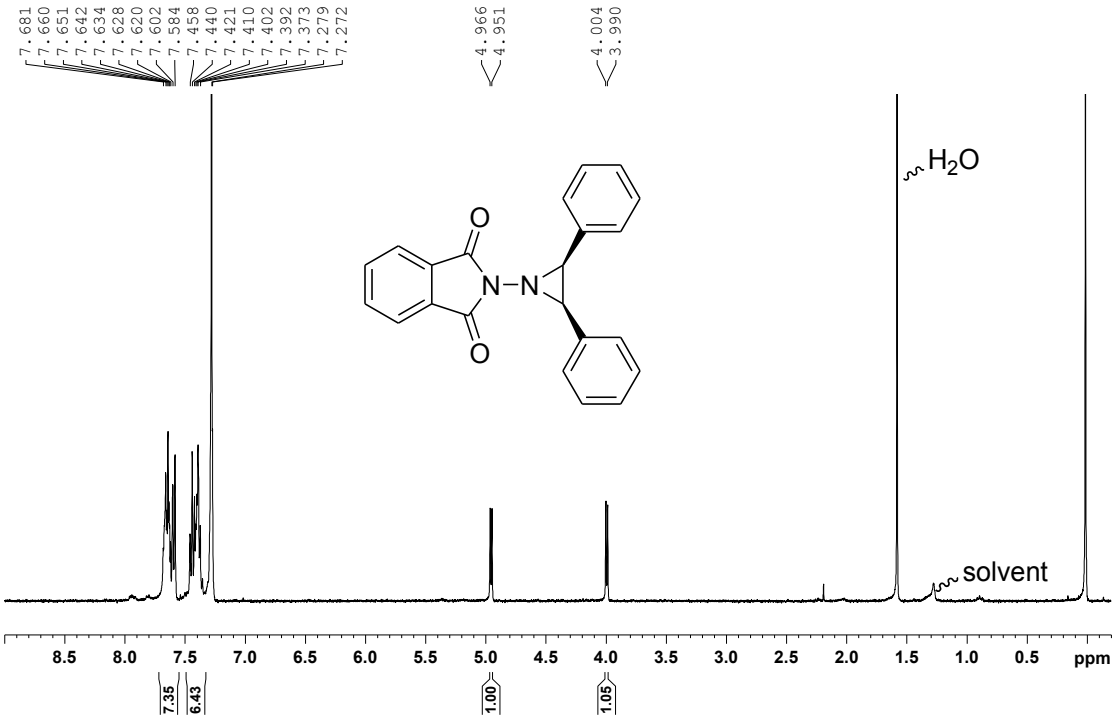
^{1}H NMR of **3e**:



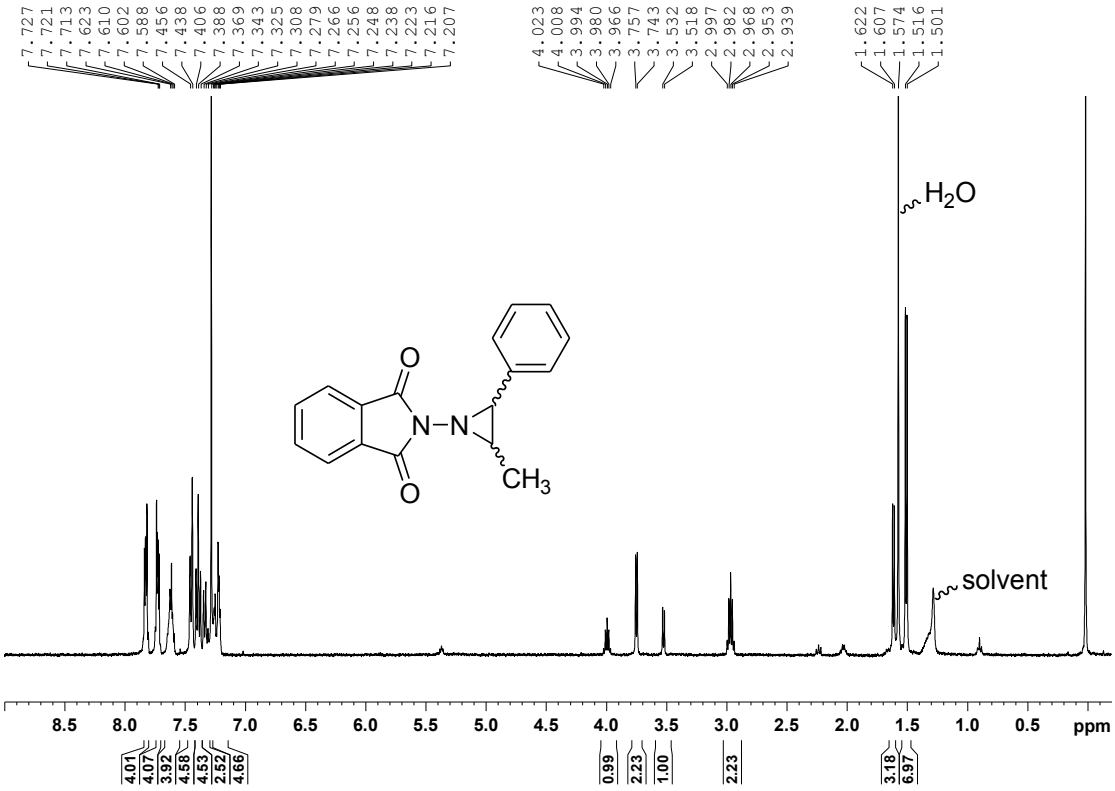
^{1}H NMR of **3f**:



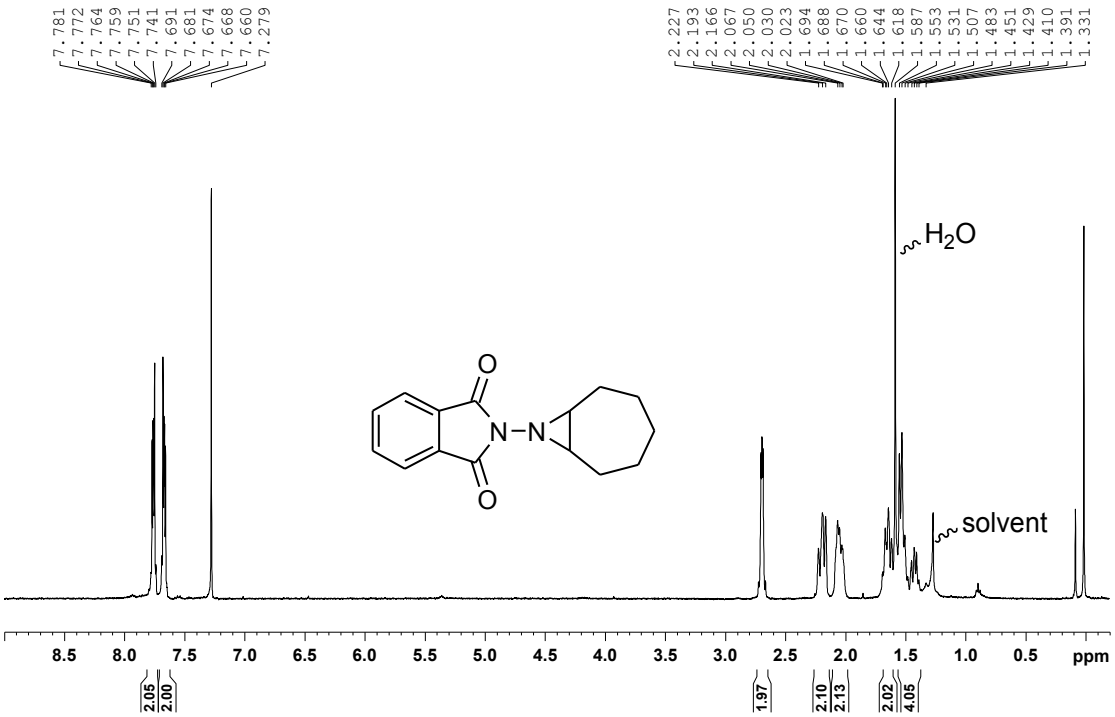
^{1}H NMR of **3g**:



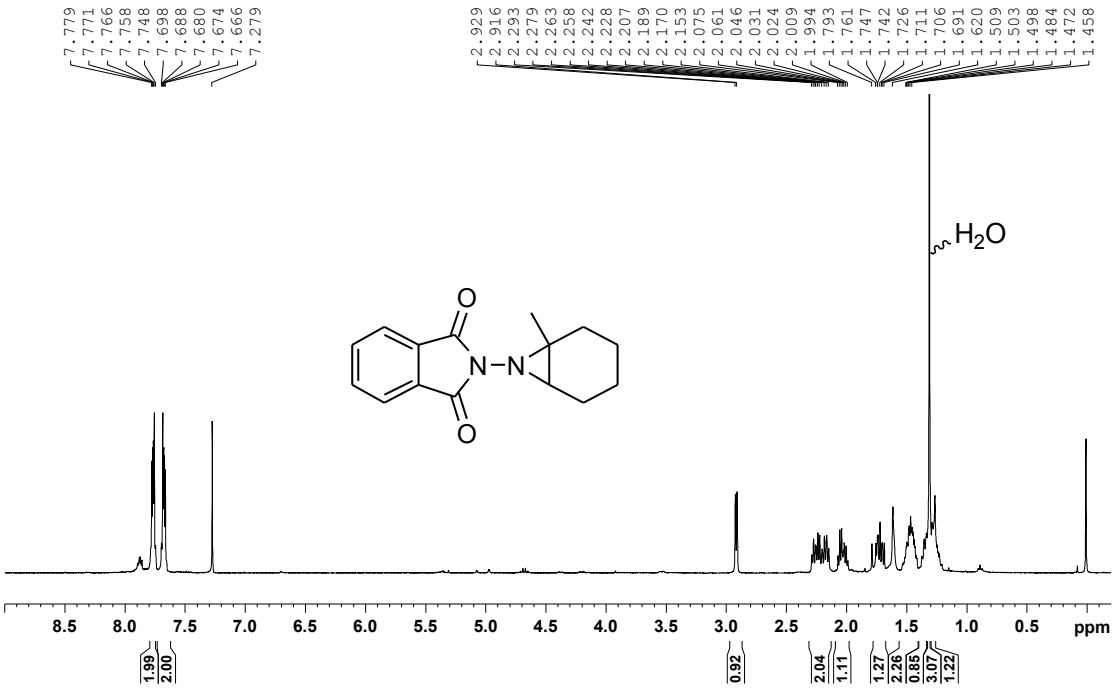
^{1}H NMR of **3h**:



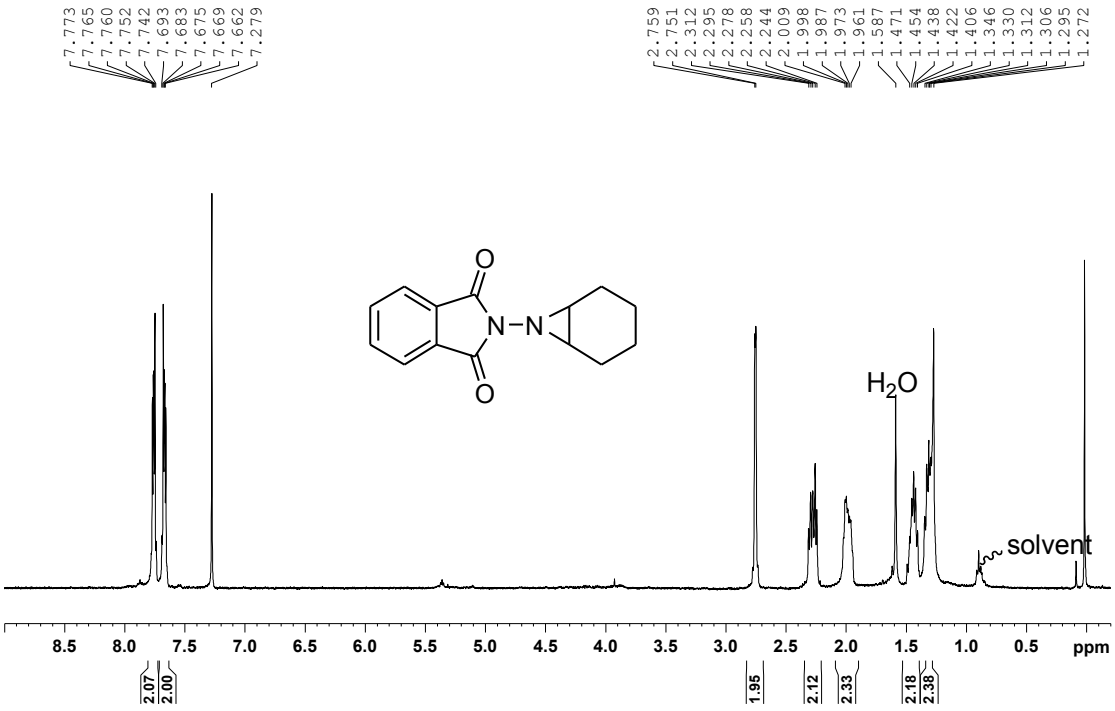
^{1}H NMR of **3i**:



^{1}H NMR of **3j**:



^{1}H NMR of **3k**:



^{1}H NMR of **3l**: