Supporting Information

Acyl-oxyallenes as *α*, *β*-Unsaturated Ketone Surrogates for Giese Radical Addition

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Contents

1. Materials and Methods

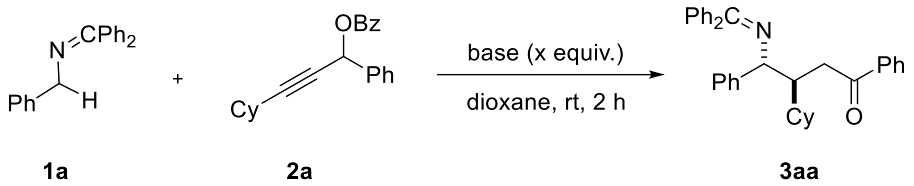
All the reactions were carried out under inert atmosphere unless otherwise noted. All the solvents used for the reactions were dried according to standard procedures. All glassware was oven dried in oven before use. All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise indicated. *t*-BuOK (98% pure from Sigma-Aldrich) and anhydrous dioxane (from J&K Scientific) were used in reactions. Anhydrous tetrahydrofuran (THF), acetonitrile (CH_3CN), and methylene chloride (CH_2Cl_2) were obtained by Glass Contour Solvent Purification System. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Flash column chromatography was performed on the Biotage® Automated Liquid Chromatography System Isolera Prime® using Santai Technologies iLOK 12-120 g silica gel cartridges and Santai Technologies SEPA FLASH 40-120 g silica gel cartridges or by using Santai Technologies™ silica gel, 60 Å (40–63 μm particle size) as stated. TLC analyses were performed on EMD TLC Silica gel 60 F_{254} Glass Plates and the spots were visualized by UV-light (254 nm) or an aqueous solution of phosphomolybdic acid, ceric sulfate, and $KMnO_4$. ^1H NMR spectra were recorded on a Bruker Ultra Shield Plus Avance III 500 MHz or a Bruker Ultra Shield Plus Avance III 400 MHz and are internally referenced to residual protic $CDCl_3$ (7.26 ppm) with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on a Bruker Ultra Shield Plus Avance III 400 MHz (101 MHz) and data are reported in terms of chemical shift relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm). ^{19}F NMR spectra were recorded on a Bruker Ultra Shield Plus Avance III 400 MHz (376 MHz). High Resolution Mass Spectra were obtained on Thermo Fisher Exactive Plus Orbitrap Mass Spectrum (ESI). X-ray analysis data was collected from Crystallography Facility at Shiyanjia lab.

2. Optimization Studies

Effect of Bases:

As shown in Table S1, 3 equivalents of K^{t}OBu were found to be optimal base

Table S1. Optimization of Bases



1a **2a** **3aa**

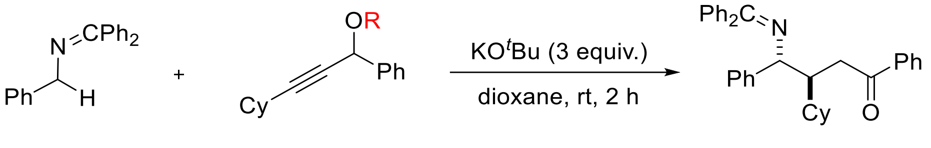
^{a}Entry	Base（x equiv.）	^{b}Yield (%)
1	K^{t}OBu (2.0 equiv.)	66
2	K^{t}OBu (3.0 equiv.)	89
3	K^{t}OBu (4.0 equiv.)	76
4	Li^{t}OBu (3.0 equiv.)	0
5	Na^{t}OBu (3.0 equiv.)	20
6	KOMe (3.0 equiv.)	46
7	NaOEt (3.0 equiv.)	0
8	NaOH (3.0 equiv.)	0
9	KOH (3.0 equiv.)	0
10	K_2CO_3 (3.0 equiv.)	0
11	LiHMDS (3.0 equiv.)	0
12	NaHMDS (3.0 equiv.)	0
13	TMG (3.0 equiv.)	0
14	Pyridine (3.0 equiv.)	0
15	NEt_3 (3.0 equiv.)	0

[a] Unless otherwise stated, the reaction was carried out under a nitrogen atmosphere at room temperature for 2 hours, using **1a** (0.1 mmol), **2a** (0.2 mmol), Base, and dioxane (1 mL). [b]The yield was determined by ^{1}H NMR of the crude mixture, using 1,3,5-trimethoxybenzene as an internal standard. dr was determined to be 10:1for all the entries.

Effect of Ester Group:

As shown in Table S2, Benzoyl group was found to be optimal ester group

Table S2: Optimization of Ester Group



1a **2a** **3aa**

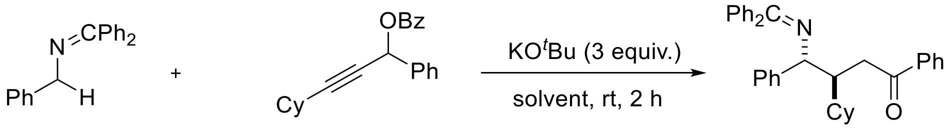
[a]Entry	-R	[b]Yield (%)
1	-Ac	60
2	-Boc	52
3	-Bz	83

[a] Unless otherwise stated, the reaction was carried out under a nitrogen atmosphere at room temperature for 2 hours, using **1a** (0.1 mmol), **2a** (0.2 mmol), K^{t}OBu (0.3 mmol), and dioxane (1 mL). [b] The yield was determined by ^{1}H NMR of the crude mixture, using 1,3,5-trimethoxybenzene as an internal standard. dr was determined to be 10:1.

Effect of Solvents:

As shown in Table S3, dioxane were found to be optimal solvent

Table S3: Optimization of Solvents



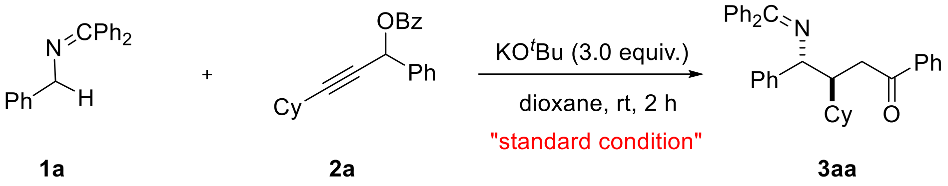
1a **2a** **3aa**

[a]Entry	Solvent	[b]Yield (%)
1	toluene	30
2	*n*-Hexane	40
3	MTBE	35
4	DCM	28
5	THF	38
6	Et_2O	35
7	Diglyme	18
8	DMSO	0
9	dioxane	83

[a] Unless otherwise stated, the reaction was carried out under a nitrogen atmosphere at room temperature for 2 hours, using **1a** (0.1 mmol), **2a** (0.2 mmol), K^{t}OBu (0.3 mmol), and solvent (1 mL). [b] The yield was determined by ^{1}H NMR of the crude mixture, using 1,3,5-trimethoxybenzene as an internal standard. dr was determined to be 10:1for all entries.

Effect of Other Conditions:

Table S4: Optimization of Other Conditions

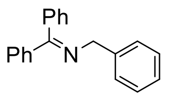


^{a}Entry	Deviation from the standard conditions	^{b}Yield（%)
1	none	89
2	2 equiv. **1a** and 1 equiv. **2a**	71
3	0.5 M vs 0.1M	55
4	0.2 M vs 0.1 M	79
5	0.05 M vs 0.1 M	82
6	air instead of N_2 atmosphere	32
7	TBAB as additive	79
8	18-crown-6 as additive	52
9	0 °C	50
10	50 °C	55
11	80 °C	0
12	dark condition	75

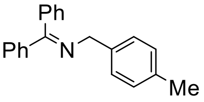
[a] Unless otherwise stated, the reaction was carried out under a nitrogen atmosphere at room temperature for 2 hours, using **1a** (0.1 mmol), **2a** (0.2 mmol), K^{t}OBu (0.3 mmol), and dioxane (1 mL). [b] The yield was determined by ^{1}H NMR, using 1,3,5-trimethoxybenzene as an internal standard. dr was determined to be 10:1for all entries.

3. Experimental Section

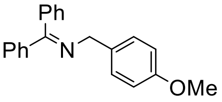
The following substrates were reported compounds and were prepared according to the following procedures.



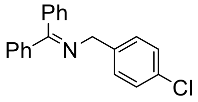
1a
ref. [1]



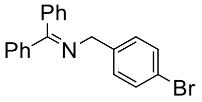
1b
ref. [2]



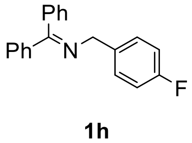
1c
ref. [1]



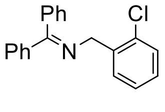
1f
ref. [1]



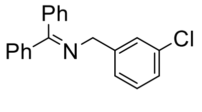
1g
ref. [2]



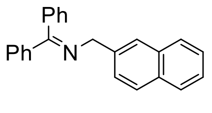
1h
ref. [2]



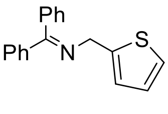
1i
ref. [1]



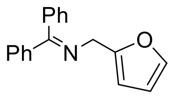
1j
ref. [1]



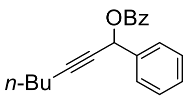
1k
ref. [3]



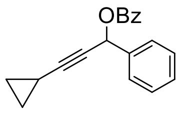
1l
ref. [2]



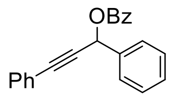
1m
ref. [2]



2b
ref. [4]

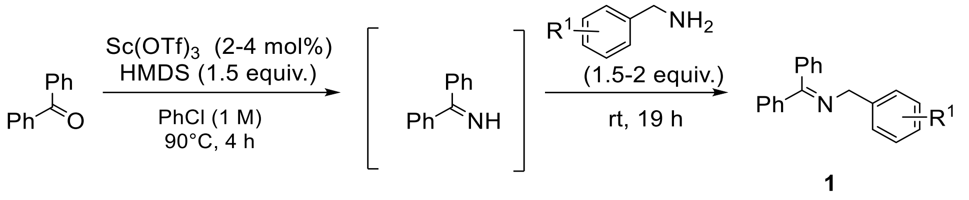


2e
ref. [5]



2j
ref. [6]

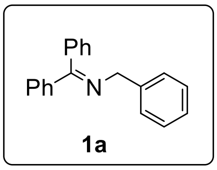
3.1 General procedure A for the preparation of *N*-benzyl ketone Imines



In a nitrogen-filled glove box, to an oven dried Schlenk tube with a magnetic stir bar was added benzophenone (1.0 equiv.), $Sc(OTf)_3$ (0.02-0.04 equiv.) and hexamethyldisilazane (1.5 equiv.) and dry chlorobenzene (1.0 M for benzophenone). The Schlenk tube was caped, removed from glove box, and stirred at 90 °C for 4h. The resulting reaction solution was cooled to room temperature, benzyl amine (1.5-2.0 equiv.) was then added. The reaction solution was stirred at room temperature for another 19h, then concentrated *in vacuo*. Purification of the crude by silica gel column chromatography afforded the title compounds **1a-1m**.

3.2 Characterization data of *N*-benzyl ketone Imines

N-benzyl-1,1-diphenylmethanimine (1a)

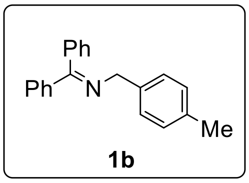


1a

The preparation of **1a** was followed according to General Procedure A from benzophenone (4.0 g, 22.0 mmol, 1.0 equiv.), Sc(OTf)$_3$ (230.0 mg, 0.4 mmol, 0.02 equiv.), HMDS (5.3 g, 33.0 mmol, 1.5 equiv.) and benzylamine (3.5 g, 33.0 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1a** as a white solid (5.8 g, 97% yield).

Spectral data for **1a**: ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.52 – 7.42 (m, 3H), 7.41 – 7.28 (m, 7H), 7.25 – 7.19 (m, 3H), 4.61 (s, 2H). This characterization data matches with the previously reported data.

N-(4-methylbenzyl)-1,1-diphenylmethanimine (1b)

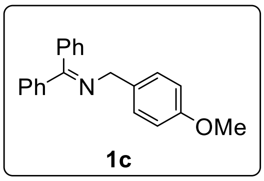


1b

The preparation of **1b** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (27.0 mg, 0.06 mmol, 0.02 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-methylbenzylamine (0.51g, 4.2 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (30% triethylamine in petroleum ether) afforded the title compound **1b** as a white solid (542 mg, 70% yield).

Spectral data for **1b**: ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.41 – 7.28 (m, 3H), 7.25 – 7.17 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.58 (s, 2H), 2.34 (s, 3H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 168.7, 140.0, 137.7, 136.9, 136.1, 130.1, 129.1, 128.7, 128.6, 128.2, 127.9, 127.7, 57.4, 21.2.This characterization data matches with the previously reported data.

N-(4-methoxybenzyl)-1,1-diphenylmethanimine (1c)

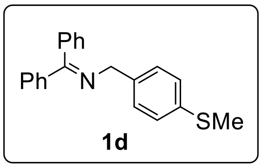


1c

The preparation of **1c** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (27.0 mg, 0.06 mmol, 0.02 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-methoxybenzylamine (0.58 g, 4.2 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1c** as a white solid (815 mg, 70% yield).

Spectral data for **1c**: ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.52 – 7.40 (m, 3H), 7.40 – 7.30 (m, 3H), 7.26 – 7.18 (m, 4H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.55 (s, 2H), 3.80 (s, 3H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 168.6, 158.5, 140.0, 136.9, 132.9, 130.1, 128.9, 128.68, 128.66, 128.6, 128.2, 127.9, 113.9, 57.0, 55.4. This characterization data matches with the previously reported data.

N-(4-(methylthio)benzyl)-1,1-diphenylmethanimine (1d)

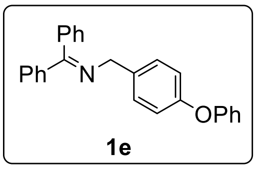


1d

The preparation of **1d** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-methylthiobenzylamine (0.86 g, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (5% triethylamine in petroleum ether) afforded the title compound **1d** as a white solid (565 mg, 65% yield).

Spectral data for **1d**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.46 (m, 3H), 7.44 – 7.34 (m, 3H), 7.33 – 7.25 (m, 4H), 7.24 (d, *J* = 5.7 Hz, 2H), 4.60 (s, 2H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 169.0, 139.8, 137.9, 136.7, 136.2, 130.2, 128.7, 128.7, 128.6, 128.3, 128.2, 127.9, 127.1, 57.1, 16.4; **IR (ATR)**: 3021, 2867, 1629, 1492, 1437, 1422, 1285, 1091, 1029, 809, 696 cm^{-1}; **HRMS (ESI)** calculated for $C_{21}H_{20}NS^+$ [M+H$^+$]: 318.1311, found: 318.1306.

N-(4-phenoxybenzyl)-1,1-diphenylmethanimine (1e)

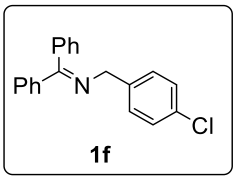


1e

The preparation of **1e** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-phenoxybenzylamine (1.1 g, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (5% triethylamine in petroleum ether) afforded the title compound **1e** as a white solid (983 mg, 99%).

Spectral data for **1e**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.55 – 7.43 (m, 3H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.39 – 7.30 (m, 6H), 7.24 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 8.0, 5.7 Hz, 4H), 4.61 (s, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 168.9, 157.7, 155.8, 139.8, 136.8, 135.8, 130.2, 129.8, 129.1, 128.72, 128.67, 128.65, 128.2, 127.9, 123.0, 119.2, 118.6, 57.0; **IR (ATR)**: 3056, 2874, 1621, 1589, 1487, 1442, 1232, 1200, 1165, 869, 763 cm^{-1}; **HRMS (ESI)** calculated for $C_{26}H_{22}NO^+$[M+H$^+$]: 364.1696, found: 364.1691.

N-(4-chlorobenzyl)-1,1-diphenylmethanimine (1f)

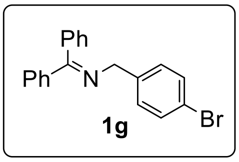


1f

The preparation of **1f** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (27.0 mg, 0.06 mmol, 0.02 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-chlorbenzylamine (0.59 g, 4.2 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1f** as a white solid (645 mg, 77%).

Spectral data for **1f**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.9 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.29 (m, 4H), 7.28 (d, *J* = 2.9 Hz, 3H), 7.19 (dd, *J* = 7.6, 1.9 Hz, 2H), 4.56 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 139.7, 139.3, 136.7, 132.3, 130.3, 129.1, 128.8, 128.7, 128.5, 128.2, 127.8, 56.8. This characterization data matches with the previously reported data.

N-(4-bromobenzyl)-1,1-diphenylmethanimine (1g)

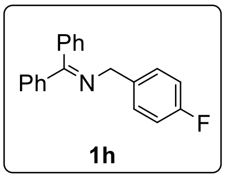


1g

The preparation of **1g** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (30.0 mg, 0.06 mmol, 0.02 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-bromobenzylamine (0.78 g, 4.2 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1g** as a white solid (955 mg, 99%).

Spectral data for **1g**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.9 Hz, 2H), 7.52 – 7.42 (m, 5H), 7.41 – 7.32 (m, 3H), 7.25 – 7.15 (m, 4H), 4.54 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 139.9, 139.7, 136.7, 131.5, 130.4, 129.5, 128.79, 128.78, 128.7, 128.3, 127.8, 120.4, 56.9. This characterization data matches with the previously reported data.

N-(4-fluorobenzyl)-1,1-diphenylmethanimine (1h)

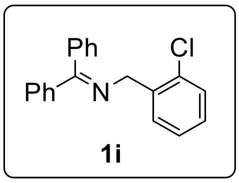


1h

The preparation of **1h** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (30.0 mg, 0.06 mmol, 0.02 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 4-flubenzylamine (526 mg, 4.2 mmol, 1.5 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1h** as a white solid (853 mg, 99%).

Spectral data for **1h**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.9 Hz, 2H), 7.53 – 7.43 (m, 3H), 7.43 – 7.26 (m, 5H), 7.20 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.56 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 161.8 (d, *J* = 244.1 Hz), 139.8, 136.7, 136.5 (d, *J* = 3.1 Hz), 130.3, 129.2 (d, *J* = 7.8 Hz), 128.8, 128.7, 128.6, 128.2, 127.8, 115.2 (d, *J* = 21.2 Hz), 56.8; **^{19}F NMR** (375 MHz, $CDCl_3$) δ 116.7. This characterization data matches with the previously reported data.

N-(2-chlorobenzyl)-1,1-diphenylmethanimine (1i)

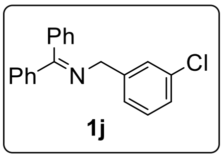


1i

The preparation of **1i** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 2-chlorobenzylamine (793 mg, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1i** as a white solid (816 mg, 97%).

Spectral data for **1i**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.44 – 7.27 (m, 5H), 7.25 – 7.15 (m, 3H), 4.67 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 139.9, 138.5, 136.6, 133.2, 130.3, 129.4, 129.2, 128.81, 128.76, 128.7, 128.3, 127.9, 127.8, 126.9, 55.0. This characterization data matches with the previously reported data.

N-(3-chlorobenzyl)-1,1-diphenylmethanimine (1j)

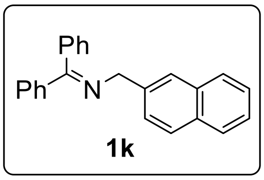


1j

The preparation of **1j** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 3-chlorobenzamine (793 mg, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (5% ethyl acetate in petroleum ether with 0.5% triethylamine) afforded the title compound **1j** as a white solid (774 mg, 92%).

Spectral data for **1j**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.44 – 7.27 (m, 5H), 7.25 – 7.15 (m, 3H), 4.67 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 142.9, 139.7, 136.7, 134.4, 130.4, 129.7, 128.80, 128.79, 128.7, 128.3, 127.9, 127.8, 126.8, 125.9, 56.9. This characterization data matches with the previously reported data.

N-(naphthalen-2-ylmethyl)-1,1-diphenylmethanimine (1k)

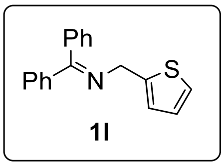


1k

The preparation of **1k** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 1-(2-naphthyl) methylamine (880 mg, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1k** as a white solid (863 mg, 97%).

Spectral data for **1k**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 3H), 7.79 – 7.67 (m, 3H), 7.56 – 7.41 (m, 6H), 7.37 (q, *J* = 6.7, 6.3 Hz, 3H), 7.26 – 7.20 (m, 2H), 4.78 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 140.0, 138.4, 136.9, 133.7, 132.6, 130.3, 128.8, 128.7, 128.2, 128.03, 127.95, 127.9, 127.8, 126.5, 126.0, 125.9, 125.5, 57.8. This characterization data matches with the previously reported data.

1,1-diphenyl-N-(thiophen-3-ylmethyl)methanimine (1l)

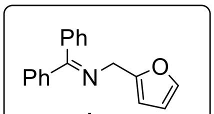


1l

The preparation of **1l** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and 2-thiophenemethylamine (634 mg, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent 10% triethylamine in petroleum ether) afforded the title compound **1l** as a white solid (416 mg, 55%).

Spectral data for **1l** : **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.7 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.33 – 7.21 (m, 3H), 7.18 – 7.09 (m, 3H), 6.87 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.79 (d, *J* = 3.4 Hz, 1H), 4.67 (s, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 169.3, 144.4, 139.6, 136.5, 130.4, 128.81, 128.78, 128.76, 128.2, 127.9, 126.8, 124.1, 123.6, 53.0. This characterization data matches with the previously reported data.

***N*-(furan-2-ylmethyl)-1,1-diphenylmethanimine (1m)**

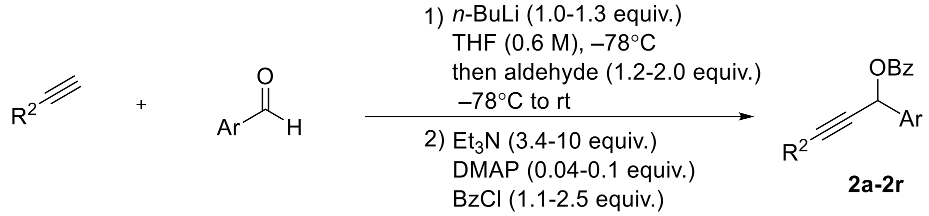


1m

The preparation of **1m** was followed according to General Procedure A from benzophenone (0.5 g, 2.8 mmol, 1.0 equiv.), Sc(OTf)$_3$ (54.0 mg, 0.1 mmol, 0.04 equiv.), HMDS (678 mg, 4.2 mmol, 1.5 equiv.) and furan-2-ylmethanamine (543 mg, 5.6 mmol, 2.0 equiv.). Purification by silica gel column chromatography with eluent (10% triethylamine in petroleum ether) afforded the title compound **1m** as a white solid (717 mg, 99%).

Spectral data for **1m**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.39 (m, 3H), 7.41 – 7.26 (m, 4H), 7.23 (d, *J* = 6.5 Hz, 2H), 6.39 – 6.28 (m, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 4.53 (s, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 170.2, 153.9, 141.8, 139.7, 136.5, 130.3, 128.8, 128.7, 128.2, 128.0, 110.4, 106.5, 51.2. This characterization data matches with the previously reported data.

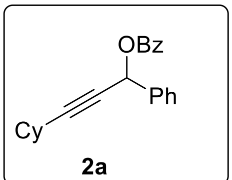
3.3 General procedure B for the preparation of Propargyl Ester



To an Oven-dried Schlenk flask equipped with a magnetic stir bar under nitrogen atmosphere was successively added with alkyne (1.0 equiv.) and THF (0.6 M for alkyne) via syringe. The solution was cooled to -78 °C before *n*-butyllithium (2.3-2.4 M in hexane, 1.0-1.3 equiv.) was added dropwise. The resulting solution was kept stirring at -78 °C for 20 minutes, and then slowly warmed to rt and stirred for 1 hour. The resulting mixture was cooled to -78 °C, and aldehyde (1.2-1.5 equiv.) was then added. The reaction mixture was allowed to slowly warm to rt and stirred at rt until the reaction was judged to be complete by TLC analysis. The reaction was quenched with adding sat. NH_4Cl (aq.) and ethyl acetate to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for twice. The combined organic layers were dried over anhydrous Na_2SO_4, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography or directly used for the next reaction without further purification.

To a solution of above product and DMAP (0.04-0.1 equiv.) in DCM (1.0 M) was added with Et_3N (3.4-10 equiv.). The resulting mixture was cooled to 0 °C, the benzoyl chloride (1.1-2.5 equiv.) was then added, and the reaction mixture was warmed to rt and stirred overnight. The reaction was quenched with adding sat. NH_4Cl (aq.) to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with DCM for two times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude product was purified by SiO_2 flash column chromatography (petroleum ether: ethyl acetate) to obtain products **2a**-**2r**.

3.4 Characterization data of Propargyl ester



2a

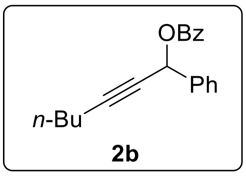
3-cyclohexyl-1-phenylprop-2-yn-1-yl benzoate (2a)

The preparation of **2a** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (833 mg, 7.7 mmol, 1.0 equiv.), *n*-butyllithium (2.4 M in hexane, 4.2 mL, 10.0 mmol, 1.3 equiv.), benzaldehyde (1.6 g, 15.4 mmol, 2.0 equiv.). Purification through SiO_2 flash column chromatography with elution (20% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.2 g, 75%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (7.6 mL, 55.0 mmol, 7.1 equiv.), DMAP (73.0 mg, 0.6 mmol, 0.07 equiv.), benzoyl chloride (1.3 mL, 11.0 mmol, 1.4 equiv.). Purification through SiO_2 flash column chromatography with elution (17% ethyl acetate in petroleum ether) afforded title compound **2a** as a pale-yellow oil (1.6 g, 89%).

Spectral data for **2a**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 6.8 Hz, 2H), 7.63 (d, J = 6.6

Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 – 7.33 (m, 5H), 6.76 (s, 1H), 2.58 – 2.42 (m, 1H), 1.87 – 1.78 (m, 2H), 1.74 – 1.66 (m, 2H), 1.57 – 1.45 (m, 3H), 1.37 – 1.26 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.65, 137.98, 133.22, 130.17, 130.01, 128.80, 128.67, 128.45, 127.87, 92.66, 76.78, 66.70, 32.5, 29.25, 25.95, 24.92; **IR (ATR)**: 2929, 2853, 1718, 1494, 1449, 1315, 1258, 1175, 1093, 1068, 1025, 937, 903, 696, 709 cm^{-1}; **HRMS (ESI)** calculated for $C_{22}H_{23}O_2^+$ [M+H$^+$]: 319.1693, found: 319.1689.

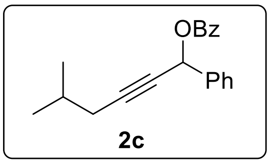
1-phenylhept-2-yn-1-yl benzoate (2b)



2b

The preparation of **2b** was followed according to General Procedure B. The propargyl alcohol was synthesized by using 1-hexyne (2.0 mL, 17.4 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 9.1 mL, 21.0 mmol, 1.2 equiv.), benzaldehyde (2.1 mL, 21.0 mmol, 1.2 equiv.), Purification through SiO_2 flash column chromatography with elution (20% ethyl acetate in petroleum ether) afforded propargyl alcohol (2.2 g, 75%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (17.0 mL, 120.0 mmol, 6.9 equiv.), DMAP (150.0 mg, 1.2 mmol, 0.07 equiv.), benzoyl chloride (2.8 mL, 24 mmol, 1.4 equiv.). Purification through SiO_2 flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2b** as a pale-yellow oil (2.9 g, 82%).

Spectral data for **2b**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.6 Hz, 1H), 7.62 (d, J = 6.6 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 – 7.34 (m, 6H), 6.72 (s, 1H), 2.33 – 2.24 (m, 2H), 1.58 – 1.48 (m, 2H), 1.49 – 1.35 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). This characterization data matches with the previously reported data.



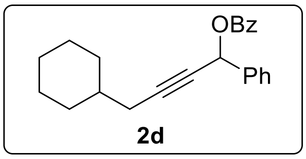
2c

5-methyl-1-phenylhex-2-yn-1-yl benzoate (2c)

The preparation of **2c** was followed according to General Procedure B. The propargyl alcohol was synthesized by using 4-methyl-1-pentyne (1.0 g, 12.0 mmol, 1.0 equiv.), *n*-butyllithium (2.4 M in hexane, 5.5 mL, 13.2 mmol, 1.1 equiv.), benzaldehyde (2.4 mL, 18.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (9% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.8 g, 80%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (12.5 mL, 90.0 mmol, 7.5 equiv.), DMAP (110.4 mg, 0.9 mmol, 0.08 equiv.), benzoyl chloride (2.6 mL, 22.5 mmol, 1.9 equiv.). Purification through SiO_2 flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2c** as a pale-yellow oil (2.1 g, 82%)

Spectral data for **2c**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, J = 6.8 Hz, 2H), 7.67 (d, J = 6.5

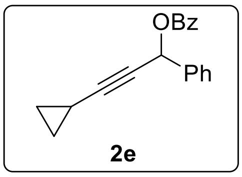
Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 – 7.37 (m, 5H), 6.78 (s, 1H), 2.22 (dd, J = 6.6, 2.0 Hz, 2H), 1.95 – 1.83 (m, 1H), 1.02 (d, J = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.56, 137.85, 133.19, 130.03, 129.92, 128.79, 128.65, 128.41, 127.77, 87.62, 77.76, 66.69, 28.07, 28.02, 22.08; **IR (ATR)**: 2868, 2858, 1718, 1601, 1494, 1451, 1342, 1316, 1175, 1141, 1093, 1068, 1025, 936, 908, 756, 696, 709, 624, 565 cm^{-1}; **HRMS (ESI)** calculated for $C_{20}H_{21}O_2^+$ [M+H$^+$]: 293.1536, found: 293.1534.


2d

4-cyclohexyl-1-phenylbut-2-yn-1-yl benzoate (2d)

The preparation of **2d** was followed according to General Procedure B. The propargyl alcohol was synthesized by using 3-cyclohexy-1-propyne (1.1 mL, 9.0 mmol, 1.0 equiv.), *n*-butyllithium (2.4 M in hexane, 4.1 mL, 9.9 mmol, 1.1 equiv.), benzaldehyde (1.8 mL, 13.5 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (9% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.1 g, 52%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (6.0 mL, 43.0 mmol, 5.0 equiv.), DMAP (52.7 mg, 0.43 mmol, 0.05 equiv.), benzoyl chloride (1.3 mL, 10.8 mmol, 1.2 equiv.). Purification through SiO_2 flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2d** as a yellow oil (1.2 g, 86%).

Spectral data for **2d**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.48 – 7.34 (m, 5H), 6.74 (s, 1H), 2.19 (dd, J = 6.7, 2.1 Hz, 2H), 1.81 (d, J = 9.7 Hz, 2H), 1.75 – 1.60 (m, 3H), 1.58 – 1.41 (m, 1H), 1.31 – 1.08 (m, 3H), 1.09 – 0.94 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 137.9, 133.2, 130.1, 130.0, 128.8, 128.7, 128.5, 127.8, 87.7, 77.7, 66.8, 37.3, 32.8, 26.8, 26.4, 26.21; **IR (ATR)**: 2922, 2851, 1718, 1449, 1315, 1258, 1175, 1093, 1067, 1025, 937, 899, 757, 709, 696, 587, 571 cm^{-1}; **HRMS (ESI)** calculated for $C_{23}H_{25}O_2^+$ [M+H$^+$]: 333.1849, found: 333.1842.

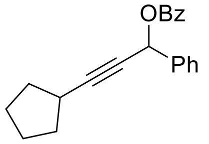

2e

3-cyclopropyl-1-phenylprop-2-yn-1-yl benzoate (2e)

The preparation of **2e** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclopropylacetylene (2.0 mL, 30.0 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 17.0 mL, 39.0 mmol, 1.3 equiv.), benzaldehyde (4.6 mL, 45.4 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (9% ethyl acetate in petroleum ether) afforded propargyl alcohol (2.3 g, 45%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (18.5 mL, 133.0 mmol, 4.4 equiv.), DMAP (163.2 mg, 1.3 mmol, 0.04 equiv.), benzoyl chloride (3.9 mL, 33.3 mmol, 1.1 equiv.).

Purification through SiO$_2$ flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2e** as a yellow oil (980 mg, 27%).

Spectral data for **2e**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.51 (m, 3H), 7.47 – 7.32 (m, 5H), 6.69 (s, 1H), 1.38 – 1.28 (m, 1H), 0.85 – 0.72 (m, 4H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.6, 137.9, 133.3, 130.1, 130.0, 128.8, 128.7, 128.5, 127.8, 91.7, 72.1, 66.7, 8.5, –0.2 . This characterization data matches with the previously reported data.



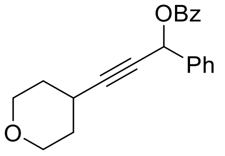
2f

3-cyclopentyl-1-phenylprop-2-yn-1-yl benzoate (2f)

The preparation of **2f** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclopentylacetylene (0.44 mL, 3.8 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.2 mmol, 1.1 equiv.), benzaldehyde (0.4 mL, 3.8 mmol, 1.5 equiv.). Purification through SiO$_2$ flash column chromatography with elution (9% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.67 g, 87%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et$_3$N (4.6 mL, 33.0 mmol, 8.7 equiv.), DMAP (41.0 mg, 0.33 mmol, 0.09 equiv.), benzoyl chloride (1.0 mL, 8.3 mmol, 2.2 equiv.). Purification through SiO$_2$ flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2f** as a yellow oil (380 mg, 38%).

Spectral data for **2f**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 6.3 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.34 (m, 5H), 6.78 (s, 1H), 2.87 – 2.66 (m, 1H), 2.01 – 1.90 (m, 2H), 1.79 – 1.64 (m, 4H), 1.63 – 1.53 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.6, 137.9, 133.1, 130.1, 129.9, 128.7, 128.6, 128.4, 127.8, 92.8, 76.2, 66.6, 33.7, 30.2, 25.1; **IR (ATR)**: 2967, 2963, 2237, 1717, 1699, 1494, 1450, 1398, 1315, 1249, 1093, 1079, 1025, 996, 906, 791, 696, 550 cm^{-1}; **HRMS (ESI)** calculated for $C_{21}H_{21}O_2^+$ [M+H$^+$]: 305.1536, found: 305.1536.

1-phenyl-3-(tetrahydro-2H-pyran-4-yl)prop-2-yn-1-yl benzoate (2g)



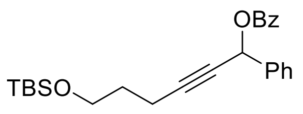
2g

The preparation of **2g** was followed according to General Procedure B. The propargyl alcohol was synthesized by using 4-ethynyltetrahydro-2H-pyran (500 mg, 4.5 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.0 mL, 4.5 mmol, 1.0 equiv.), benzaldehyde (0.6 mL, 5.9 mmol, 1.3 equiv.). Purification through SiO$_2$ flash column chromatography with elution (20% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.0 g, 99%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et$_3$N

(6.2 mL, 45.0 mmol, 10.0 equiv.), DMAP (56.0 mg, 0.5 mmol, 0.1 equiv.), benzoyl chloride (1.3 mL, 11.3 mmol, 2.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2g** as a yellow oil (1.2 g, 83%).

Spectral data for **2g**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.9 Hz, 2H), 7.62 (d, *J* = 6.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.35 (m, 5H), 6.74 (s, 1H), 3.95 – 3.83 (m, 2H), 3.58 – 3.43 (m, 2H), 2.79 – 2.63 (m, 1H), 1.95 – 1.81 (m, 2H), 1.80 – 1.64 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 137.6, 133.3, 129.9, 128.9, 128.7, 128.4, 127.7, 90.4, 78.0, 66.4, 66.3, 31.9, 26.3; **IR (ATR)**: 2950, 2947, 1718, 1600, 1494, 1451, 1316, 1248, 1176, 1127, 1093, 1066, 1024, 998, 904, 765, 710, 697, 599, 586, 583 cm^{-1}; **HRMS (ESI)** calculated for $C_{21}H_{21}O_3^+$ [M+H$^+$]: 321.1485, found: 321.1482.

6-((tert-butyldimethylsilyl)oxy)-1-phenylhex-2-yn-1-yl benzoate (2h)

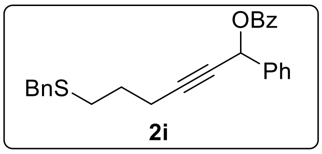


2h

The preparation of **2h** was followed according to General Procedure B. The propargyl alcohol was synthesized by using tert-butyldimethyl(4-pentynyloxy)silane (1.0 g, 6.0 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.6 mL, 6.0 mmol, 1.0 equiv.), benzaldehyde (0.9 mL, 9.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (9% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.74 g, 41%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (4.6 mL, 33.0 mmol, 5.5 equiv.), DMAP (41.0 mg, 0.33 mmol, 0.06 equiv.), benzoyl chloride (1.0 mL, 8.3 mmol, 1.4 equiv.). Purification through SiO_2 flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2h** as a yellow oil (812 mg, 60%).

Spectral data for **2h**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.33 (m, 5H), 6.70 (s, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.43 – 2.32 (m, 2H), 1.82 – 1.67 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 137.8, 133.3, 130.03, 129.99, 128.9, 128.7, 128.5, 127.8, 88.2, 77.1, 66.7, 61.6, 31.5, 26.0, 18.4, 15.4, -5.3; **IR (ATR)**: 2952, 2928, 2855, 1720, 1471, 1451, 1316, 1249, 1094, 1068, 1026, 973, 938, 834, 775, 709, 696, 663, 588 cm^{-1}; **HRMS (ESI)** calculated for $C_{25}H_{33}O_3Si^+$ [M+H$^+$]: 409.2193, found: 409.2188.

6-(benzylthio)-1-phenylhex-2-yn-1-yl benzoate (2i)

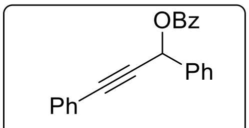


2i

The preparation of **2i** was followed according to General Procedure B. The propargyl alcohol was synthesized by using benzyl(pent-4-yn-1-yl)sulfane (1.4 g, 7.4 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 3.5 mL, 8.1 mmol, 1.1 equiv.), benzaldehyde (1.5 mL, 11.1 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.5 g, 70%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (3.5 mL, 25.0 mmol, 3.4 equiv.), DMAP (61.0 mg, 0.5 mmol, 0.07 equiv.), benzoyl chloride (1.5 mL, 12.5 mmol, 1.7 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2i** as a yellow oil (1.8 g, 90%).

Spectral data for **2i**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.9 Hz, 2H), 7.61 (d, *J* = 6.3 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.37 (m, 5H), 7.30 (d, *J* = 4.3 Hz, 4H), 7.28 – 7.19 (m, 1H), 6.71 (s, 1H), 3.69 (s, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.37 (m, 2H), 1.80 (p, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 138.5, 137.7, 133.3, 130.0, 128.9, 128.7, 128.6, 128.5, 127.1, 127.1, 87.4, 77.6, 66.6, 36.3, 30.4, 28.0, 18.1; **IR (ATR)**: 2982, 2928, 1712, 1600, 1449, 1312, 1268, 1266, 1171, 1092, 1068, 1025, 993, 898, 858, 754, 669, 667, 663, 477 cm^{-1}; **HRMS (ESI)** calculated for $C_{26}H_{25}O_2S^+$ [M+H$^+$]: 401.1570, found: 401.1568.

1,3-diphenylprop-2-yn-1-yl benzoate (2j)

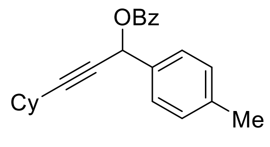


2j

The preparation of **2j** was followed according to General Procedure B. Benzoylation reaction of the 1,3-diphenylprop-2-yn-1-ol (1.8 g, 8.6 mmol) with Et_3N (12.0 mL, 86.0 mmol, 10.0 equiv.), DMAP (105.0 mg, 0.9 mmol, 0.1 equiv.), benzoyl chloride (2.0 mL, 17.2 mmol, 2.0 equiv.). Purification though SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2j** as a yellow oil (1.8 g, 78%).

Spectral data for **2j**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 2H), 7.71 (d, *J* = 6.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.49 – 7.39 (m, 5H), 7.37 – 7.29 (m, 3H), 6.98 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.60, 137.37, 133.38, 132.08, 130.07, 129.92, 129.08, 128.93, 128.85, 128.52, 128.40, 127.92, 122.26, 87.39, 85.74, 66.74. This characterization data matches with the previously reported data.

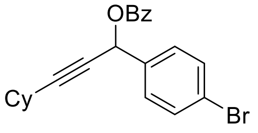
3-cyclohexyl-1-(p-tolyl)prop-2-yn-1-yl benzoate (2k)



2k

The preparation of **2k** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.6 mL, 4.6 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.2 mL, 5.0 mmol, 1.1 equiv.), *p*-tolualdehyde (0.8 mL, 7.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.0 g, 99%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (3.0 mL, 22.0 mmol, 5.0 equiv.), DMAP (54.0 mg, 0.44 mmol, 0.1 equiv.), benzoyl chloride (1.3 mL, 11.0 mmol, 2.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2k** as a yellow oil (1.5 g, 99%).

Spectral data for **2k**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.30 – 7.24 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 2.54 – 2.43 (m, 1H), 2.38 (s, 3H), 1.88 – 1.78 (m, 2H), 1.75 – 1.64 (m, 2H), 1.55 – 1.40 (m, 3H), 1.37 – 1.21 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 138.2, 137.8, 133.1, 129.9, 129.5, 128.5, 128.3, 124.8, 92.4, 76.8, 66.6, 32.4, 29.1, 25.0, 24.8, 21.5; **IR (ATR)**: 2929, 2854, 1718, 1601, 1514, 1450, 1315, 1257, 1175, 1094, 1068, 1025, 919, 813, 764, 709, 686, 573, 549 cm$^{-1;}$ **HRMS (ESI)** calculated for $C_{23}H_{25}O_2^+$ [M+H$^+$]: 355.1669, found: 355.1669.



2l

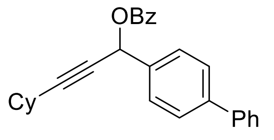
1-(4-bromophenyl)-3-cyclohexylprop-2-yn-1-yl benzoate (2l)

The preparation of **2l** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.6 mL, 4.6 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.2 mL, 5.0 mmol, 1.1 equiv.), 4-bromobenzaldehyde (1.3 g, 7.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.1 g, 82%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.4 mL, 17.0 mmol, 3.7 equiv.), DMAP (41.0 mg, 0.34 mmol, 0.1 equiv.), benzoyl chloride (1.0 mL, 8.5 mmol, 1.8 equiv.). Purification through SiO_2 flash column chromatography with elution (11% ethyl acetate in petroleum ether) afforded title compound **2l** as a yellow oil (1.2 g, 80%).

Spectral data for **2l**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.48 (m, 5H), 7.43 (t, *J* = 8.4, 7.1 Hz, 2H), 6.69 (s, 1H), 2.53 – 2.40 (m, 1H), 1.86 – 1.77 (m, 2H), 1.75 – 1.65 (m, 2H), 1.55 – 1.42 (m, 3H), 1.37 – 1.26 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 137.1, 133.4, 131.8, 130.0, 129.9, 129.6, 128.5, 122.9, 93.1, 76.3, 66.0, 32.4, 29.2, 25.9, 24.9;

IR (ATR): 2930, 2854, 1718, 1585, 1487, 1450, 1407, 1316, 1290, 1257, 1175, 1093, 1068, 1025, 1012, 926, 820, 755, 709, 686, 667, 551 cm^{-1}; **HRMS (ESI)** calculated for $C_{22}H_{22}BrO_2^+$ [M+H$^+$]: 397.0798, found: 397.0794.

1-([1,1'-biphenyl]-4-yl)-3-cyclohexylprop-2-yn-1-yl benzoate (2m)

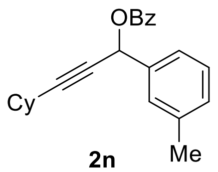


2m

The preparation of **2m** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.5 mL, 3.8 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.2 mmol, 1.1 equiv.), 4-biphenylcarboxaldehyde (1.1 g, 6.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.1 g, 99%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.6 mL, 19.0 mmol, 5.0 equiv.), DMAP (46.0 mg, 0.4 mmol, 0.1 equiv.), benzoyl chloride (1.1 mL, 9.5 mmol, 2.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2m** as a yellow oil (1.4 g, 93%).

Spectral data for **2m**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.66 – 7.60 (m, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.82 (s, 1H), 2.58 – 2.47 (m, 1H), 1.92 – 1.81 (m, 2H), 1.80 – 1.68 (m, 2H), 1.59 – 1.48 (m, 3H), 1.39 – 1.28 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 141.8, 140.7, 137.0, 133.2, 130.2, 130.0, 128.9, 128.5, 128.4, 127.6, 127.4, 127.3, 92.8, 76.8, 66.5, 32.5, 29.3, 26.0, 24.9; **IR (ATR)**: 2928, 2852, 1717, 1600, 1485, 1450, 1315, 1290, 1175, 1093, 1068, 1025, 993, 904, 765, 709, 666, 551 cm^{-1}; **HRMS (ESI)** calculated for $C_{28}H_{27}O_2^+$ [M+H$^+$]: 395.2006, found: 395.2002.

3-cyclohexyl-1-(m-tolyl)prop-2-yn-1-yl benzoate (2n)

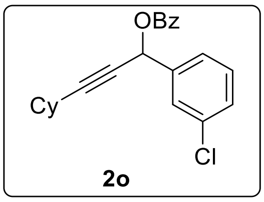


2n

The preparation of **2n** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.6 mL, 4.6 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.2 mL, 5.0 mmol, 1.1 equiv.), *m*-tolualdehyde (0.8 mL, 7.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (33% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.0 g, 99%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.4 mL, 17.0 mmol, 3.7 equiv.), DMAP (56.0 mg, 0.46 mmol, 0.1 equiv.), benzoyl chloride (1.3 mL,11.5 mmol, 2.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2n** as a yellow oil (0.9 g, 61%).

Spectral data for **2n**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 2.53 – 2.44 (m, 1H), 2.38 (s, 3H), 1.87 – 1.77 (m, 2H), 1.76 – 1.66 (m, 2H), 1.55 – 1.44 (m, 3H), 1.37 – 1.22 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 138.4, 137.9, 133.2, 130.3, 130.0, 129.6, 128.60, 128.58, 128.5, 125.0, 92.5, 66.8, 32.5, 29.3, 26.0, 24.9, 21.6; **IR (ATR)**: 2930, 2854, 1719, 1601, 1450, 1315, 1257, 1175, 1093, 1068, 1025, 935, 900, 788, 747, 710 cm^{-1}; **HRMS (ESI)** calculated for $C_{23}H_{25}O_2^+$ [M+H$^+$]: 333.1849, found: 333.1850.

1-(3-chlorophenyl)-3-cyclohexylprop-2-yn-1-yl benzoate (2o)

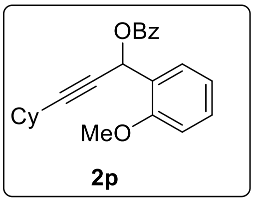


2o

The preparation of **2o** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.5 mL, 3.8 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.2 mmol, 1.1 equiv.), 3-chlorobenzaldehyde (0.7 mL, 6.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.9 g, 99%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.6 mL, 19.0 mmol, 5.0 equiv.), DMAP (46.0 mg, 0.4 mmol, 0.1 equiv.), benzoyl chloride (1.1 mL, 9.5 mmol, 2.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2o** as a yellow oil (1.1 g, 82%).

Spectral data for **2o**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.0 Hz, 2H), 7.63 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.37 – 7.30 (m, 2H), 6.70 (s, 1H), 2.55 – 2.43 (m, 1H), 1.88 – 1.78 (m, 2H), 1.75 – 1.65 (m, 2H), 1.57 – 1.42 (m, 3H), 1.38 – 1.28 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 139.9, 134.5, 133.4, 130.02, 129.95, 129.9, 129.0, 128.5, 128.0, 126.0, 93.2, 76.2, 65.9, 32.4, 29.2, 25.9, 24.9; **IR (ATR)**: 2929, 2853, 1719, 1599, 1577, 1449, 1433, 1315, 1259, 1246, 1195, 1176, 1092, 1068, 1025, 934, 877, 786, 756, 709, 689, 671 cm^{-1}; **HRMS (ESI)** calculated for $C_{22}H_{21}O_2ClNa^+$ [M+Na$^+$]: 375.1122, found: 375.1118.

3-cyclohexyl-1-(2-methoxyphenyl)prop-2-yn-1-yl benzoate (2p)

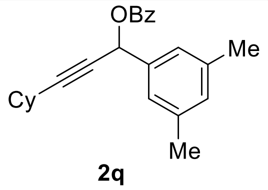


2p

The preparation of **2p** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.5 mL, 3.8 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.2 mmol, 1.1 equiv.), *o*-anisaldehyde (0.7 mL, 6.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.7 g, 81%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et$_3$N (2.0 mL, 15.0 mmol, 4.0 equiv.), DMAP (37.0 mg, 0.4 mmol, 0.8 equiv.), benzoyl chloride (0.9 mL, 7.5 mmol, 2.0 equiv.). Purification through SiO$_2$ flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2p** as a yellow oil (0.9 g, 88%).

Spectral data for **2p**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.07 (d, J = 7.0 Hz, 2H), 7.83 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.41 – 7.32 (m, 1H), 7.10 – 7.02 (m, 2H), 6.90 (d, J = 7.3 Hz, 1H), 3.80 (s, 3H), 2.60 – 2.41 (m, 1H), 1.88 – 1.79 (m, 2H), 1.76 – 1.67 (m, 2H), 1.56 – 1.46 (m, 3H), 1.38 – 1.25 (m, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.5, 157.0, 132.9, 130.4, 130.2, 129.9, 129.1, 128.3, 126.0, 120.5, 110.8, 91.9, 76.8, 61.6, 55.6, 32.5, 29.2, 25.9, 24.9; **IR (ATR)**: 2929, 2853, 1719, 1602, 1589, 1492, 1463, 1445, 1315, 1287, 1245, 1174, 1162, 1094, 1068, 1049, 1025, 945, 919, 901, 753, 710, 687, 597 cm^{-1}; **HRMS (ESI)** calculated for C$_{23}$H$_{25}$O$_3^+$ [M+H$^+$]: 349.1798, found: 349.1797.

3-cyclohexyl-1-(3,5-dimethylphenyl)prop-2-yn-1-yl benzoate (2q)

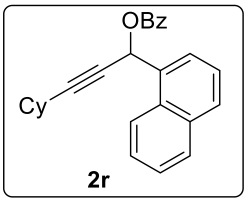


2q

The preparation of **2q** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.6 mL, 4.6 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 2.2 mL, 5.0 mmol, 1.1 equiv.), 3,5-dimethylbenzaldehyde (0.9 mL, 7.0 mmol, 1.5 equiv.). Purification through SiO$_2$ flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (1.0 g, 90%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et$_3$N (2.4 mL, 17.0 mmol, 4.0 equiv.), DMAP (56.0 mg, 0.46 mmol, 0.1 equiv.), benzoyl chloride (1.3 mL, 11.5 mmol, 2.5 equiv.). Purification through SiO$_2$ flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2q** as a yellow oil (1.4 g, 96%).

Spectral data for **2q**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.10 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.25 (s, 2H), 7.00 (s, 1H), 6.70 (s, 1H), 2.55 – 2.44 (m, 1H), 2.36 (s, 6H), 1.88 – 1.79 (m, 2H), 1.78 – 1.70 (m, 2H), 1.58 – 1.47 (m, 3H), 1.39 – 1.28 (m, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.7, 138.2, 137.8, 133.1, 130.5, 130.3, 130.0, 128.4, 125.7, 92.3, 77.0, 66.8, 32.5, 29.2, 26.0, 24.9, 21.4; **IR (ATR)**: 2930, 2855, 1718, 1603, 1450, 1315, 1262, 1176, 1094, 1068, 1025, 933, 849, 755, 711, 666 cm^{-1}; **HRMS (ESI)** calculated for C$_{24}$H$_{27}$O$_2^+$ [M+H$^+$]: 347.2006, found: 347.2006.

3-cyclohexyl-1-(naphthalen-1-yl)prop-2-yn-1-yl benzoate (2r)

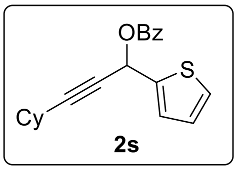


2r

The preparation of **2r** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.4 mL, 3.7 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.0 mmol, 1.1 equiv.), 1-naphthaldehyde (0.9 mL, 5.6 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.9 g, 92%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.4 mL, 17.0 mmol, 4.6 equiv.), DMAP (41.0 mg, 0.34 mmol, 0.1 equiv.), benzoyl chloride (1.0 mL,8.5 mmol, 2.3 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2r** as a yellow oil (0.9 g, 71%).

Spectral data for **2r**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.08(m, 3H), 7.93 – 7.82 (m, 3H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 2.63 – 2.45 (m, 1H), 1.91 – 1.82 (m, 2H), 1.79 – 1.69 (m, 2H), 1.59 – 1.47 (m, 3H), 1.40 – 1.29 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 135.3, 133.5, 133.2, 133.1, 130.1, 130.0, 128.6, 128.5, 127.8, 127.2, 126.6, 126.4, 125.4, 93.0, 66.9, 32.5, 29.3, 25.9, 24.9; **IR (ATR)**: 3062, 3030, 2916, 1717, 1601, 1584, 1494, 1451, 1315, 1248, 1175, 1094, 1068, 1025, 937, 909, 756, 709, 697, 629, 588, 565, 471 cm^{-1}; **HRMS (ESI)** calculated for $C_{26}H_{25}O_2^+$ [M+H$^+$]: 369.1849, found: 369.1849.

3-cyclohexyl-1-(naphthalen-1-yl)prop-2-yn-1-yl benzoate (2s)



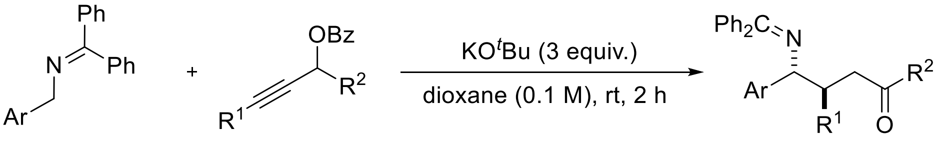
2s

The preparation of **2s** was followed according to General Procedure B. The propargyl alcohol was synthesized by using cyclohexylacetylene (0.5 mL, 3.8 mmol, 1.0 equiv.), *n*-butyllithium (2.3 M in hexane, 1.8 mL, 4.2 mmol, 1.1 equiv.), thiophenecarboxaldehyde (0.6 mL, 6.0 mmol, 1.5 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded propargyl alcohol (0.9 g, 95%) as a yellow oil. Benzoylation reaction of the above propargyl alcohol with Et_3N (2.5 mL, 18.0 mmol, 4.7 equiv.), DMAP (44.0 mg, 0.4 mmol, 0.1 equiv.), benzoyl chloride (1.0 mL, 9.0 mmol, 2.4 equiv.). Purification through SiO_2 flash column chromatography with elution (10% ethyl acetate in petroleum ether) afforded title compound **2s** as a yellow oil (1.2 g, 99%).

Spectral data for **2s**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.33 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.95 (d, *J* = 1.9 Hz, 1H), 2.55 – 2.46 (m, 1H), 1.87 – 1.80 (m, 2H), 1.76 – 1.69

(m, 2H), 1.56 – 1.48 (m, 3H), 1.38 – 1.30 (m, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.6, 141.3, 133.3, 130.1, 130.0, 128.5, 127.6, 126.9, 126.8, 92.2, 76.5, 61.9, 32.4, 29.2, 26.0, 24.9; **IR (ATR)**: 2929, 2854, 1718, 1601, 1494, 1451, 1315, 1258, 1175, 1093, 1067, 1025, 937, 904, 756, 709, 686, 597, 565 cm^{-1}; **HRMS (ESI)** calculated for $C_{20}H_{21}O_2S^+$ [M+H$^+$]: 325.1257, found: 325.1259.

3.5 General procedure C for the preparation of γ -Aminoketones



(1 equiv.)
1a-1m

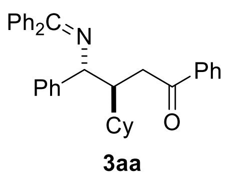
(2 equiv.)
2a-2r

3aa-3ma
3ab-3ar

In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a - 1m** (0.2 mmol, 1.0 equiv.), K^{t}OBu (0.6 mmol, 3.0 equiv.) and 1,4 - dioxane (2 mL). The reaction mixture was stirred at room temperature for 5 min and alkynes **2a - 2r** (0.4 mmol, 2.0 equiv.) were subsequently added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a pad of celite, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO$_2$ flash column chromatography to obtain products **3aa-3ma** and **3ab-3ar**. The diastereoselectivity (anti/syn ratio) of the reaction was confirmed by analyzing the ^{1}H NMR of crude product.

3.6 Characterization data of γ -Aminoketones

3-cyclohexyl-4-((diphenylmethylene)amino)-1,4-diphenylbutan-1-one (3aa)



3aa

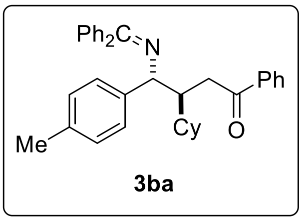
The preparation of **3aa** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 10:1 mixture of anti and syn isomer. **3aa** was isolated as a pale-yellow film (81 mg, 83%) and was diastereoisomeric pure.

R$_f$ = 0.56 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.31 (m, 9H), 7.28 – 7.27 (m, 3H), 7.23 – 7.15 (m, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 4.68 (d, *J* = 4.8 Hz, 1H), 3.28 (dd, *J* = 16.9, 4.2 Hz, 1H), 3.16 (dd, *J* = 16.9, 7.3 Hz, 1H), 2.87 – 2.70 (m, 1H), 1.71 – 1.56 (m, 3H), 1.54 – 1.42 (m, 2H), 1.33 – 1.16 (m, 1H), 1.13 – 1.03

(m, 3H), 1.03 – 0.81 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 200.9, 167.4, 144.8, 140.0, 137.6, 136.9, 132.5, 130.1, 128.8, 128.6, 128.4, 128.3, 128.3, 128.3, 128.1, 127.8, 127.6, 126.6, 66.8, 47.9, 40.1, 37.6, 31.4, 30.3, 26.9, 26.8, 26.7; **IR (ATR)**: 2921, 2850, 1680, 1620, 1597, 1579, 1491, 1446, 1314, 1272, 1002, 773, 749, 692 cm^{-1}; **HRMS (ESI)**: calculated for $C_{35}H_{36}NO^+$ [M+H$^+$]: 486.2791, found: 486.2791.

3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenyl-4-(*p*-tolyl)butan-1-one (3ba)



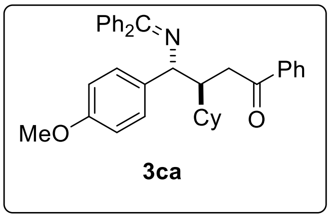
3ba

The preparation of **3ba** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 7:1 mixture of anti and syn isomer. **3ba** was isolated as a yellow oil (72 mg, 72%) and was diastereoisomeric pure.

R$_f$ = 0.50 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.83 (d, *J* = 7.1 Hz, 2H), 7.64 (d, *J* = 6.9 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.28 (m, 8H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 5.9 Hz, 2H), 4.61 (d, *J* = 4.8 Hz, 1H), 3.22 (dd, *J* = 16.9, 4.2 Hz, 1H), 3.11 (dd, *J* = 16.9, 7.4 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.29 (s, 3H), 1.63 – 1.53 (m, 3H), 1.52 – 1.39 (m, 2H), 1.22 – 1.14 (m, 1H), 1.08 – 0.98 (m, 3H), 0.98 – 0.83 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 201.0, 167.2, 141.8, 140.1, 137.6, 137.0, 136.0, 132.5, 130.0, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 66.6, 48.0, 40.1, 37.6, 31.5, 30.3, 26.9, 26.8, 26.7, 21.2; **IR (ATR)**: 2922, 2850, 1682, 1622, 1446, 1314, 1273, 1179, 1002, 753, 730, 692 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NO^+$ [M+H$^+$]: 500.2948, found: 500.2948.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-1-phenylbutan-1-one (3ca)



3ca

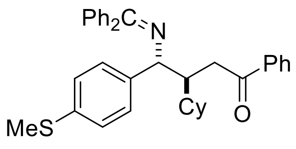
The preparation of **3ca** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ca** was isolated as a white solid (68 mg, 66%) and was diastereoisomeric pure.

R$_f$ = 0.54 [5% ethyl acetate in petroleum ether (containing 0.5% triethylamine)].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 6.7 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.32 (m, 8H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 6.2 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.59 (d, *J* = 5.0 Hz, 1H), 3.77 (s, 3H), 3.23 (dd, *J* = 16.9, 4.2 Hz, 1H), 3.11 (dd, *J* = 16.9, 7.2 Hz, 1H), 2.77 – 2.65 (m, 1H), 1.84 – 1.66 (m, 1H), 1.63 – 1.52 (m, 2H), 1.46 (m, 2H), 1.26 – 1.17 (m, 1H), 1.08 – 1.01 (m, 3H), 1.01 – 0.77 (m, 2H); **^{13}C NMR** (101 MHz,

$CDCl_3$): δ 201.0, 167.2, 158.2, 140.0, 137.6, 137.0, 136.9, 132.5, 130.0, 128.8, 128.5, 128.4, 128.32, 128.25, 128.1, 127.8, 113.7, 66.3, 55.3, 48.0, 40.0, 37.6, 31.5, 30.2, 26.9, 26.8, 26.7; **IR (ATR)**: 2957, 2930, 2859, 1453, 1270, 1131, 1057, 1028, 1002, 919, 755, 728, 697 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{37}NO_2Na^+$ [$M+Na^+$]: 538.2716, found: 538.2711.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(4-(methylthio)phenyl)-1-phenylbutan-1-one (3da)



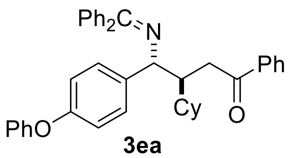
3da

The preparation of **3da** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3da** was isolated as a yellow solid (72 mg, 68%) and was diastereoisomeric pure.

$R_f = 0.34$ [5% ethyl acetate in petroleum ether (containing 0.5% triethylamine)].

^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.84 (d, J = 7.7 Hz, 2H), 7.64 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.42 – 7.31 (m, 8H), 7.20 – 7.09 (m, 4H), 6.95 (d, J = 7.1 Hz, 2H), 4.59 (d, J = 4.9 Hz, 1H), 3.21 (dd, J = 17.0, 4.2 Hz, 1H), 3.11 (dd, J = 16.7, 7.1 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.45 (s, 3H), 1.63 – 1.56 (m, 3H), 1.48 – 1.41 (m, 2H), 1.24 – 1.15 (m, 1H), 1.08 – 0.98 (m, 3H), 0.95 – 0.85 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.8, 167.6, 141.8, 139.9, 137.5, 136.9, 136.1, 132.6, 130.1, 128.8, 128.6, 128.4, 128.30, 128.28, 128.10, 128.08, 127.7, 126.7, 66.4, 47.8, 40.0, 37.5, 31.5, 30.3, 26.9, 26.8, 26.7, 16.1; **IR (ATR)**: 2921, 2851, 1683, 1617, 1597, 1577, 1489, 1445, 1314, 1253, 1002, 754, 737, 704, 695, 684 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NOS^+$ [$M+H^+$]: 532.2669, found: 532.2669.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(4-phenoxyphenyl)-1-phenylbutan-1-one (3ea)



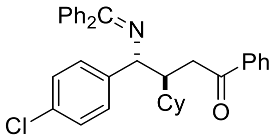
3ea

The preparation of **3ea** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ea** was isolated as a white solid (72 mg, 62%) and was diastereoisomeric pure.

$R_f = 0.45$ [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.0 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.42 – 7.28 (m, 10H), 7.19 (d, J = 8.3 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.02 – 6.92 (m, 4H), 6.89 (d, J = 8.6 Hz, 2H), 4.62 (d, J = 4.9 Hz, 1H), 3.30 (dd, J = 17.0, 4.4 Hz, 1H), 3.09 (dd, J = 16.9, 7.0 Hz, 1H), 2.83 – 2.67 (m, 1H), 1.63 – 1.52 (m, 3H), 1.52 – 1.42 (m, 2H), 1.28 – 1.16 (m, 1H), 1.08 – 1.02 (m, 3H), 1.01 – 0.82 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.8, 167.4, 157.5, 155.6, 139.9, 139.8, 137.6, 136.9, 132.6, 130.1, 129.8, 128.84, 128.78, 128.6, 128.4, 128.3, 128.1, 127.8, 123.1, 118.9, 118.7, 66.3, 47.9, 40.1, 37.2, 31.5, 30.2, 26.9, 26.8, 26.7; **IR (ATR)**: 2922, 2850, 1683, 1589, 1505, 1489, 1447, 1233, 1166, 749, 690 cm^{-1};**HRMS (ESI)** calculated for $C_{41}H_{39}NO_2K^+$ [$M+K^+$]: 616.2612, found: 616.2612.

4-(4-chlorophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenylbutan-1-one (3fa)



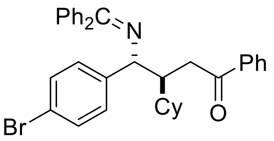
3fa

The preparation of **3fa** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 3:1 mixture of anti and syn isomer. **3fa** was isolated as a milky white gummy (62 mg, 60% combined) consisting of two diastereomers (~2:1 isolated dr).

R_f = 0.50 [5% ethyl acetate in petroleum ether (containing 0.5% triethylamine)].

These reported data are for the mixture of diastereomers. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.3 Hz, 1.3 H), 7.77 (d, *J* = 7.7 Hz, 0.35H), 7.69 – 7.60 (m, 2.35H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.42 – 7.30 (m, 8H), 7.16 (m, 4H), 6.91 (dd, *J* = 14.7, 6.5 Hz, 2H), 4.60 (d, *J* = 4.9 Hz, 0.65H), 4.35 (d, *J* = 4.9 Hz, 0.35H), 3.19 (dd, *J* = 17.1, 4.5 Hz, 0.65H), 3.11 (dd, *J* = 17.1, 6.8 Hz, 0.65H), 2.94 – 2.81 (m, 0.70H), 2.75 – 2.69 (m, 0.65H), 2.66 (dd, *J* = 15.7, 4.3 Hz, 0.35H), 1.65 – 1.56 (m, 4H), 1.48 – 1.42 (m, 1H), 1.22 – 1.14 (m, 1H), 1.11 – 0.98 (m, 3H), 0.96 – 0.81 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.6, 200.0, 167.9, 167.2, 143.4, 142.0, 139.9, 139.8, 137.53, 137.48, 136.9, 136.8, 132.6, 132.5, 132.2, 130.2, 130.1, 129.9, 128.9, 128.8, 128.7, 128.52, 128.48, 128.44, 128.36, 128.35, 128.31, 128.29, 128.25, 128.2, 128.1, 128.0, 127.74, 127.65, 67.6, 66.2, 47.8, 47.1, 40.1, 38.6, 37.4, 36.6, 32.7, 31.5, 30.2, 28.5, 27.0, 26.9, 26.83, 26.77, 26.6; **IR (ATR)**: 2923, 2850, 1682, 1597, 1488, 1446, 1314, 1274, 1089, 1014, 1002, 827, 752, 733, 691 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{35}ClO^+$ [$M+H^+$]: 520.2402, found: 520.2402.

4-(4-bromophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenylbutan-1-one (3ga)



3ga

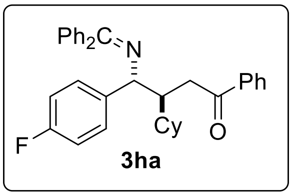
The preparation of **3ga** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ga** was isolated as a yellow solid (112 mg, 99% combined) consisting of two diastereomers (5:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R_f = 0.31 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 6.8 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.49 (t, *J* =

7.3 Hz, 1H), 7.41 – 7.31 (m, 10H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 7.1 Hz, 2H), 4.60 (d, *J* = 4.2 Hz, 1H), 3.20 (dd, *J* = 17.0, 4.0 Hz, 1H), 3.12 (dd, *J* = 17.1, 7.0 Hz, 1H), 2.77 – 2.67 (m, 1H), 1.67 – 1.53 (m, 3H), 1.50 – 1.40 (m, 2H), 1.22 – 1.13 (m, 1H), 1.08 – 1.00 (m, 3H), 0.96 – 0.85 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.6, 168.0, 143.9, 139.7, 137.5, 136.7, 132.7, 131.4, 130.2, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.6, 120.4, 66.2, 47.8, 40.0, 37.3, 31.5, 30.2, 26.8, 26.7, 26.6; **IR (ATR)**: 2922, 2850, 1682, 1622, 1597, 1577, 1485, 1446, 1072, 1010, 908, 824, 752, 732, 691 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{35}BrNO^+$ [M+H$^+$]: 564.1897, found: 564.1897.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(4-fluorophenyl)-1-phenylbutan-1-one (3ha)



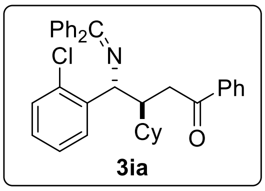
3ha

The preparation of **3ha** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 3:1 mixture of anti and syn isomer. **3ha** was isolated as a white solid (95 mg, 94% combined) consisting of two diastereomers (4:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R$_f$ = 0.38 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.42 – 7.32 (m, 8H), 7.18 (dd, *J* = 8.7, 5.6 Hz, 2H), 6.96 – 6.88 (m, 4H), 4.61 (d, *J* = 4.9 Hz, 1H), 3.21 (dd, *J* = 16.9, 4.4 Hz, 1H), 3.10 (dd, *J* = 17.2, 6.9 Hz, 1H), 2.78 – 2.67 (m, 1H), 1.62 – 1.56 (m, 3H), 1.49 – 1.41 (m, 2H), 1.20 – 1.13 (m, 1H), 1.08 – 0.99 (m, 3H), 0.95 – 0.85 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.7, 167.7, 161.5 (d, *J* = 242. 0 Hz), 140.5 (d, *J* = 3.3 Hz), 139.8, 137.5, 136.8, 132.6, 130.2, 129.0 (d, *J* = 7.8 Hz), 128.8, 128.6, 128.4, 128.32, 128.25, 128.23, 128.1, 127.7, 115.1 (d, *J* = 21.1 Hz), 66.1, 47.9, 40.0, 37.4, 31.5, 30.2, 26.9, 26.8, 26.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.5; **IR (ATR)**: 2923, 2850, 1683, 1597, 1506, 1446, 1314, 1274, 1220, 1155, 1002, 834, 753, 732, 692 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{34}FNONa^+$ [M+Na$^+$]: 526.2517, found: 526.2518.

4-(2-chlorophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenylbutan-1-one (3ia)



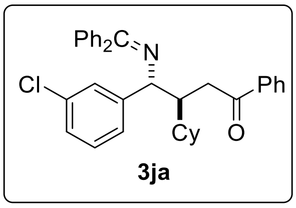
3ia

The preparation of **3ia** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ia** was isolated as a white solid (99 mg, 95% combined) consisting of two diastereomers (2:1 isolated dr).

R$_f$ = 0.28 [0.5% triethylamine in petroleum ether].

These reported data are for the mixture of diastereomers. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 5H), 7.74 – 7.67 (m, 6H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.51 – 7.21 (m, 29H), 7.16 – 7.08 (m, 4H), 6.99 – 6.88 (m, 9H), 5.10 (d, *J* = 3.7 Hz, 2H), 4.92 (d, *J* = 8.8 Hz, 1H), 3.49 (dd, *J* = 17.1, 4.4 Hz, 2H), 3.19 (dd, *J* = 17.1, 7.3 Hz, 2H), 3.10 – 3.00 (m, 1H), 2.93 (dd, *J* = 16.7, 6.9 Hz, 1H), 2.76 (m, *J* = 7.5, 4.3 Hz, 2H), 2.62 (dd, *J* = 16.7, 5.0 Hz, 1H), 1.70 – 1.54 (m, 15H), 1.28 – 1.20 (m, 3H), 1.13 – 0.90 (m, 15H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.8, 200.0, 168.2, 167.8, 142.7, 141.1, 140.1, 139.9, 137.6, 137.3, 137.2, 137.0, 132.6, 132.5, 131.7, 130.2, 130.12, 130.09, 129.5, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.19, 128.18, 128.1, 128.0, 127.82, 127.78, 127.7, 127.6, 127.0, 126.7, 63.3, 63.0, 47.6, 45.4, 40.7, 38.9, 37.2, 35.5, 32.6, 31.0, 30.9, 27.7, 27.2, 27.0, 26.90, 26.87, 26.85, 26.7; **IR (ATR):** 2923, 2850, 1683, 1617, 1597, 1446, 1314, 1272, 1215, 1030, 1002, 908, 750, 734, 692 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{34}ClNONa^+$ [M+Na$^+$]: 542.2221, found: 542.2211.

4-(3-chlorophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenylbutan-1-one (3ja)

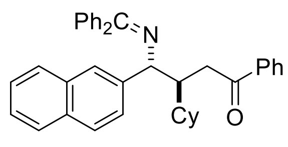


3ja

The preparation of **3ja** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ja** was isolated as a white solid (82 mg, 79% combined) consisting of two diastereomers (2:1 isolated dr). R_f = 0.20 [0.5% triethylamine in petroleum ether].

These reported data are for the mixture of diastereomers. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.0 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.51 – 7.46 (m, 1H), 7.44 – 7.30 (m, 9H), 7.26 – 7.05 (m, 4H), 6.91 (dd, *J* = 13.2, 6.8 Hz, 2H), 4.61 (d, *J* = 4.7 Hz, 0.6H), 4.35 (d, *J* = 7.2 Hz, 0.4H), 3.21 (dd, *J* = 17.1, 4.4 Hz, 0.6H), 3.12 (dd, *J* = 17.1, 7.0 Hz, 0.6H), 2.95 – 2.82 (m, 0.8H), 2.74 – 2.68 (m, 0.6H), 2.65 (dd, *J* = 16.3, 4.7 Hz, 0.4H), 1.62 – 1.55 (m, 4H), 1.46 – 1.41 (m, 1H), 1.21 – 1.15 (m, 1H), 1.11 – 0.98 (m, 3H), 0.95 – 0.84 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.5, 200.0, 168.1, 167.4, 147.0, 145.6, 139.8, 139.7, 137.5, 137.4, 136.8, 136.7, 134.2, 134.0, 132.6, 130.3, 130.2, 129.6, 129.5, 128.8, 128.74, 128.73, 128.59, 128.56, 128.5, 128.39, 128.37, 128.31, 128.25, 128.2, 128.1, 128.0, 127.8, 127.68, 127.65, 127.1, 126.9, 126.7, 126.6, 125.8, 67.8, 66.4, 47.9, 47.1, 40.1, 38.6, 37.3, 36.7, 32.6, 31.5, 30.3, 28.5, 27.0, 26.9, 26.82, 26.77, 26.6; **IR (ATR)**: 2922, 2850, 1682, 1622, 1595, 1576, 1446, 1314, 1272, 1179, 1001, 782, 753, 690 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{34}ClNONa^+$ [M+Na$^+$]: 542.2221, found: 542.2215.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(naphthalen-2-yl)-1-phenylbutan-1-one (3ma)



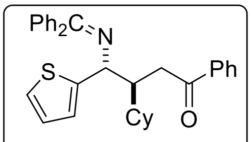
3ka

The preparation of **3ka** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ka** was isolated as a white solid (90 mg, 84% combined) consisting of two diastereomers (5:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R$_f$ = 0.17 [0.5% triethylamine in petroleum ether].

^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.84 – 7.76 (m, 4H), 7.76 – 7.69 (m, 3H), 7.67 – 7.61 (m, 1H), 7.46 – 7.40 (m, 6H), 7.40 – 7.30 (m, 6H), 6.98 (d, *J* = 7.2 Hz, 2H), 4.85 (d, *J* = 4.8 Hz, 1H), 3.32 (dd, *J* = 17.1, 4.3 Hz, 1H), 3.27 – 3.17 (m, 1H), 2.94 – 2.76 (m, 1H), 1.70 – 1.59 (m, 3H), 1.57 – 1.50 (m, 2H), 1.30 – 1.23 (m, 1H), 1.10 – 1.02 (m, 3H), 1.02 – 0.90 (m, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$): δ 200.9, 167.9, 142.5, 140.0, 137.5, 136.9, 133.5, 132.6, 132.5, 130.2, 128.9, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 126.2, 126.0, 125.9, 125.5, 66.9, 47.8, 40.3, 37.5, 31.5, 30.5, 26.9, 26.8, 26.7; **IR (ATR)**: 2922, 2849, 1683, 1622, 1597, 1446, 1270, 1002, 779, 748, 691, 641 cm^{-1}; **HRMS (ESI)** calculated for $C_{39}H_{37}NONa^+$ [M+Na$^+$]: 558.2767, found: 558.2755.

3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenyl-4-(thiophen-2-yl)butan-1-one (3ka)



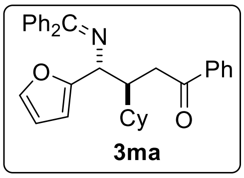
3la

The preparation of **3la** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 3:1 mixture of anti and syn isomer. **3la** was isolated as a white solid (87 mg, 88% combined) consisting of two diastereomers (3:1 isolated dr).

R$_f$ = 0.40 [0.5% triethylamine in petroleum ether].

These reported data are for the mixture of diastereomers.^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.93 (d, *J* = 7.0 Hz, 6H), 7.86 (d, *J* = 7.0 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 6H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 4H), 7.46 – 7.33 (m, 30H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 3H), 7.13 – 7.06 (m, 8H), 6.92 (dd, *J* = 5.0 Hz, 3H), 6.90 (dd, *J* = 5.2 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 3H), 6.79 (d, *J* = 3.5 Hz,1H), 4.96 (d, *J* = 3.7 Hz, 3H), 4.89 (d, *J* = 5.8 Hz, 1H), 3.43 – 3.29 (m, 4H), 3.24 (dd, *J* = 7.6 Hz, 3H), 2.82 – 2.68 (m, 5H), 1.70 – 1.53 (m, 13H), 1.50 – 1.40 (m, 7H), 1.30 – 1.19 (m, 4H), 1.15 – 1.00 (m, 11H), 1.01 – 0.82 (m, 9H); ^{13}**C NMR** (101 MHz, CDCl$_3$): δ 200.5, 200.0, 168.4, 167.0, 148.2, 146.5, 139.8, 139.6, 137.6, 137.5, 136.5, 132.62, 132.59, 130.3, 130.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.41, 128.36, 128.3, 128.22, 128.15, 128.1, 127.73, 127.71, 126.6, 126.1, 124.3, 123.9, 123.8, 123.4, 63.5, 63.3, 48.2, 47.0, 40.1, 39.2, 37.7, 37.1, 32.1, 31.5, 30.4, 29.4, 26.9, 26.8, 26.71, 26.66, 26.6; **IR (ATR)**: 2922, 2847, 1615, 1494, 1446, 1343, 1266, 1024, 759, 695, 639 cm^{-1}; **HRMS (ESI)** calculated for $C_{33}H_{34}NOS^+$ [M+H$^+$]: 492.2330, found: 492.2330.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-(furan-2-yl)-1-phenylbutan-1-one (3la)



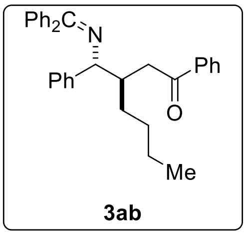
3ma

The preparation of **3ma** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ma** was isolated as a brown liquid (66 mg, 69%) and was diastereoisomeric pure.

R$_f$ = 0.22 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.68 (d, *J* = 6.9 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.39 (m, 6H), 7.39 – 7.30 (m, 3H), 7.14 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.27 – 6.19 (m, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 4.77 (d, *J* = 3.5 Hz, 1H), 3.44 (dd, *J* = 17.5, 3.7 Hz, 1H), 3.20 (dd, *J* = 17.5, 7.6 Hz, 1H), 2.91 – 2.78 (m, 1H), 1.65 – 1.53 (m, 3H), 1.48 – 1.41 (m, 2H), 1.22 – 1.16 (m, 1H), 1.10 – 1.00 (m, 3H), 0.91 – 0.83 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.5, 169.4, 156.3, 141.4, 140.0, 137.6, 136.6, 132.7, 130.3, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 110.1, 106.6, 61.7, 44.4, 40.2, 38.0, 31.2, 30.7, 26.9, 26.7, 26.6; **IR (ATR)**: 2921, 2851, 1683, 1623, 1447, 1282, 1002, 766, 751, 730, 698, 687 cm^{-1}; **HRMS (ESI)** calculated for $C_{33}H_{33}NO_2Na^+$ [M+Na$^+$]: 498.2403, found: 498.2397.

3-(((diphenylmethylene)amino)(phenyl)methyl)-1-phenylheptan-1-one (3ab)



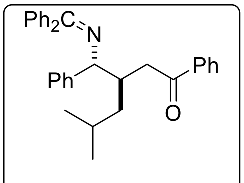
3ab

The preparation of **3ab** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ab** was isolated as a white solid (87 mg, 95% combined) consisting of two diastereomers (2:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R$_f$ = 0.25 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.33 (m, 8H), 7.33 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.00 (d, *J* = 7.3 Hz, 2H), 4.59 (d, *J* = 4.4 Hz, 1H), 3.33 (dd, *J* = 16.3, 3.5 Hz, 1H), 3.07 (dd, *J* = 16.2, 9.0 Hz, 1H), 2.76 – 2.51 (m, 1H), 1.33 – 1.21 (m, 2H), 1.20 – 1.10 (m, 2H), 1.11 – 0.96 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDfCl_3$): δ 201.0, 168.0, 144.3, 140.0, 137.4, 136.7, 132.7, 130.1, 128.8, 128.5, 128.4, 128.32, 128.30, 128.2, 127.9, 127.6, 126.7, 67.5, 43.2, 39.8, 31.8, 29.2, 23.0, 14.1; **IR (ATR)**: 2950, 2928, 2858, 1683, 1447, 1314, 1289, 1178, 1028, 1001, 774, 747, 696 cm^{-1}; **HRMS (ESI)** calculated for $C_{33}H_{33}NONa^+$ [M+Na$^+$]: 482.2454, found: 482.2450.

3-(((diphenylmethylene)amino)(phenyl)methyl)-5-methyl-1-phenylhexan-1-one (3ac)



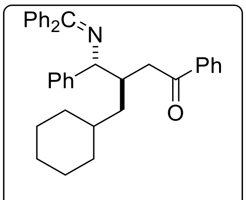
3ac

The preparation of **3ac** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2.6:1 mixture of anti and syn isomer. **3ac** was isolated as yellow solid (78 mg, 85% combined) consisting of two diastereomers (2:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R_f = = 0.30 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 6.9 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.33 (m, 8H), 7.28 (d, *J* = 4.4 Hz, 4H), 7.24 – 7.19 (m, 1H), 6.95 (d, *J* = 6.8 Hz, 2H), 4.53 (d, *J* = 4.0 Hz, 1H), 3.31 (dd, *J* = 16.2, 3.7 Hz, 1H), 3.03 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.78 – 2.61 (m, 1H), 1.34 – 1.04 (m, 3H), 0.75 (d, *J* = 6.3 Hz, 3H), 0.72 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 201.1, 168.0, 144.4, 140.1, 137.5, 136.7, 132.7, 130.2, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.6, 126.7, 67.6, 41.6, 40.9, 40.0, 25.1, 23.2, 22.3; **IR (ATR)**: 2954, 2870, 1679, 1623, 1599, 1445, 1313, 1272, 1027, 1005, 775, 746, 692 cm^{-1}; **HRMS (ESI)** calculated for $C_{33}H_{33}NONa^+$ [M+Na$^+$]: 482.2454, found: 482.2453.

3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenyl-4-(*p*-tolyl)butan-1-one (3ad)



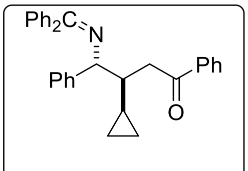
3ad

The preparation of **3ad** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ad** was isolated as a yellow solid (83 mg, 83% combined) consisting of two diastereomers (2:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization of the major isomer.

R_f = 0.30 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 12.1, 6.9 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.32 (m, 9H), 7.29 – 7.27 (m, 3H), 7.24 – 7.19 (m, 1H), 6.96 (d, *J* = 7.1 Hz, 2H), 4.54 (d, *J* = 3.7 Hz, 1H), 3.28 (dd, *J* = 16.2, 3.3 Hz, 1H), 3.03 (dd, *J* = 16.2, 9.1 Hz, 1H), 2.80 – 2.60 (m, 1H), 1.65 – 1.43 (m, 3H), 1.31 – 1.22 (m, 1H), 1.19 – 1.09 (m, 2H), 1.06 – 0.94 (m, 3H), 0.93 – 0.81 (m, 2H), 0.76 – 0.63 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 201.0, 168.0, 144.4, 140.0, 137.4, 136.5, 132.6, 130.0, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.4, 126.6, 67.1, 39.9, 39.8, 34.3, 334.0, 32.7, 26.6, 26.3, 26.2; **IR (ATR)**: 2919, 2848, 1685, 1623, 1597, 1490, 1447, 1315, 1290, 1026, 1001, 783, 752, 743, 691 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NO^+$ [M+H$^+$]: 500.2948, found: 500.2948.

3-cyclopropyl-4-((diphenylmethylene)amino)-1,4-diphenylbutan-1-one (3ae)

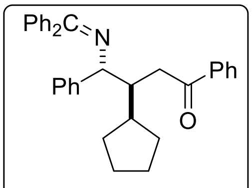


3ae

The preparation of **3ae** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 3:1 mixture of anti and syn isomer. **3ae** was isolated as a yellow oil (74 mg, 83% combined) consisting of two diastereomers (3:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization of the major isomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.36 (m, 8H), 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 7.02 (d, *J* = 6.8 Hz, 2H), 4.65 (d, *J* = 4.6 Hz, 1H), 3.34 (dd, *J* = 14.9, 4.0 Hz, 1H), 3.25 (dd, *J* = 14.8, 9.0 Hz, 1H), 1.96 – 1.78 (m, 1H), 0.78 – 0.55 (m, 1H), 0.38 – 0.26 (m, 1H), 0.19 – 0.10 (m, 1H), 0.07 – -0.05 (m, 1H), -0.11 – -0.29 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 201.4, 167.9, 144.0, 140.0, 137.6, 136.8, 132.6, 130.2, 128.7, 128.5, 128.42, 128.39, 128.3, 128.22, 128.18, 127.9, 127.6, 126.7, 69.9, 49.6, 40.5, 15.0, 5.1, 4.5,; **IR (ATR)**: 2992, 1684, 1624, 1447, 1917, 1002, 778, 745, 697 cm^{-1}; **HRMS (ESI)** calculated for $C_{32}H_{29}NONa^+$ [M+Na$^+$]:466.2141, found: 466.2144.

3-cyclopentyl-4-((diphenylmethylene)amino)-1,4-diphenylbutan-1-one (3af)



3af

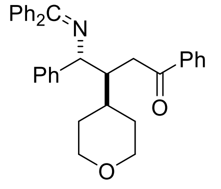
The preparation of **3af** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 4:1 mixture of anti and syn isomer. **3af** was isolated as white solid (90 mg, 95% combined) consisting of two diastereomers (4:1 isolated dr). A single crystal sample was used for characterization.

R$_f$ = 0.20 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.30 (m, 8H), 7.25 – 7.20 (m, 4H), 7.19 – 7.14 (m, 1H), 6.96 (d, *J* = 7.3 Hz, 2H), 4.63 (d, *J* = 3.3 Hz, 1H), 3.49 (dd, *J* = 17.3, 3.7 Hz, 1H), 3.10 (dd, *J* = 17.3, 6.8 Hz, 1H), 2.79 – 2.67 (m, 1H), 1.77 – 1.69 (m, 1H), 1.61 – 1.48 (m, 3H), 1.46 – 1.35 (m, 3H), 1.11 – 0.98 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) : δ 201.0, 167.7, 144.7, 140.1, 137.7, 136.6, 132.5, 130.1, 128.8, 128.6, 128.4, 128.3, 128.22, 128.20, 128.1, 127.9, 127.5, 126.6, 68.2, 47.5, 44.0, 38.7, 31.2, 30.7, 25.3, 24.9; **IR (ATR)**: 2950, 2867, 1683, 1490, 1446, 1315, 1290, 1209, 1002, 779, 759, 750, 699, 689 cm^{-1}; **HRMS (ESI)** calculated for $C_{34}H_{34}NO^+$ [M+H$^+$]: 472.2635, found: 472.2635.

3-cyclohexyl-4-((diphenylmethylene)amino)-1-phenyl-4-(*p*-tolyl)butan-1-one (3ag)

The preparation of **3ag** was followed according to General Procedure C. ^{1}H NMR analysis of



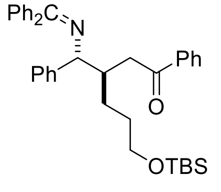
3ag

the crude revealed a 5:1 mixture of anti and syn isomer. **3ag** was isolated as a white solid (89 mg, 91%) and consisting of two diastereomers (5:1 isolated dr). A small amount of diastereoisomeric mixture (< 30 mg) was further purified by preparative TLC (0.5% triethylamine in petroleum ether) to obtain the major isomer for characterization.

R_f = 0.40 [5% ethyl acetate in petroleum ether (containing 0.5% triethylamine)].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 1H), 7.47 – 7.29 (m, 9H), 7.28 – 7.23 (m, 3H), 7.21 – 7.10 (m, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 4.67 (d, *J* = 4.4 Hz, 1H), 3.92 – 3.71 (m, 2H), 3.33 (dd, *J* = 17.1, 3.8 Hz, 1H), 3.26 – 3.08 (m, 3H), 2.85 – 2.69 (m, 1H), 1.58 – 1.42 (m, 1H), 1.37 – 1.22 (m, 4H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 200.4, 167.8, 144.4, 139.8, 137.4, 136.6, 132.7, 130.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.5, 126.8, 68.4, 68.3, 66.0, 47.2, 37.8, 37.1, 31.4, 30.6; **IR (ATR)**: 2916, 2835, 1683, 1445, 1316, 1243, 1001, 778, 753, 691, 659, 640, 606, 564, 53 cm^{-1}; **HRMS (ESI)** calculated for $C_{34}H_{34}NO_2^+$ [M+H$^+$]: 488.2584, found: 488.2584.

6-((tert-butyldimethylsilyl)oxy)-3-(((diphenylmethylene)amino)(phenyl)methyl)-1-phenylhexan-1-one (3ah)



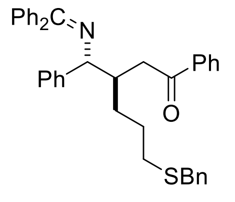
3ah

The preparation of **3ah** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 3:1 mixture of anti and syn isomer. **3ah** was isolated as a yellow liquid (85 mg, 74% combined) consisting of two diastereomers (2:1 isolated dr).

R_f = 0.22 [0.5% triethylamine in petroleum ether].

These reported data are for the mixture of diastereomers. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.91 – 7.83 (m, 2H), 7.80 – 7.73 (m, 2H), 7.62 – 7.53 (m, 1H), 7.49 – 7.37 (m, 8H), 7.37 – 7.29 (m, 4H), 7.30 – 7.23 (m, 1H), 7.03 (d, *J* = 6.1 Hz, 1.4H), 6.95 (d, *J* = 7.0 Hz, 0.6H), 4.58 (d, *J* = 4.8 Hz, 0.7H), 4.53 (d, *J* = 4.9 Hz, 0.3H), 3.56 (t, *J* = 6.1 Hz, 0.7H), 3.53 – 3.46 (m, 1.3H), 3.35 (dd, *J* = 16.2, 3.7 Hz, 0.7H), 3.29 – 3.18 (m, 0.3H), 3.09 (dd, *J* = 16.2, 8.8 Hz, 0.7H), 2.78 – 2.66 (m, 1.3H), 1.77 – 1.27 (m, 4H), 0.91 (s, 2.7H), 0.88 (s, 6.3H), 0.05 (s, 1.8H), 0.01 (s, 4.2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 200.9, 200.2, 168.1, 167.3, 144.1, 143.3, 140.0, 137.4, 136.81, 136.76, 132.8, 132.7, 130.1, 130.0, 128.8, 128.7, 128.54, 128.51, 128.49, 128.34, 128.31, 128.22, 128.20, 128.14, 128.10, 127.9, 127.73, 127.66, 126.82, 126.75, 68.3, 67.9, 63.5, 63.4, 42.9, 42.2, 40.1, 39.8, 30.5, 30.3, 28.3, 26.8, 26.08, 26.06, 18.4, 18.4, -5.17, -5.19, -5.22; **IR (ATR)**: 2927, 2855, 1683, 1447, 1254, 1096, 1002, 833, 774, 750, 694 cm^{-1}; **HRMS (ESI)** calculated for $C_{38}H_{45}NO_2SiNa^+$ [M+Na$^+$]: 598.3112, found: 598.3107.

6-(benzylthio)-3-(((diphenylmethylene)amino)(phenyl)methyl)-1-phenylhexan-1-one (3ai)



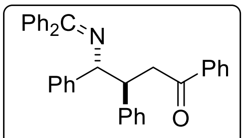
3ai

The preparation of **3ai** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 4:1 mixture of anti and syn isomer. **3ai** was isolated as a pale-yellow liquid (69 mg, 61% combined) consisting of two diastereomers (2:1 isolated dr).

R_f = 0.52 [5% ethyl acetate in petroleum ether (containing 0.5% triethylamine)].

These reported data are for the mixture of diastereomers.**^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.75 – 7.66 (m, 2H), 7.61 – 7.46 (m, 2H), 7.44 – 7.34 (m, 8H), 7.32 – 7.27 (m, 3H), 7.25 – 7.19 (m, 6H), 6.96 (d, *J* = 6.4 Hz, 1.2H), 6.88 (d, *J* = 6.9 Hz, 0.8H), 4.50 (d, *J* = 4.7 Hz, 0.6H), 4.44 (d, *J* = 5.1 Hz, 0.3H), 3.60 (s, 0.8H), 3.57 (s, 1.2H), 3.28 (dd, *J* = 16.4, 3.5 Hz, 0.6H), 3.17 (dd, *J* = 15.8, 4.7 Hz, 0.4H), 3.00 (dd, *J* = 16.3, 9.0 Hz, 0.6H), 2.71 – 2.57 (m, 1.4H), 2.32 – 2.22 (m, 2H), 1.45 – 1.27 (m, 4H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 200.7, 200.0, 168.1, 167.4, 144.0, 143.2, 139.9, 138.70, 138.67, 137.3, 136.74, 136.68, 132.9, 132.8, 131.1, 130.2, 130.1, 129.4, 129.3, 128.93, 128.91, 128.8, 128.7, 128.64, 128.60, 128.55, 128.52, 128.45, 128.41, 128.38, 128.37, 128.30, 128.26, 128.20, 128.18, 128.15, 128.1, 127.8, 127.70, 127.65, 126.9, 126.8, 68.4, 67.8, 42.7, 42.0, 40.2, 39.8, 36.3, 31.6, 31.5, 31.4, 30.0, 27.1, 26.9; **IR (ATR):** 2920, 2848, 1674, 1624, 1446, 1277, 1123, 821, 744, 696 cm^{-1}; **HRMS (ESI)** calculated for $C_{39}H_{37}NOSNa^+$ [M+Na$^+$]: 590.2488, found: 590.2488.

4-((diphenylmethylene)amino)-1,3,4-triphenylbutan-1-one (3aj)



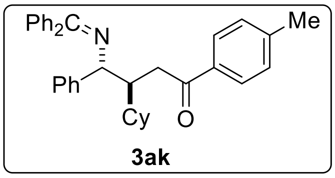
3aj

The preparation of **3aj** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 9:1 mixture of anti and syn isomer. **3aj** was isolated as a yellow liquid (69 mg, 72%) and was diastereoisomeric pure.

R_f = 0.30 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.36 – 7.31 (m, 2H), 7.30 – 7.20 (m, 6H), 7.19 – 7.13 (m, 1H), 7.13 – 7.08 (m, 3H), 7.06 – 7.02 (m, 2H), 6.54 (d, *J* = 7.3 Hz, 2H), 4.60 (d, *J* = 5.5 Hz, 1H), 4.03 – 3.95 (m, 1H), 3.74 (dd, *J* = 16.8, 10.3 Hz, 1H), 3.50 (dd, *J* = 16.9, 3.8 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 199.4, 168.1, 143.3, 142.1, 139.7, 137.4, 136.7, 132.8, 130.2, 128.7, 128.7, 128.5, 128.2, 128.2, 128.1, 127.6, 127.4, 126.8, 126.4, 71.1, 49.8, 39.4; **HRMS (ESI)** calculated for $C_{35}H_{30}NO^+$ [M+H$^+$]: 480.2322, found: 480.2325.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenyl-1-(p-tolyl)butan-1-one (3ak)

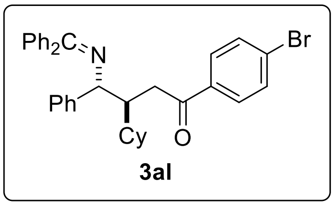

3ak

The preparation of **3ak** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3ak** was isolated as a yellow solid (85 mg, 85% combined) consisting of two diastereomers (4:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R_f = 0.51 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.35 (m, 6H), 7.31 – 7.27 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 3H), 7.00 (d, *J* = 7.0 Hz, 2H), 4.69 (d, *J* = 4.7 Hz, 1H), 3.25 (dd, *J* = 16.9, 4.0 Hz, 1H), 3.16 (dd, *J* = 16.8, 7.4 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.41 (s, 3H), 1.66 – 1.56 (m, 3H), 1.54 – 1.45 (m, 2H), 1.26 – 1.18 (m, 1H), 1.11 – 1.01 (m, 3H), 1.00 – 0.89 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.6, 167.4, 144.9, 143.2, 140.0, 136.9, 135.0, 130.0, 129.1, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 126.6, 66.8, 48.0, 40.1, 37.4, 31.4, 30.3, 26.9, 26.8, 26.7, 21.7; **IR (ATR)**: 2921, 2850, 1675, 1607, 1446, 1314, 1273, 1179, 1029, 809, 772, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NO^+$ [M+H$^+$]: 500.2948, found: 500.2948.

1-(4-bromophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenylbutan-1-one (3al)

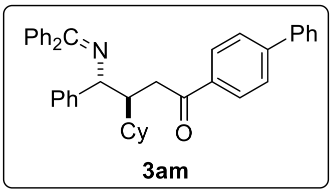

3al

The preparation of **3al** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3al** was isolated as a white solid (108 mg, 96% combined) consisting of two diastereomers (5:1 isolated dr). A small amount of diastereoisomeric mixture (< 30 mg) was further purified by preparative TLC (0.5% triethylamine in petroleum ether) to obtain the major isomer for characterization.

R_f = 0.36 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.62 (m, 4H), 7.48 (d, J = 8.6 Hz, 2H), 7.45 – 7.28 (m, 6H), 7.26 – 7.16 (m, 5H), 6.95 (d, *J* = 5.9 Hz, 2H), 4.64 (d, *J* = 4.9 Hz, 1H), 3.24 (dd, *J* = 16.6, 4.4 Hz, 1H), 3.04 (dd, *J* = 16.7, 7.1 Hz, 1H), 2.76 – 2.65 (m, 1H), 1.64 – 1.55 (m, 3H), 1.52 – 1.44 (m, 2H), 1.25 – 1.19 (m, 1H), 1.09 – 0.99 (m, 3H), 0.96 – 0.84 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 200.0, 167.6, 144.7, 139.8, 136.8, 136.2, 131.6, 130.1, 129.9, 128.7, 128.6, 128.34, 128.28, 128.1, 127.7, 127.6, 127.5, 126.7, 66.8, 48.4, 40.0, 37.5, 31.4, 30.2, 26.83, 26.76, 26.65; **IR (ATR)**: 2922, 2850, 1683, 1583, 1446, 1275, 1070, 1001, 773, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{35}BrNO^+$ [M+H$^+$]: 564.1897, found: 564.1897.

1-([1,1'-biphenyl]-4-yl)-3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenylbutan-1-one (3am)



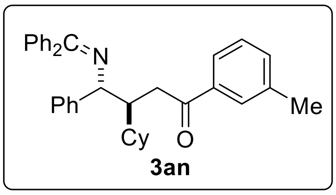
3am

The preparation of **3am** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 7:1 mixture of anti and syn isomer. **3am** was isolated as a white solid (70 mg, 62% combined) consisting of two diastereomers (4:1 isolated dr).

R$_f$ = 0.36 [0.5% triethylamine in petroleum ether].

These reported data are for the mixture of diastereomers.**^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.94 (d, J = 8.0 Hz, 1.6H), 7.78 (d, J = 8.1 Hz, 0.4H), 7.74 – 7.66 (m, 2H), 7.68 – 7.55 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.45 – 7.31 (m, 8H), 7.31 – 7.27 (m, 3H), 7.25 – 7.15 (m, 1H), 7.03 – 6.92 (m, 2H), 4.71 (d, J = 4.9 Hz, 0.8H), 4.45 (d, J = 7.3 Hz, 0.2H), 3.32 (dd, J = 16.7, 4.2 Hz, 0.8H), 3.19 (dd, J = 16.8, 7.2 Hz, 0.8H), 3.05 – 2.90 (m, 0.4H), 2.87 – 2.77 (m, 0.8H), 2.72 (dd, J = 15.9, 5.2 Hz, 0.2H), 1.72 – 1.59 (m, 3H), 1.57 – 1.49 (m, 2H), 1.29 – 1.20 (m, 1H), 1.14 – 1.03 (m, 3H), 1.02 – 0.89 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 200.5, 199.9, 167.4, 166.6, 145.12, 145.09, 144.8,143.4, 140.2, 140.1, 139.9, 136.9, 136.2, 130.0, 129.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.32, 128.26, 128.21, 128.18, 128.1, 128.08, 128.05, 127.9, 127.7, 127.6, 127.34, 127.30, 127.0, 126.9, 126.6, 68.2, 66.8, 48.1, 47.1, 40.1, 38.7, 37.6, 36.9, 32.6, 31.4, 30.2, 29.8, 28.4, 27.1, 26.9, 26.8, 26.7; **IR (ATR)**: 2921, 2849, 1675, 1602, 1489, 1447, 1273, 1181, 1003, 762, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{41}H_{39}NOK^+$ [M+K$^+$]: 600.2663, found: 600.2664.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenyl-1-(*m*-tolyl)butan-1-one (3an)



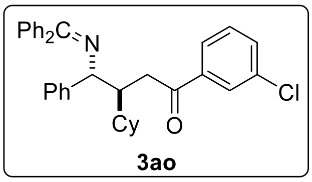
3an

The preparation of **3an** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 9:1 mixture of anti and syn isomer. **3an** was isolated as a yellow solid (98.8 mg, 99% combined) consisting of two diastereomers (9:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

R$_f$ = 0.41 [0.5% triethylamine in petroleum ether].

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 – 7.56 (m, 4H), 7.42 – 7.30 (m, 6H), 7.29 – 7.21 (m, 6H), 7.20 – 7.15 (m, 1H), 6.95 (d, J = 6.2 Hz, 2H), 4.63 (d, J = 4.9 Hz, 1H), 3.21 (dd, J = 16.8, 4.2 Hz, 1H), 3.10 (dd, J = 16.8, 7.4 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.34 (s, 3H), 1.60 – 1.53 (m, 3H), 1.50 – 1.40 (m, 2H), 1.25 – 1.13 (m, 1H), 1.07 – 0.97 (m, 3H), 0.96 – 0.81 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 201.3, 167.4, 144.9, 140.0, 138.1, 137.6, 136.9, 133.3, 130.0, 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 127.8, 127.6, 126.6, 125.5, 66.9, 48.0, 40.0, 37.7, 31.4, 30.2, 26.9, 26.8, 26.7, 21.5; **IR (ATR)**: 2922, 2851, 1682, 1489, 1446, 1314, 1283, 1028, 1001, 752, 694 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NO^+$ [M+H$^+$]: 500.2948, found: 500.2948.

1-(3-chlorophenyl)-3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenylbutan-1-one (3ao)

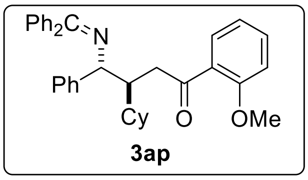


3ao

The preparation of **3ao** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed an 8:1 mixture of anti and syn isomer. **3ao** was isolated as yellow liquid (68 mg, 66%) and was diastereoisomeric pure.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.34 (m, 5H), 7.33 – 7.28 (m, 3H), 7.24 – 7.21 (m, 2H), 7.20 – 7.16 (m, 3H), 6.92 (d, *J* = 7.0 Hz, 2H), 4.59 (d, *J* = 5.2 Hz, 1H), 3.19 (dd, *J* = 16.7, 4.7 Hz, 1H), 3.01 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.77 – 2.65 (m, 1H), 1.61 – 1.52 (m, 3H), 1.47 – 1.40 (m, 2H), 1.22 – 1.15 (m, 1H), 1.05 – 0.97 (m, 3H), 0.93 – 0.82 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 199.6, 167.6, 144.6, 139.7, 139.1, 136.8, 134.7, 132.4, 130.1, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 126.7, 126.4, 66.8, 48.3, 39.9, 37.7, 31.5, 30.1, 26.82, 26.75, 26.7; **IR (ATR)**: 2921, 2850, 1684, 1571, 1490, 1447, 1278, 1211, 754, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{35}ClNO^+$ [M+H$^+$]: 520.2402, found: 520.2402.

3-cyclohexyl-4-((diphenylmethylene)amino)-1-(2-methoxyphenyl)-4-phenylbutan-1-one (3ap)

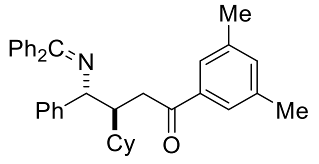


3ap

The preparation of **3ap** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ap** was isolated as a pale-yellow solid (86 mg, 84% combined) consisting of two diastereomers (2:1 isolated dr). Analytical sample of the major isomer was obtained via further recrystallization in MeOH for characterization.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.29 (m, 8H), 7.25 – 7.20 (m, 3H), 7.21 – 7.11 (m, 2H), 6.93 (d, *J* = 6.6 Hz, 2H), 6.90 – 6.79 (m, 2H), 4.58 (d, *J* = 5.3 Hz, 1H), 3.79 (s, 3H), 3.33 – 3.13 (m, 2H), 2.79 – 2.60 (m, 1H), 1.66 – 1.52 (m, 3H), 1.50 – 1.40 (m, 2H), 1.20 – 1.11 (m, 1H), 1.08 – 0.97 (m, 3H), 0.95 – 0.80 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$): δ 203.5, 166.7, 157.8, 145.0, 140.1, 137.0, 132.5, 130.4, 129.9, 129.6, 128.8, 128.4, 128.2, 128.0, 127.8, 127.6, 126.4, 120.5, 111.3, 67.0, 55.5, 47.3, 42.7, 40.0, 31.4, 30.1, 26.9, 26.8, 26.7; **IR (ATR)**: 2921, 2849, 1674, 1596, 1485, 1446, 1435, 1285, 1241, 1026, 754, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{36}H_{38}NO_2^+$ [M+H$^+$]: 516.2897, found: 516.2897.

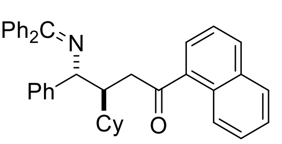
3-cyclohexyl-1-(3,5-dimethylphenyl)-4-((diphenylmethylene)amino)-4-phenylbutan-1-one (3aq)


3aq

The preparation of **3aq** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed an 8:1 mixture of anti and syn isomer. **3aq** was isolated as white solid (90 mg, 88%) and was diastereoisomeric pure.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 6.6 Hz, 2H), 7.64 – 7.44 (m, 9H), 7.45 – 7.39 (m, 4H), 7.37 – 7.32 (m, 1H), 7.11 (d, *J* = 6.5 Hz, 2H), 4.80 (d, *J* = 5.0 Hz, 1H), 3.37 (dd, *J* = 16.6, 4.2 Hz, 1H), 3.25 (dd, *J* = 16.6, 7.4 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.47 (s, 6H), 1.86 – 1.71 (m, 3H), 1.68 – 1.57 (m, 2H), 1.41 – 1.29 (m, 1H), 1.26 – 1.14 (m, 3H), 1.14 – 1.00 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 167.3, 144.9, 140.0, 137.9, 137.6, 136.9, 134.1, 130.0, 128.8, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 126.5, 126.1, 67.0, 48.1, 40.0, 37.7, 31.3, 30.2, 26.9, 26.8, 26.7, 21.4; **IR (ATR)**: 2921, 2850, 1683, 1601, 1490, 1446, 1314, 1293, 1180, 1157, 1029, 851, 773, 760 cm^{-1}; **HRMS (ESI)** calculated for $C_{37}H_{39}NONa^+$ [M+Na$^+$]: 536.2924, found: 536.2925.

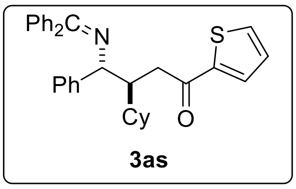
3-cyclohexyl-4-((diphenylmethylene)amino)-1-(naphthalen-1-yl)-4-phenylbutan-1-one (3ar)


3ar

The preparation of **3ar** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 2:1 mixture of anti and syn isomer. **3ar** was isolated as white solid (75 mg, 70% combined) consisting of two diastereomers (2:1 isolated dr). A small amount of diastereoisomeric mixture was further purified by preparative TLC (0.5% triethylamine in petroleum ether) to obtain the major isomer for characterization.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (brs, 1H), 7.97 – 7.73 (m, 5H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.41 – 7.30 (m, 7H), 7.25 – 7.18 (m, 3H), 6.97 (d, *J* = 6.4 Hz, 2H), 4.68 (d, *J* = 4.8 Hz, 1H), 3.40 (dd, *J* = 16.5, 4.2 Hz, 1H), 3.23 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.78 (s, 1H), 1.64 – 1.49 (m, 5H), 1.26 – 1.20 (m, 1H), 1.08 – 1.01 (m, 3H), 0.99 – 0.88 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 201.2, 167.5, 144.9, 140.0, 137.0, 135.4, 134.9, 132.6, 130.1, 129.7, 129.7, 128.8, 128.6, 128.2, 128.1, 127.8, 127.7, 126.7, 126.6, 124.5, 67.0, 48.5, 40.2, 37.7, 31.4, 30.3, 26.9, 26.9, 26.7; **IR (ATR)**: 3064, 3028, 2931, 1678, 1622, 1598, 1578, 1491, 1447, 1314, 1287, 1073, 1028, 1001, 774, 749, 692 cm^{-1}; **HRMS (ESI)** calculated for $C_{39}H_{38}NO^+$ [M+H$^+$]: 536.2948, found: 536.2948.

3-cyclohexyl-4-((diphenylmethylene)amino)-4-phenyl-1-(thiophen-2-yl)butan-1-one (3as)

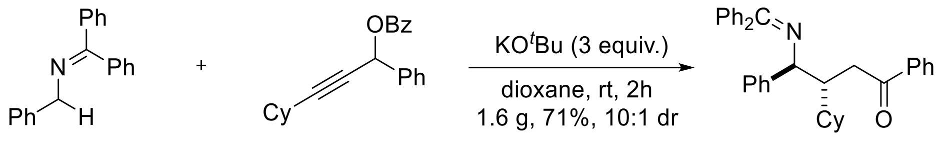


3as

The preparation of **3as** was followed according to General Procedure C. ^{1}H NMR analysis of the crude revealed a 5:1 mixture of anti and syn isomer. **3as** was isolated as a pale-yellow oil (85 mg, 87% combined) consisting of two diastereomers (8:1 isolated dr). A small amount of diastereoisomeric mixture (< 30 mg) was further purified by preparative TLC (0.5% triethylamine in petroleum ether) to obtain the major isomer for characterization.

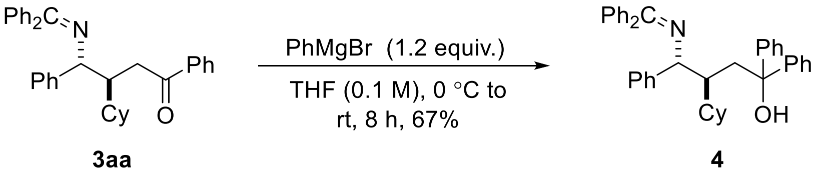
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.0 Hz, 2H), 7.61 (d, J = 3.7 Hz, 1H), 7.52 (d, J = 5.0 Hz, 1H), 7.48 – 7.36 (m, 5H), 7.38 – 7.29 (m, 3H), 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.05 – 7.01 (m, 1H), 6.99 (d, J = 6.3 Hz, 2H), 4.66 (d, J = 5.0 Hz, 1H), 3.19 (dd, J = 16.5, 4.6 Hz, 1H), 3.09 (dd, J = 16.6, 7.1 Hz, 1H), 2.85 – 2.73 (m, 1H), 1.69 – 1.56 (m, 3H), 1.56 – 1.48 (m, 2H), 1.30 – 1.22 (m, 1H), 1.11 – 1.01 (m, 3H), 1.01 – 0.90 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.5, 167.4, 145.0, 144.8, 139.8, 136.9, 132.9, 131.5, 130.0, 128.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 126.6, 66.7, 48.3, 39.9, 38.3, 31.4, 30.1, 26.9, 26.8, 26.7; **IR (ATR)**: 2922, 2850, 1654, 1622, 1446, 1415, 1275, 1238, 1028, 773, 724, 695 cm^{-1}; **HRMS (ESI)** calculated for $C_{33}H_{34}NOS^+$ [$M+H^+$]: 492.2334, found: 492.2333.

3.7 Synthetic Application



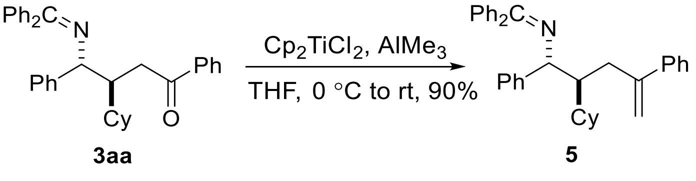
1a **2a** **3aa**

In a nitrogen-filled glove box, to an oven dried flask with a magnetic stir bar was charged with imines **1a** (1.2 g, 4.6 mmol, 1.0 equiv.), K^{t}OBu (1.5 g, 13.8 mmol, 3.0 equiv.) and 1,4 -dioxane (50 mL). The reaction mixture was stirred at room temperature for 5 min and alkynes **2a** (2.9 g, 9.2 mmol, 2.0 equiv.) were subsequently added. The flask was sealed with a rubber septum, removed from glovebox and stirred at rt for 2h. The reaction mixture was diluted with 120 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a pad of celite, rinsed with petroleum ether (220 mL × 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography with elution (triethylamine:petroleum ether = 5: 100) to obtain products **3aa** (1.6 g, 71%) as a single diastereoisomer. The diastereoselectivity (anti/syn ratio) of the reaction was confirmed by analyzing the ^{1}H NMR of crude product.



To a stirring solution of **3aa** (97 mg, 0.2 mmol, 1.0 equiv.) in THF (2.0 mL) at 0 °C under nitrogen atmosphere was added PhMgBr solution (1 M in THF, 0.24 mL, 0.24 mmol, 1.2 equiv.) dropwise. The resulting solution was warmed to room temperature and stirred at for 8 h. The reaction was quenched by adding aq. NH_4Cl (10 mL) at 0 °C. 10 mL ethyl acetate was added, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL × 2). The organic phases were combined, dried over anhydrous sodium sulfate, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (2:1) as the eluent, yielding title product **4** as a film (76.0 mg, 67%).

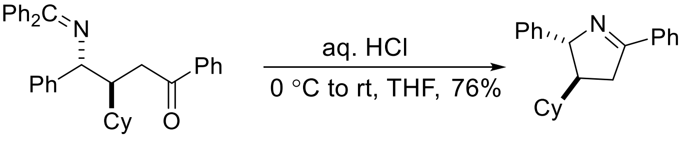
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.44 7.37 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.11 (m, 9H), 7.08 (d, *J* = 6.3 Hz, 2H), 6.85 (d, *J* = 6.1 Hz, 2H), 4.34 (d, *J* = 9.7 Hz, 1H), 2.54 (d, *J* = 14.3 Hz, 1H), 2.38 (t, *J* = 8.5 Hz, 1H), 2.26 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.60 – 1.55 (m, 1H), 1.33 – 1.28 (m, 2H), 0.99 – 0.83 (m, 5H), 0.83 – 0.74 (m, 1H), 0.47 (q, *J* = 11.6 Hz, 1H), 0.26 (d, *J* = 13.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.1, 151.2, 147.8, 145.0, 138.7, 136.8, 132.6, 130.8, 130.2, 129.0, 128.7, 128.5, 128.4, 128.29, 128.26, 127.9, 127.6, 127.5, 127.2, 126.9, 126.5, 126.2, 126.0, 76.4, 67.7, 45.4, 40.6, 39.2, 30.7, 27.1, 27.0, 26.8, 26.6; **IR (ATR)**: 3056, 2919, 2850, 1618, 1597, 1491, 1445, 1316, 1161, 1061, 1029, 998, 919, 771, 752, 696, 557 cm^{-1}; **HRMS (ESI)** calculated for $C_{22}H_{26}N^+$ [M+H$^+$]: 564.3261, found: 564.3261.



Synthesis of Tebbe reagent: to a stirring suspension of titanocene dichloride (602.2 mg, 2.4 mmol, 1.0 equiv.) in toluene (2.4 mL) at room temperature was added dropwise a solution of $AlMe_3$ (2 M in hexanes, 2.45 mL, 2.0 equiv.). The resulting dark red solution was stirred at room temperature for 2 days, then used directly.

To a stirring solution of **3aa** (97 mg, 0.2 mmol, 1.0 equiv.) in THF (2 mL) at 0 °C was added dropwise the above prepared Tebbe reagent (0.5 M, 1.2 mL, 0.6 mmol, 3.0 equiv.). The resulting solution was stirred at 0 °C for 5 mins, then warmed to room temperature, and stirred for 30 mins. The reaction mixture was diluted with 3 mL Et_2O, and then quenched by dropwise addition of aq. NaOH (0.1 M, 0.2 mL) until gas ceased. The mixture was dried over anhydrous magnesium sulfate, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (20:1) containing 5% triethylamine as the eluent, yielding desired product **5** (87 mg, 90%) as a colorless film.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 6.1 Hz, 2H), 7.41 – 7.34 (m, 6H), 7.24 – 7.13 (m, 8H), 7.10 – 7.05 (m, 2H), 6.95 (d, *J* = 5.7 Hz, 2H), 5.21 (s, 1H), 5.07 (s, 1H), 4.51 (d, *J* = 4.4 Hz, 1H), 3.01 (d, *J* = 14.9 Hz, 1H), 2.74 (dd, *J* = 15.0, 9.9 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.56 – 1.44 (m, 2H), 1.34 – 1.24 (m, 3H), 1.04 – 0.96 (m, 4H), 0.87 – 0.83 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.3, 149.2, 145.8, 141.1, 140.3, 137.2, 129.9, 128.8, 128.4, 128.20, 128.15, 128.11, 128.08, 127.9, 127.8, 127.0, 126.6, 126.3, 113.7, 67.3, 49.5, 39.9, 33.1, 30.7, 30.3, 27.4, 27.2, 27.0; **HRMS (ESI)** calculated for $C_{36}H_{38}N^+$ [$M+H^+$]: 484.2999, found: 484.2997.

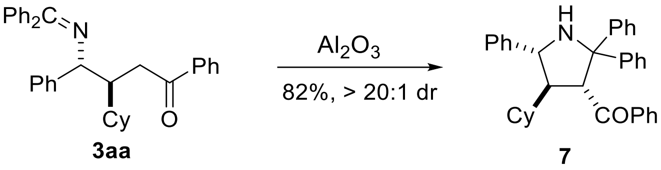


3aa

6

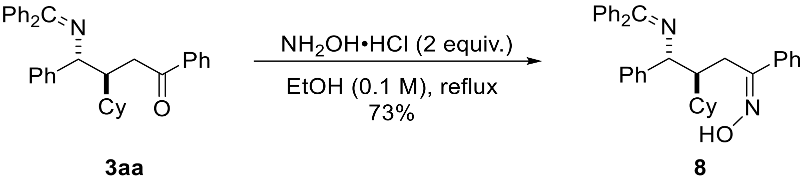
To s stirring solution of **3aa** (97 mg, 0.2 mmol, 1.0 equiv.) in THF (2.0 mL) at 0 °C was added aq. HCl (1 M, 1 mL, 1 mmol, 10 equiv.) dropwise, and the resulting solution mixture was warmed to room temperature and stirred for 5 mins. The reaction was quenched by adding 1N aqueous NaOH solution until a pH of 10 reached. After stirring for 5 mins, dichloromethane (5 mL) was added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The organic phases were combined and dried over anhydrous sodium sulfate, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (20:1) as the eluent, yielding desired **6** (46 mg, 76%) as a colorless film.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.31 (m, 3H), 7.29 – 7.23 (m, 2H), 7.19 – 7.14 (m, 3H), 5.01 (d, *J* = 5.9 Hz, 1H), 3.32 – 3.00 (m, 1H), 2.77 (dd, *J* = 17.2, 6.5 Hz, 1H), 2.31 – 2.04 (m, 1H), 1.74 – 1.52 (m, 4H), 1.46 – 1.30 (m, 1H), 1.26 – 1.10 (m, 4H), 1.09 – 0.95 (m, 1H), 0.95 – 0.78 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.9, 144.7, 134.6, 130.7, 128.57, 128.55, 128.0, 127.2, 126.9, 79.5, 52.4, 41.6, 38.9, 31.7, 30.4, 26.7, 26.53, 26.48; **HRMS (ESI)** calculated for $C_{22}H_{26}N^+$ [M+H$^+$]: 304.2060, found: 304.2055.



γ-aminoketone **3aa** (97 mg, 0.2 mmol) was subjected to a neutral alumina (25 g) packed column chromatography with petroleum ether/ethyl acetate (20:1) as the eluent (elution flow rate < 5 mL/min). The collected solution was concentrated *in vacuo*, affording the title product **7** (80 mg, 82%, >20:1 dr isolated) as a colorless film.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.5 Hz, 4H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.37 (m, 6H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 6.99 – 6.84 (m, 3H), 5.29 (d, *J* = 3.4 Hz, 1H), 3.89 (d, *J* = 7.9 Hz, 1H), 3.45 (brs, 1H), 2.77 – 2.66 (m, 1H), 1.89 (d, *J* = 12.8 Hz, 1H), 1.64 (d, *J* = 12.8 Hz, 1H), 1.50 – 1.40 (m, 3H), 1.24 – 1.13 (m, 2H), 0.99 – 0.88 (m, 3H), 0.53 – 0.37 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 204.7, 146.7, 144.3, 143.7, 138.9, 132.7, 128.74, 128.69, 128.6, 128.2, 127.7, 127.5, 127.0, 126.9, 126.6, 126.3, 76.4, 66.9, 60.3, 56.8, 41.8, 33.0, 32.4, 26.4, 26.3, 26.0; **HRMS (ESI)** calculated for $C_{35}H_{36}NO^+$ [M+H$^+$]: 486.2791, found: 486.2789.

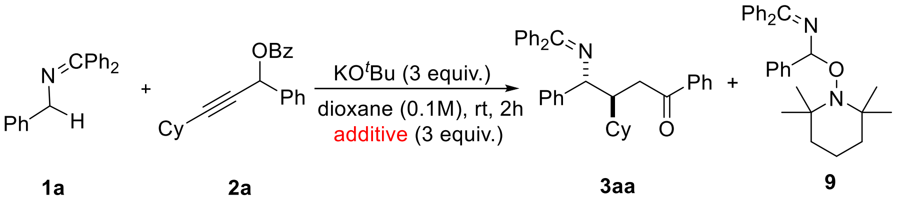


To a stirring solution of **3aa** (97 mg, 0.2 mmol, 1.0 equiv.) in EtOH (2.0 mL) at rt was added, $NH_2OH·HCl$ (28 mg, 0.4 mmol, 2.0 equiv.) and Et_3N (50.6 mg, 0.5 mmol, 2.5 equiv.). The mixture was heated under reflux for 8 h until the reaction was judged to be complete by TLC analysis. The reaction mixture was cooled to room temperature, ethyl acetate (10.0 mL) and water (10.0 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL × 2). The organic phases were combined and dried over anhydrous sodium sulfate, filtered through a coarse fritted glass funnel, and the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:4) as the eluent, yielding product **8** (73.0 mg, 73%).

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.95 (d, *J* = 6.0 Hz, 2H), 7.46 – 7.44 (m, 7H), 7.43 – 7.39 (m, 5H), 7.37 – 7.30 (m, 5H), 7.26 – 7.23 (m, 1H), 5.11 (d, *J* = 5.8 Hz, 1H), 3.27 – 3.15 (m, 1H), 2.86 (dd, *J* = 17.1, 6.1 Hz, 1H), 2.32 – 2.21 (m, 1H), 1.80 – 1.65 (m, 5H), 1.60 – 1.34 (m, 1H), 1.32 – 1.15 (m, 3H), 1.12 – 1.03 (m, 1H), 1.02 – 0.93 (m, 1H); ^{13}**C NMR** (101 MHz, $CDCl_3$):δ 173.4, 157.6, 144.5, 136.4, 134.2, 132.9, 130.8, 129.5, 129.4, 129.1, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.2, 126.9, 79.2, 52.2, 41.5, 38.9, 31.6, 30.3, 26.6, 26.5, 26.4; **IR (ATR)**: 3246, 2920, 2848, 1617, 1492, 1444, 1328, 1160, 1076, 994, 932, 917, 762, 692, 657 cm^{-1}; **HRMS (ESI)** calculated for $C_{35}H_{37}N_2O^+$ [M+H$^+$]: 501.2900, found: 501.2900.

3.8 Mechanism Experiment

I. Radical Trapping Experiment



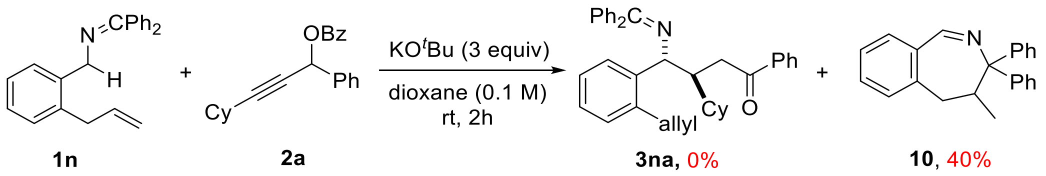
entries	additive	yield of **3aa**
1	none	83%
2	TEMPO	0% (25% for **9**)
3	BHT	0%

In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (54 mg, 0.2 mmol, 1.0 equiv.), K^{t}OBu (0.6 mmol, 3.0 equiv.), additive (0.6 mmol, 3.0 equiv.) and 1,4 -dioxane (2 mL). The reaction mixture was stirred at room temperature for 5 min and propargyl ester **2a** (0.4 mmol, 2.0 equiv.) were subsequently added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*.

The reactions were checked by ^{1}H NMR and HRMS analysis and no desired product was formed. When TEMPO was employed, the crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), yielding byproduct **9** (21 mg, 25%) as a colorless film.

Spectral data for **9**: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.43 (m, 3H), 7.38 – 7.27 (m, 8H), 7.23 – 7.17 (m, 2H), 5.84 (s, 1H), 1.64 – 1.29 (m, 6H), 1.27 (s, 3H), 1.21 (s, 3H), 1.07 (s, 3H), 0.72 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.4, 141.1, 139.4, 136.8, 130.0, 128.7, 128.2, 128.0, 127.9, 127.8, 127.5, 127.1, 97.1, 60.2, 59.3, 40.5, 40.0, 34.9, 33.1, 20.6, 20.4, 17.2. This characterization data matches with the previously reported data.[7]

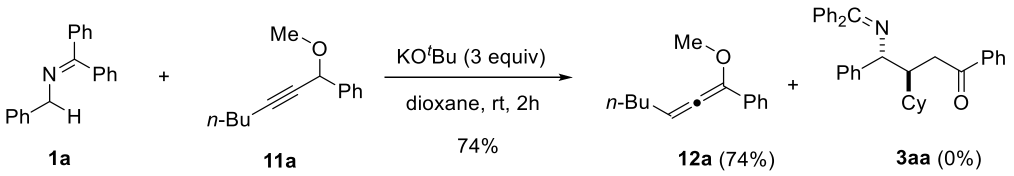
II. Radical Clock Experiment



In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1n** (62 mg, 0.2 mmol, 1.0 equiv.), K^{t}OBu (67 mg, 0.6 mmol, 3.0 equiv.), additive (0.6 mmol, 3.0 equiv.) and 1,4 -dioxane (2 mL). The reaction mixture was stirred at room temperature for 5 min and propargyl ester **2a** (128 mg, 0.4 mmol, 2.0 equiv.) was subsequently added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO$_2$ flash column chromatography (0.5% triethylamine in petroleum ether), yielding cyclization byproduct **10** (25 mg, 40%) as a colorless film. No desired product **3na** was isolated.

Spectral data for **10**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.93 (s, 1H), 7.71 (dd, J = 8.4, 1.4 Hz, 2H), 7.55 (dd, J = 7.1, 2.1 Hz, 1H), 7.37 – 7.27 (m, 6H), 7.20 (q, J = 7.3 Hz, 3H), 7.16 – 7.05 (m, 2H), 3.61 – 3.42 (m, 1H), 3.07 (dd, J = 16.9, 2.9 Hz, 1H), 2.86 (dd, J = 17.1, 5.9 Hz, 1H), 0.88 (d, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 160.4, 147.8, 147.5, 140.1, 134.9, 133.7, 130.6, 130.5, 128.4, 128.0, 127.9, 126.6, 126.3, 126.1, 126.0, 74.7, 38.6, 36.5, 15.2; **HRMS (ESI)** calculated for $C_{23}H_{22}N^+$ [M+H$^+$]: 312.1747, found: 312.1741.

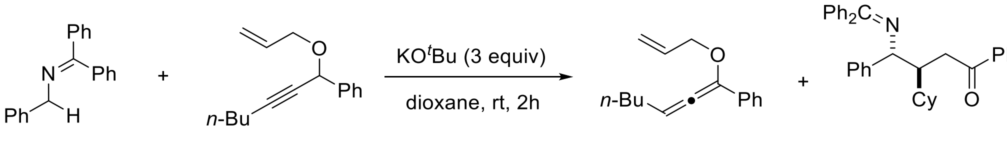
III. Control Experiment



In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (54 mg, 0.2 mmol, 1.0 equiv.), K^{t}OBu (67 mg, 0.6 mmol, 3.0 equiv.), and 1,4 -dioxane (2 mL). The reaction mixture was stirred at room temperature for 5 min and propargyl ether **11a** (81 mg, 0.4 mmol, 2.0 equiv.) was subsequently added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), yielding allene **12a** (28 mg, 74%) as a colorless film. No desired product **3aa** was isolated.

Note: compound **12a** was contaminated with minor unidentified impurity. Further purification led to decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.24 (t, *J* = 6.4 Hz, 1H), 3.60 (s, 3H), 2.28 – 2.17 (m, 2H), 1.56 – 1.47 (m, 2H), 1.42 (dt, *J* = 14.8, 7.0 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 134.5, 134.1, 128.2, 127.4, 125.0, 109.8, 56.2, 31.5, 31.0, 22.5, 14.0; **HRMS (ESI)** calculated for $C_{13}H_{19}N^+$ [M+H$^+$]: 191.1430, found: 191.1428.

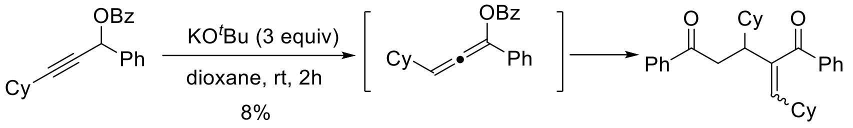


1a **11b** **12b** (62%) **3aa** (0%)

In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (54 mg, 0.2 mmol, 1.0 equiv.), K^{t}OBu (67 mg, 0.6 mmol, 3.0 equiv.), and 1,4 -dioxane (2 mL). The reaction mixture was stirred at room temperature for 5 min and propargyl ether **11b** (91 mg, 0.4 mmol, 2.0 equiv.) were subsequently added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), yielding allene **12b** (26.8 mg, 62%) as a colorless film. No desired product **3aa** was isolated.

Note: compound **12b** was contaminated with minor unidentified impurity. Further purification led to decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.35 (m, 3H), 6.25 (t, *J* = 6.5 Hz, 1H), 6.11 (m, 1H), 5.44 (dd, *J* = 17.3, 1.8 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.7 Hz, 1H), 4.33 (m, 2H), 2.27 (q, *J* = 7.0 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.45 (q, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.7, 134.5, 134.1, 128.2, 127.4, 125.1, 116.9, 109.5, 69.4, 31.4, 31.0, 22.5, 14.0; **HRMS (ESI)** calculated for $C_{15}H_{21}O^+$ [M+H$^+$]: 217.1587, found: 217.1585.

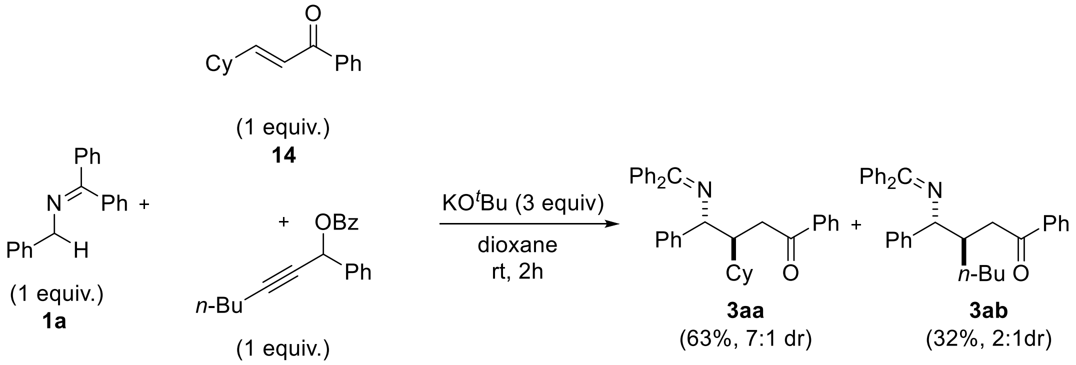


2a **13**

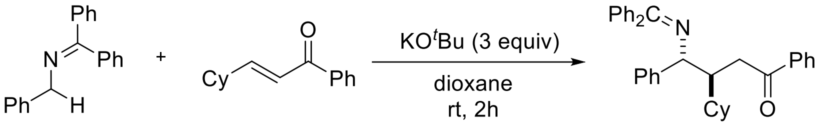
In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with K^{t}OBu (67 mg, 0.6 mmol, 3.0 equiv.), and 1,4 -dioxane (2 mL). Alkynes **2a** (91 mg, 0.4 mmol, 2.0 equiv.) were added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography (petroleum ether), yielding **13** (13.0 mg, 8%) as a colorless residue.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 13.1, 7.7 Hz, 3H), 7.64 – 7.32 (m, 7H), 5.47 (d, *J* = 10.4 Hz, 1H), 3.26 (dd, *J* = 17.0, 9.2 Hz, 1H), 3.11 – 3.04 (m, 1H), 3.04 – 2.96 (m, 1H), 1.82 – 1.67 (m, 5H), 1.57 – 1.39 (m, 6H), 1.24 – 0.80 (m, 11H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 200.0, 139.7, 138.3, 138.0, 137.6, 133.1, 133.0, 129.5, 128.7, 128.5, 128.1, 45.7, 40.6, 38.85, 38.80, 32.9, 31.8, 29.8, 28.2, 26.74, 26.71, 26.65, 25.8, 25.43, 25.40; **HRMS (ESI)** calculated for $C_{30}H_{37}O_2^+$ [M+H$^+$]: 429.2788, found: 429.2786.

V. Competitive experiment



In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (27 mg, 0.1 mmol, 1.0 equiv.), K^{t}OBu (34 mg, 0.3 mmol, 3.0 equiv.), and 1,4 -dioxane (1 mL). The reaction mixture was stirred at room temperature for 5 minutes, propargyl ester **2b** (29 mg, 0.1 mmol, 1.0 equiv.) and *α,β*-unsaturated ketone **14** (21 mg, 0.1 mmol, 1.0 equiv.) were added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. ^{1}H NMR analysis of the crude revealed a 7:1 mixture of anti and syn isomer for **3aa** and 2:1 mixture of anti and syn isomer for **3ab**. The crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), respectively yielding **3aa** (30.5 mg, 63% combined, 10:1 isolated dr) as a colorless film along with **3ab** (14.7 mg, 32% combined, 2:1 isolated dr) as a colorless film.



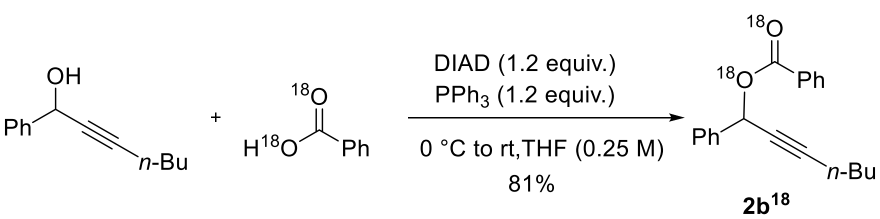
(1 equiv.)
1a

(2 equiv.)
14

3aa
(90%, 7:1 dr)

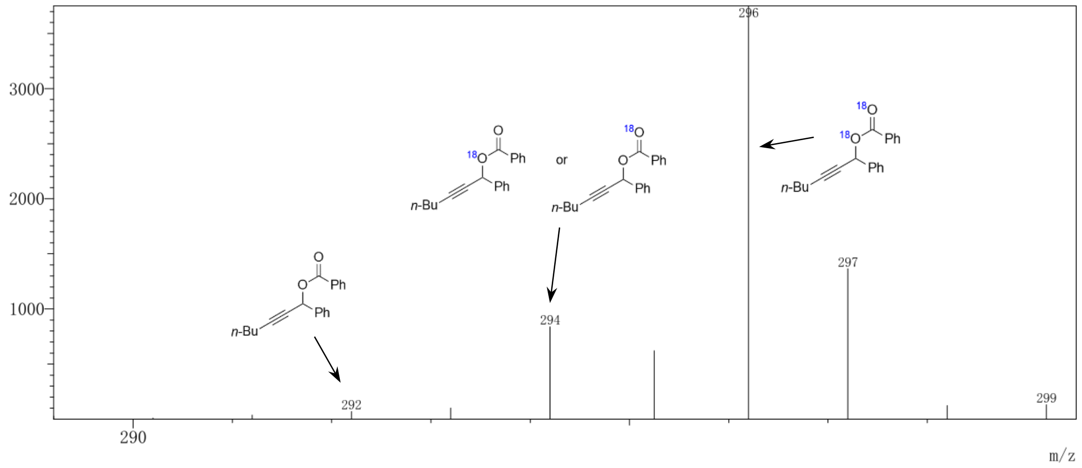
In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (27 mg, 0.1 mmol, 1.0 equiv.), K^{t}OBu (34 mg, 0.3 mmol, 3.0 equiv.), and 1,4 -dioxane (1 mL). The reaction mixture was stirred at room temperature for 5 minutes, and *α,β*-unsaturated ketone **17** (42 mg, 0.2 mmol, 2.0 equiv.) was added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. ^{1}H NMR analysis of the crude revealed a 7:1 mixture of anti and syn isomer for **3aa**. The crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), yielding **3aa** (30.5 mg, 90% combined, 7:1 isolated dr) as a colorless film.

V. Labelling experiment.

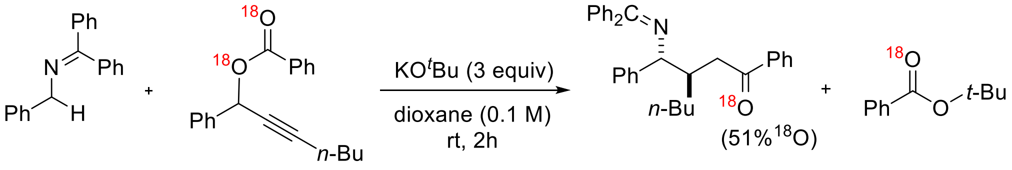


2b^{18}

To a stirring solution of 1-phenylhept-2-yn-1-ol (338 mg, 1.8 mmol, 1.0 equiv.), ^{18}O enriched benzoic acid[8] (230 mg, 1.8 mmol, 1.0 equiv.), and triphenylphosphine (566 mg, 2.2 mmol, 1.2 equiv.) in THF (0.25 M, 7.2 mL) at 0 °C was added DIAD (0.4 mL, 2.2 mmol, 1.2 equiv.) dropwise. The resulting solution was warmed to room temperature, and stirred for 24 h. The reaction was quenched by adding 10 mL of aq. $NaHCO_3$ solution and extracted three times with ethyl acetate (15 mL X 3). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate, and filtered through a coarse fritted glass funnel. The filtrate was concentrated *in vacuo*. Purification by silica gel column chromatography using 10% ethyl acetate in petroleum ether as the eluent afforded the title compound **2b**^{18}(430 mg, 81%) as a colorless oil.



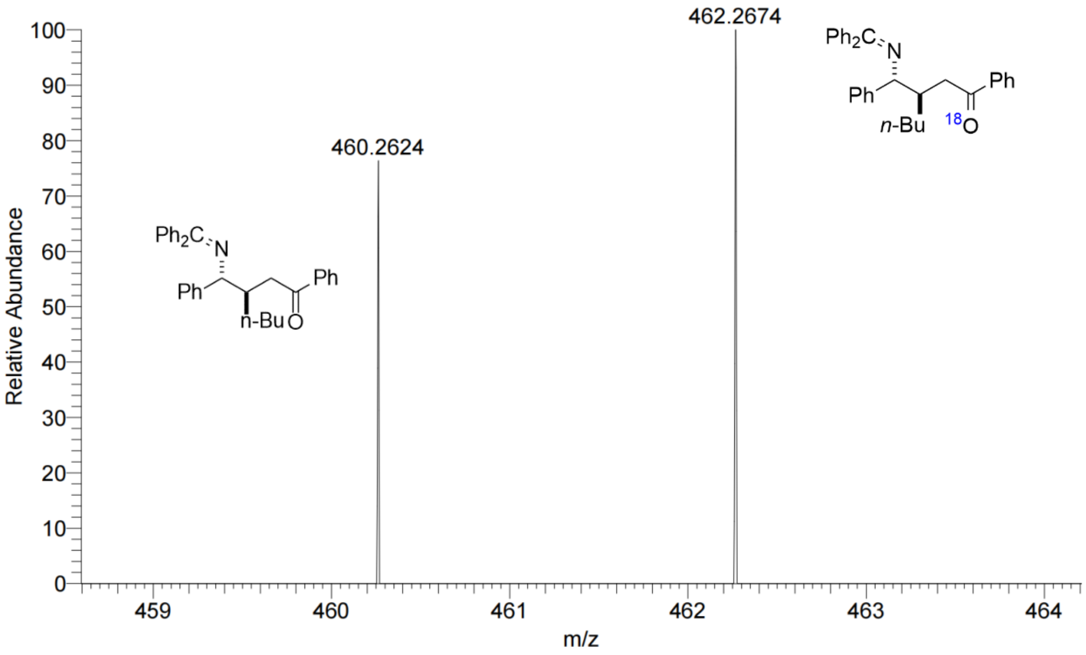
The O^{18} enrichment of compound **2b^{18}** was determined by Gas chromatography - mass spectrometry (GC-MS) analysis to be 93%. The relative abundance of [M], [M + 2], and [M + 4] peaks are 0.02, 0.16 and 1.28, respectively. The abundance of ^{18}O in **2b** is therefore calculated as: $(1.28 + 0.16 \times 1/2) / (1.28 + 0.16 + 0.02) \times 100\% = 93\%$.



1a **2b^{18}** **3ab^{18}**, 74% **15^{18}**, 90%

In a nitrogen-filled glove box, to an oven dried 1-dram vial with a magnetic stir bar was charged with imines **1a** (27 mg, 0.1 mmol, 1.0 equiv.), K^{t}OBu (34 mg, 0.3 mmol, 3.0 equiv.), and 1,4 -dioxane (1 mL). The reaction mixture was stirred at room temperature for 5 minutes, and propargyl ester **2b^{18}** (59 mg, 0.2 mmol, 2.0 equiv.) was added. The vial was caped, removed from glovebox and stirred at rt for 2h. The reaction mixture was added via glass pipet into a 10 mL vial containing 5 mL of petroleum ether to allow the salts to precipitate. The resulting mixture was filtered through a coarse fritted glass funnel, rinsed with petroleum ether (5 mL X 2) and the filtrate was concentrated *in vacuo*. The crude was purified though SiO_2 flash column chromatography (0.5% triethylamine in petroleum ether), affording titled compound **3a^{18}** (34.0 mg, 74%, 2:1 isolated dr) as a colorless film along with compound **15^{18}**(32 mg, 90%).

The O^{18} enrichment of compound **3ab^{18}** was determined by HRMS analysis to be 57%. In HRMS, The relative abundance of [M], [M + 2] peaks for **3a^{18}** were 76 and 100, respectively. The O^{18} content was calculated as 100/(76+100)×100% = 57%.



4. X-Ray Analysis of Compound 3af

The X-ray crystal structure of **3af** (CCDC: 2407137). The crystal was obtained by slow evaporation of a solution of dichloromethane and petroleum ether.

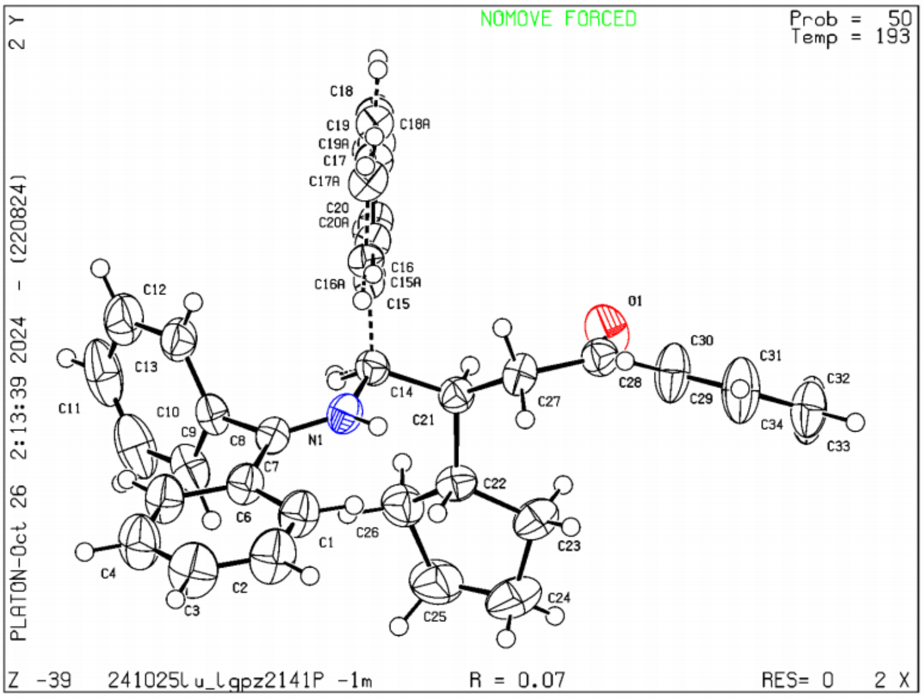


Table 1 Crystal data and structure refinement for 241025LU_LGPZ214150_0m.

Identification code	**3af**
Empirical formula	$C_{34}H_{34}NO$
Formula weight	472.62
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	9.2433(5)
b/Å	11.6116(7)
c/Å	13.7296(8)
α/°	72.825(2)
β/°	80.564(2)
γ/°	69.791(2)
Volume/Å^3	1318.05(13)
Z	2
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.070
F(000)	506.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.868 to 54.93
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 15$, $-17 \leqslant l \leqslant 17$
Reflections collected	12578
Independent reflections	5985 [R_{int} = 0.0453, R_{sigma} = 0.0771]
Data/restraints/parameters	5985/181/380
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1440
Final R indexes [all data]	R_1 = 0.1303, wR_2 = 0.1777
Largest diff. peak/hole / e Å^{-3}	0.20/-0.46

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 241025LU_LGPZ214150_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	10482(2)	2201.0(18)	1282.7(13)	62.2(5)
N1	5046(2)	3113.5(17)	3154.3(14)	41.0(5)
C1	3492(3)	1777(2)	4808.5(19)	54.0(7)
C2	2701(4)	1224(3)	5661(2)	69.0(9)
C3	1141(4)	1770(3)	5847(2)	72.1(9)
C4	362(3)	2876(3)	5178(2)	68.7(8)
C5	1135(3)	3446(3)	4328.1(19)	55.2(7)
C6	2721(3)	2902(2)	4138.4(18)	44.0(6)
C7	3576(3)	3528(2)	3240.1(16)	37.8(5)
C8	2637(2)	4645(2)	2480.8(17)	40.2(5)
C9	1913(3)	4479(3)	1749(2)	57.1(7)
C10	1085(3)	5530(4)	1029(2)	74.7(10)
C11	958(3)	6720(4)	1060(3)	79.9(11)
C12	1637(3)	6902(3)	1787(3)	72.1(9)

C13	2489(3)	5866(2)	2501(2)	52.2(7)
C14	5889(2)	3710(2)	2263.3(17)	38.2(5)
C15	6425(14)	4744(9)	2387(6)	39.6(17)
C16	6645(8)	4831(6)	3336(6)	49.0(15)
C16A	6388(15)	4563(12)	3665(10)	45(2)
C17	7182(6)	5761(6)	3438(5)	53.3(15)
C17A	6921(12)	5389(10)	3959(10)	58(2)
C18	7521(6)	6607(6)	2573(6)	56.5(16)
C18A	7438(12)	6285(12)	3185(13)	56(2)
C19	7271(6)	6572(5)	1601(6)	53.8(14)
C19A	7393(13)	6395(12)	2158(11)	53(2)
C20	6727(8)	5638(7)	1521(5)	43.5(13)
C20A	6883(16)	5551(15)	1909(10)	51(2)
C21	7275(2)	2689(2)	1896.4(17)	38.2(5)
C22	6728(3)	1728(2)	1623.8(17)	42.3(6)
C23	7979(3)	647(2)	1260(2)	54.0(7)
C24	7089(4)	90(3)	798(3)	76.5(9)
C25	5791(4)	1222(3)	280(3)	75.9(9)
C26	5633(3)	2299(3)	758(2)	54.7(7)
C27	8541(3)	2044(2)	2649.5(17)	43.0(6)
C28	10150(3)	1645(2)	2144.4(18)	42.4(6)
C29	11353(2)	540(2)	2723.6(17)	39.1(5)
C30	11310(3)	167(3)	3770.1(19)	61.2(8)
C31	12436(3)	-890(3)	4270(2)	71.2(9)
C32	13589(3)	-1596(3)	3732(2)	64.4(8)
C33	13639(3)	-1240(3)	2696(2)	78.4(10)
C34	12552(3)	-171(3)	2193(2)	65.0(8

Table 3 Anisotropic Displacement Parameters (Å2×103) for 241025LU_LGPZ214150_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23
O1	51.7(11)	71.0(13)	49.1(11)	7.2(10)
N1	41.8(11)	36.1(10)	38.0(11)	-4.6(9)
C1	55.5(15)	48.5(15)	45.3(14)	-3.2(12)
C2	73(2)	59.1(18)	50.2(17)	7.2(14)
C3	75(2)	75(2)	49.7(17)	-1.2(16)
C4	54.1(17)	73(2)	60.2(18)	-8.3(16)
C5	47.9(15)	53.4(16)	49.0(15)	-3.3(13)
C6	44.5(13)	41.4(13)	39.6(13)	-6.7(11)
C7	37.5(12)	35.9(12)	37.8(12)	-11.2(10)
C8	30.6(11)	46.4(14)	37.4(12)	-4.5(11)
C9	39.4(14)	76.4(19)	55.3(16)	-19.7(15)
C10	43.5(16)	121(3)	44.9(17)	-10.4(19)
C11	39.1(16)	97(3)	61(2)	23.8(19)
C12	48.8(16)	47.2(16)	91(2)	13.3(16)
C13	42.0(14)	41.8(14)	62.1(17)	-5.8(13)
C14	33.8(11)	34.9(12)	43.1(13)	-4.7(10)
C15	28(2)	33(3)	55(4)	-17(3)
C15A	27(3)	35(4)	67(5)	-17(4)
C16	40(2)	40(3)	67(4)	-19(2)
C16A	40(4)	39(4)	63(5)	-23(4)
C17	42(2)	51(3)	75(4)	-30(3)
C17A	51(4)	45(4)	79(5)	-24(4)
C18	42(2)	50(3)	90(5)	-36(3)
C18A	42(4)	44(5)	85(5)	-25(5)

C19	42(2)	41(2)	79(4)	-20(3)
C19A	42(3)	46(4)	76(5)	-26(4)
C20	33(2)	37(2)	61(3)	-15(3)
C20A	40(3)	42(3)	69(5)	-20(4)
C21	38.0(12)	36.0(12)	38.5(12)	-7.0(10)
C22	51.3(14)	41.2(13)	37.2(13)	-11.3(11)
C23	68.7(18)	45.1(14)	48.7(15)	-16.0(12)
C24	103(3)	57.1(19)	82(2)	-32.1(17)
C25	81(2)	89(2)	81(2)	-44(2)
C26	51.6(15)	64.3(17)	55.7(16)	-23.8(14)
C27	41.8(13)	40.6(13)	40.1(13)	-11.6(11)
C28	41.2(13)	42.9(13)	43.3(14)	-12.2(11)
C29	34.1(12)	43.7(13)	38.7(13)	-14.8(11)
C30	48.5(15)	75.8(19)	40.4(15)	-21.9(14)
C31	53.9(17)	87(2)	40.9(15)	-7.0(15)
C32	47.0(15)	65.4(18)	63.4(19)	-15.4(15)
C33	54.7(18)	96(2)	61.1(19)	-37.2(18)
C34	45.7(15)	89(2)	40.5(14)	-20.7(15)

Table 4 Bond Lengths for 241025LU_LGPZ214150_0m.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C28	1.215(3)	C16	C17	1.383(9)
N1	C7	1.273(3)	C16A	C17A	1.395(17)
N1	C14	1.463(3)	C17	C18	1.370(8)
C1	C2	1.384(3)	C17A	C18A	1.401(14)
C1	C6	1.387(3)	C18	C19	1.406(8)
C2	C3	1.375(4)	C18A	C19A	1.384(17)
C3	C4	1.376(4)	C19	C20	1.381(9)
C4	C5	1.381(3)	C19A	C20A	1.367(19)
C5	C6	1.396(3)	C21	C22	1.530(3)
C6	C7	1.491(3)	C21	C27	1.527(3)
C7	C8	1.498(3)	C22	C23	1.530(3)
C8	C9	1.385(3)	C22	C26	1.530(3)
C8	C13	1.385(3)	C23	C24	1.510(4)
C9	C10	1.394(4)	C24	C25	1.520(4)
C10	C11	1.359(5)	C25	C26	1.530(4)
C11	C12	1.362(5)	C27	C28	1.511(3)
C12	C13	1.390(4)	C28	C29	1.489(3)
C14	C15	1.508(7)	C29	C30	1.371(3)
C14	C15A	1.533(13)	C29	C34	1.378(3)
C14	C21	1.547(3)	C30	C31	1.383(3)
C15	C16	1.388(9)	C31	C32	1.360(4)
C15	C20	1.390(9)	C32	C33	1.357(4)
C15A	C16A	1.379(19)	C33	C34	1.373(4)
C15A	C20A	1.398(19)			

Table 5 Bond Angles for 241025LU_LGPZ214150_0m.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C14	119.83(19)	C15A	C16A	C17A	121.1(10)
C2	C1	C6	120.2(3)	C18	C17	C16	118.6(6)
C3	C2	C1	120.6(3)	C16A	C17A	C18A	117.7(10)
C2	C3	C4	119.5(3)	C17	C18	C19	121.1(5)
C3	C4	C5	120.6(3)	C19A	C18A	C17A	122.5(11)
C4	C5	C6	120.1(3)	C20	C19	C18	119.1(5)
C1	C6	C5	118.8(2)	C20A	C19A	C18A	117.6(11)
C1	C6	C7	120.5(2)	C19	C20	C15	120.8(5)
C5	C6	C7	120.6(2)	C19A	C20A	C15A	122.5(11)

N1	C7	C6	119.7(2)	C22	C21	C14	110.67(18)
N1	C7	C8	123.1(2)	C27	C21	C14	113.06(18)
C6	C7	C8	117.24(19)	C27	C21	C22	112.12(19)
C9	C8	C7	121.0(2)	C21	C22	C26	114.47(19)
C13	C8	C7	120.0(2)	C23	C22	C21	116.6(2)
C13	C8	C9	119.0(2)	C23	C22	C26	102.47(19)
C8	C9	C10	120.1(3)	C24	C23	C22	103.9(2)
C11	C10	C9	119.9(3)	C23	C24	C25	104.9(2)
C10	C11	C12	120.7(3)	C24	C25	C26	106.2(2)
C11	C12	C13	120.2(3)	C22	C26	C25	106.5(2)
C8	C13	C12	120.0(3)	C28	C27	C21	113.73(19)
N1	C14	C15	116.2(3)	O1	C28	C27	121.7(2)
N1	C14	C15A	103.6(7)	O1	C28	C29	119.5(2)
N1	C14	C21	110.30(17)	C29	C28	C27	118.7(2)
C15	C14	C21	109.7(5)	C30	C29	C28	123.1(2)
C15A	C14	C21	113.8(9)	C30	C29	C34	117.7(2)
C16	C15	C14	122.5(6)	C34	C29	C28	119.1(2)
C16	C15	C20	118.4(6)	C29	C30	C31	120.7(2)
C20	C15	C14	119.1(6)	C32	C31	C30	120.6(3)
C16A	C15A	C14	124.2(12)	C33	C32	C31	119.2(3)
C16A	C15A	C20A	118.6(11)	C32	C33	C34	120.6(3)
C20A	C15A	C14	117.0(12)	C33	C34	C29	121.1(2)
C17	C16	C15	122.0(5)				

Table 6 Torsion Angles for 241025LU_LGPZ214150_0m.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C28	C29	C30	154.2(3)	C14	C21	C27	C28	-147.80(19)
O1	C28	C29	C34	-27.7(3)	C15	C14	C21	C22	-172.2(4)
N1	C7	C8	C9	101.1(3)	C15	C14	C21	C27	61.1(4)
N1	C7	C8	C13	-78.6(3)	C15	C16	C17	C18	-0.8(9)
N1	C14	C15	C16	23.1(11)	C15A	C14	C21	C22	174.5(8)
N1	C14	C15	C20	-157.5(6)	C15A	C14	C21	C27	47.8(8)
N1	C14	C15A	C16A	19(2)	C15A	C16A	C17A	C18A	-0.7(17)
N1	C14	C15A	C20A	-166.2(14)	C16	C15	C20	C19	1.7(11)
N1	C14	C21	C22	58.6(2)	C16	C17	C18	C19	2.6(8)
N1	C14	C21	C27	-68.1(2)	C16A	C15A	C20A	C19A	-2(2)
C1	C2	C3	C4	0.1(5)	C16A	C17A	C18A	C19A	1.9(16)
C1	C6	C7	N1	-8.5(3)	C17	C18	C19	C20	-2.3(8)
C1	C6	C7	C8	172.4(2)	C17A	C18A	C19A	C20A	-2.9(17)
C2	C1	C6	C5	-1.3(4)	C18	C19	C20	C15	0.1(9)
C2	C1	C6	C7	177.8(2)	C18A	C19A	C20A	C15A	3(2)
C2	C3	C4	C5	-0.6(5)	C20	C15	C16	C17	-1.3(11)
C3	C4	C5	C6	0.2(5)	C20A	C15A	C16A	C17A	1(2)
C4	C5	C6	C1	0.8(4)	C21	C14	C15	C16	-102.8(8)
C4	C5	C6	C7	-178.3(2)	C21	C14	C15	C20	76.5(9)
C5	C6	C7	N1	170.6(2)	C21	C14	C15A	C16A	-101.2(17)
C5	C6	C7	C8	-8.5(3)	C21	C14	C15A	C20A	74.0(17)
C6	C1	C2	C3	0.9(5)	C21	C22	C23	C24	-165.6(2)
C6	C7	C8	C9	-79.8(3)	C21	C22	C26	C25	155.2(2)
C6	C7	C8	C13	100.5(2)	C21	C27	C28	O1	28.1(3)
C7	N1	C14	C15	93.8(6)	C21	C27	C28	C29	-152.0(2)
C7	N1	C14	C15A	97.2(10)	C22	C21	C27	C28	86.2(2)
C7	N1	C14	C21	-140.6(2)	C22	C23	C24	C25	36.7(3)
C7	C8	C9	C10	-177.9(2)	C23	C22	C26	C25	27.9(3)
C7	C8	C13	C12	179.1(2)	C23	C24	C25	C26	-19.0(3)
C8	C9	C10	C11	-1.6(4)	C24	C25	C26	C22	-5.9(3)

C9	C8	C13	C12	-0.6(3)	C26	C22	C23	C24	-39.8(3)
C9	C10	C11	C12	0.3(4)	C27	C21	C22	C23	-52.0(3)
C10	C11	C12	C13	0.9(4)	C27	C21	C22	C26	-171.55(19)
C11	C12	C13	C8	-0.7(4)	C27	C28	C29	C30	-25.8(4)
C13	C8	C9	C10	1.7(3)	C27	C28	C29	C34	152.3(2)
C14	N1	C7	C6	178.79(19)	C28	C29	C30	C31	178.1(3)
C14	N1	C7	C8	-2.1(3)	C28	C29	C34	C33	-176.2(3)
C14	C15	C16	C17	178.0(7)	C29	C30	C31	C32	-1.5(5)
C14	C15	C20	C19	-177.7(7)	C30	C29	C34	C33	2.0(4)
C14	C15A	C16A	C17A	175.8(15)	C30	C31	C32	C33	1.1(5)
C14	C15A	C20A	C19A	-177.2(14)	C31	C32	C33	C34	0.9(5)
C14	C21	C22	C23	-179.2(2)	C32	C33	C34	C29	-2.4(5)
C14	C21	C22	C26	61.2(2)	C34	C29	C30	C31	0.0(4)

Table 7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 241025LU_LGPZ214150_0m.

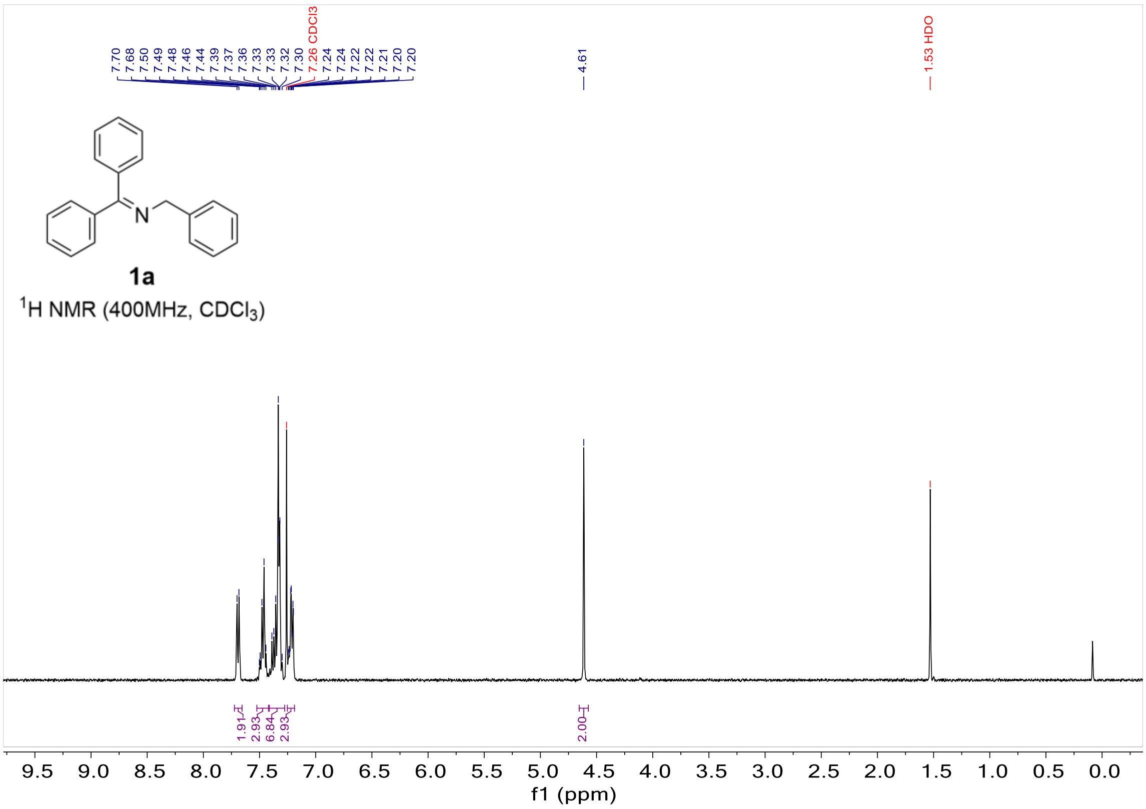
Atom	x	y	z	U(eq)
H1	5554.47	2470.33	3629.49	49
H1A	4567.26	1385.19	4682.46	65
H2	3241.6	459.3	6121	83
H3	605.14	1386.02	6433.62	86
H4	-718.22	3250.1	5301.32	82
H5	586	4210.59	3871.79	66
H9	1979.66	3647.86	1738.15	69
H10	611.09	5414.29	516.19	90
H11	388.78	7433.82	568.95	96
H12	1526.73	7739.16	1806.2	87
H13	2971.23	5994.71	3002.1	63
H14	5166.12	4109.5	1701.33	46
H14A	5179.6	4193.77	1699.24	46
H16	6420.29	4234.72	3932.13	59
H16A	6041.68	3939.65	4173.87	54
H17	7312.42	5810.71	4095.13	64
H17A	6932.6	5346.09	4659.32	70
H18	7930.52	7228.48	2631.02	68
H18A	7833.61	6837.83	3372.4	67
H19	7475	7182.09	1006.92	65
H19A	7705.03	7034.06	1644.48	64
H20	6556.06	5607.02	866.86	52
H20A	6887.34	5588.19	1208.1	61
H21	7743.39	3136.42	1251.06	46
H22	6160.8	1336.82	2246.72	51
H23A	8723.26	973.16	744.97	65
H23B	8546.6	5.51	1839.95	65
H24A	6667.46	-518.04	1333.76	92
H24B	7760.06	-356.15	293.98	92
H25A	4813.81	1013.4	398.74	91
H25B	6045.76	1469.87	-465.32	91
H26A	5922.09	2998.52	242.27	66
H26B	4555.02	2638.88	1028.07	66
H27A	8496.87	2635.13	3054.56	52
H27B	8333.47	1284.88	3128.72	52
H30	10497.42	639.21	4156.39	73
H31	12402.6	-1123.8	4995.23	85
H32	14350.03	-2329.18	4078.16	77
H33	14432.38	-1734.94	2315.29	94

H34	12628.15	81.68	1467.31	78

Table 8 Atomic Occupancy for 241025LU_LGPZ214150_0m.

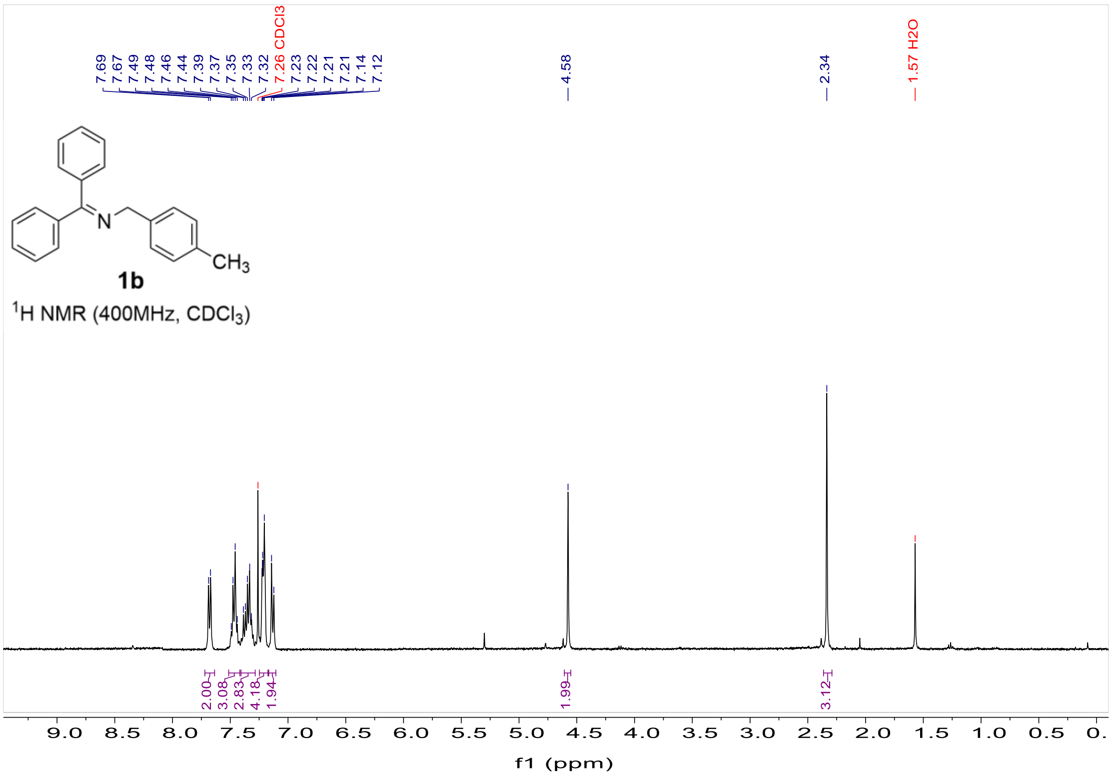
Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H14	0.652(8)	H14A	0.348(8)	C15	0.652(8)
C15A	0.348(8)	C16	0.652(8)	H16	0.652(8)
C16A	0.348(8)	H16A	0.348(8)	C17	0.652(8)
H17	0.652(8)	C17A	0.348(8)	H17A	0.348(8)
C18	0.652(8)	H18	0.652(8)	C18A	0.348(8)
H18A	0.348(8)	C19	0.652(8)	H19	0.652(8)
C19A	0.348(8)	H19A	0.348(8)	C20	0.652(8)
H20	0.652(8)	C20A	0.348(8)	H20A	0.348(8)

5. NMR Spectra



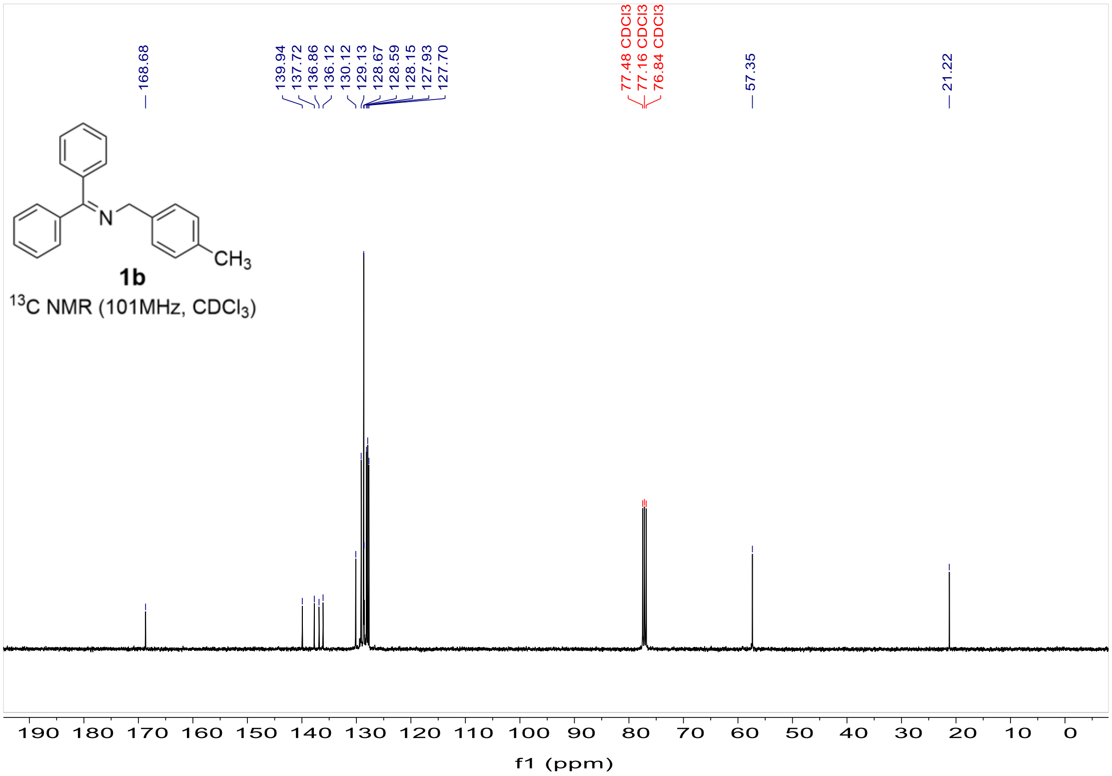
1a

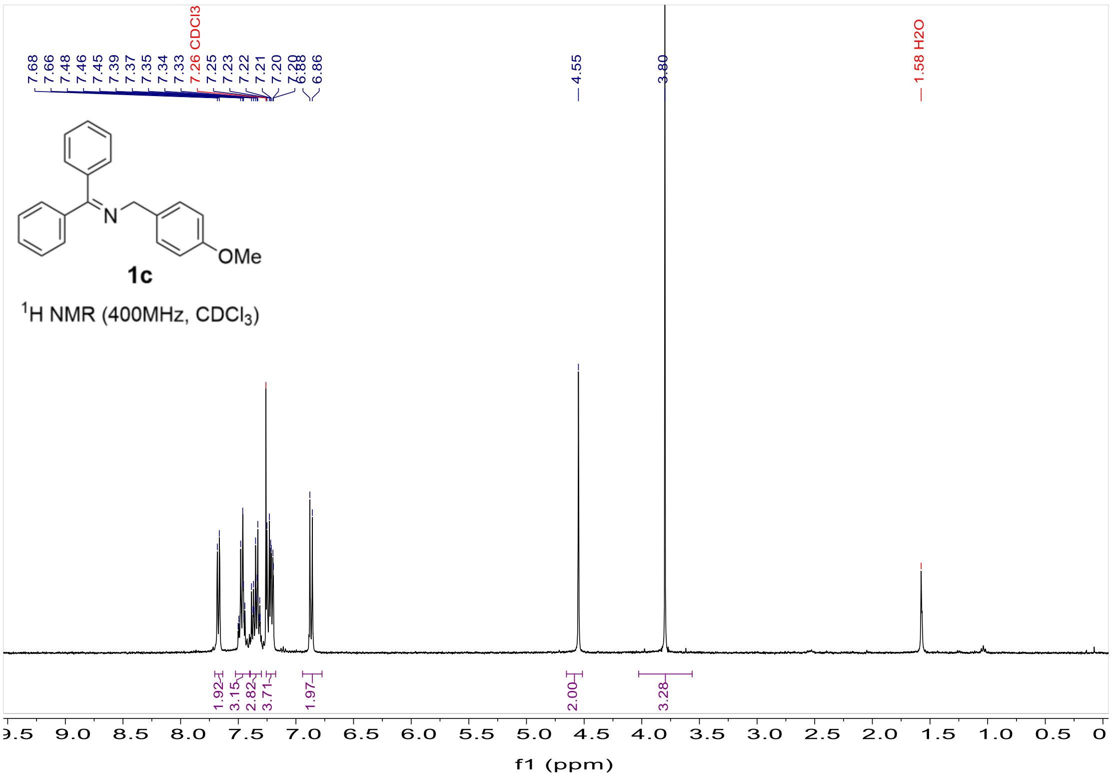
^{1}H NMR (400MHz, $CDCl_3$)

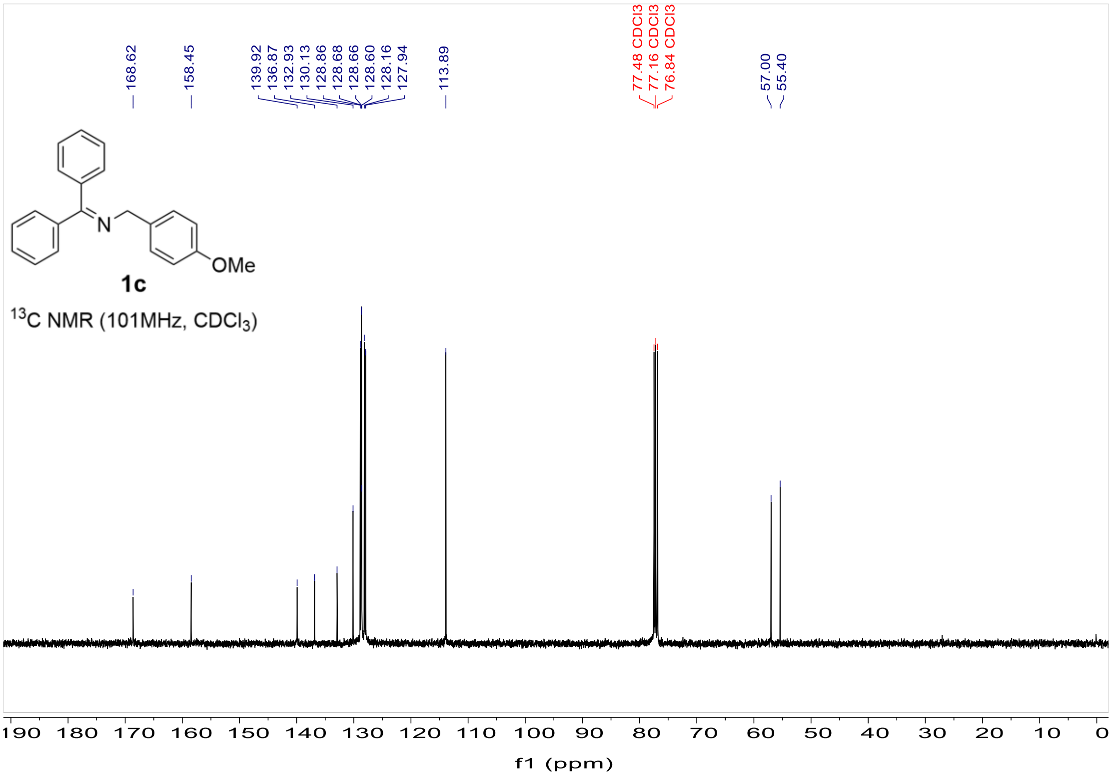


1b

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

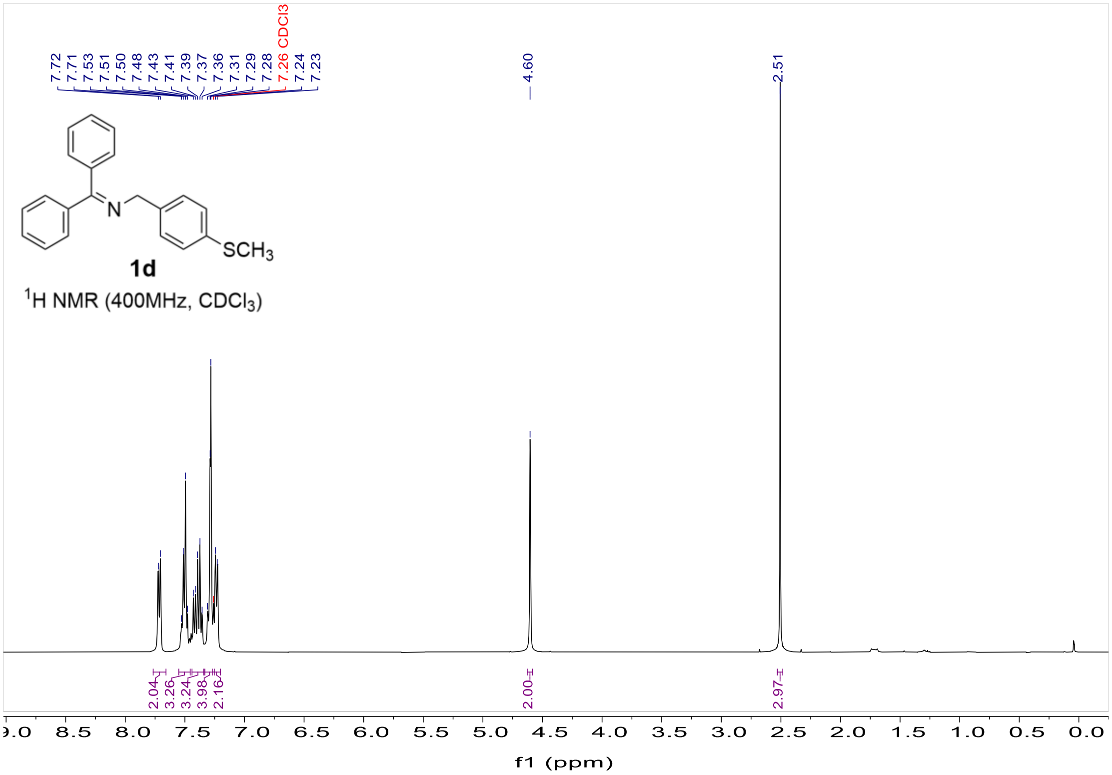

168.68
139.94
137.72
136.86
136.12
130.12
129.13
128.67
128.59
128.15
127.93
127.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.35
21.22
N
CH3
1b
13C NMR (101MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.68
7.66
7.48
7.46
7.45
7.39
7.37
7.35
7.34
7.33
7.26 CDCl3
7.25
7.23
7.22
7.21
7.20
6.88
6.86
4.55
3.80
1.58 H2O
N
OMe
1c
1H NMR (400MHz, CDCl3)
1.92
3.15
2.82
3.71
1.97
2.00
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



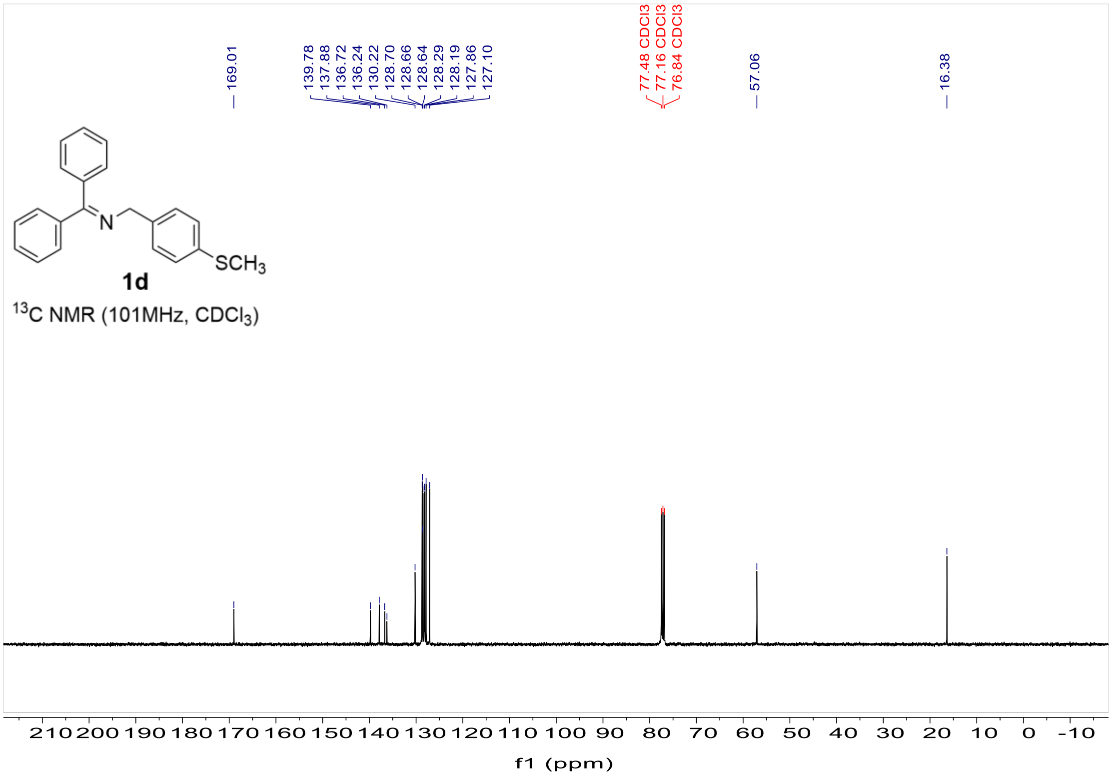
1c

^{13}C NMR (101MHz, CDCl$_3$)

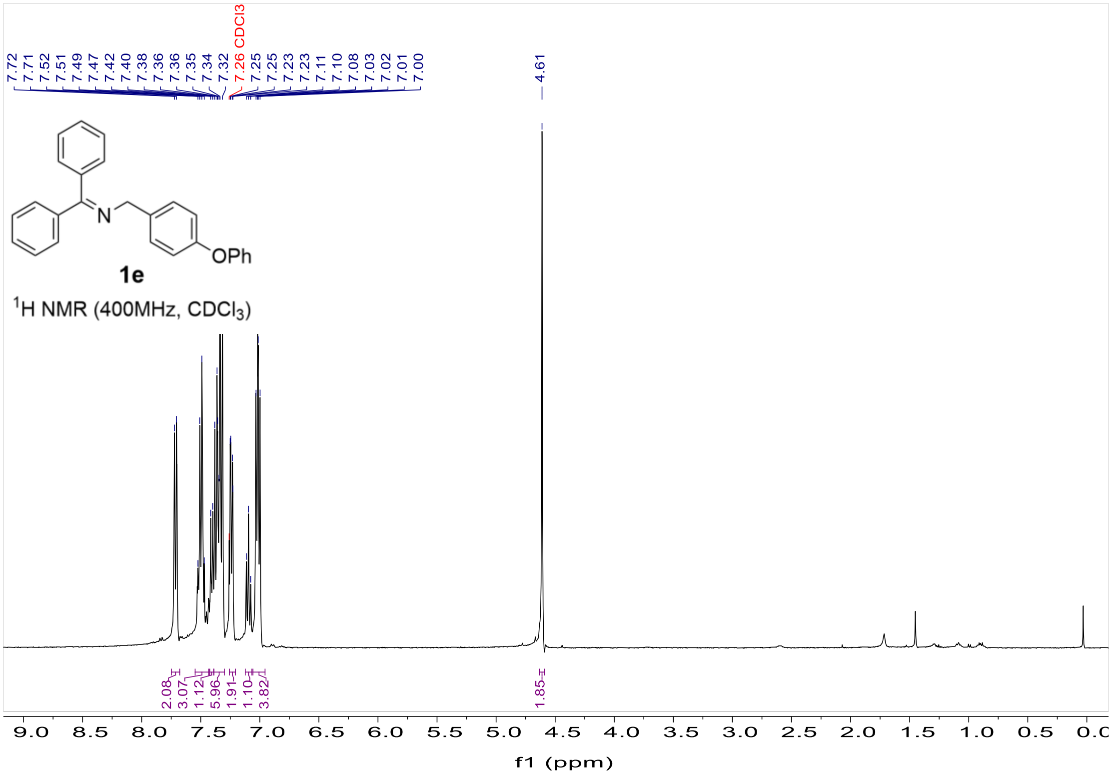


1d

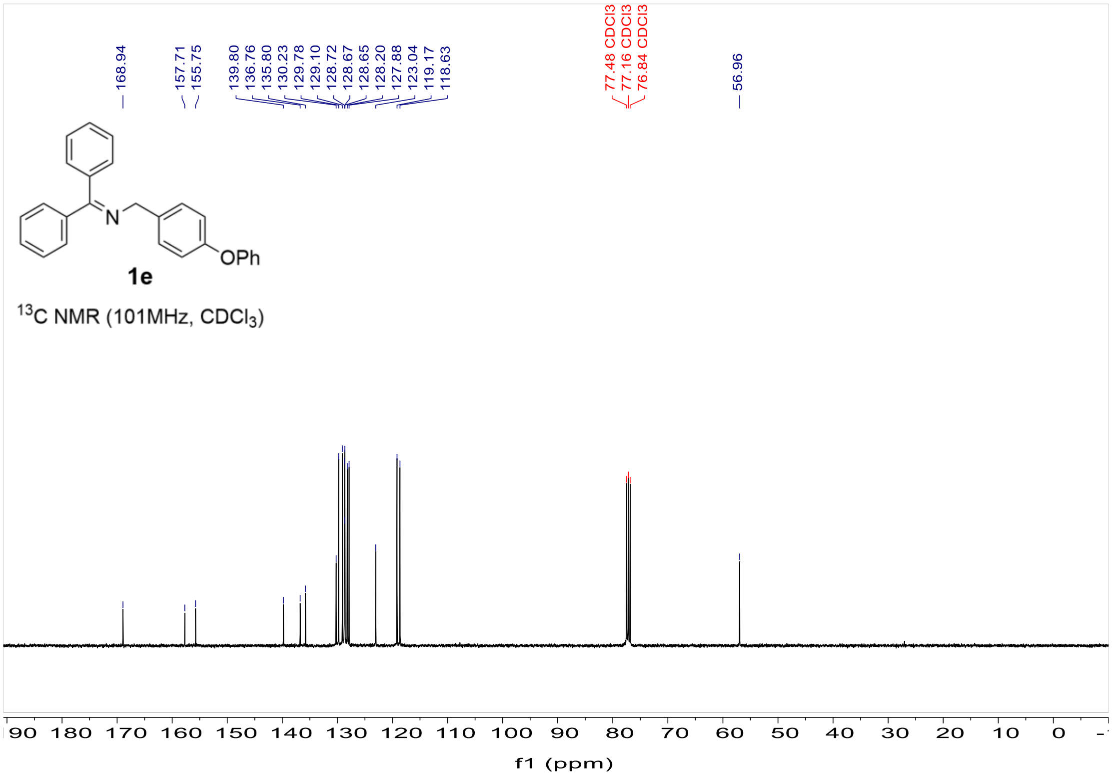
^{1}H NMR (400MHz, CDCl$_3$)



169.01
139.78
137.88
136.72
136.24
130.22
128.70
128.66
128.64
128.29
128.19
127.86
127.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.06
16.38
N
SCH3
1d
13C NMR (101MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

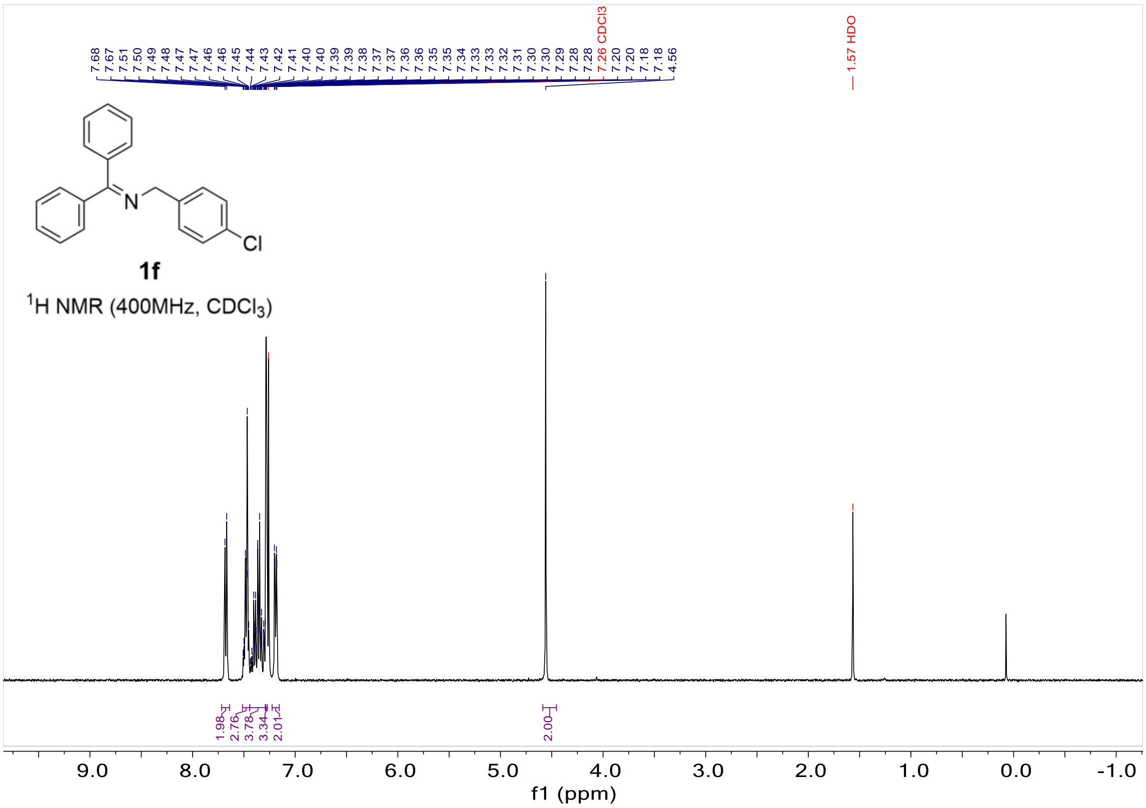


7.72
7.71
7.52
7.51
7.49
7.47
7.42
7.40
7.38
7.36
7.36
7.35
7.34
7.32
7.26 CDCl3
7.25
7.25
7.23
7.23
7.11
7.10
7.08
7.03
7.02
7.01
7.00
4.61
N
OPh
1e
1H NMR (400MHz, CDCl3)
2.08
3.07
1.12
5.96
1.91
1.10
3.82
1.85
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



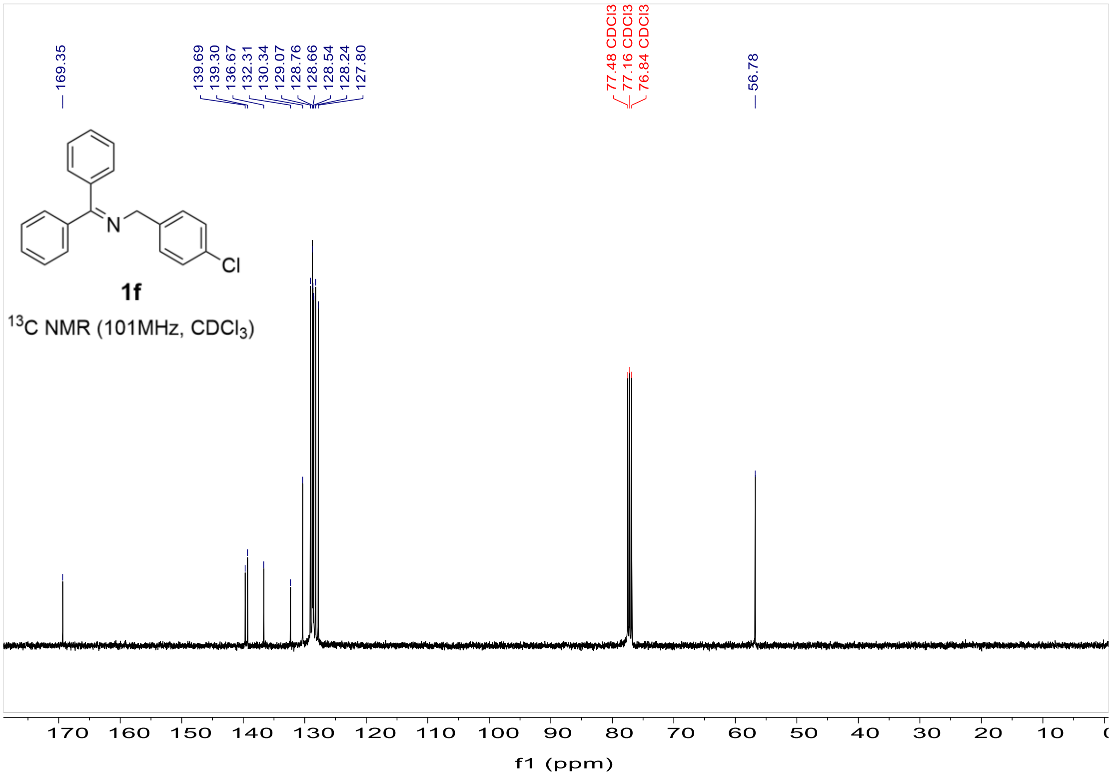
1e

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



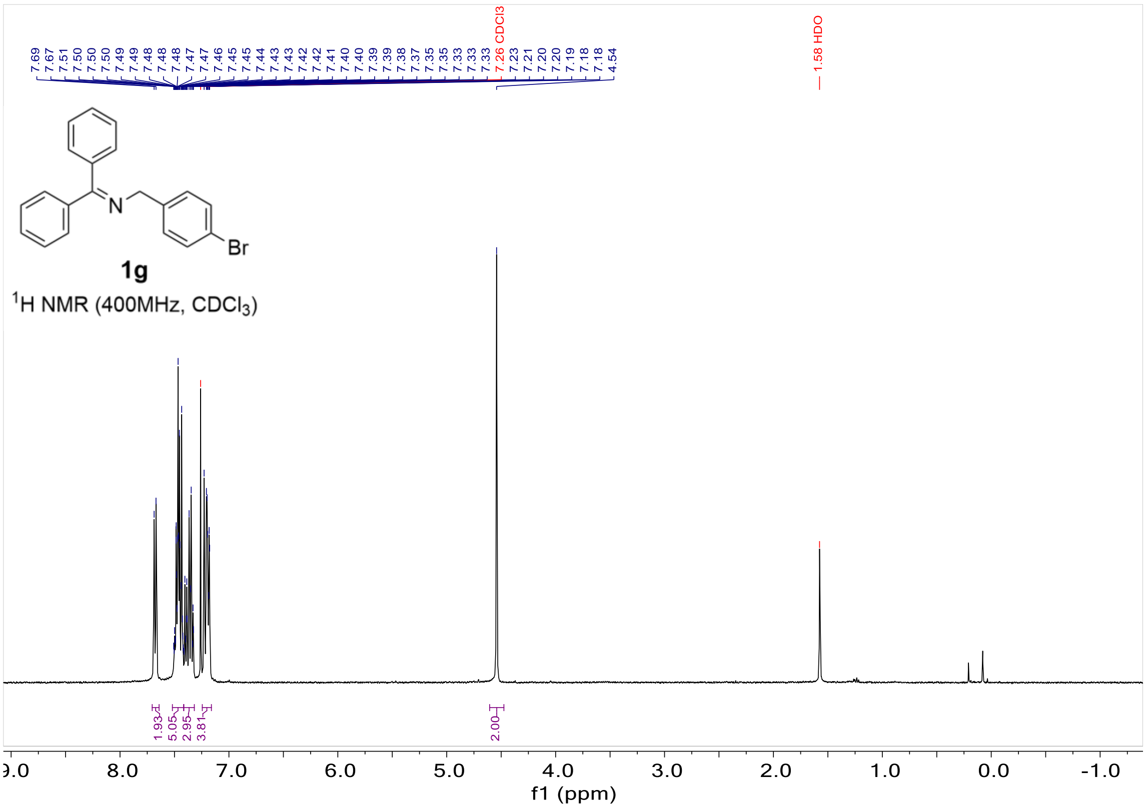
1f

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



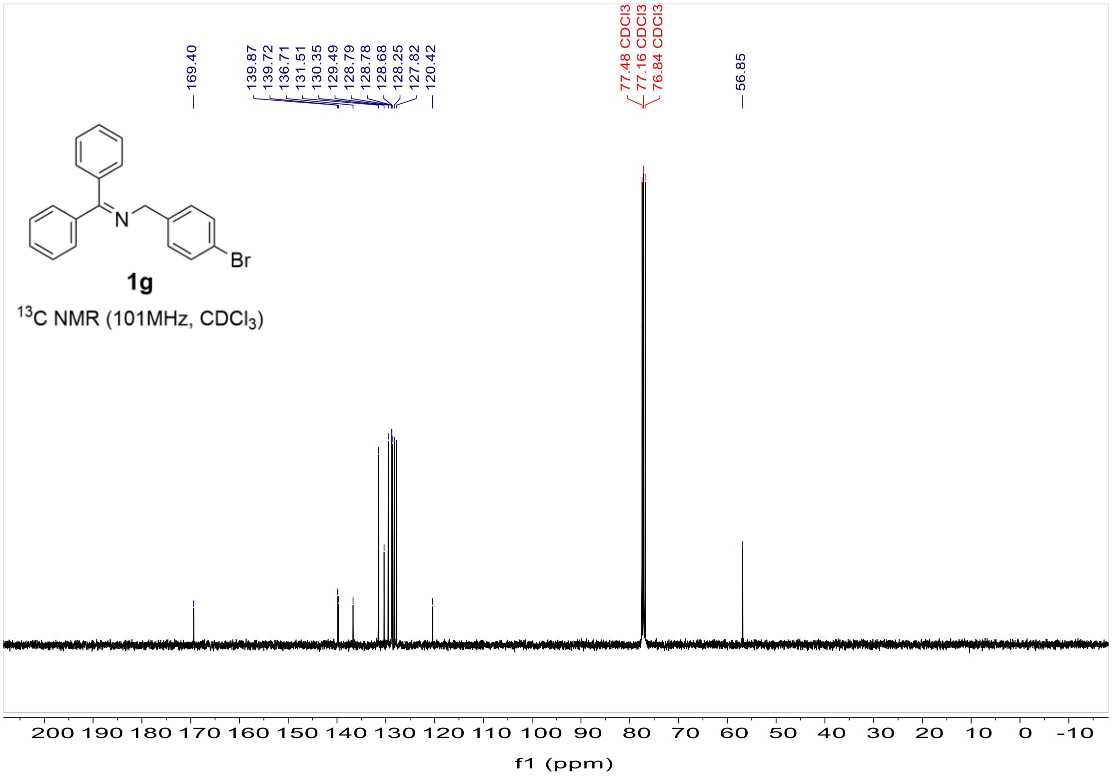
1f

^{13}C NMR (101MHz, CDCl$_3$)



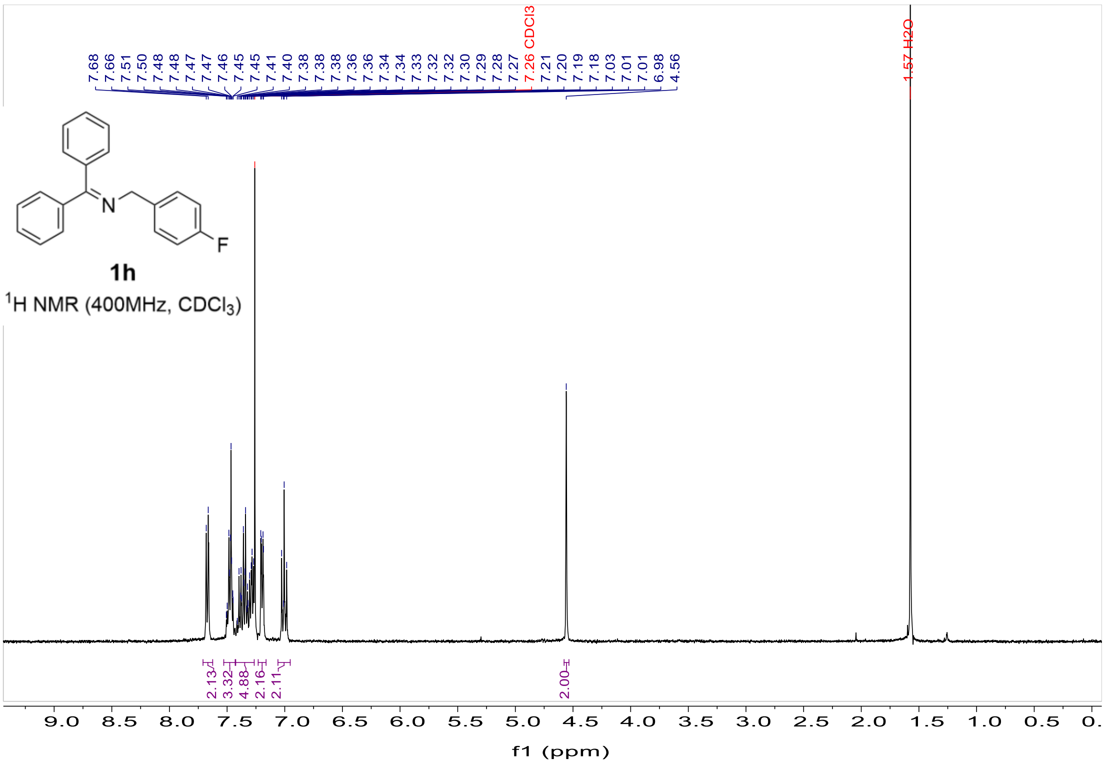
1g

^{1}H NMR (400MHz, CDCl$_3$)



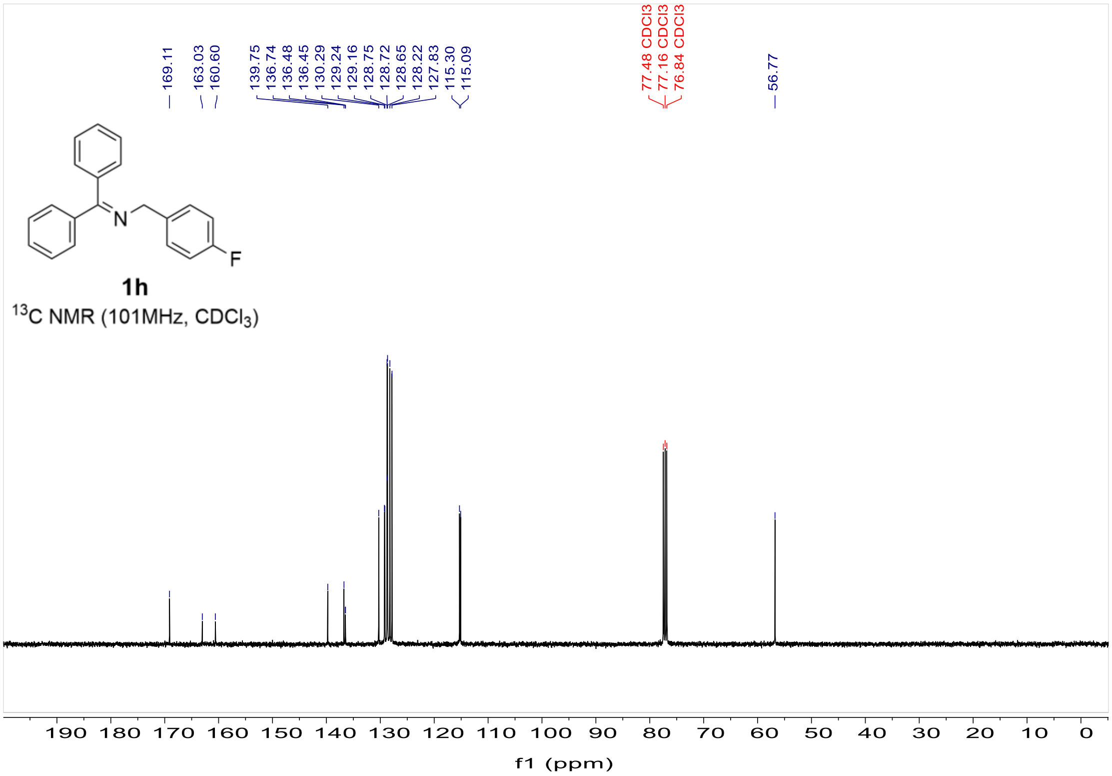
1g

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

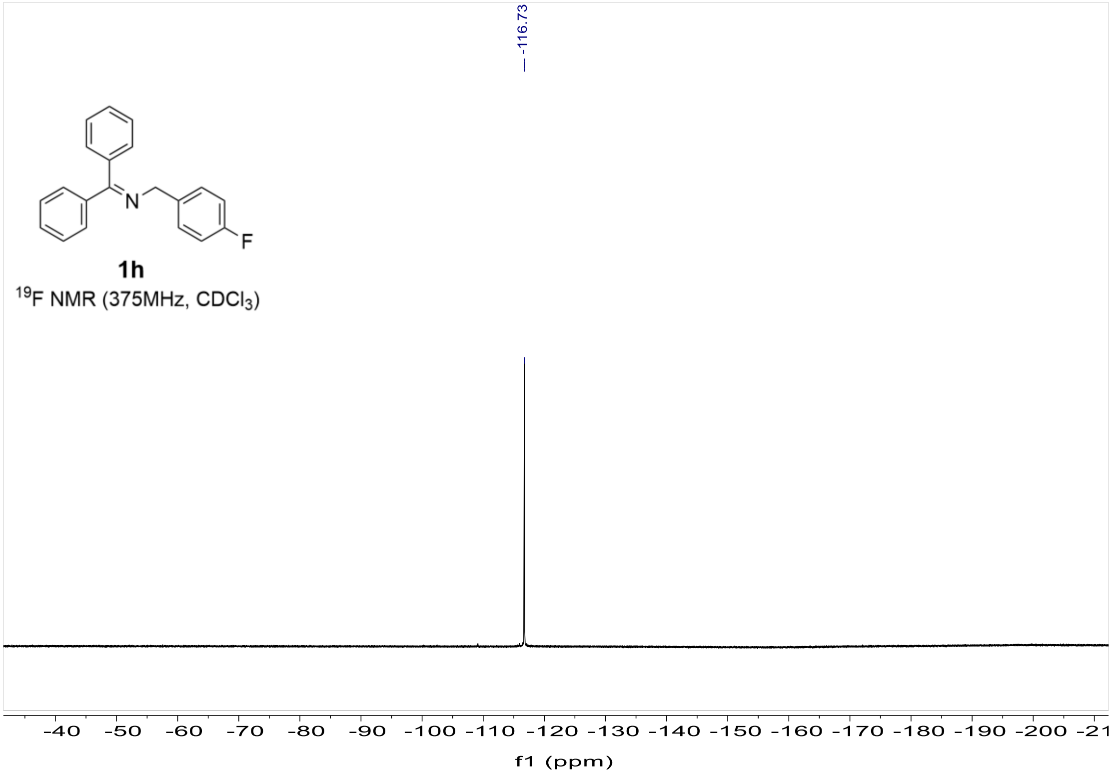


1h

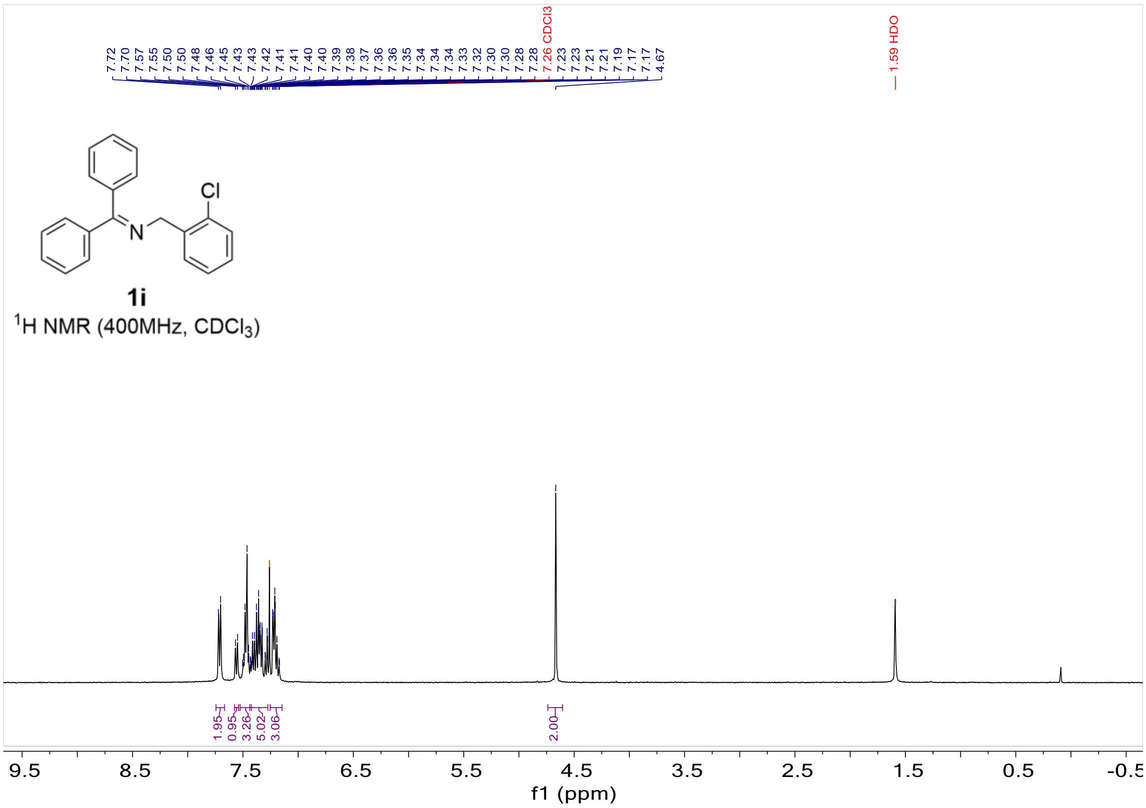
^{1}H NMR (400MHz, $CDCl_3$)


1h

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

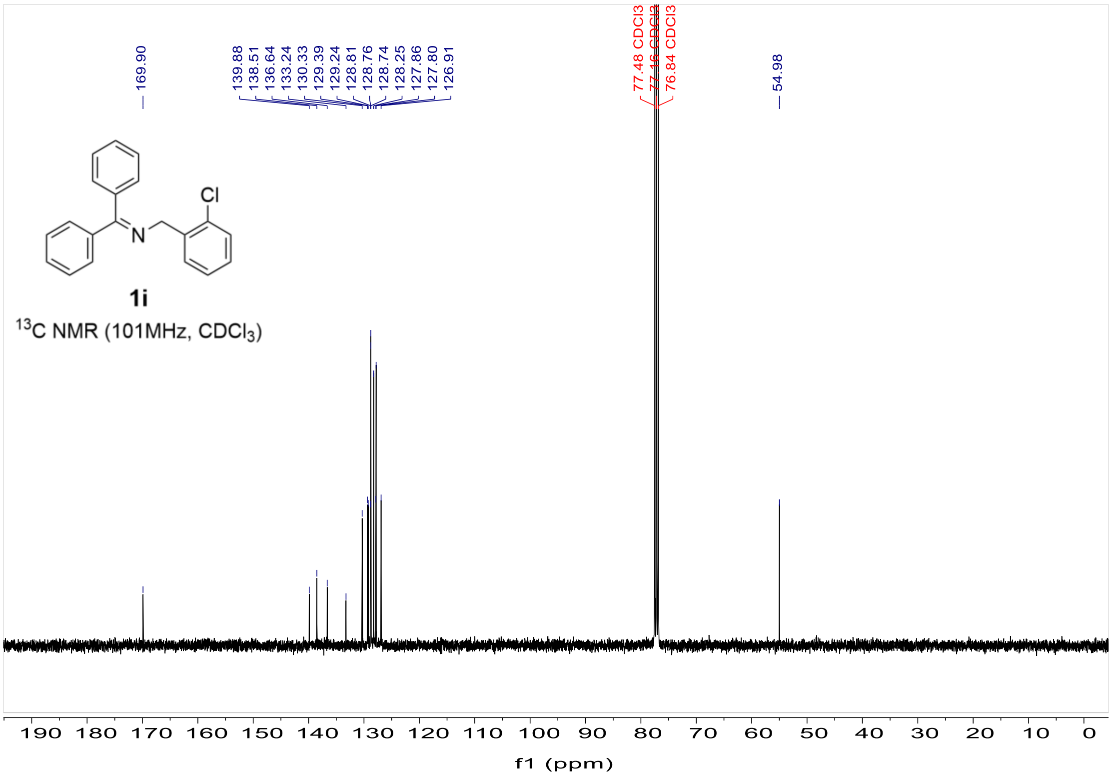

1h

^{19}F NMR (375MHz, $CDCl_3$)



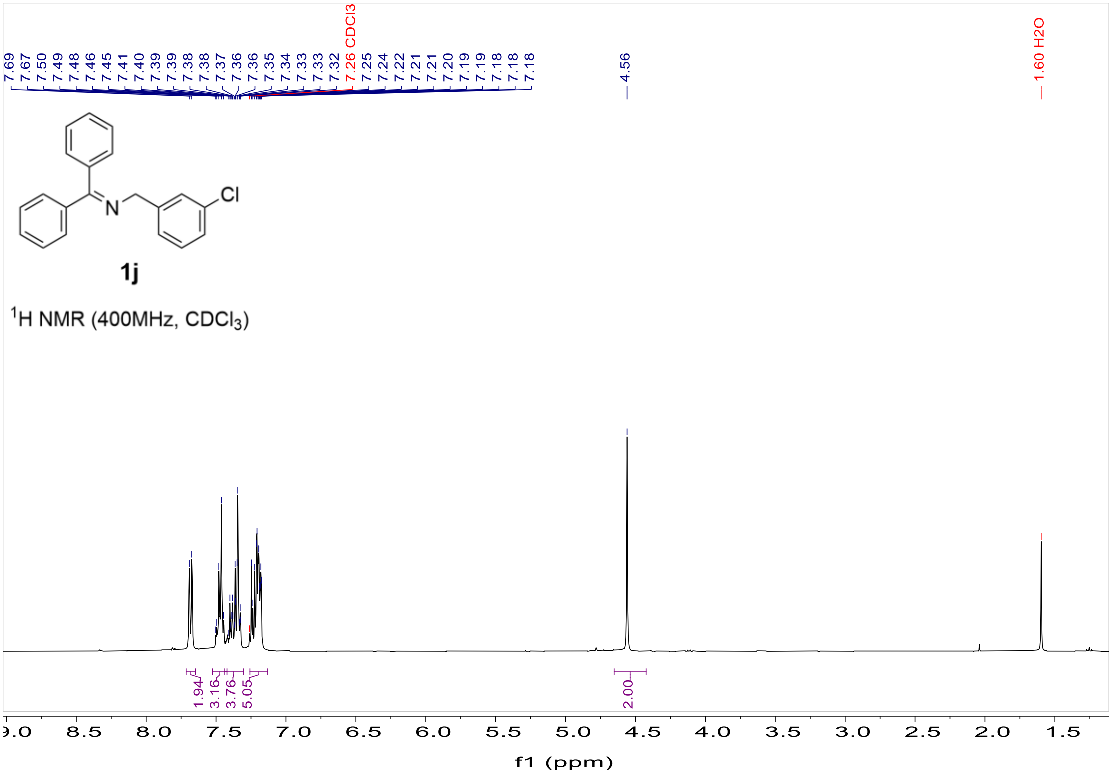
1i

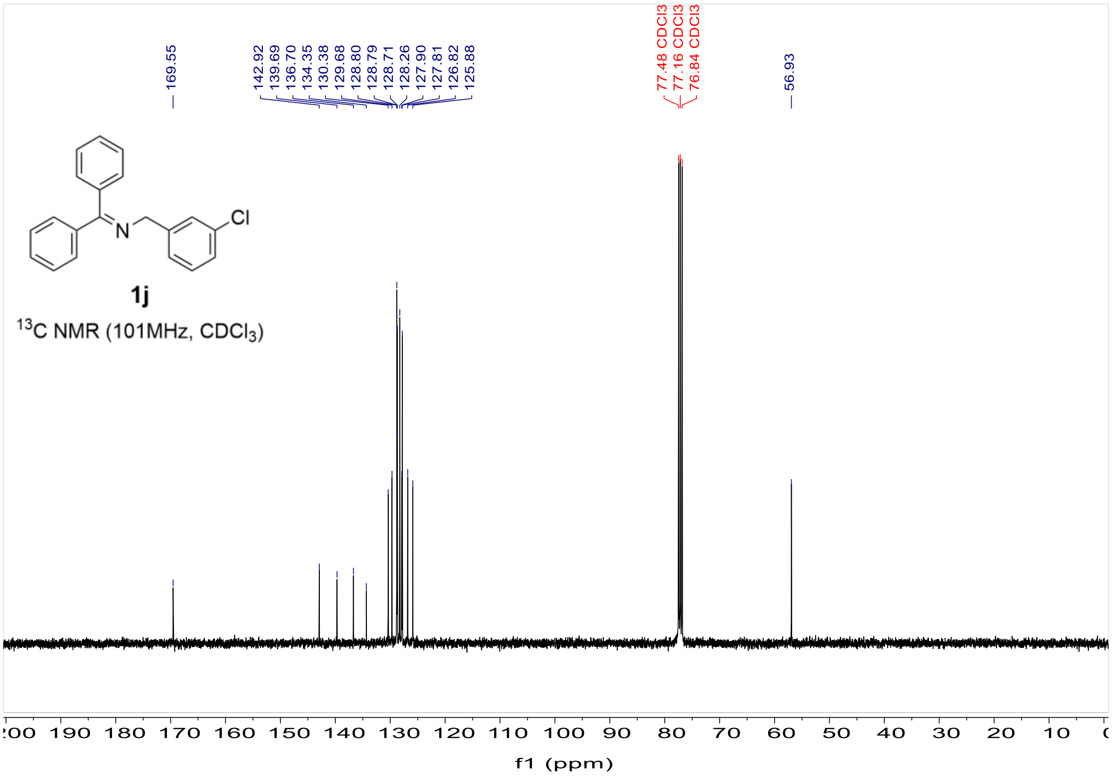
^{1}H NMR (400MHz, $CDCl_3$)

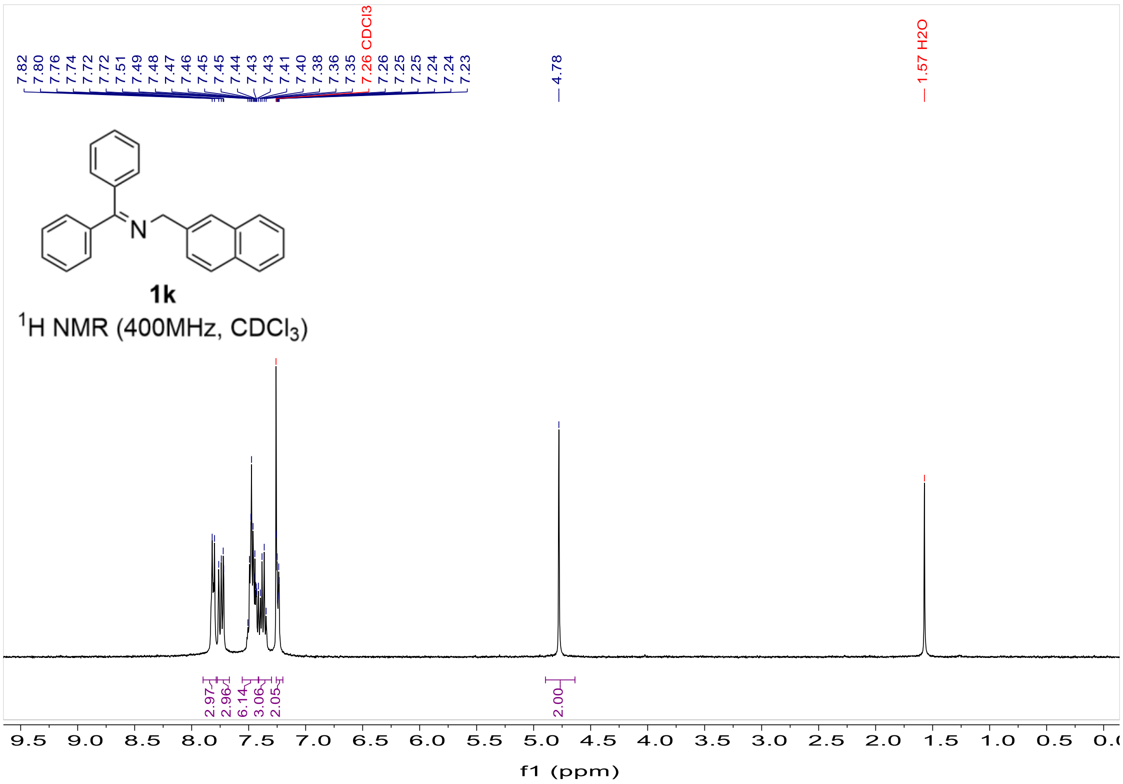


1i

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

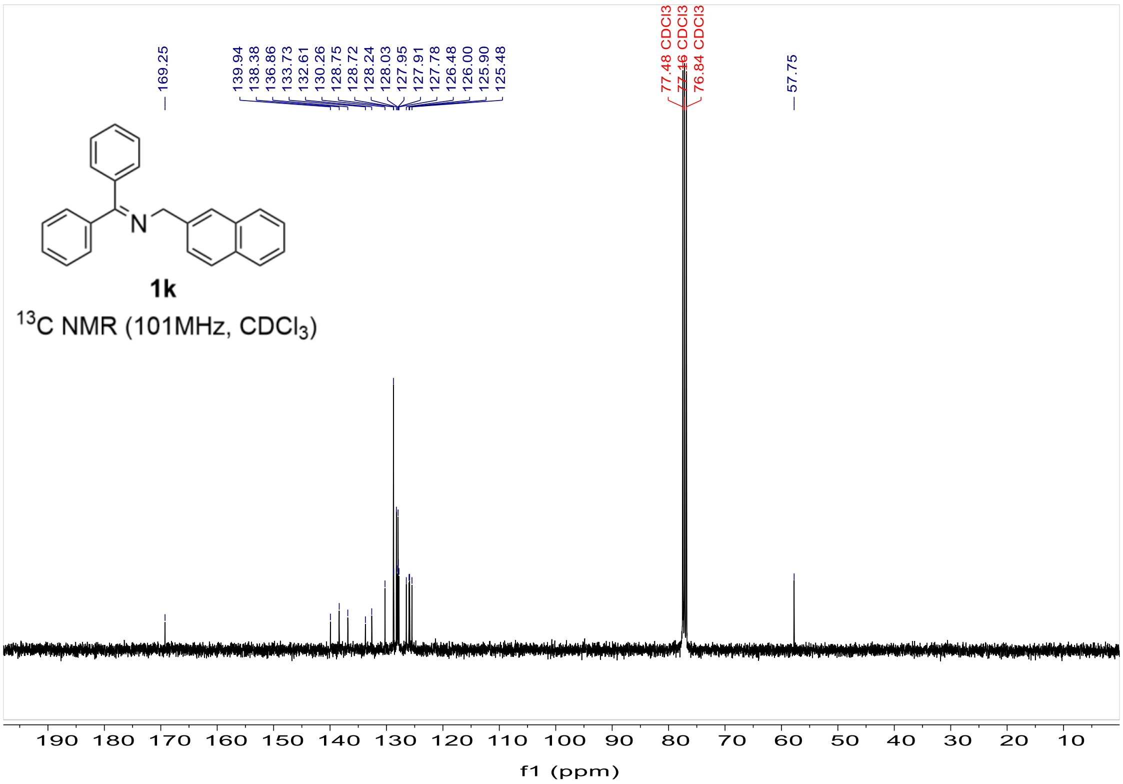

7.69
7.67
7.50
7.49
7.48
7.46
7.45
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.26 CDCl3
7.25
7.24
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
4.56
1.60 H2O
Cl
N
1j
¹H NMR (400MHz, CDCl₃)
1.94
3.16
3.76
5.05
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


169.55
142.92
139.69
136.70
134.35
130.38
129.68
128.80
128.79
128.71
128.26
127.90
127.81
126.82
125.88
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.93
Cl
N
1j
¹³C NMR (101MHz, CDCl₃)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



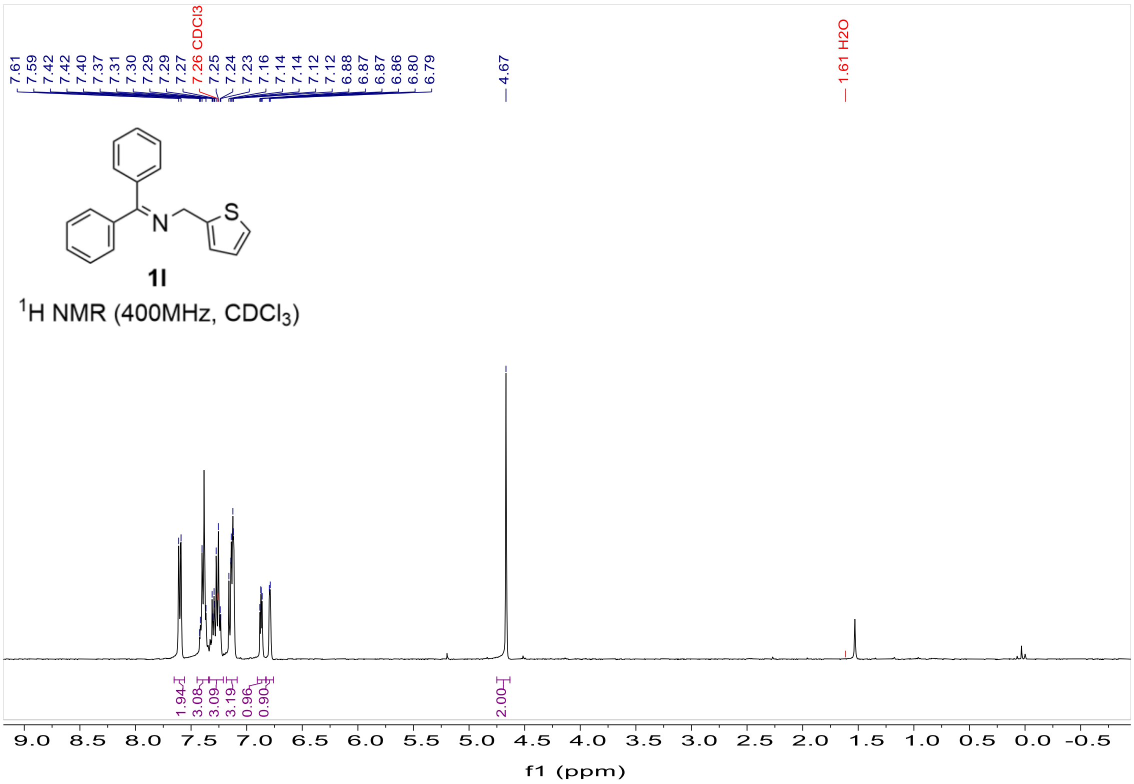
1k

^{1}H NMR (400MHz, CDCl$_3$)



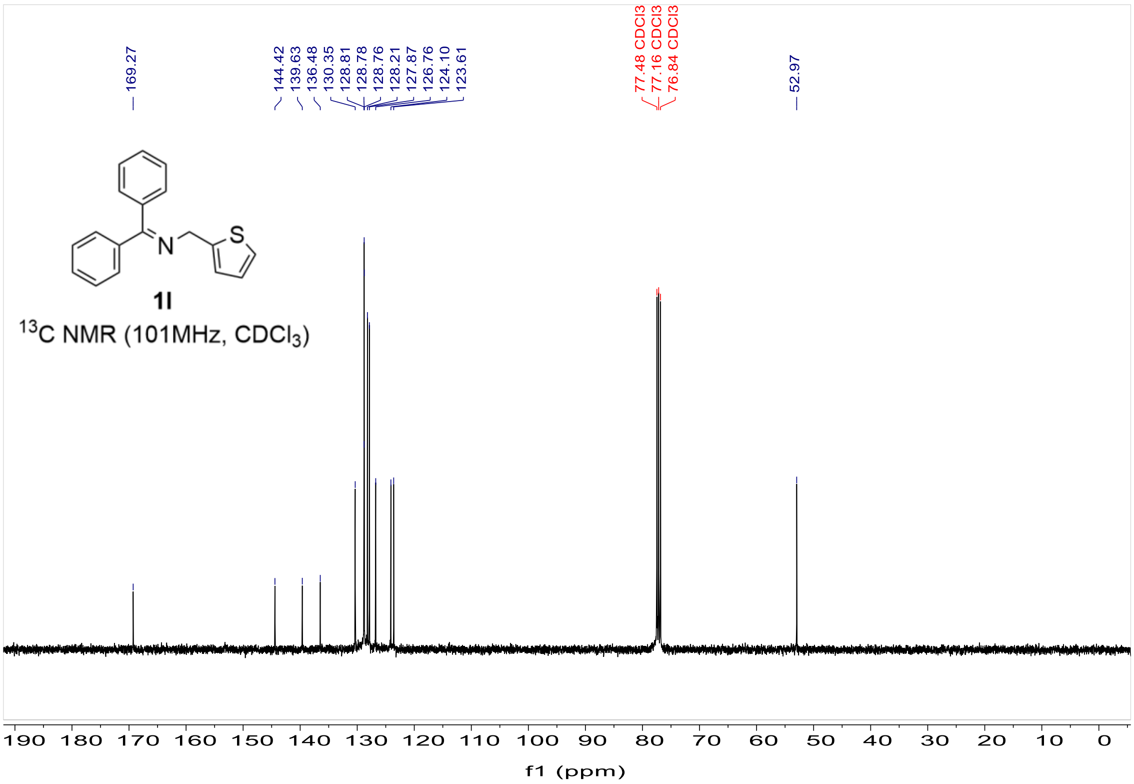
1k

^{13}C NMR (101MHz, CDCl$_3$)



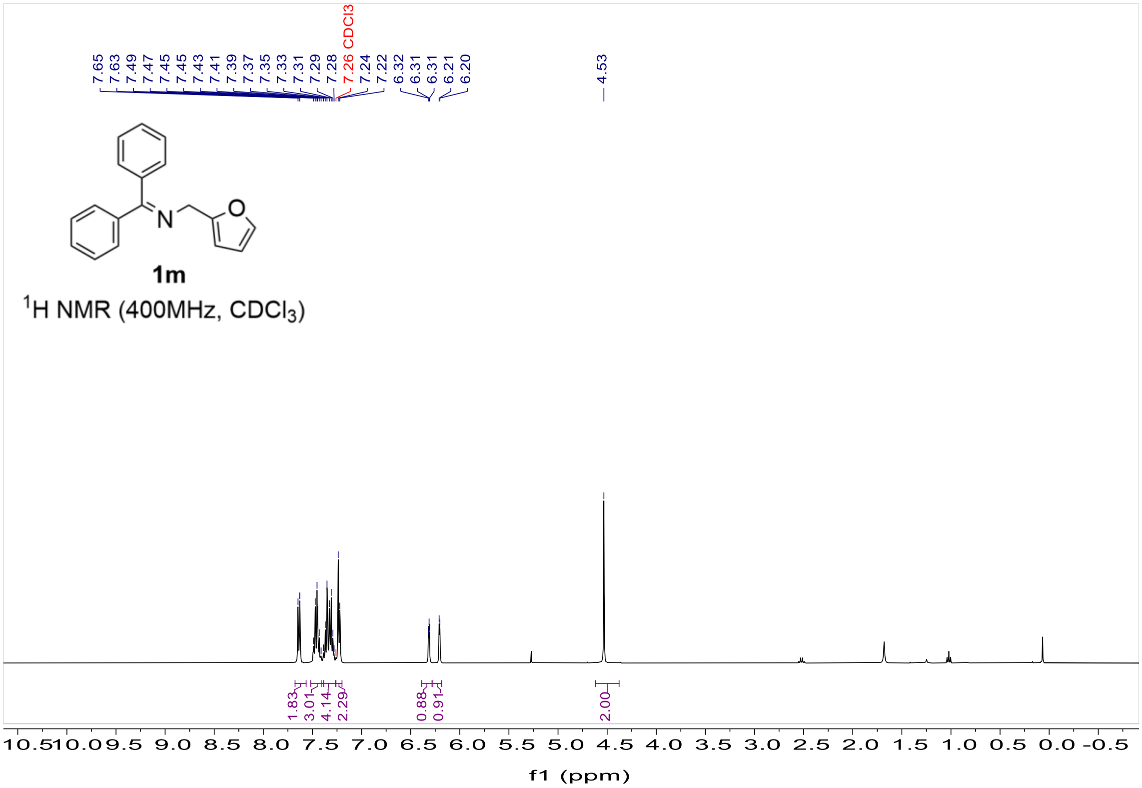
1l

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



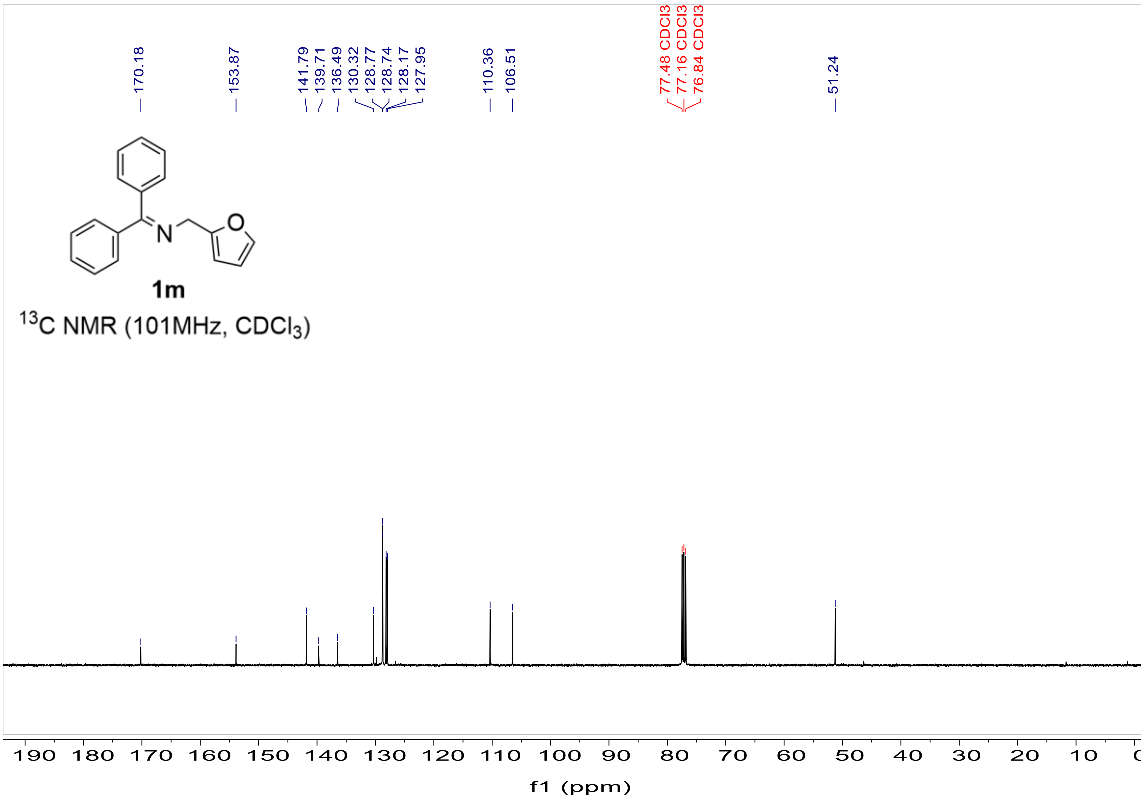
1l

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



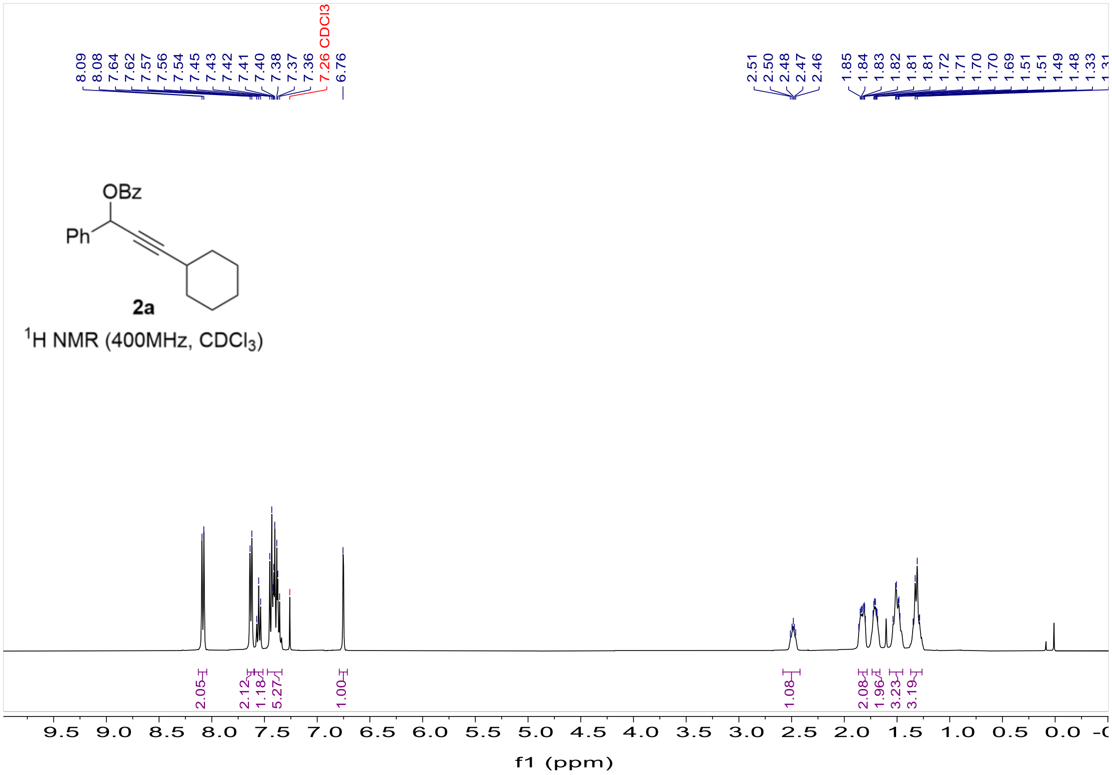
1m

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



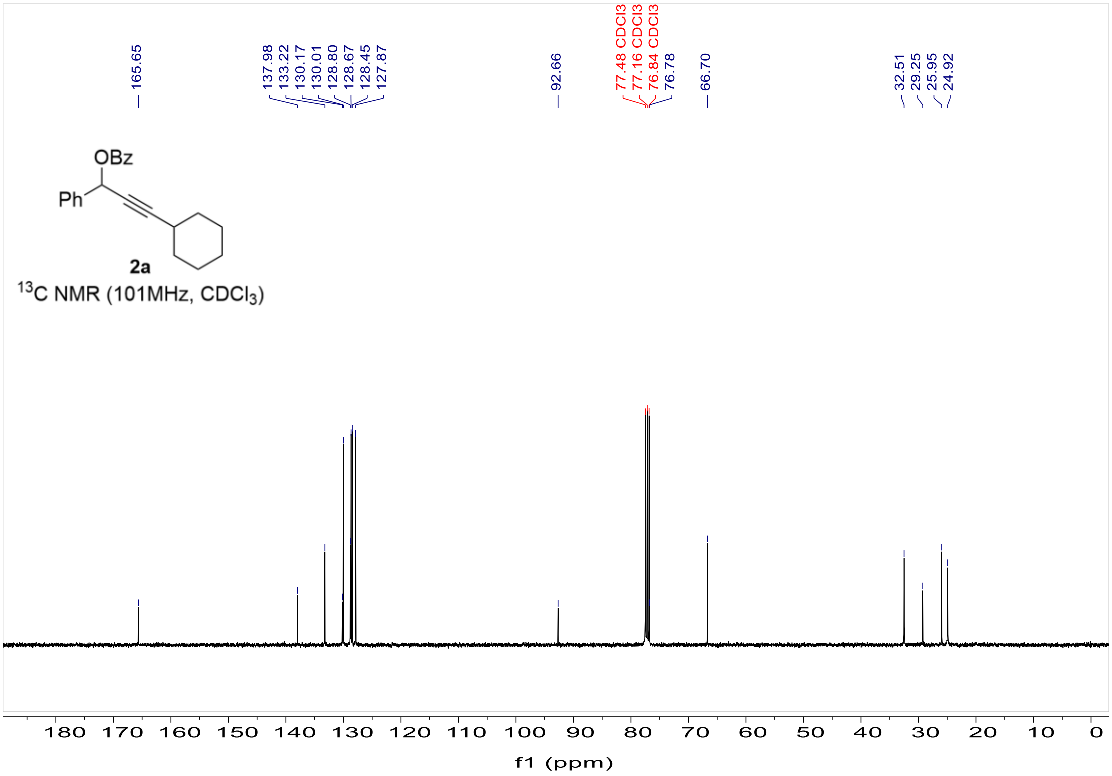
1m

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



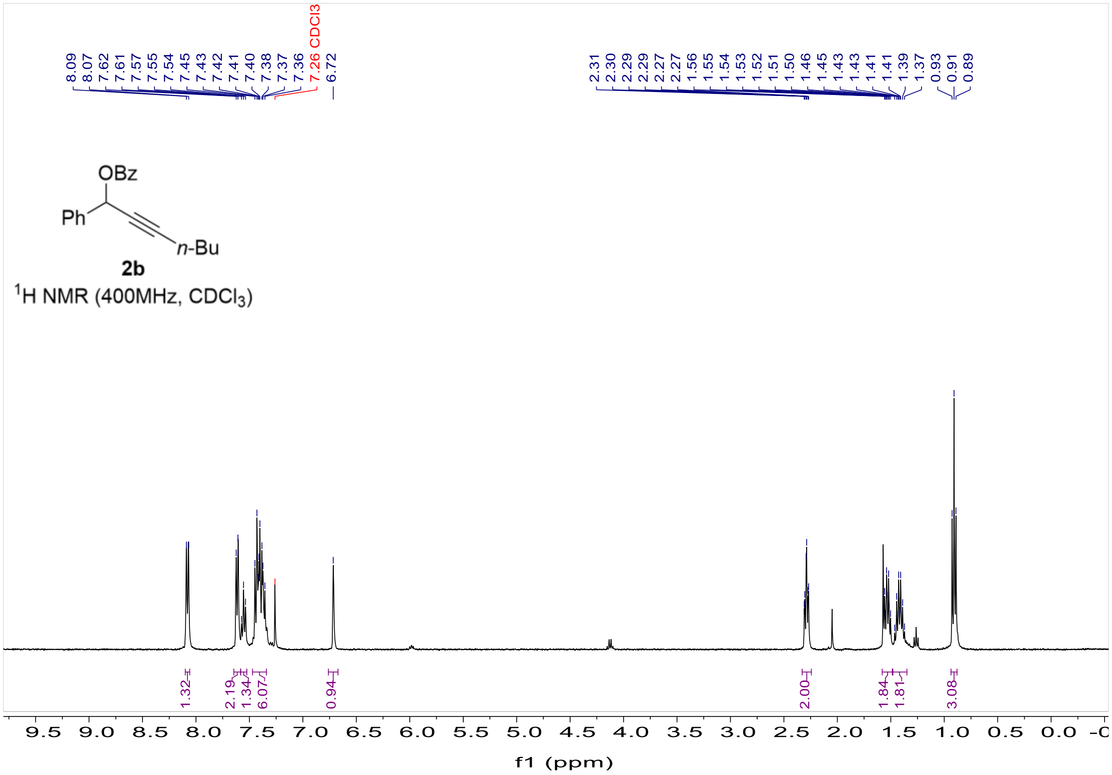
2a

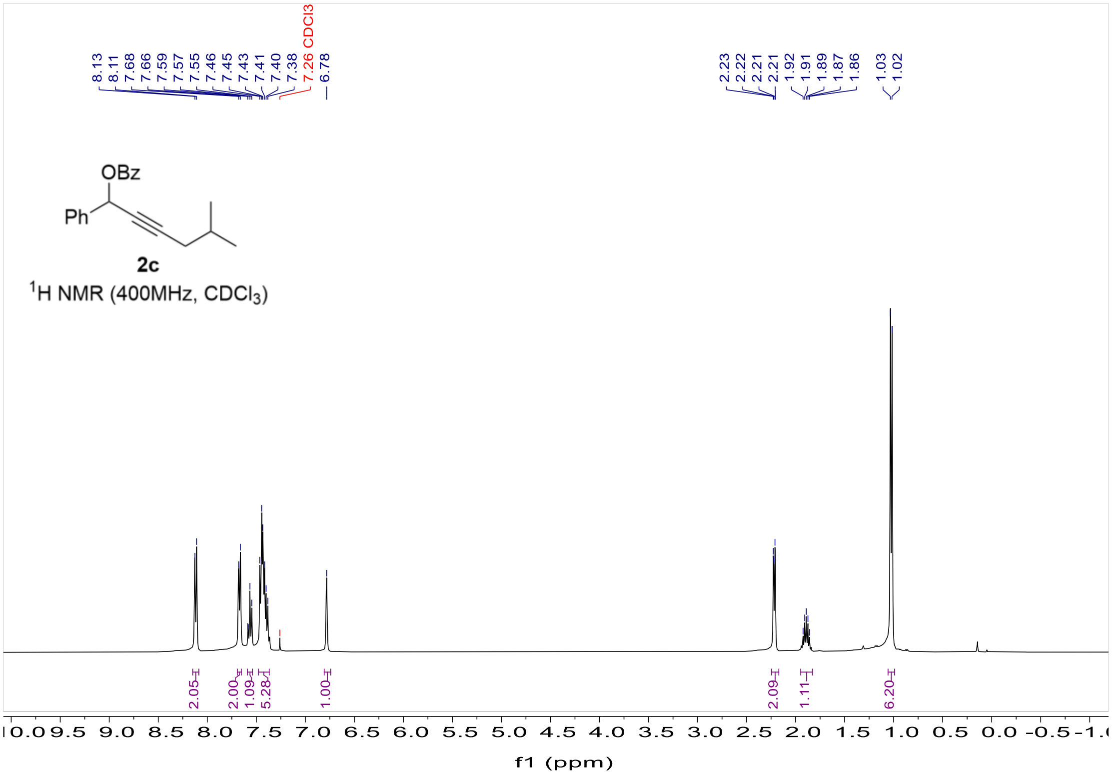
^{1}H NMR (400MHz, CDCl$_3$)

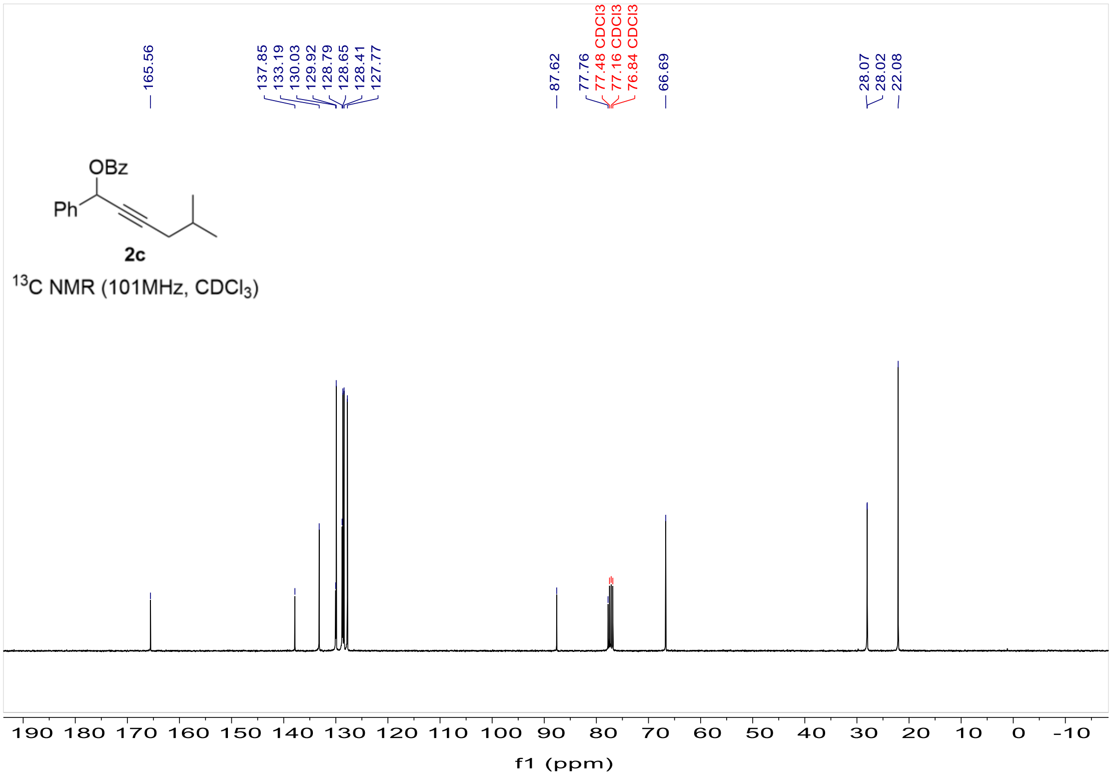


2a

^{13}C NMR (101MHz, CDCl$_3$)

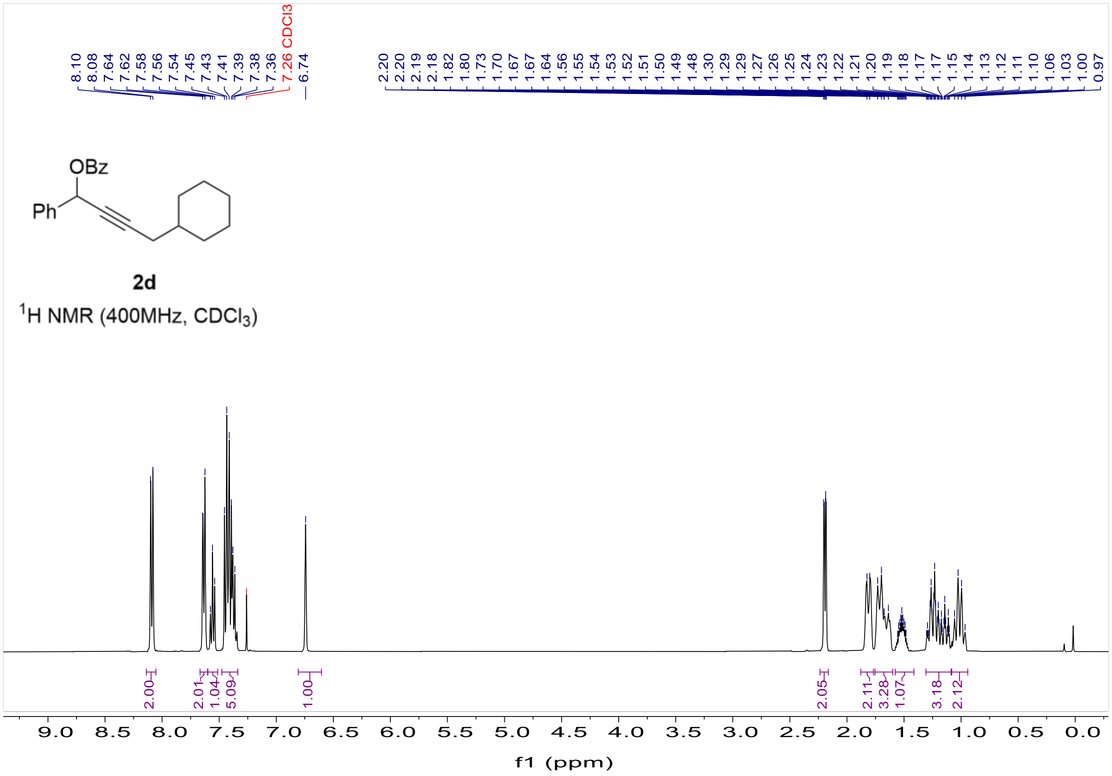

8.09
8.07
7.62
7.61
7.57
7.55
7.54
7.45
7.43
7.42
7.41
7.40
7.38
7.37
7.36
7.26 CDCl3
6.72
2.31
2.30
2.29
2.29
2.27
2.27
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.46
1.45
1.43
1.43
1.41
1.41
1.39
1.37
0.93
0.91
0.89
OBz
Ph
n-Bu
2b
^{1}H NMR (400MHz, CDCl$_3$)
1.32
2.19
1.34
6.07
0.94
2.00
1.84
1.81
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.13
8.11
7.68
7.66
7.59
7.57
7.55
7.46
7.45
7.43
7.41
7.40
7.38
7.26 CDCl3
6.78
2.23
2.22
2.21
2.21
1.92
1.91
1.89
1.87
1.86
1.03
1.02
OBz
Ph
2c
^{1}H NMR (400MHz, CDCl$_3$)
2.05
2.00
1.09
5.28
1.00
2.09
1.11
6.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



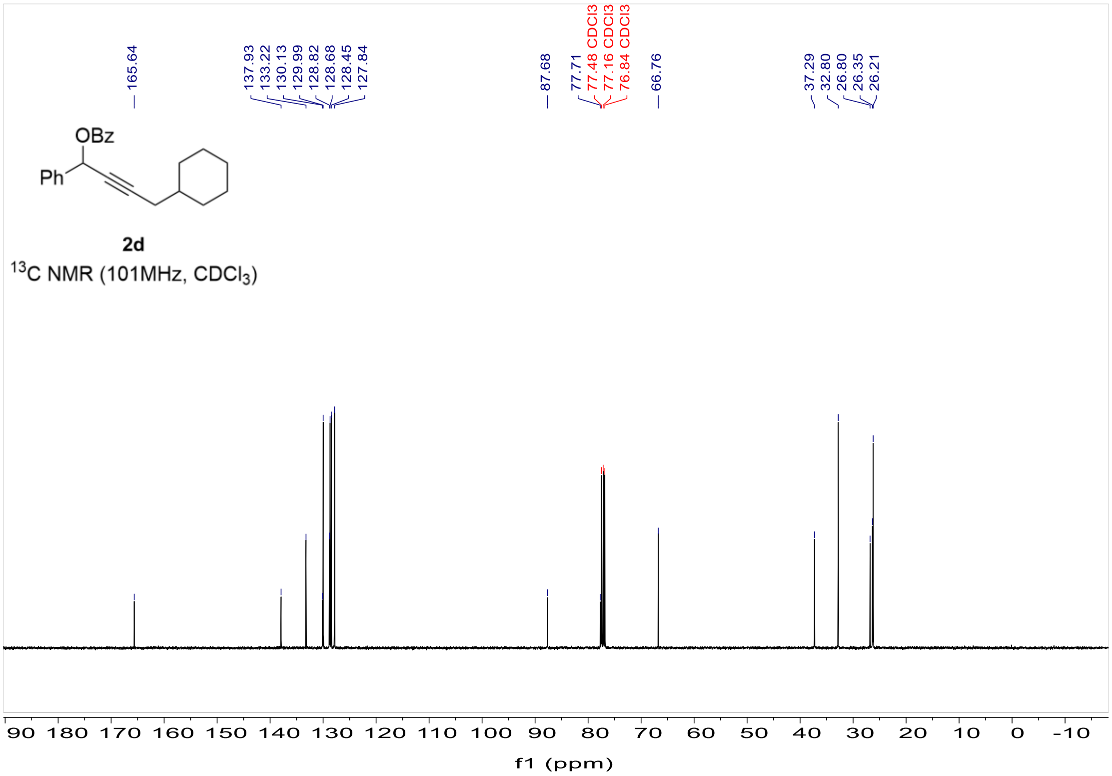
2c

^{13}C NMR (101MHz, CDCl$_3$)

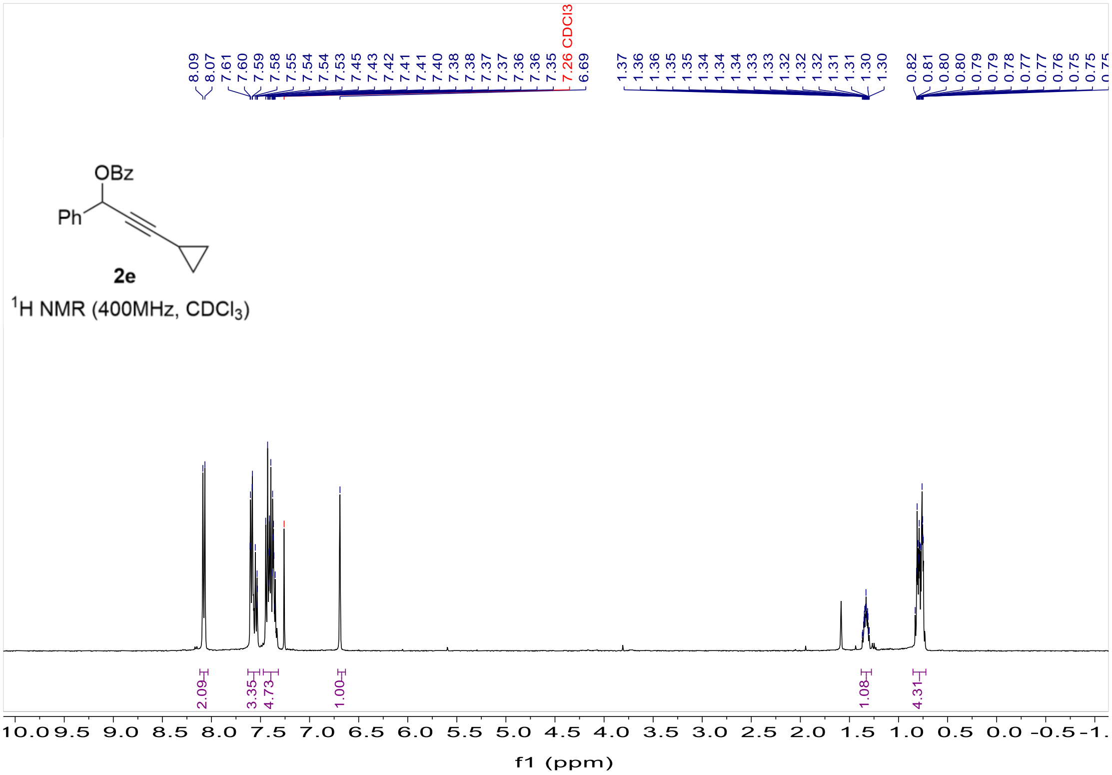


2d

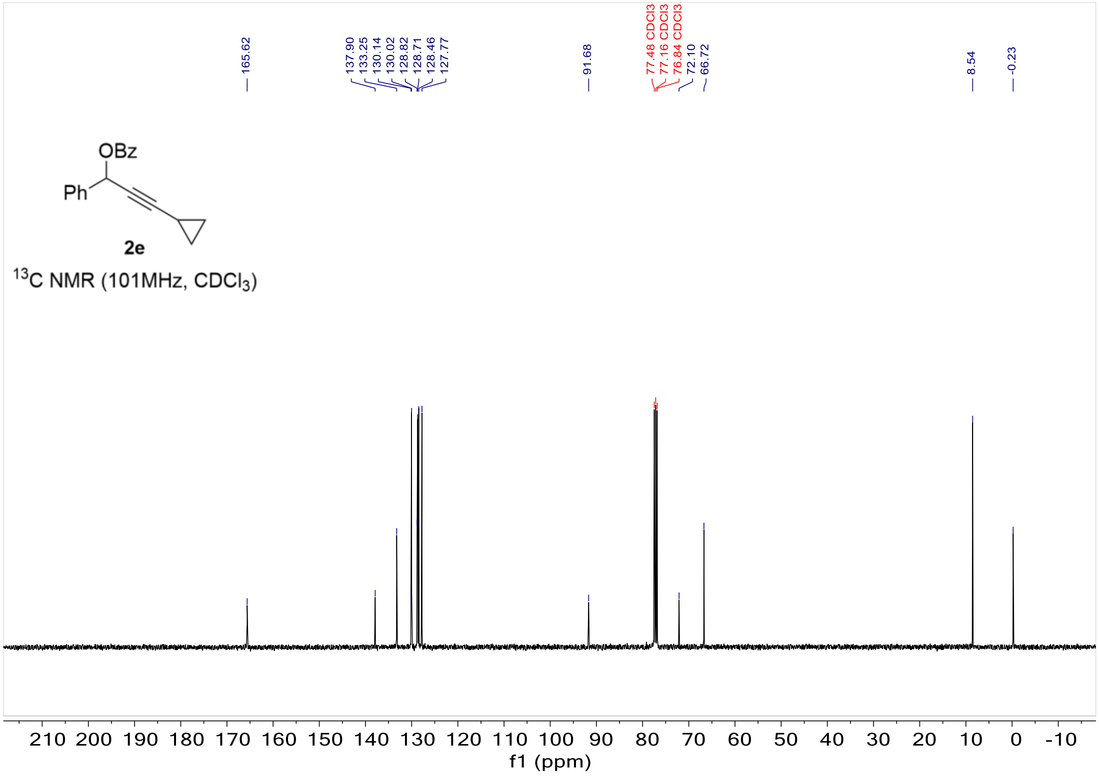
^{1}H NMR (400MHz, CDCl$_3$)

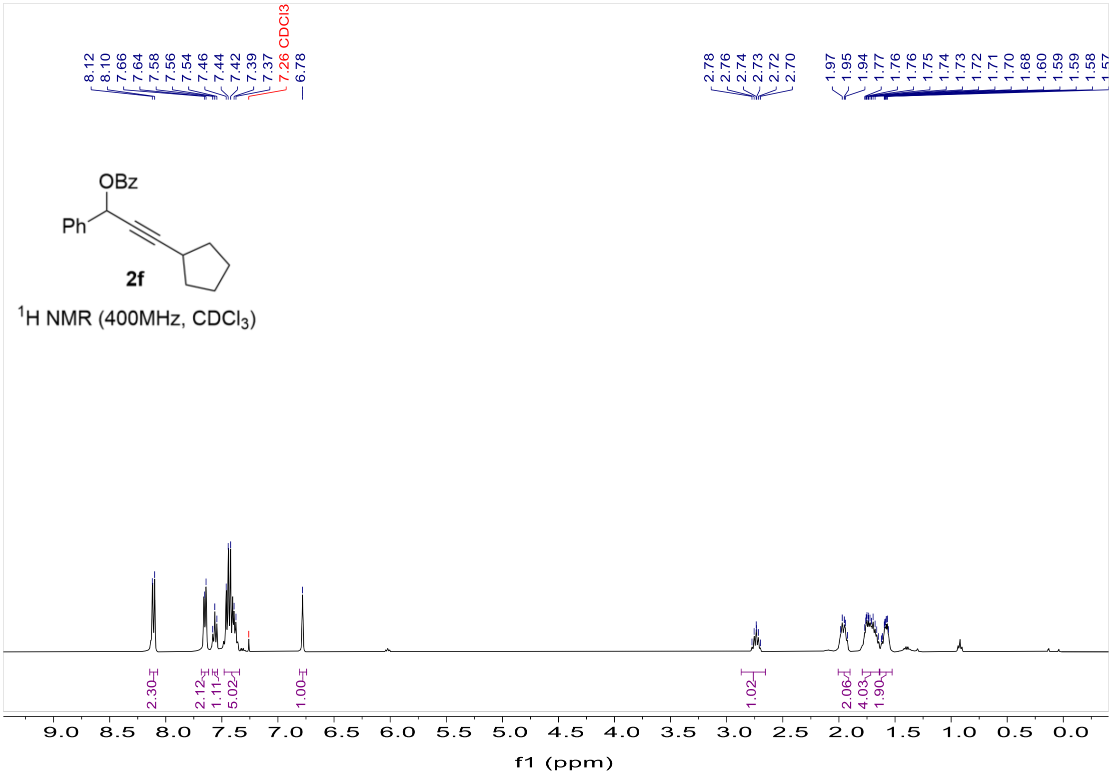

2d

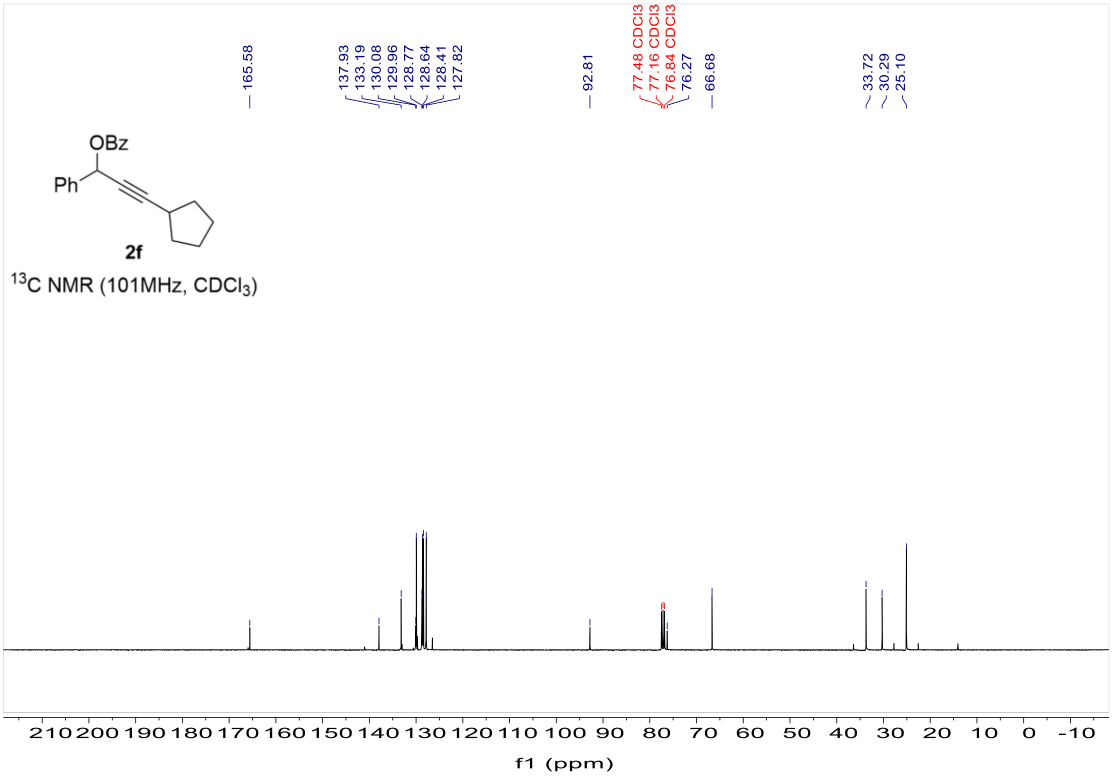
^{13}C NMR (101MHz, CDCl$_3$)


2e

^{1}H NMR (400MHz, CDCl$_3$)

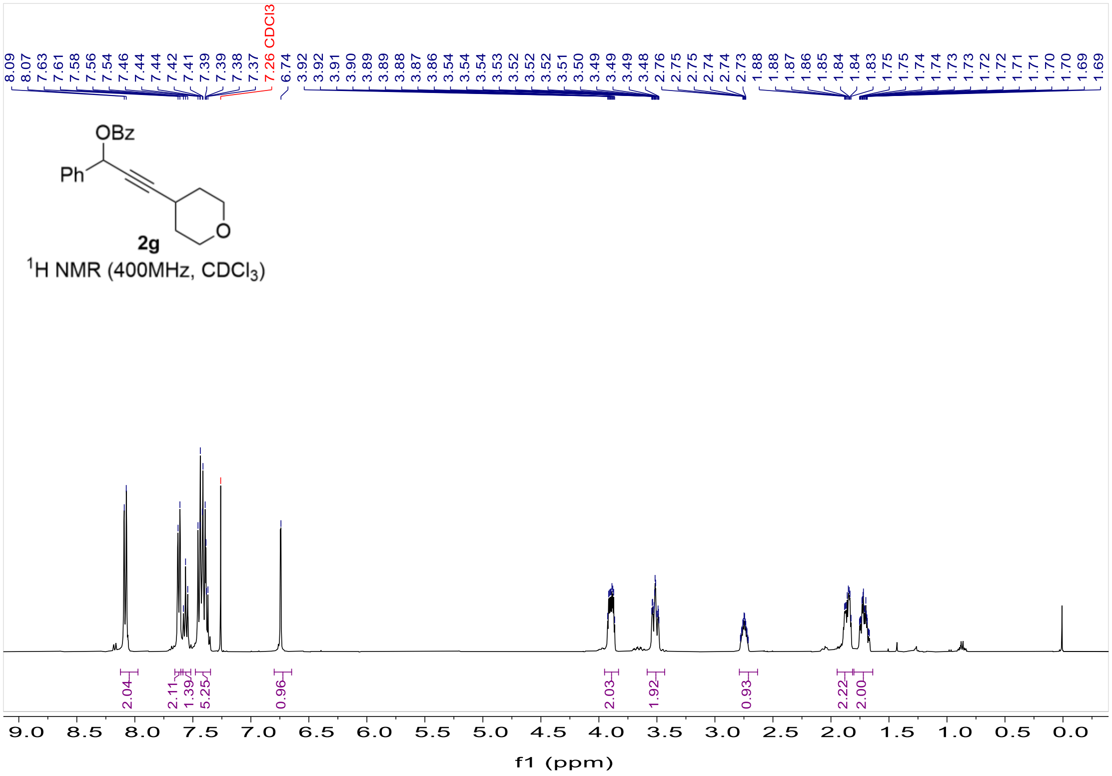

165.62
137.90
133.25
130.14
130.02
128.82
128.71
128.46
127.77
91.68
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.10
66.72
8.54
-0.23
OBz
Ph
2e
^{13}C NMR (101MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.12
8.10
7.66
7.64
7.58
7.56
7.54
7.46
7.44
7.42
7.39
7.37
7.26 CDCl3
6.78
2.78
2.76
2.74
2.73
2.72
2.70
1.97
1.95
1.94
1.77
1.76
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.68
1.60
1.59
1.59
1.58
1.57
OBz
Ph
2f
^{1}H NMR (400MHz, CDCl$_3$)
2.30
2.12
1.11
5.02
1.00
1.02
2.06
4.03
1.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



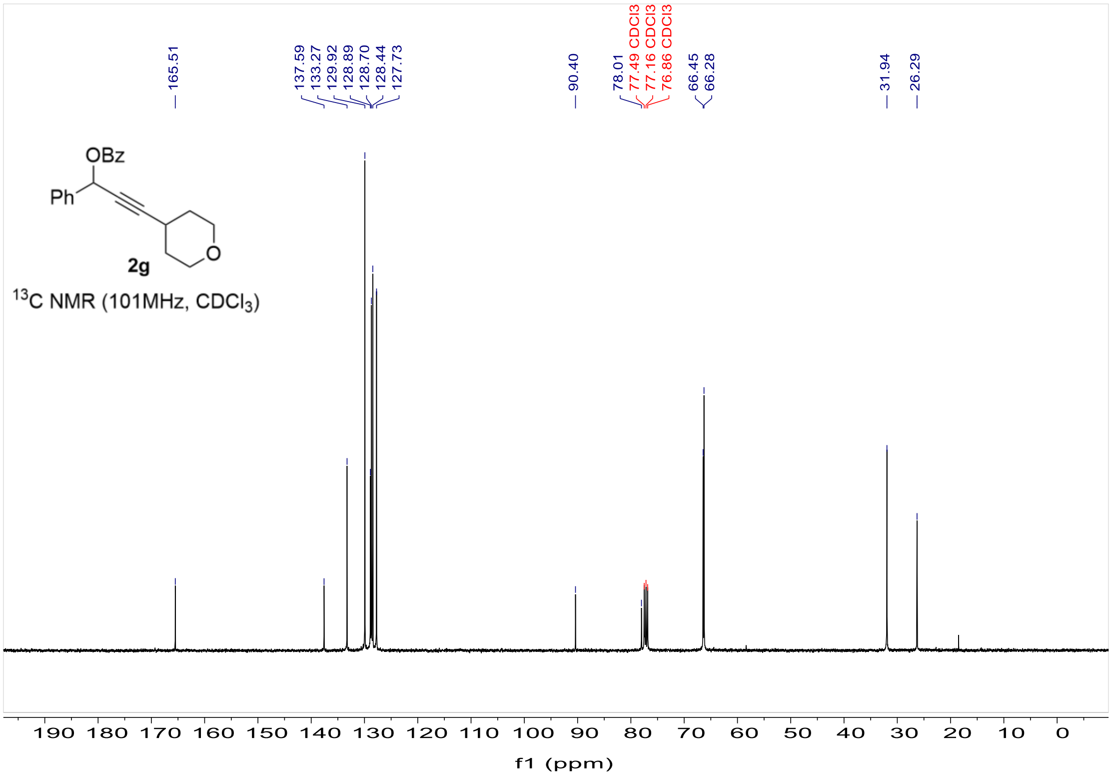
2f

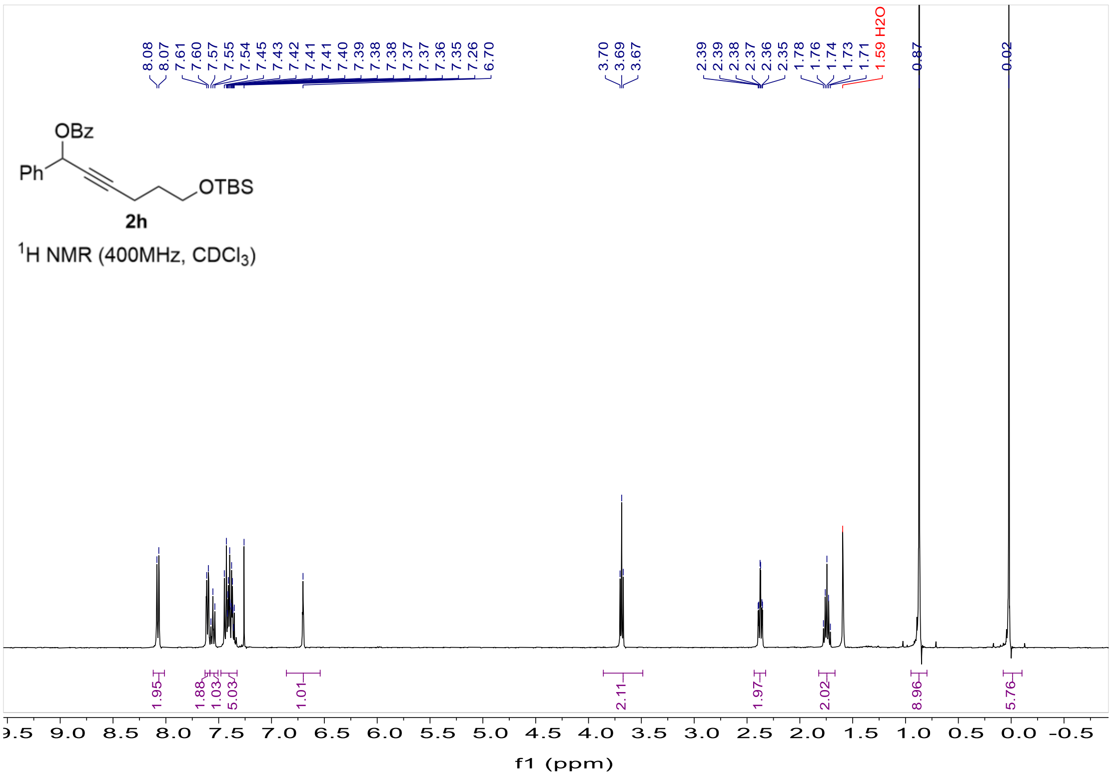
^{13}C NMR (101MHz, CDCl$_3$)

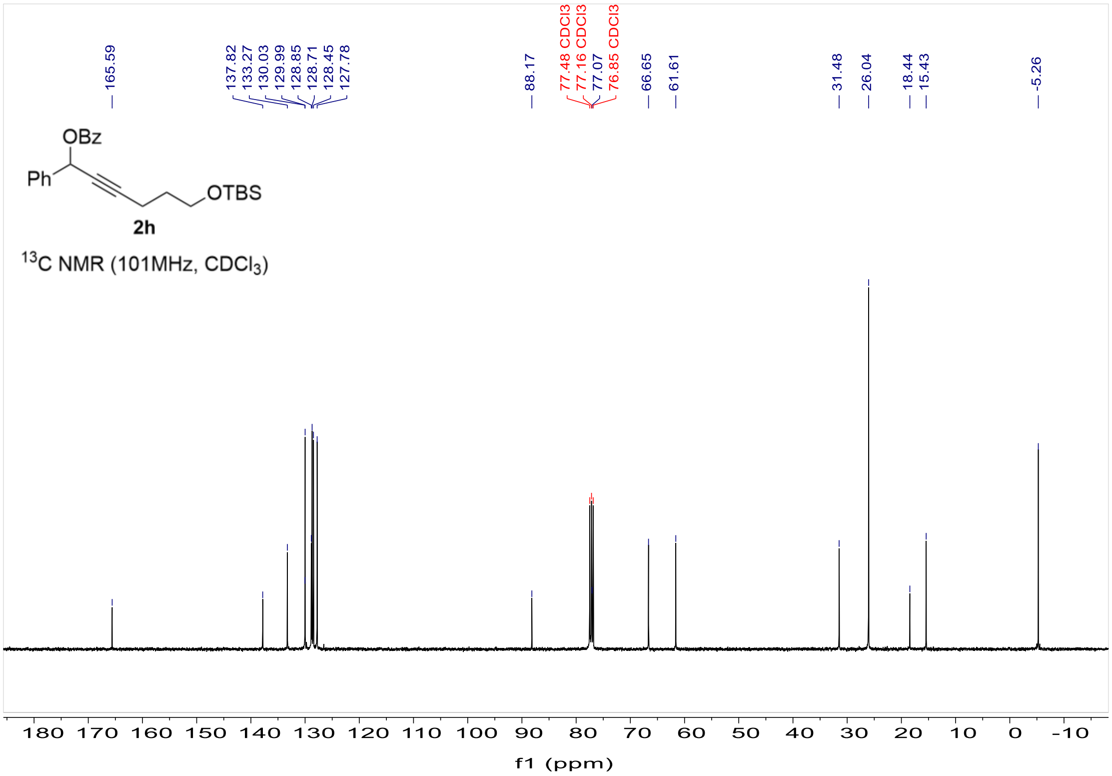


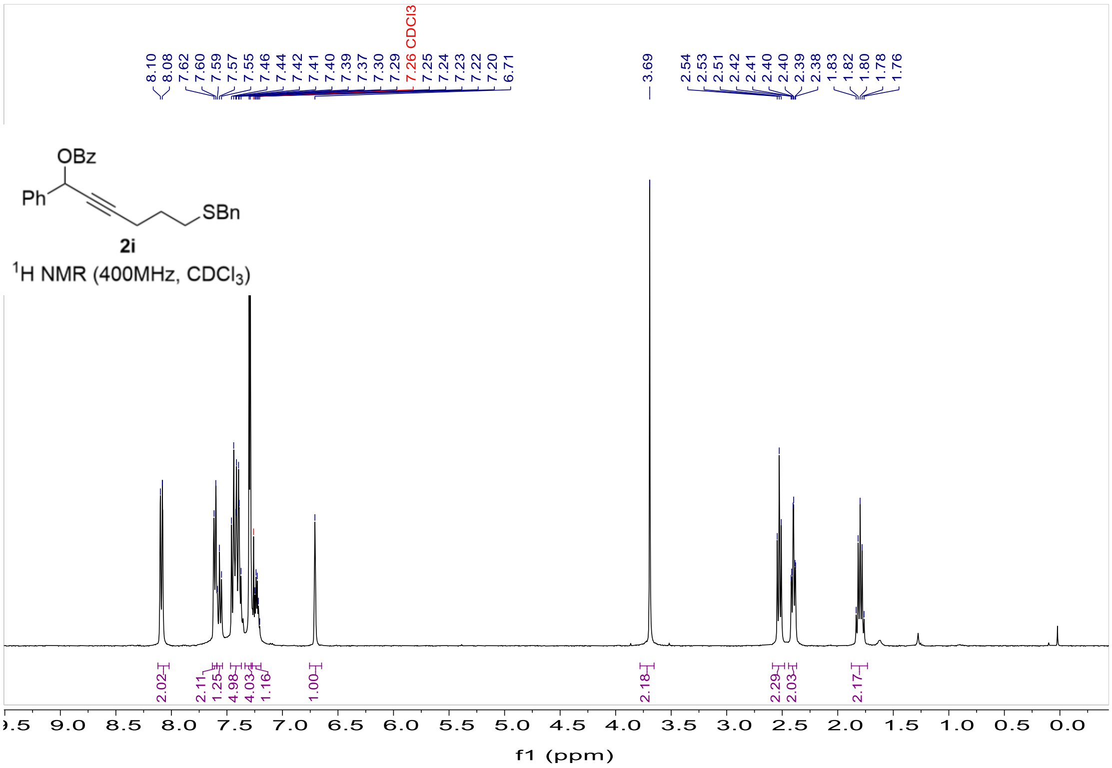
2g

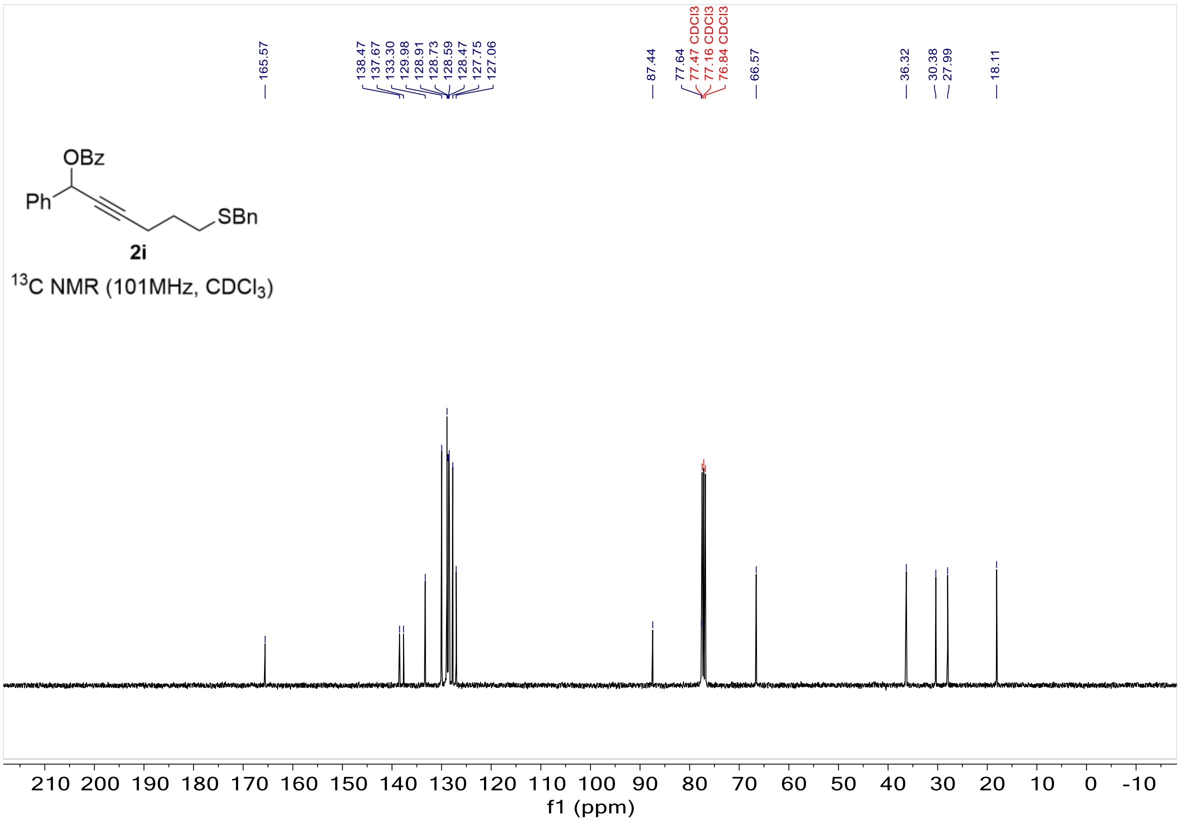
^{1}H NMR (400MHz, CDCl$_3$)

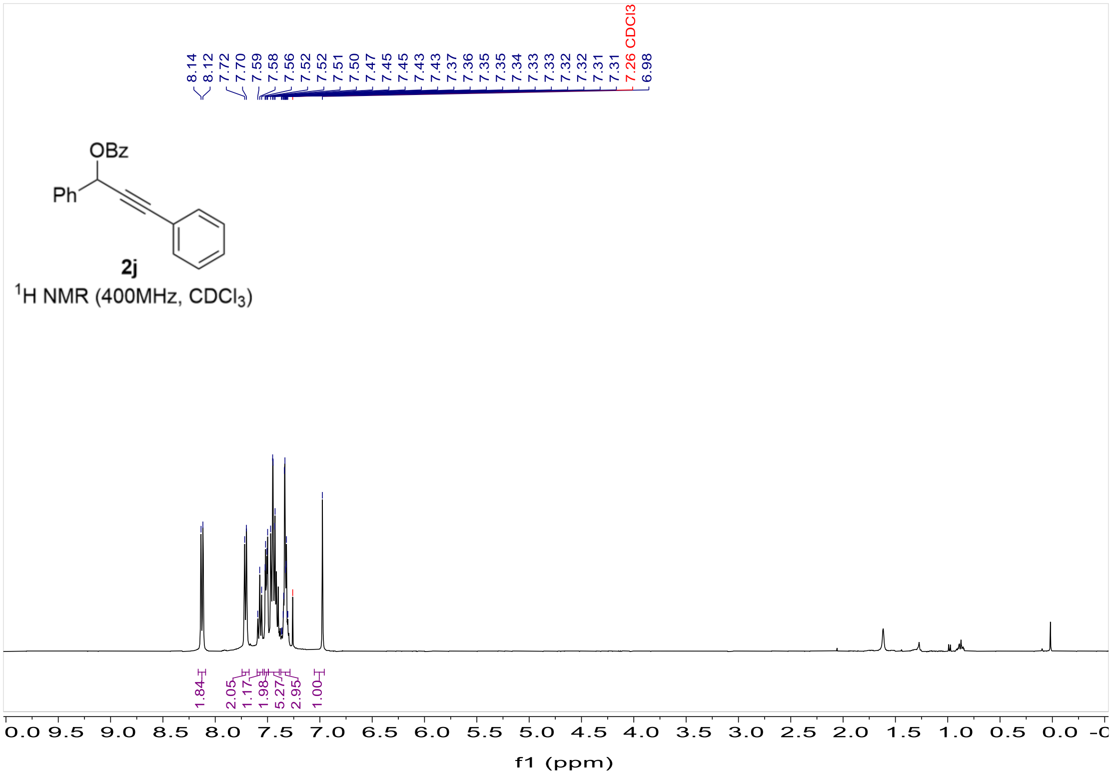

165.51
137.59
133.27
129.92
128.89
128.70
128.44
127.73
90.40
78.01
77.49 CDCl3
77.16 CDCl3
76.86 CDCl3
66.45
66.28
31.94
26.29
OBz
Ph
O
2g
13C NMR (101MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

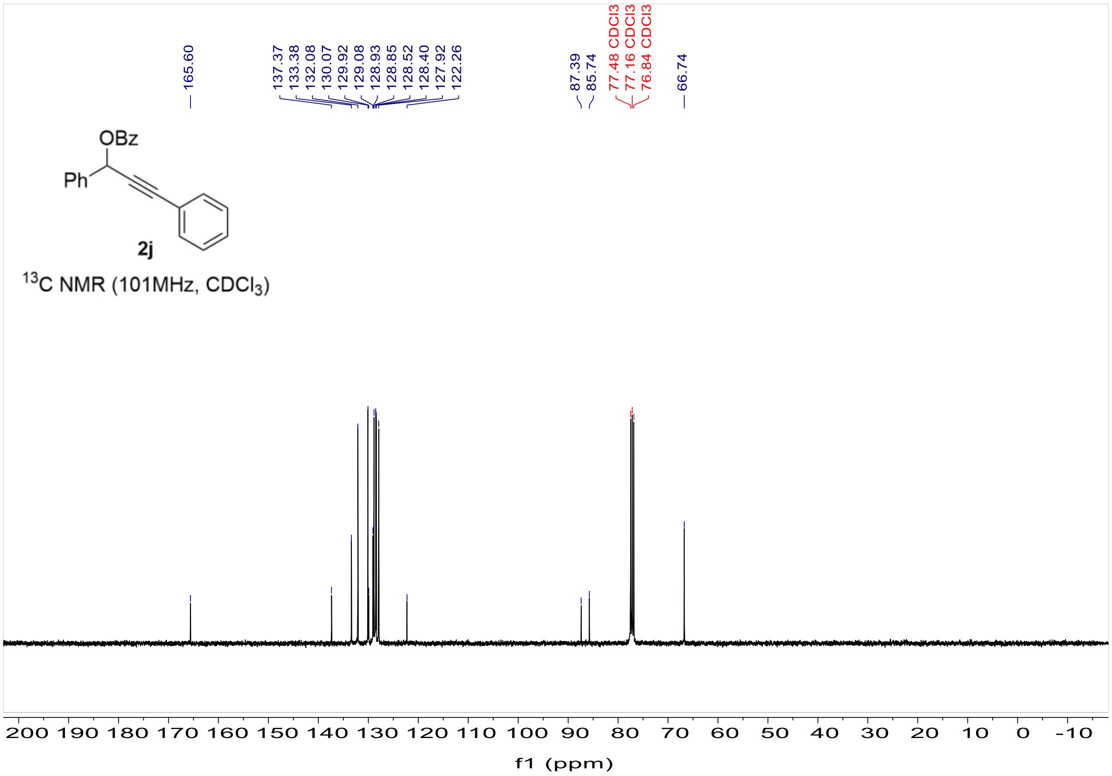

8.08
8.07
7.61
7.60
7.57
7.55
7.54
7.45
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.26
6.70
3.70
3.69
3.67
2.39
2.39
2.38
2.37
2.36
2.35
1.78
1.76
1.74
1.73
1.71
1.59 H2O
0.87
0.02
1.95
1.88
1.03
5.03
1.01
2.11
1.97
2.02
8.96
5.76
OBz
Ph
OTBS
2h
1H NMR (400MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

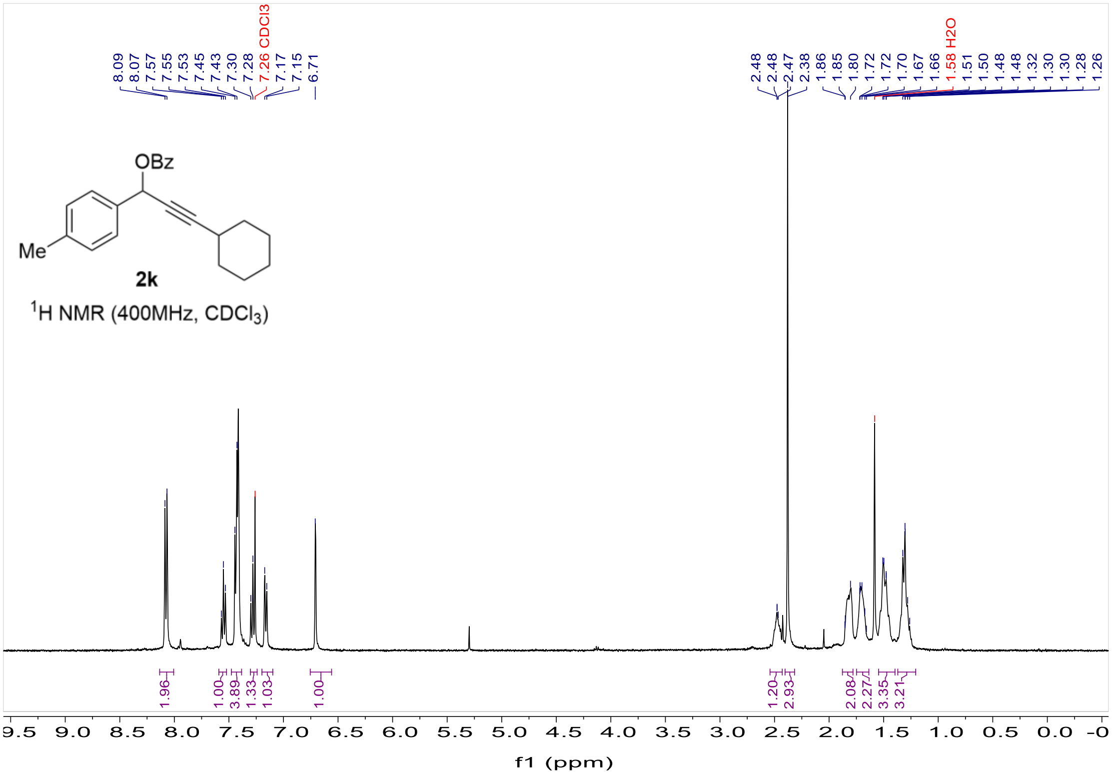

165.59
137.82
133.27
130.03
129.99
128.85
128.71
128.45
127.78
88.17
77.48 CDCl3
77.16 CDCl3
77.07
76.85 CDCl3
66.65
61.61
31.48
26.04
18.44
15.43
-5.26
OBz
Ph
OTBS
2h
13C NMR (101MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

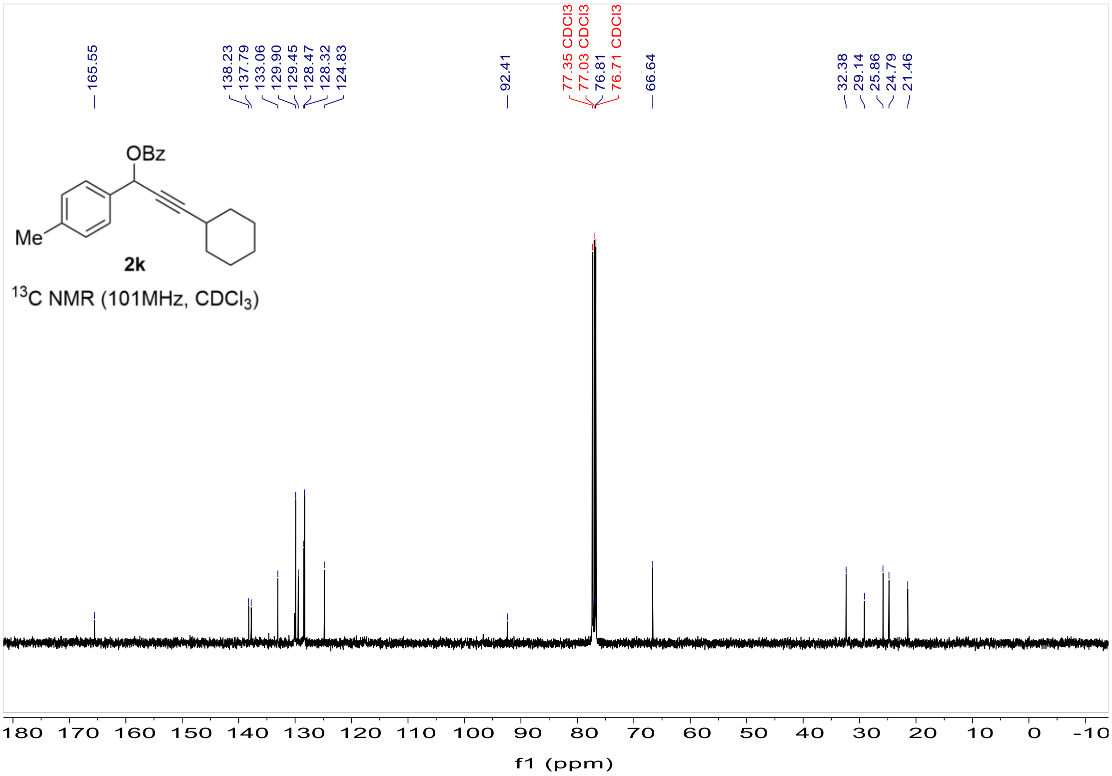

8.10
8.08
7.62
7.60
7.59
7.57
7.55
7.46
7.44
7.42
7.41
7.40
7.39
7.37
7.30
7.29
7.26 CDCl3
7.25
7.24
7.23
7.22
7.20
6.71
3.69
2.54
2.53
2.51
2.42
2.41
2.40
2.40
2.39
2.38
1.83
1.82
1.80
1.78
1.76
OBz
Ph
SBn
2i
1H NMR (400MHz, CDCl3)
2.02
2.11
1.25
4.98
4.03
1.16
1.00
2.18
2.29
2.03
2.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.57
138.47
137.67
133.30
129.98
128.91
128.73
128.59
128.47
127.75
127.06
87.44
77.64
77.47 CDCl3
77.16 CDCl3
76.84 CDCl3
66.57
36.32
30.38
27.99
18.11
OBz
Ph
SBn
2i
^{13}C NMR (101MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.14
8.12
7.72
7.70
7.59
7.58
7.56
7.52
7.52
7.51
7.50
7.47
7.45
7.45
7.43
7.43
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.26 CDCl3
6.98
OBz
Ph
2j
^{1}H NMR (400MHz, CDCl$_3$)
1.84
2.05
1.17
1.98
5.27
2.95
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

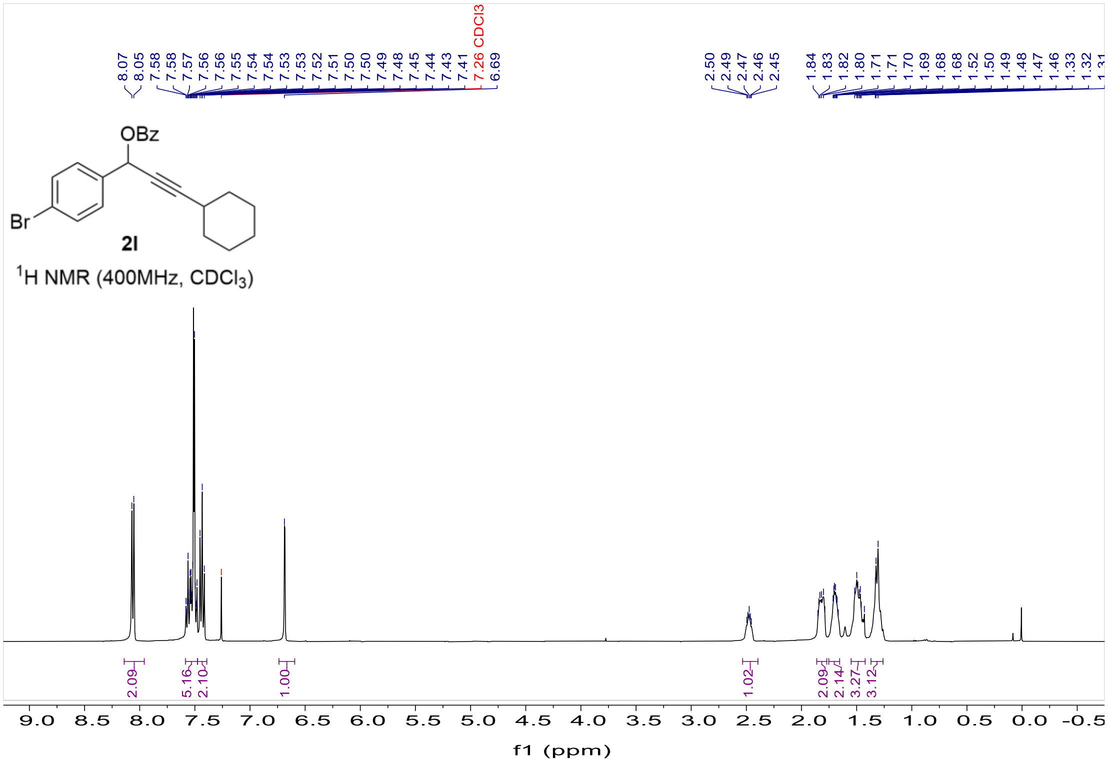

165.60
137.37
133.38
132.08
130.07
129.92
129.08
128.93
128.85
128.52
128.40
127.92
122.26
87.39
85.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.74
OBz
Ph
2j
^{13}C NMR (101MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
8.07
7.57
7.55
7.53
7.45
7.43
7.30
7.28
7.26 CDCl3
7.17
7.15
6.71
2.48
2.48
2.47
2.38
1.86
1.85
1.80
1.72
1.70
1.67
1.66
1.58 H2O
1.51
1.50
1.48
1.48
1.32
1.30
1.28
1.26
OBz
Me
2k
^{1}H NMR (400MHz, CDCl$_3$)
1.96
1.00
3.89
1.33
1.03
1.00
1.20
2.93
2.08
2.27
3.35
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



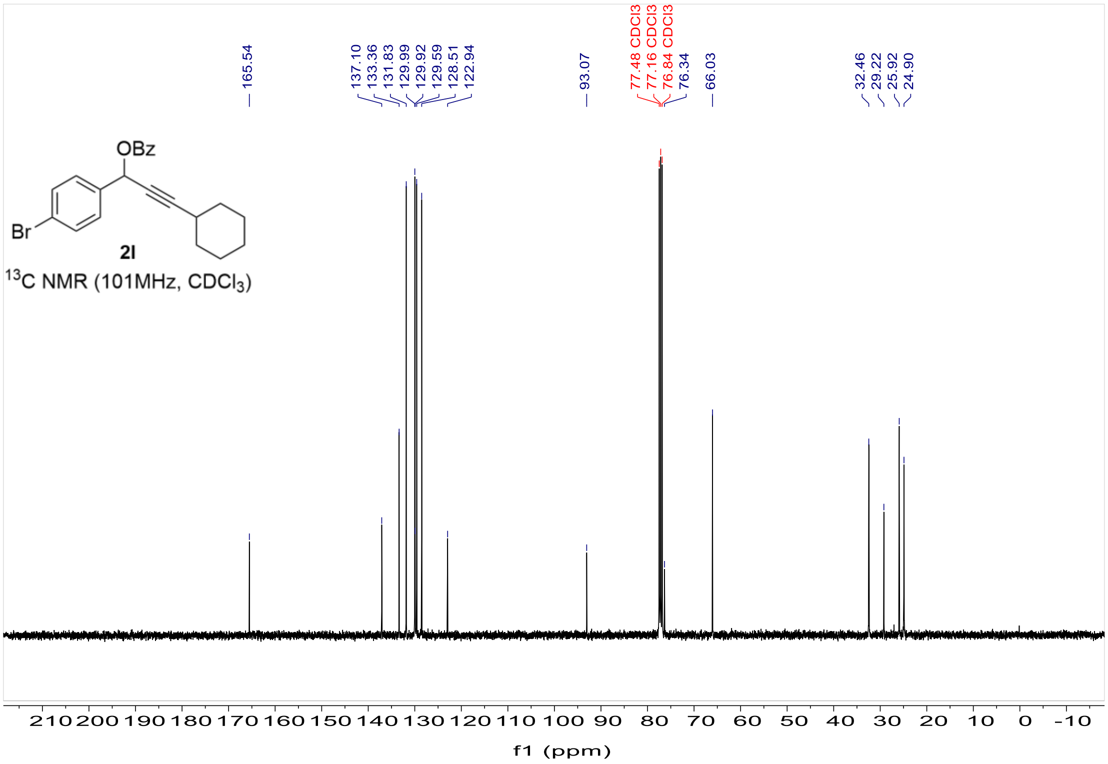
2k

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



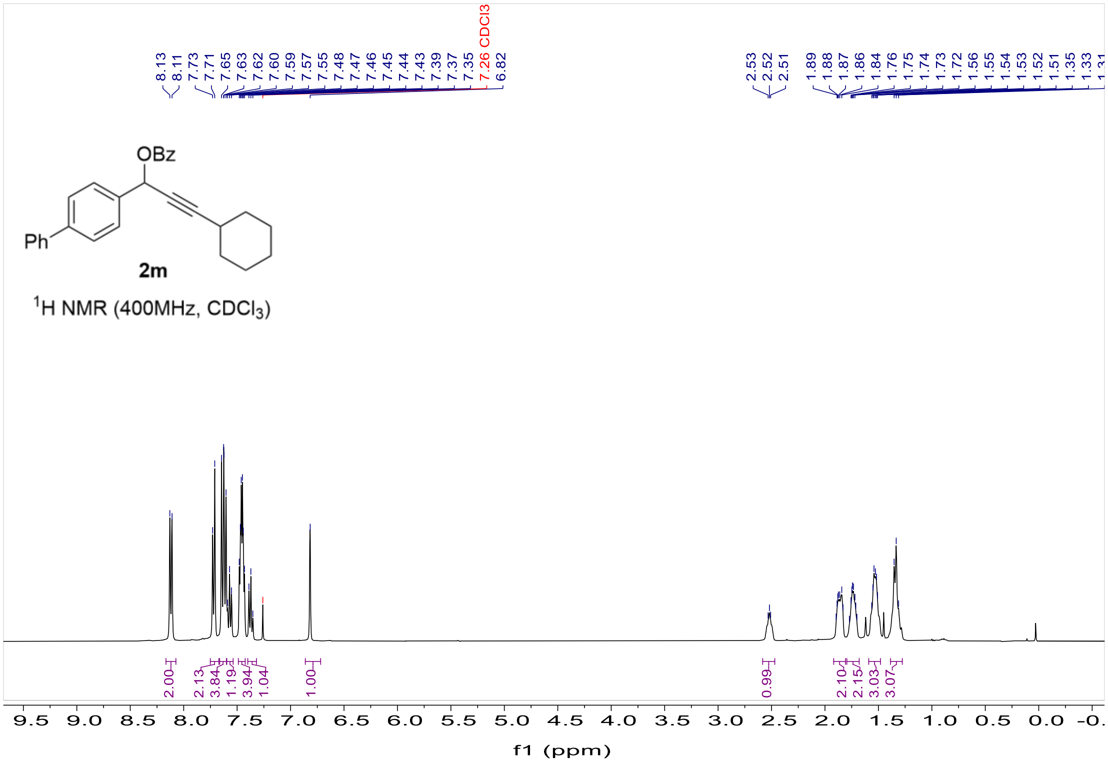
2l

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



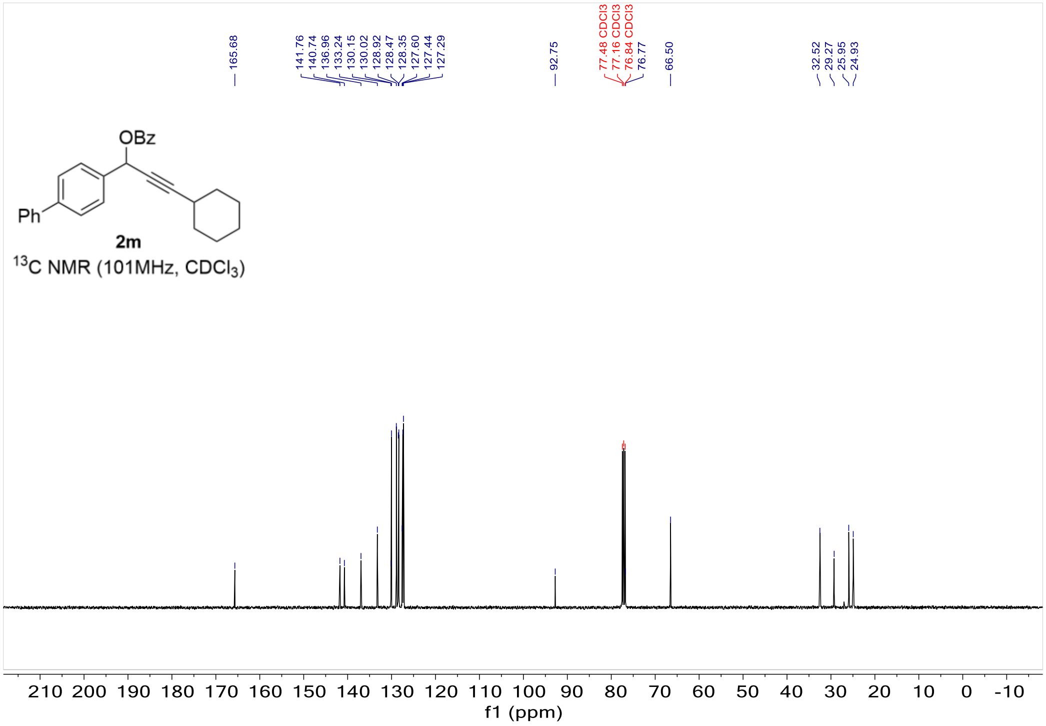
2l

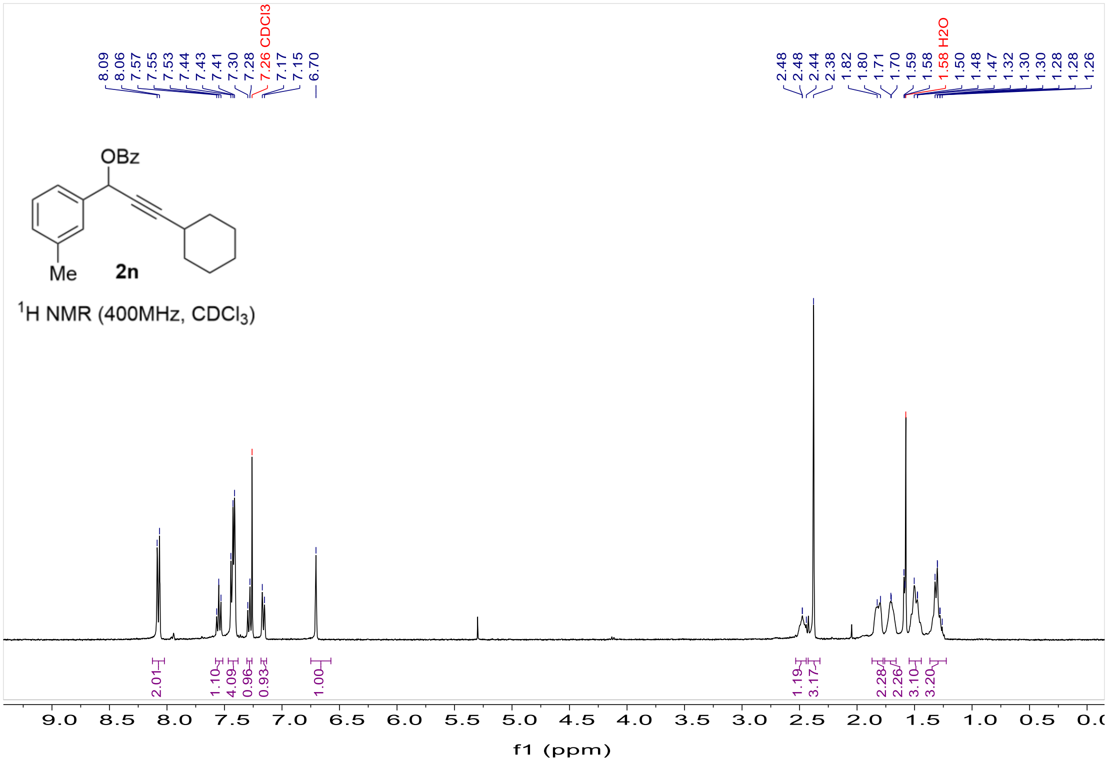
^{13}C NMR (101MHz, CDCl$_3$)

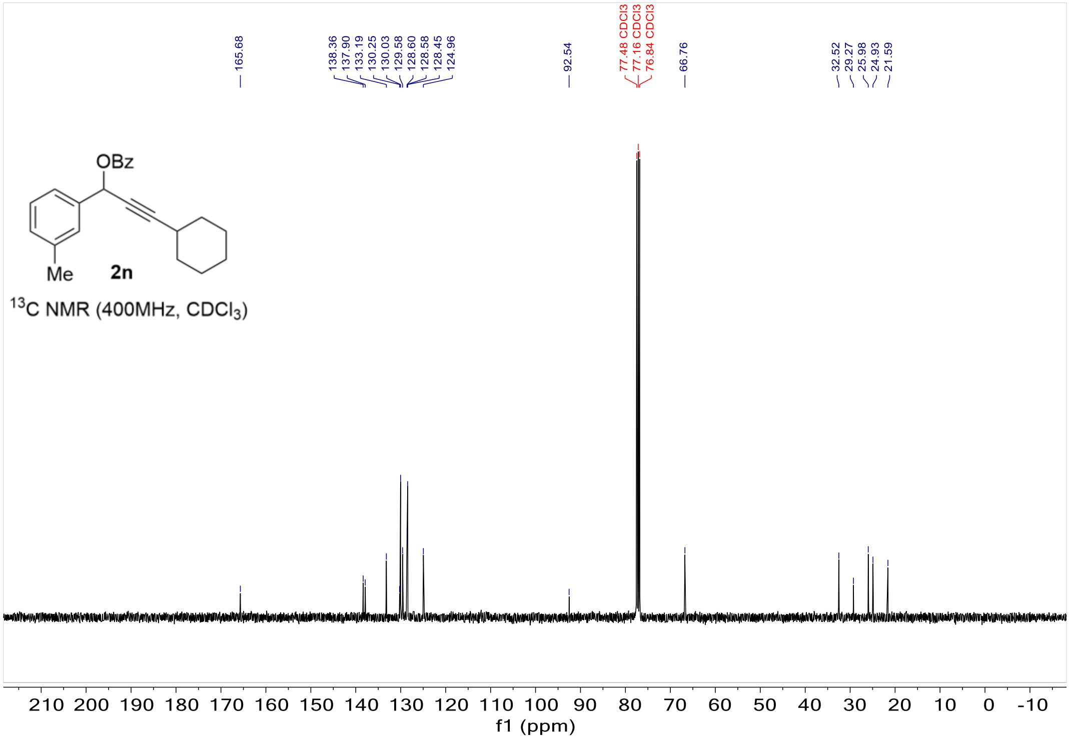


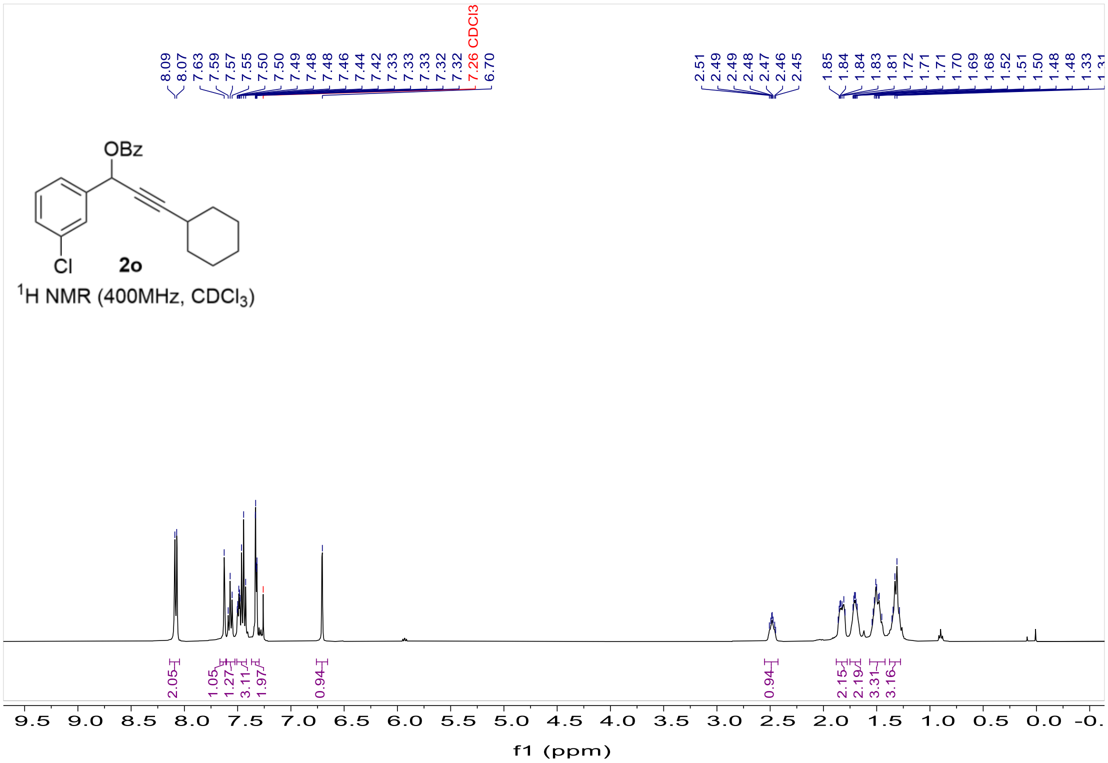
2m

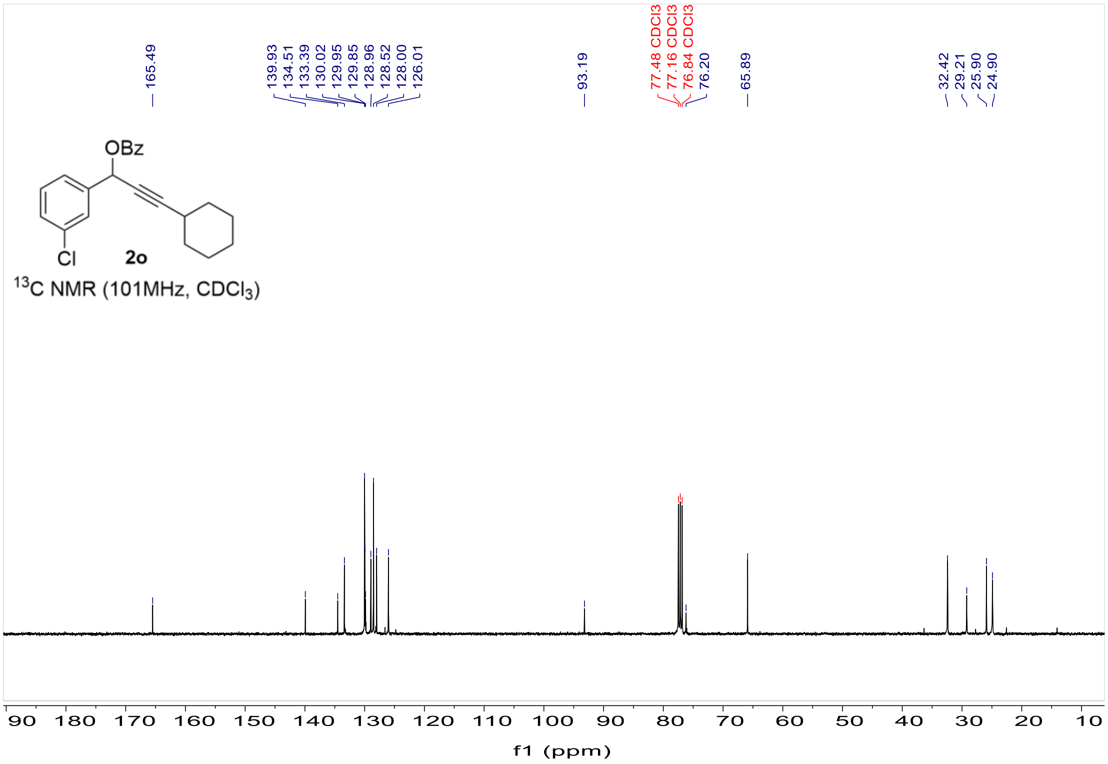
^{1}H NMR (400MHz, CDCl$_3$)


165.68
141.76
140.74
136.96
133.24
130.15
130.02
128.92
128.47
128.35
127.60
127.44
127.29
92.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.77
66.50
32.52
29.27
25.95
24.93
OBz
Ph
2m
13C NMR (101MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
8.06
7.57
7.55
7.53
7.44
7.43
7.41
7.30
7.28
7.26 CDCl3
7.17
7.15
6.70
2.48
2.48
2.44
2.38
1.82
1.80
1.71
1.70
1.59
1.58
1.58 H2O
1.50
1.48
1.47
1.32
1.30
1.30
1.28
1.28
1.26
OBz
Me
2n
1H NMR (400MHz, CDCl3)
2.01
1.10
4.09
0.96
0.93
1.00
1.19
3.17
2.28
2.26
3.10
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

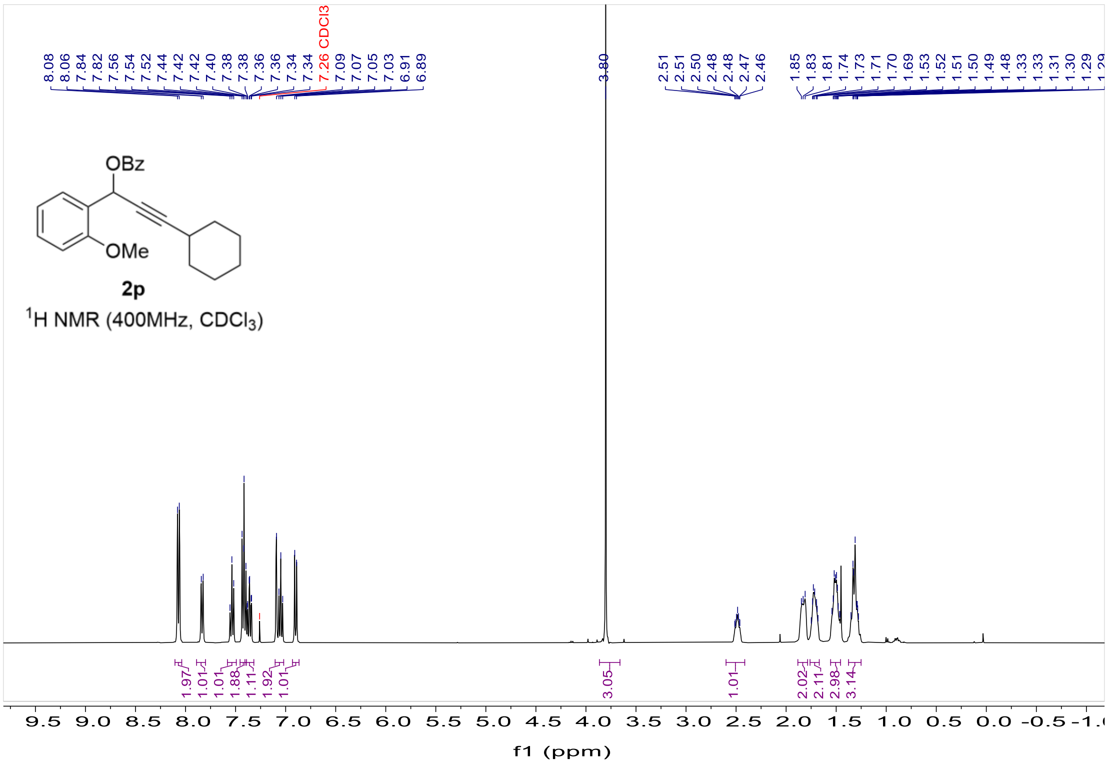

165.68
138.36
137.90
133.19
130.25
130.03
129.58
128.60
128.58
128.45
124.96
92.54
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.76
32.52
29.27
25.98
24.93
21.59
OBz
Me
2n
^{13}C NMR (400MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
8.07
7.63
7.59
7.57
7.55
7.50
7.49
7.48
7.46
7.44
7.42
7.33
7.33
7.32
7.32
7.26 CDCl3
6.70
2.51
2.49
2.49
2.48
2.47
2.46
2.45
1.85
1.84
1.84
1.83
1.81
1.72
1.71
1.71
1.70
1.69
1.68
1.52
1.51
1.50
1.48
1.33
OBz
Cl
2o
^{1}H NMR (400MHz, CDCl$_3$)
2.05
1.05
1.27
3.11
1.97
0.94
0.94
2.15
2.19
3.31
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



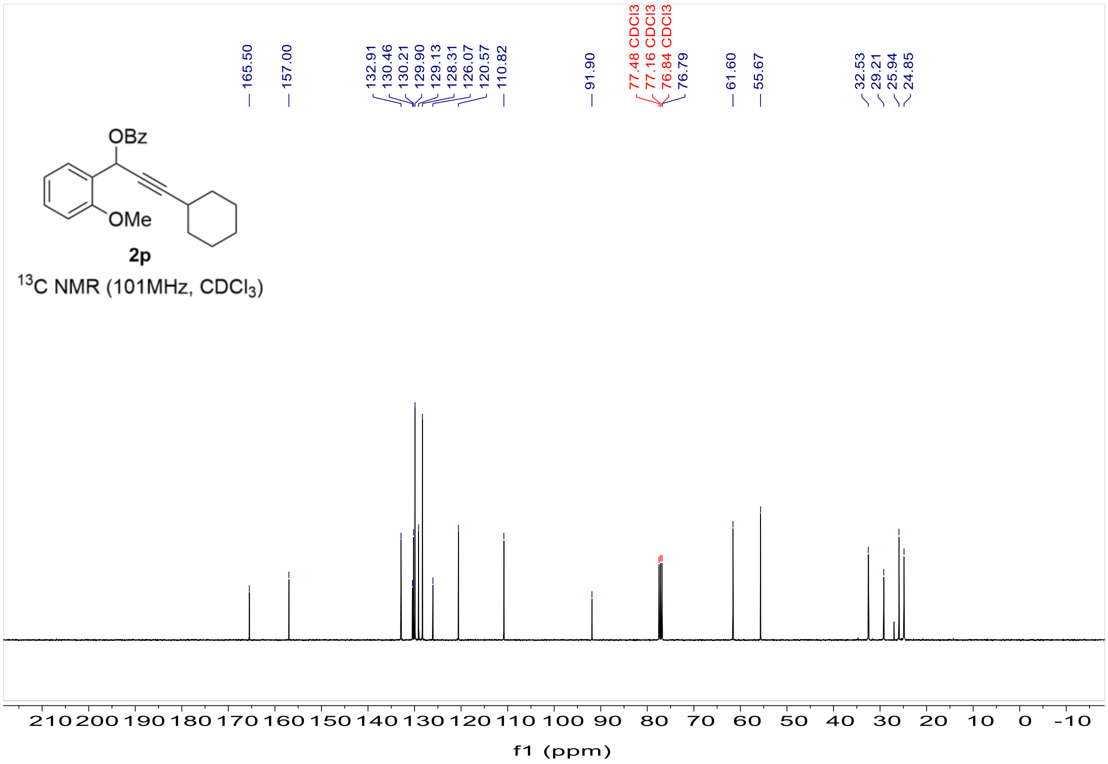
2o

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

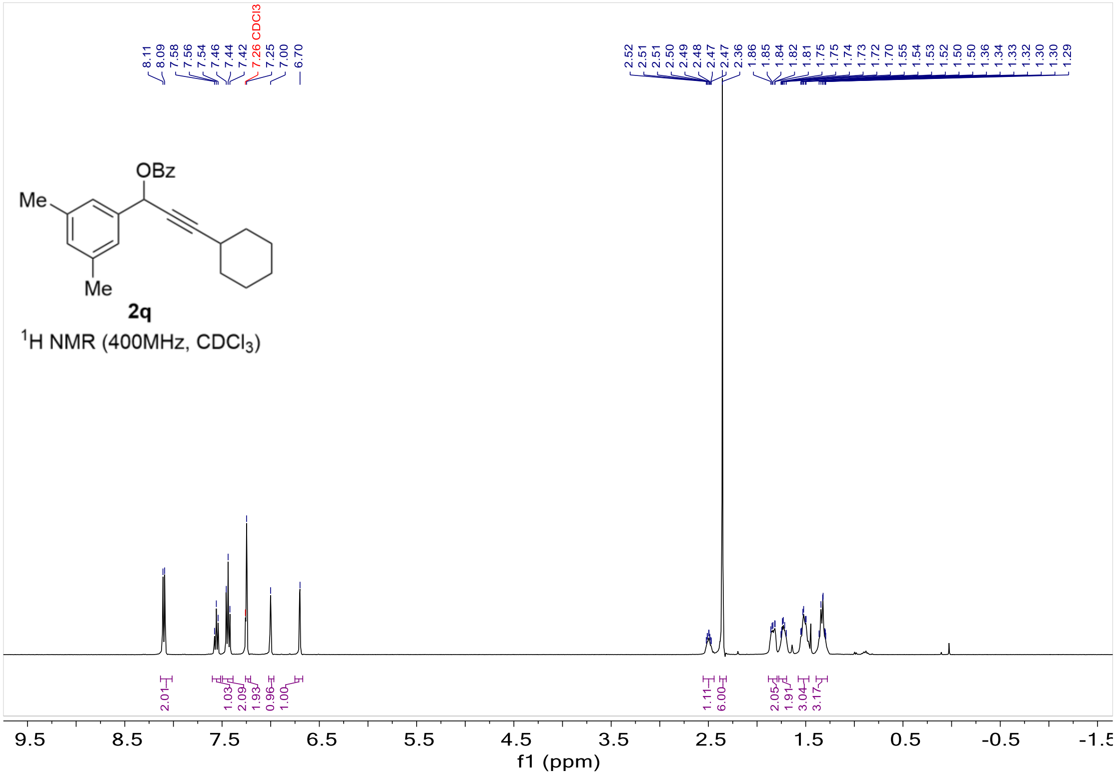


2p

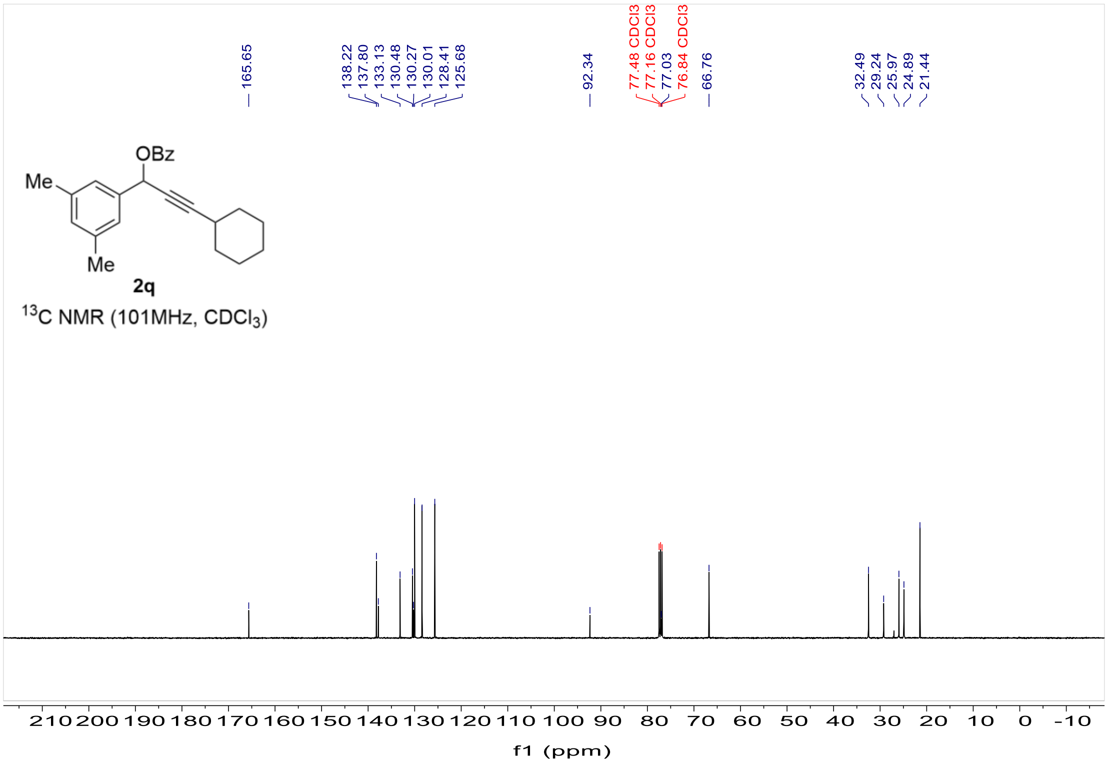
^{1}H NMR (400MHz, $CDCl_3$)


2p

^{13}C NMR (101MHz, CDCl$_3$)

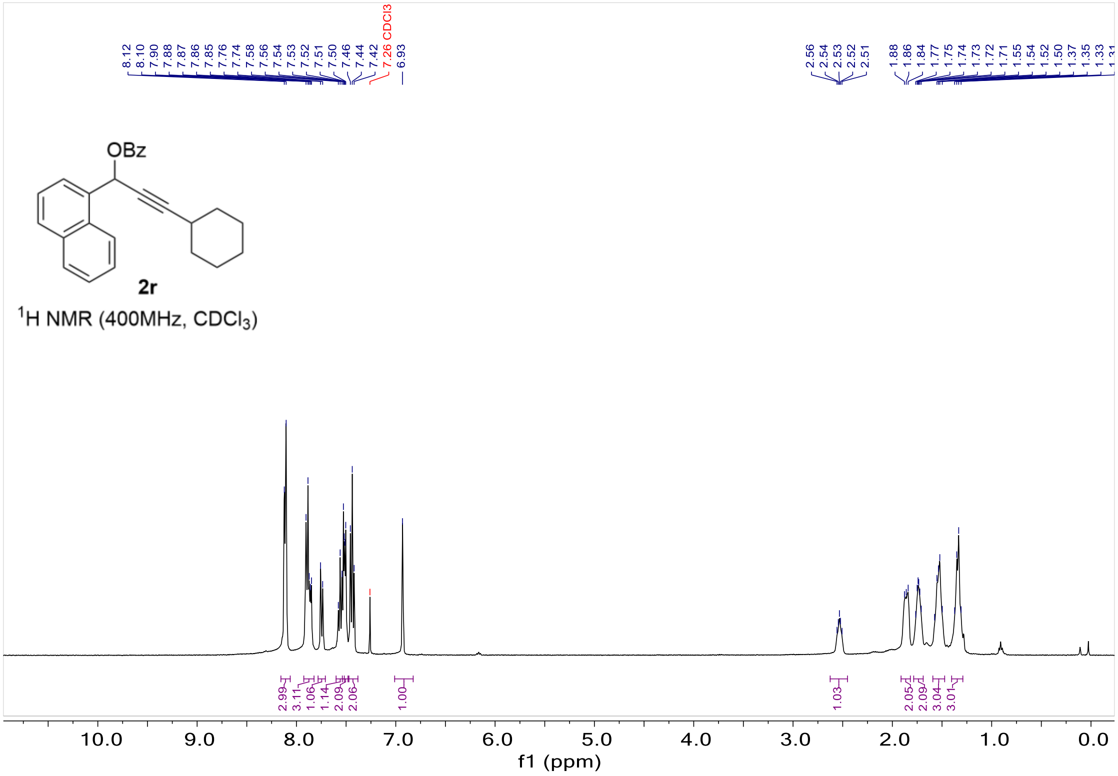

2q

^{1}H NMR (400MHz, CDCl$_3$)



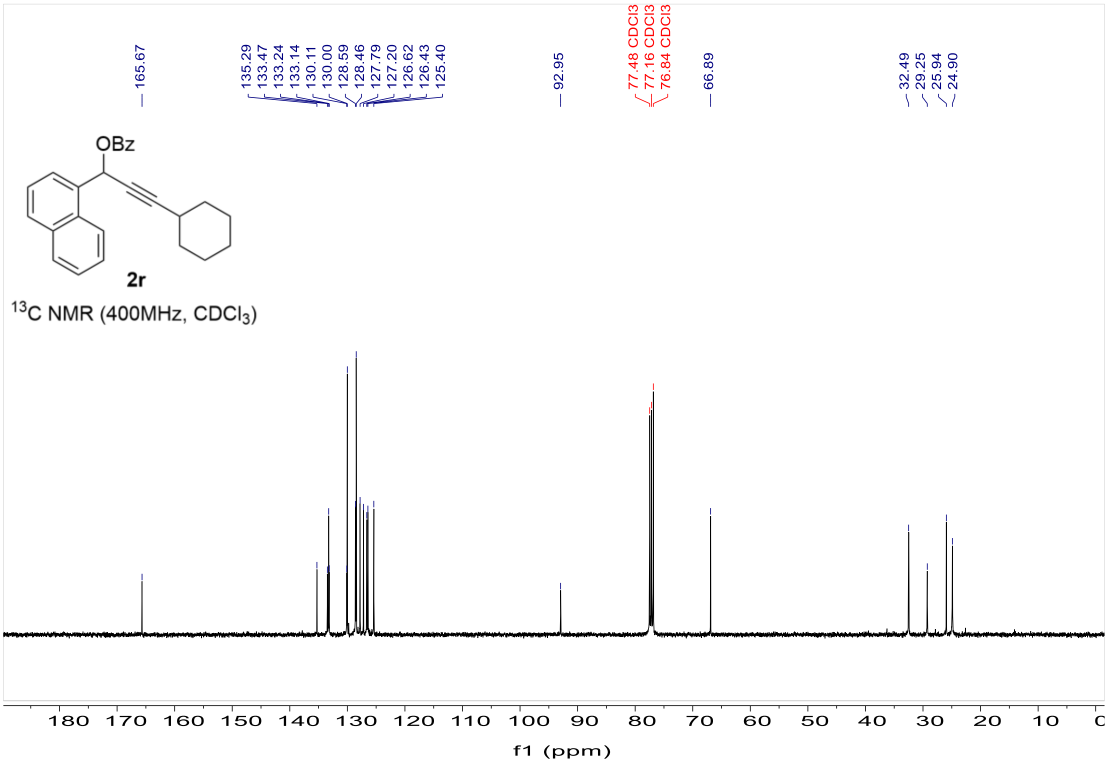
2q

^{13}C NMR (101MHz, CDCl$_3$)



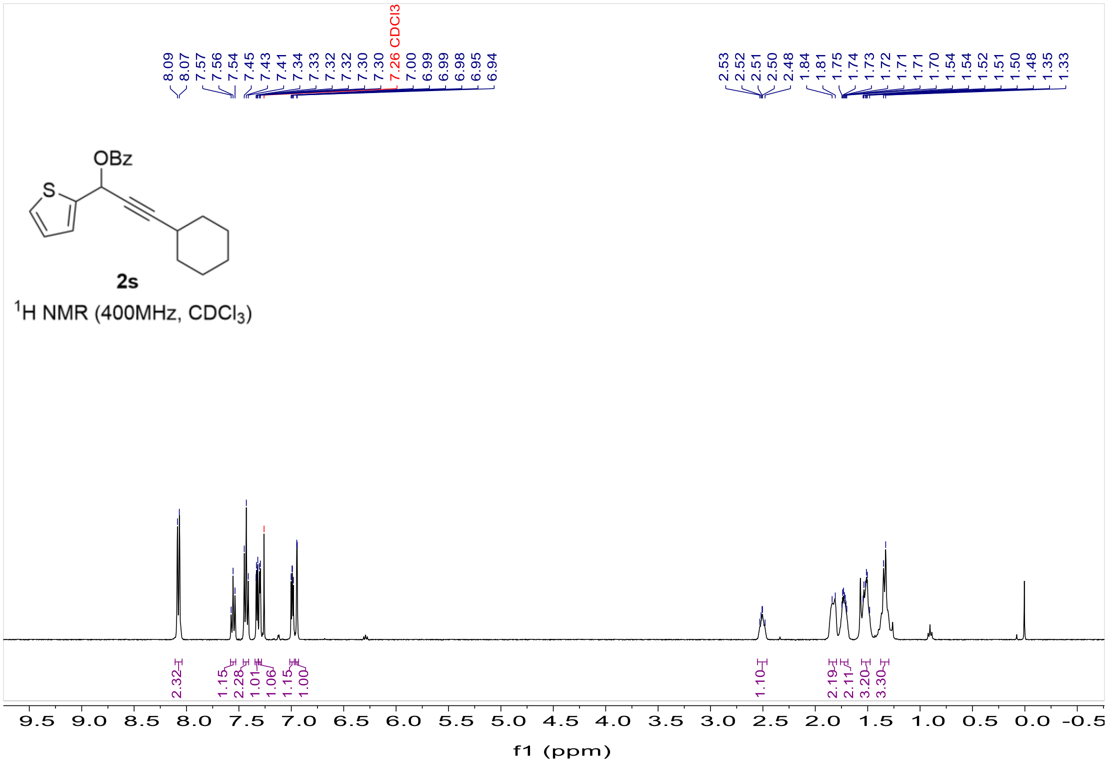
2r

^{1}H NMR (400MHz, CDCl$_3$)



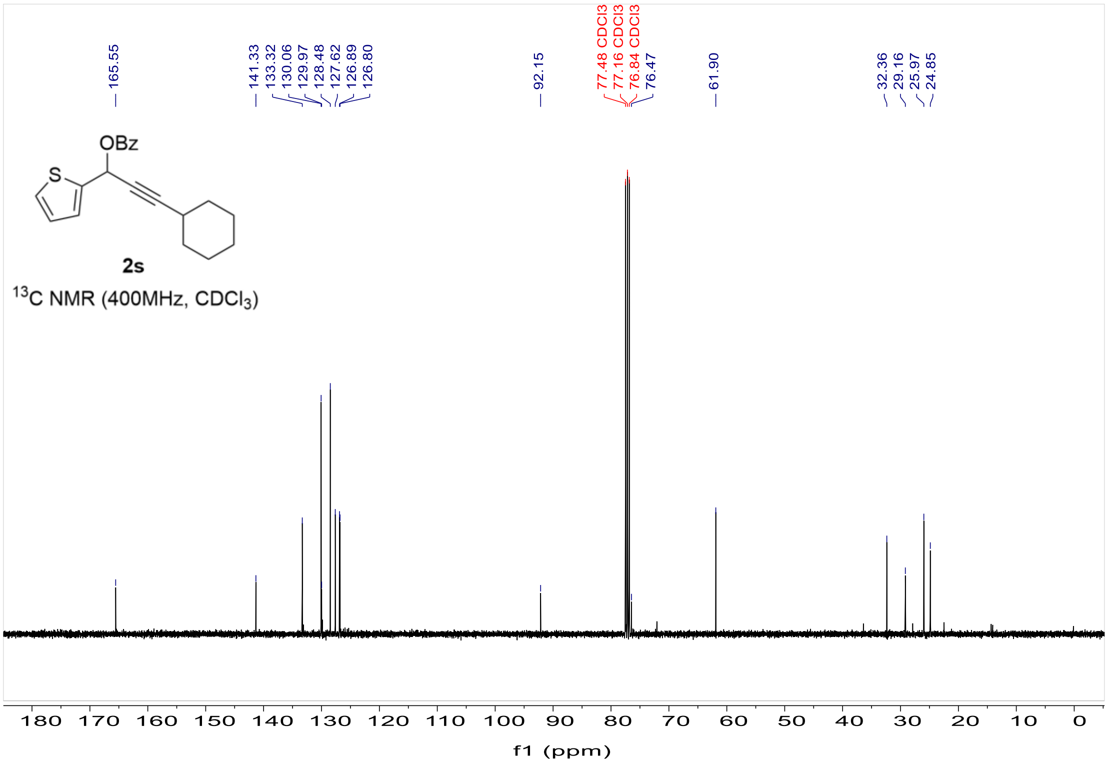
2r

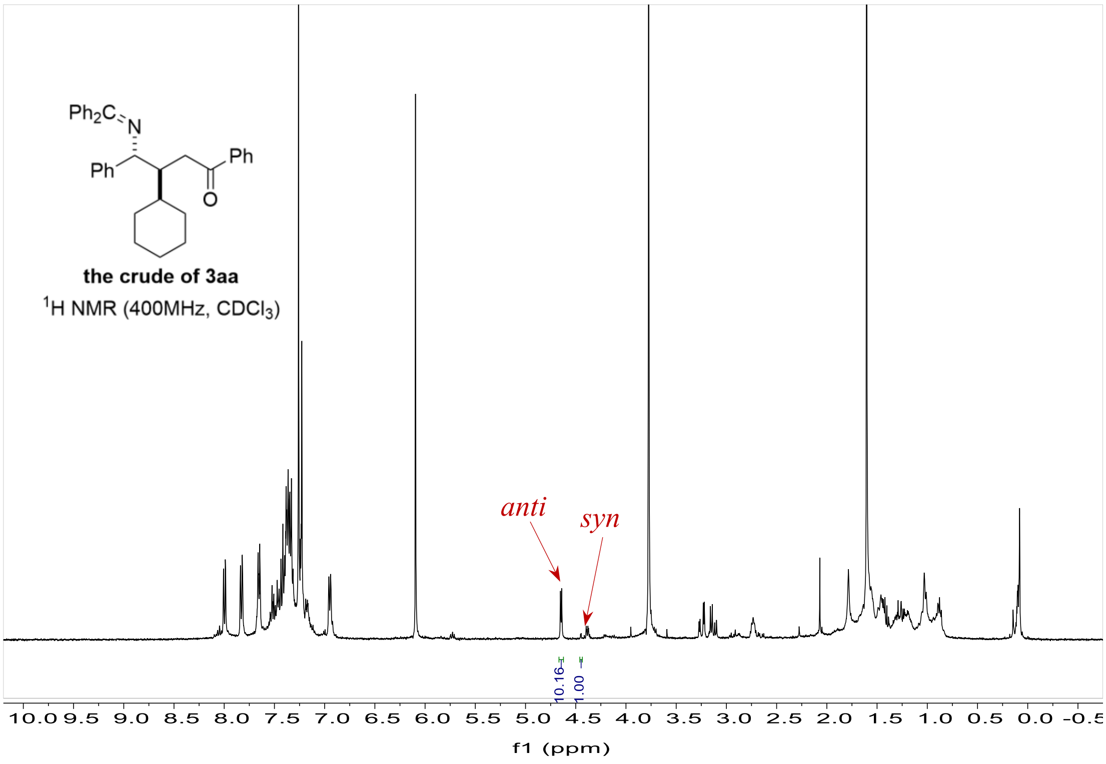
^{13}C NMR (400MHz, $CDCl_3$)

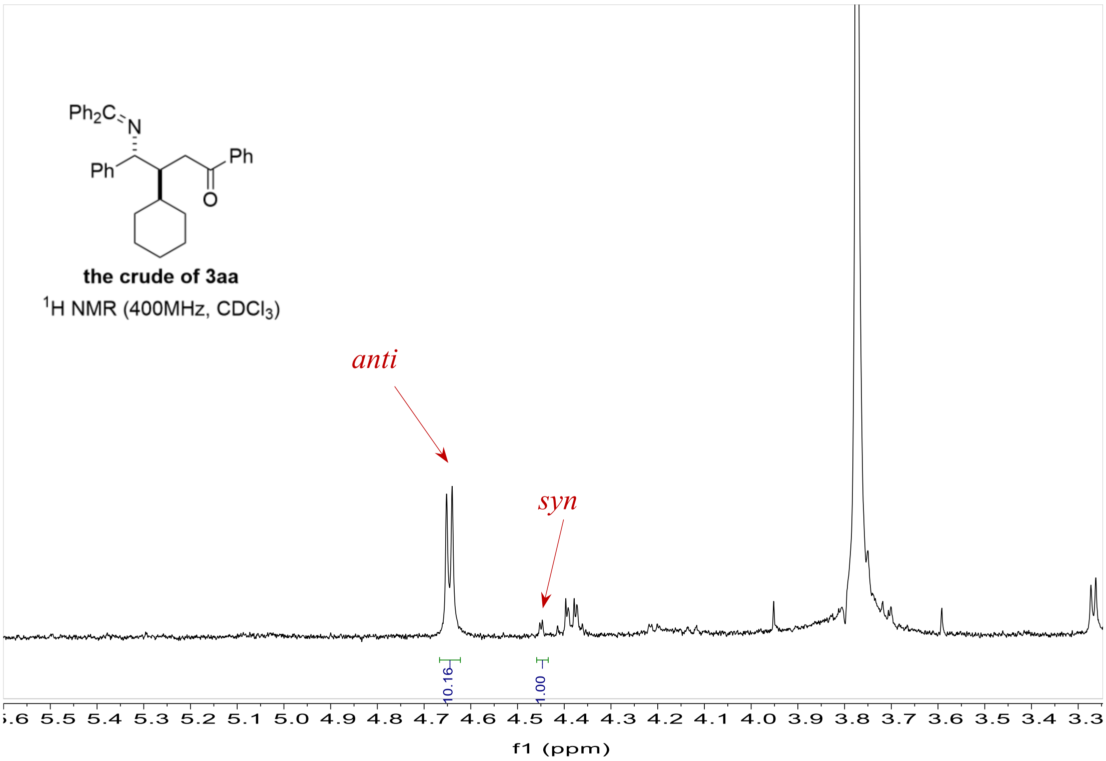


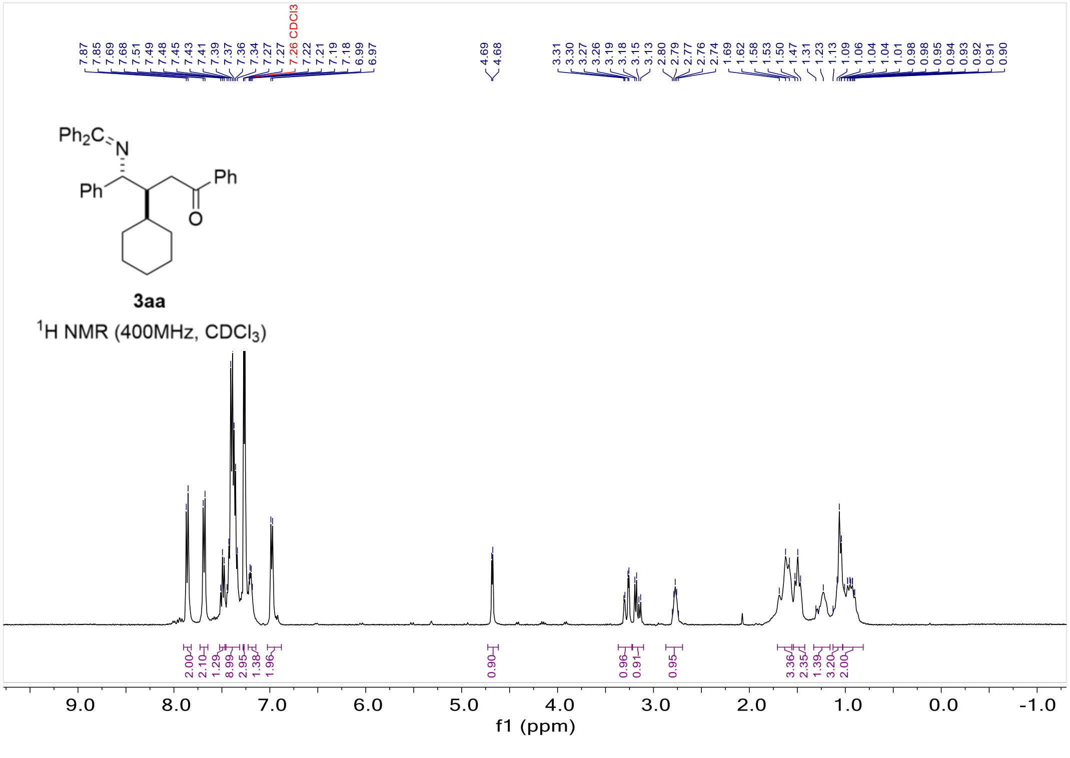
2s

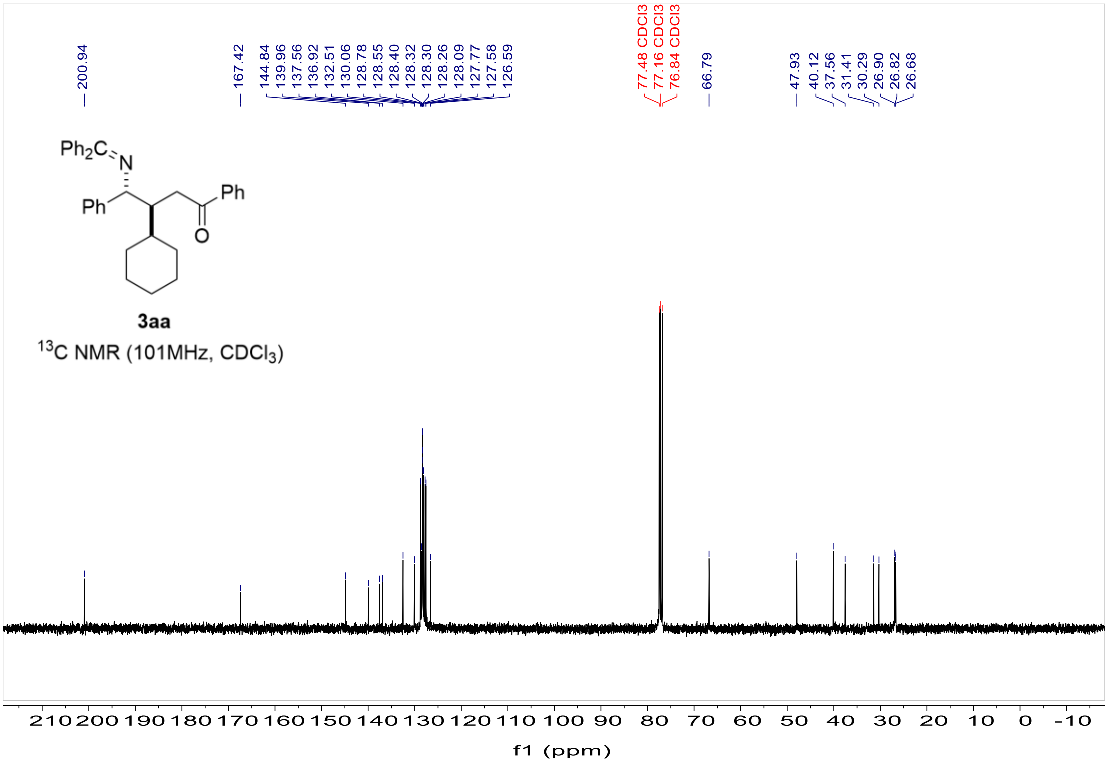
^{1}H NMR (400MHz, $CDCl_3$)


165.55
141.33
133.32
130.06
129.97
128.48
127.62
126.89
126.80
92.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.47
61.90
32.36
29.16
25.97
24.85
OBz
S
2s
^{13}C NMR (400MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph$_2$C
N
Ph
Ph
O
the crude of 3aa
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
10.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

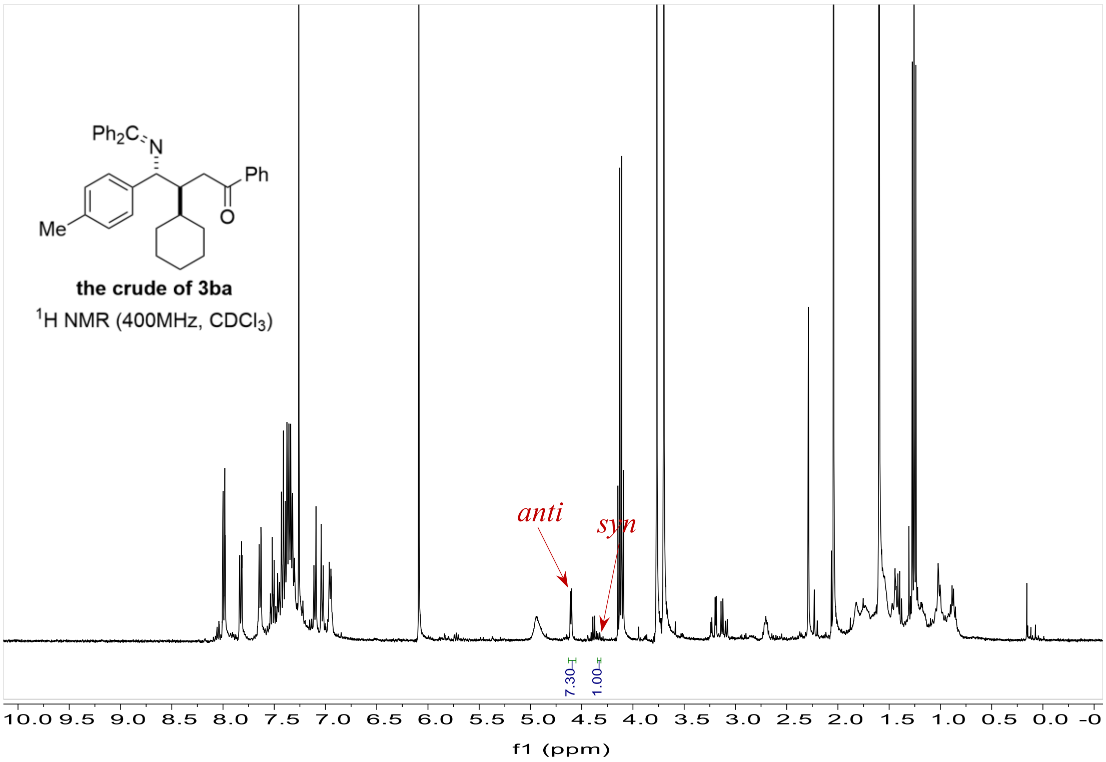

Ph2C
N
Ph
Ph
O
the crude of 3aa
1H NMR (400MHz, CDCl3)
anti
syn
10.16
1.00
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
f1 (ppm)


7.87
7.85
7.69
7.68
7.51
7.49
7.48
7.45
7.43
7.41
7.39
7.37
7.36
7.34
7.27
7.26 CDCl3
7.22
7.21
7.19
7.18
6.99
6.97
4.69
4.68
3.31
3.30
3.27
3.26
3.19
3.18
3.15
3.13
2.80
2.79
2.77
2.76
2.74
1.69
1.62
1.58
1.53
1.50
1.47
1.31
1.23
1.13
1.09
1.06
1.04
1.04
1.01
0.98
0.98
0.95
0.94
0.93
0.92
0.91
0.90
Ph2C
N
Ph
Ph
O
3aa
1H NMR (400MHz, CDCl3)
2.00
2.10
1.29
8.99
2.95
1.38
1.96
0.90
0.96
0.91
0.95
3.36
2.35
1.39
3.20
2.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)



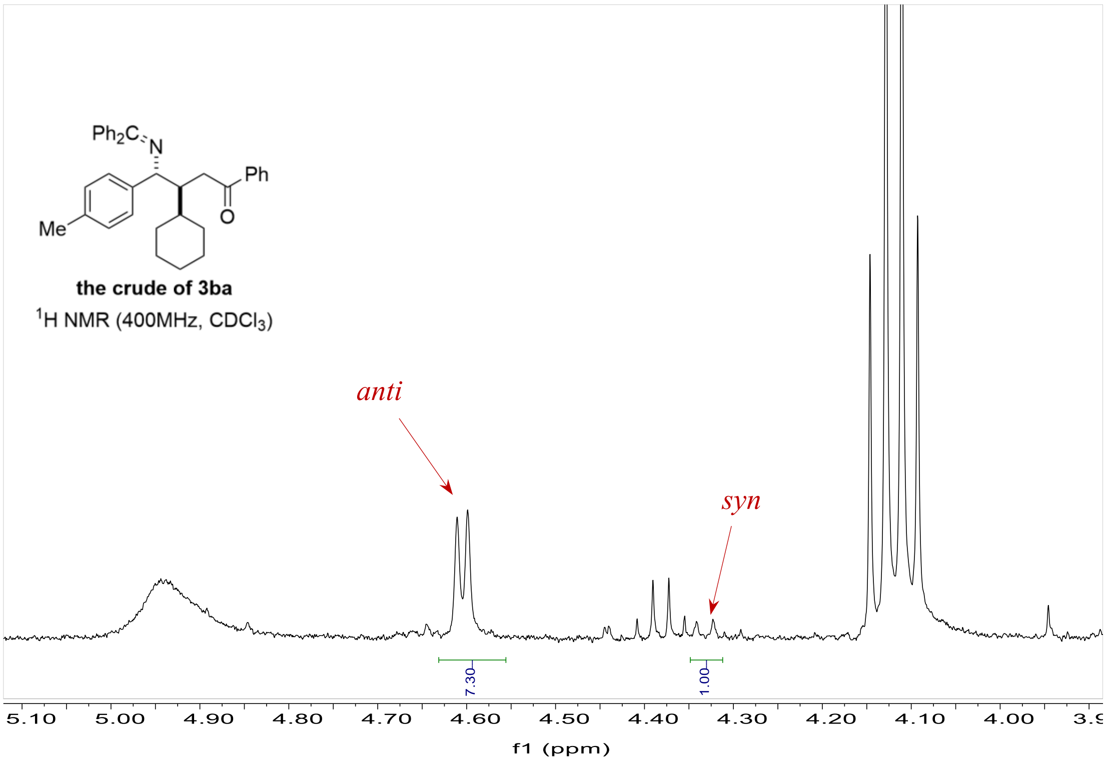
3aa

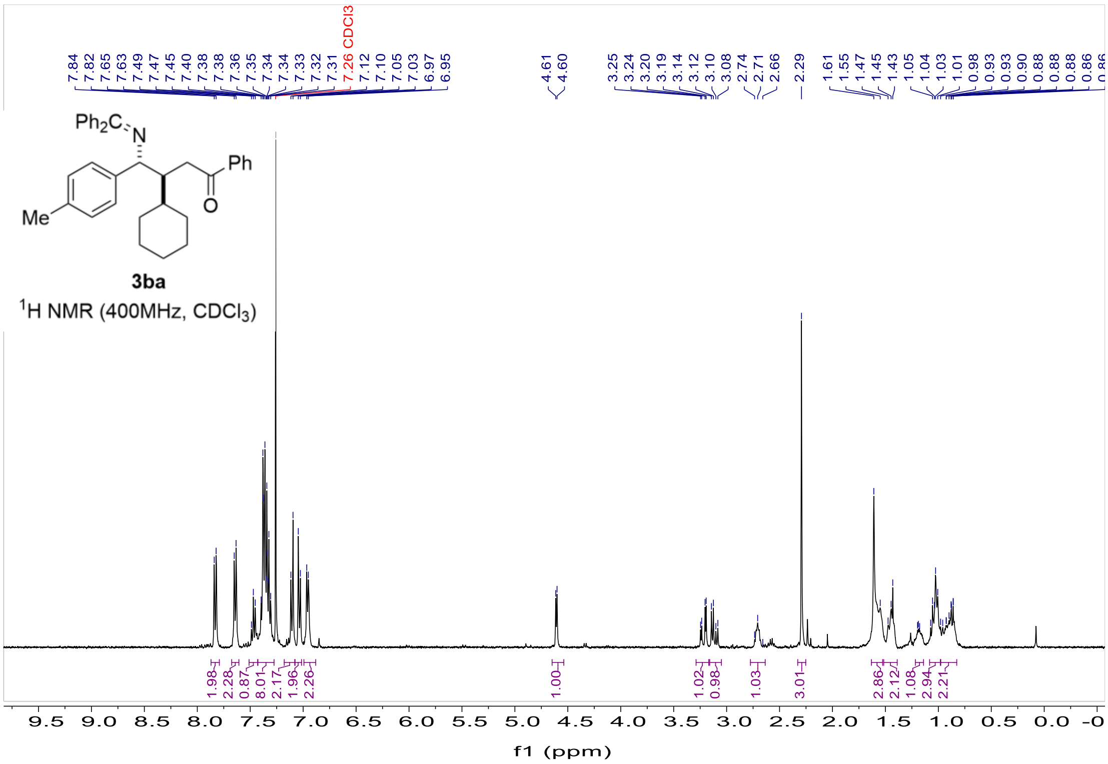
^{13}C NMR (101MHz, CDCl$_3$)

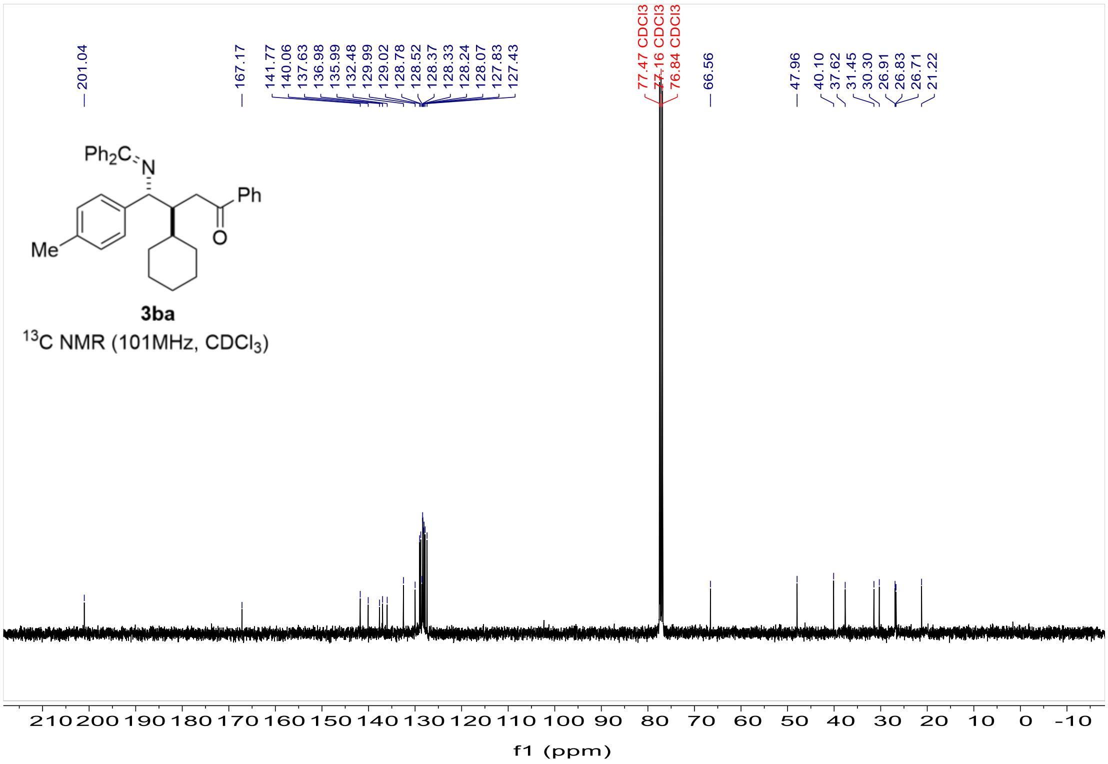


the crude of 3ba

^{1}H NMR (400MHz, CDCl$_3$)

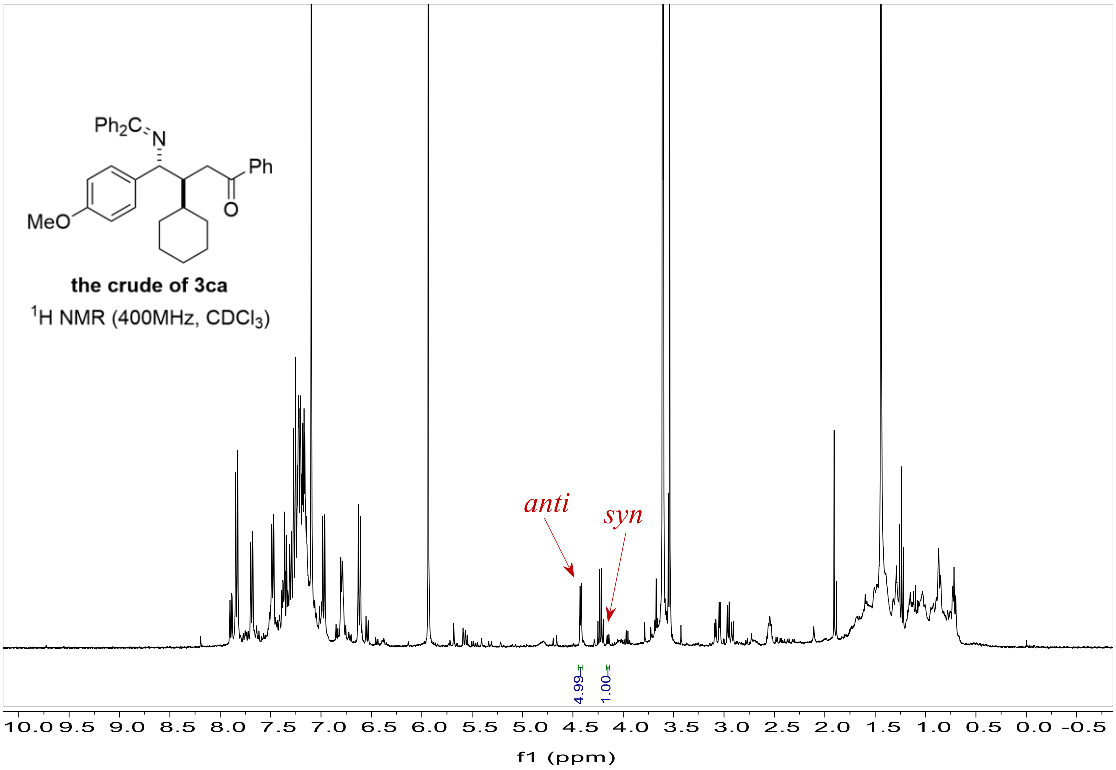

Ph2C
N
Ph
O
Me
the crude of 3ba
1H NMR (400MHz, CDCl3)
anti
syn
7.30
1.00
5.10
5.00
4.90
4.80
4.70
4.60
4.50
4.40
4.30
4.20
4.10
4.00
f1 (ppm)


7.84
7.82
7.65
7.63
7.49
7.47
7.45
7.40
7.38
7.38
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.26 CDCl3
7.12
7.10
7.05
7.03
6.97
6.95
4.61
4.60
3.25
3.24
3.20
3.19
3.14
3.12
3.10
3.08
2.74
2.71
2.66
2.29
1.61
1.55
1.47
1.45
1.43
1.05
1.04
1.03
1.01
0.98
0.93
0.93
0.90
0.88
0.88
0.86
Ph2C
N
Ph
O
Me
3ba
1H NMR (400MHz, CDCl3)
1.98
2.28
0.87
8.01
2.17
1.96
2.26
1.00
1.02
0.98
1.03
3.01
2.86
2.12
1.08
2.94
2.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



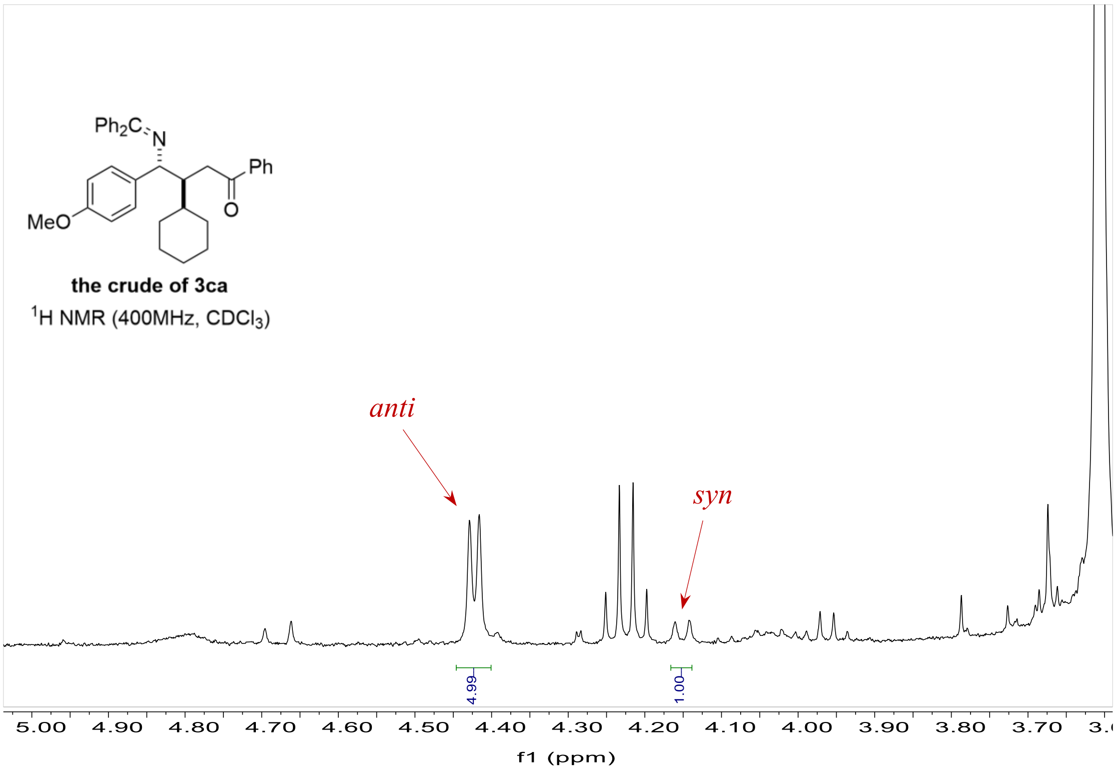
3ba

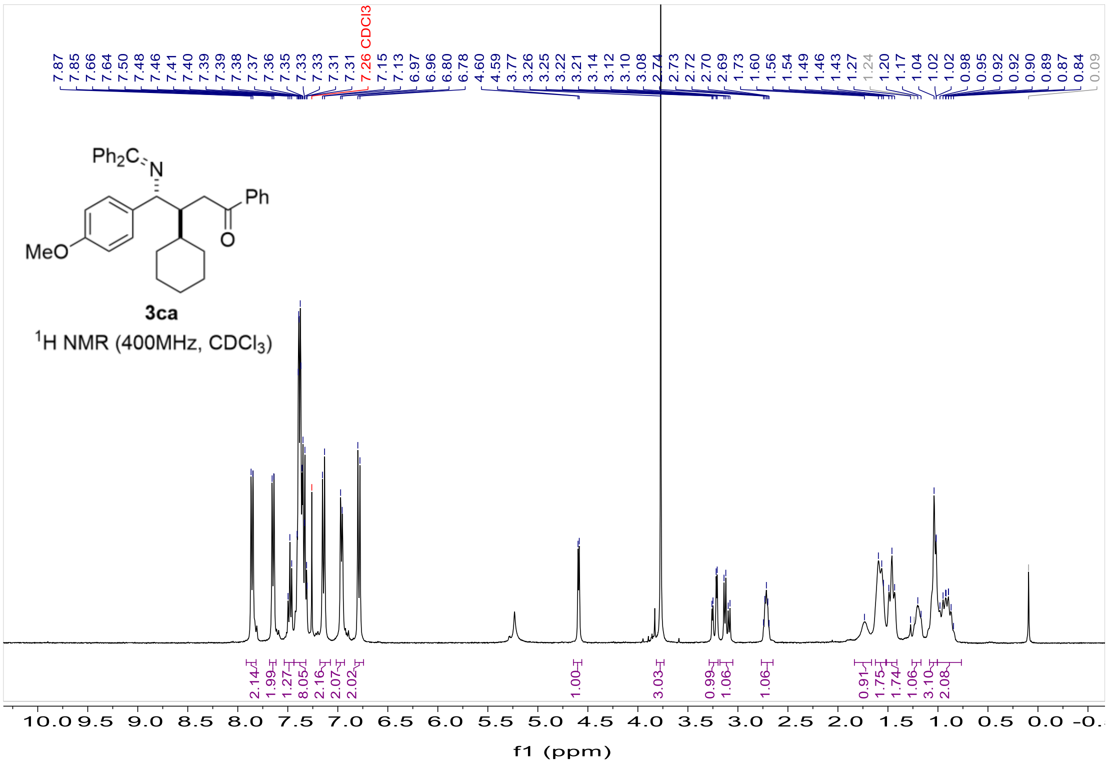
^{13}C NMR (101MHz, CDCl$_3$)

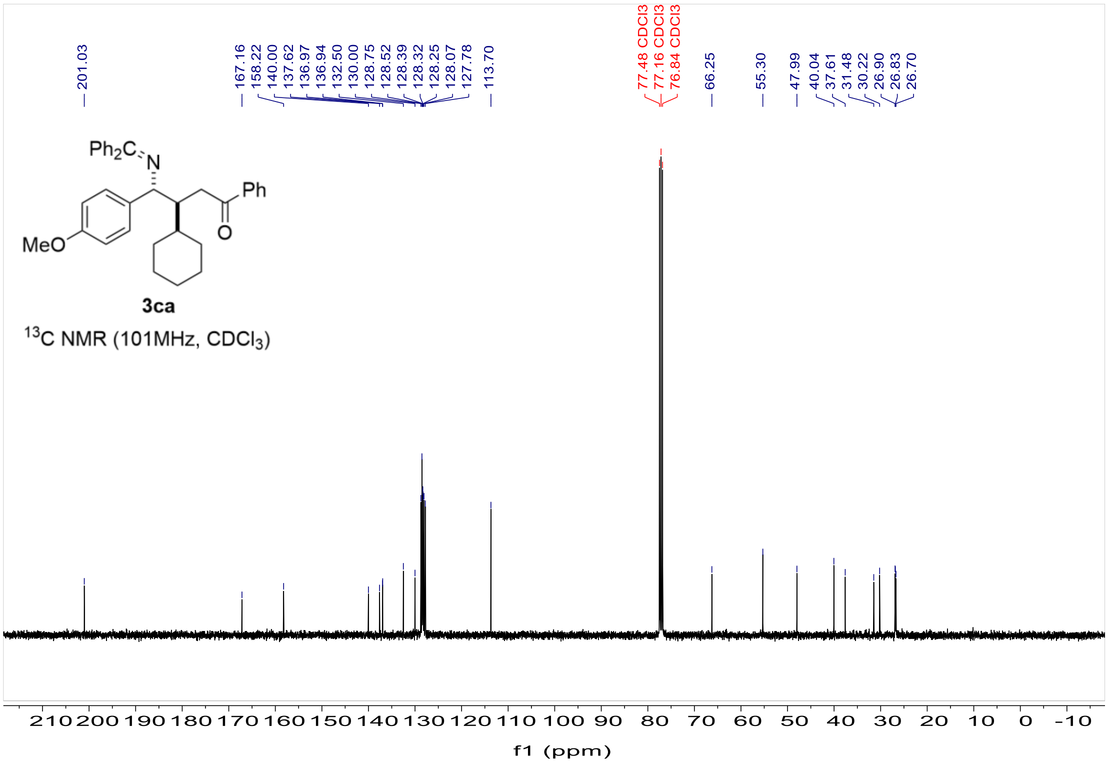


the crude of 3ca

^{1}H NMR (400MHz, CDCl$_3$)

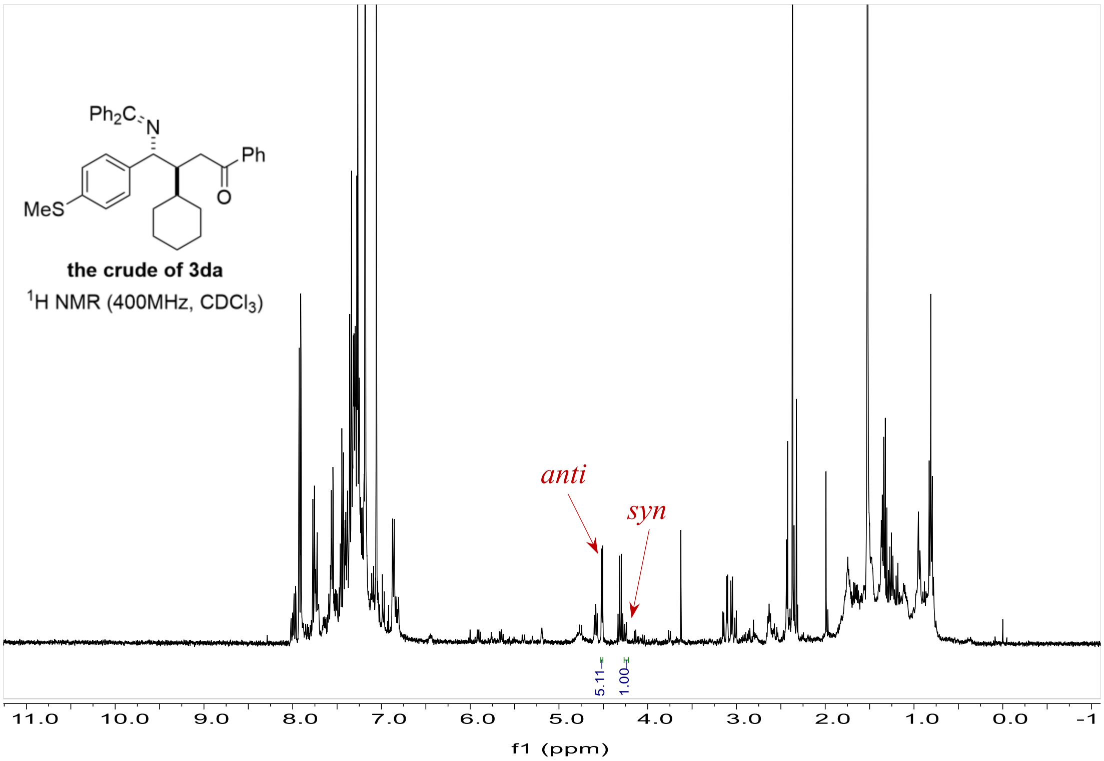

Ph2C N Ph MeO O
the crude of 3ca
1H NMR (400MHz, CDCl3)
anti
syn
4.99
1.00
5.00 4.90 4.80 4.70 4.60 4.50 4.40 4.30 4.20 4.10 4.00 3.90 3.80 3.70 3.
f1 (ppm)


7.87 7.85 7.66 7.64 7.50 7.48 7.46 7.41 7.40 7.39 7.39 7.38 7.37 7.36 7.35 7.33 7.33 7.31 7.26 CDCl3 7.15 7.13 6.97 6.96 6.80 6.78 4.60 4.59 3.77 3.26 3.25 3.22 3.21 3.14 3.12 3.10 3.08 2.74 2.73 2.72 2.70 2.69 1.73 1.60 1.56 1.54 1.49 1.46 1.43 1.27 1.24 1.20 1.17 1.04 1.02 0.98 0.95 0.92 0.90 0.89 0.87 0.84 0.09
Ph2C N Ph MeO O
3ca
1H NMR (400MHz, CDCl3)
2.14 1.99 1.27 8.05 2.16 2.07 2.02 1.00 3.03 0.99 1.06 1.06 0.91 1.75 1.74 1.06 3.10 2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



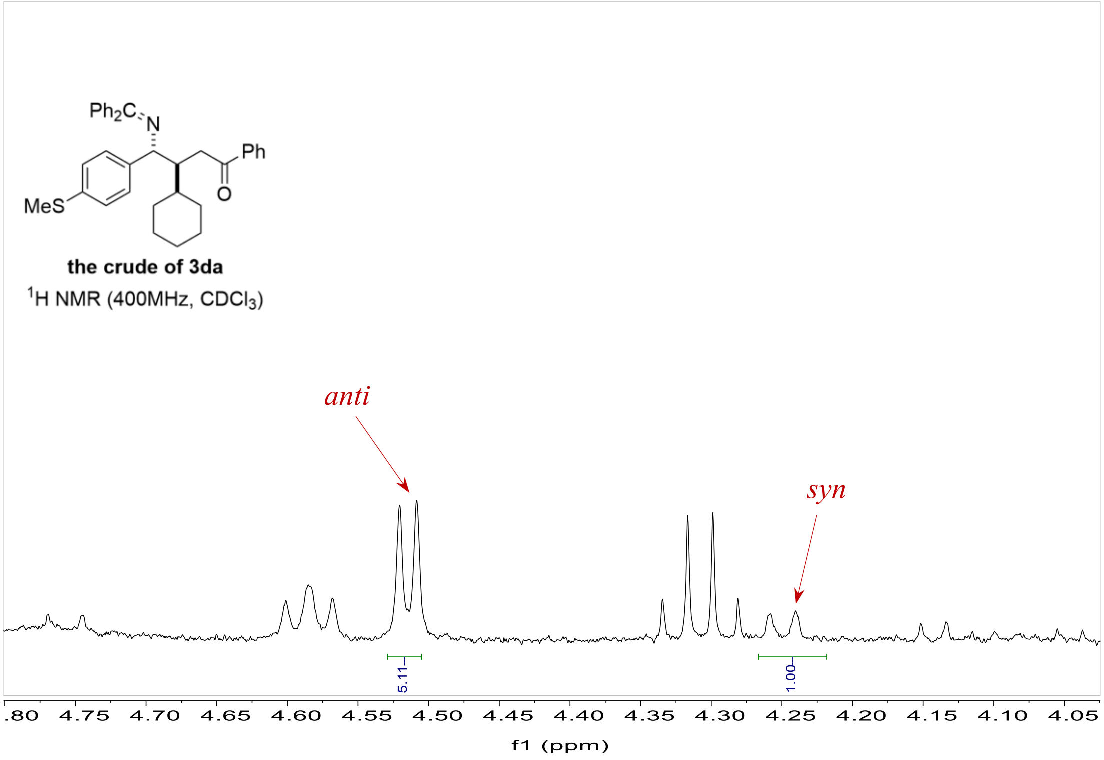
3ca

^{13}C NMR (101MHz, CDCl$_3$)



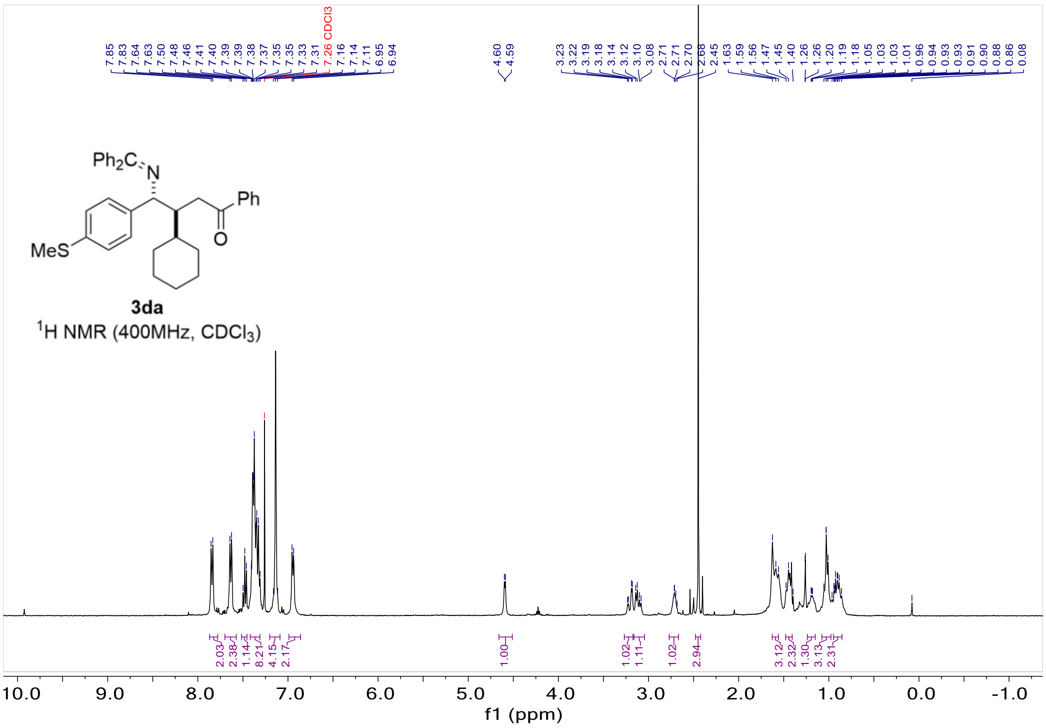
the crude of 3da

^{1}H NMR (400MHz, CDCl$_3$)



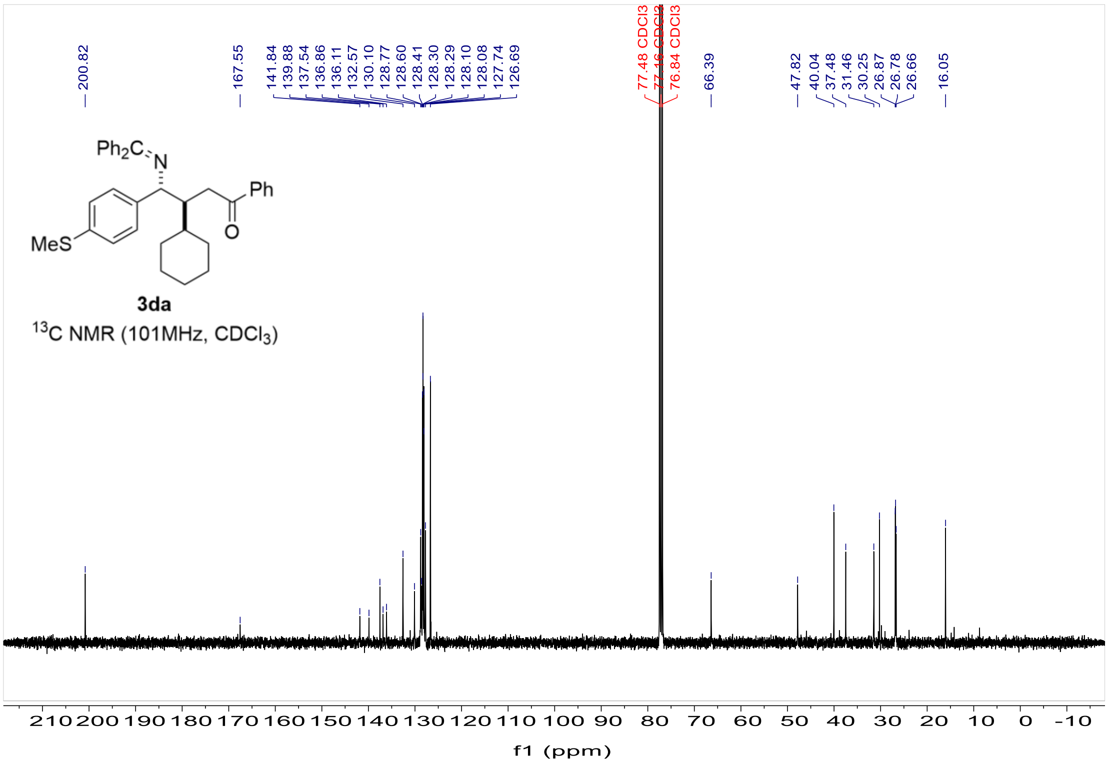
the crude of 3da

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



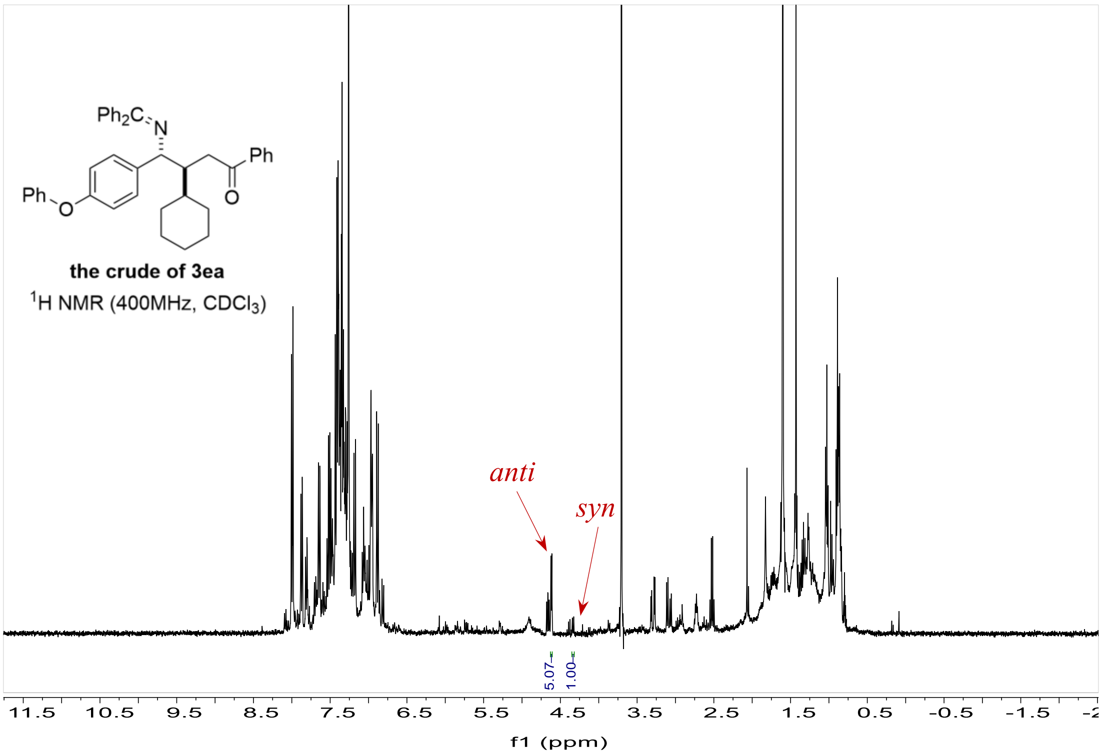
3da

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



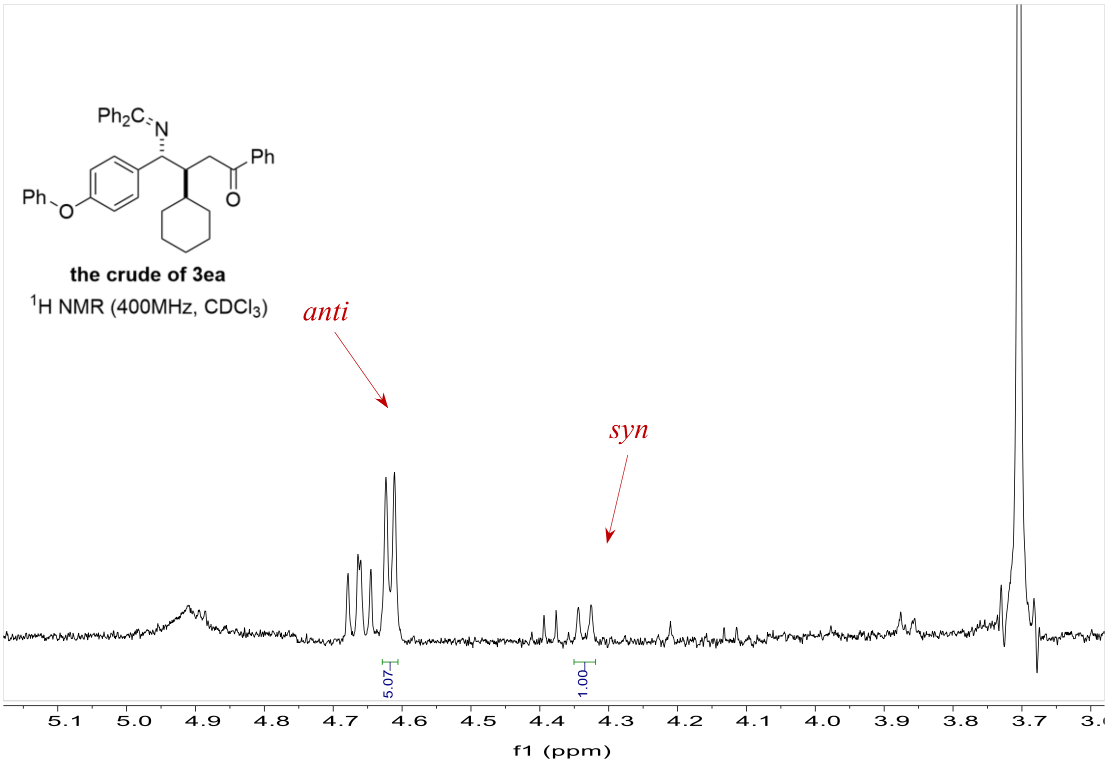
3da

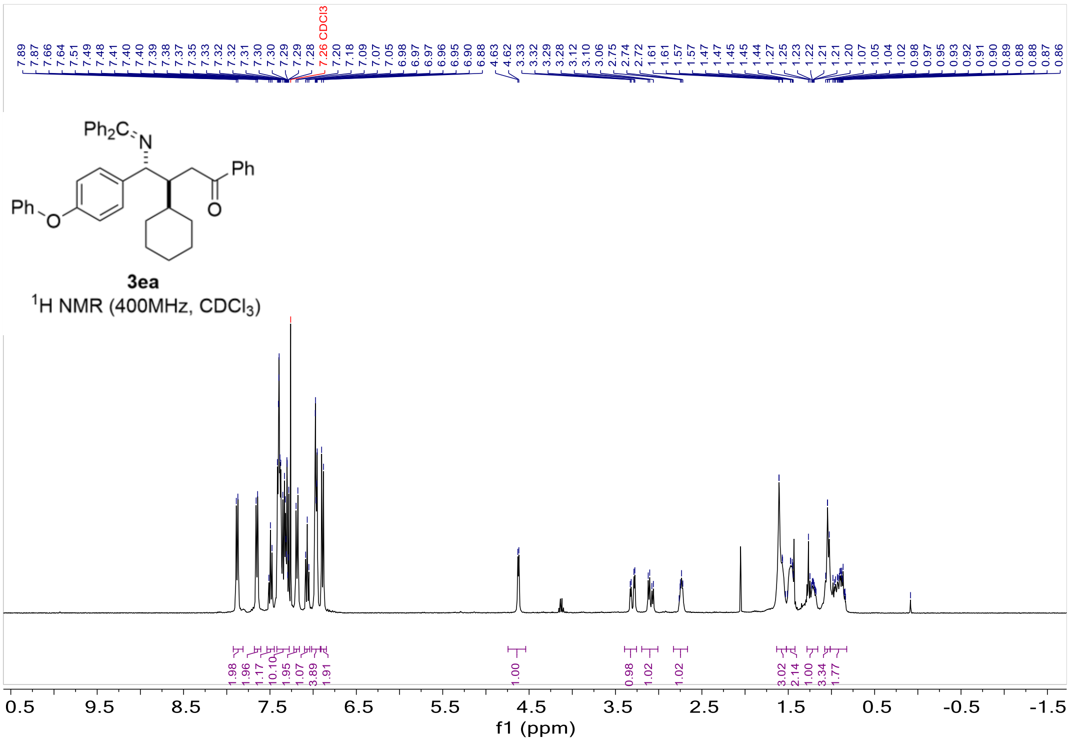
^{13}C NMR (101MHz, CDCl$_3$)

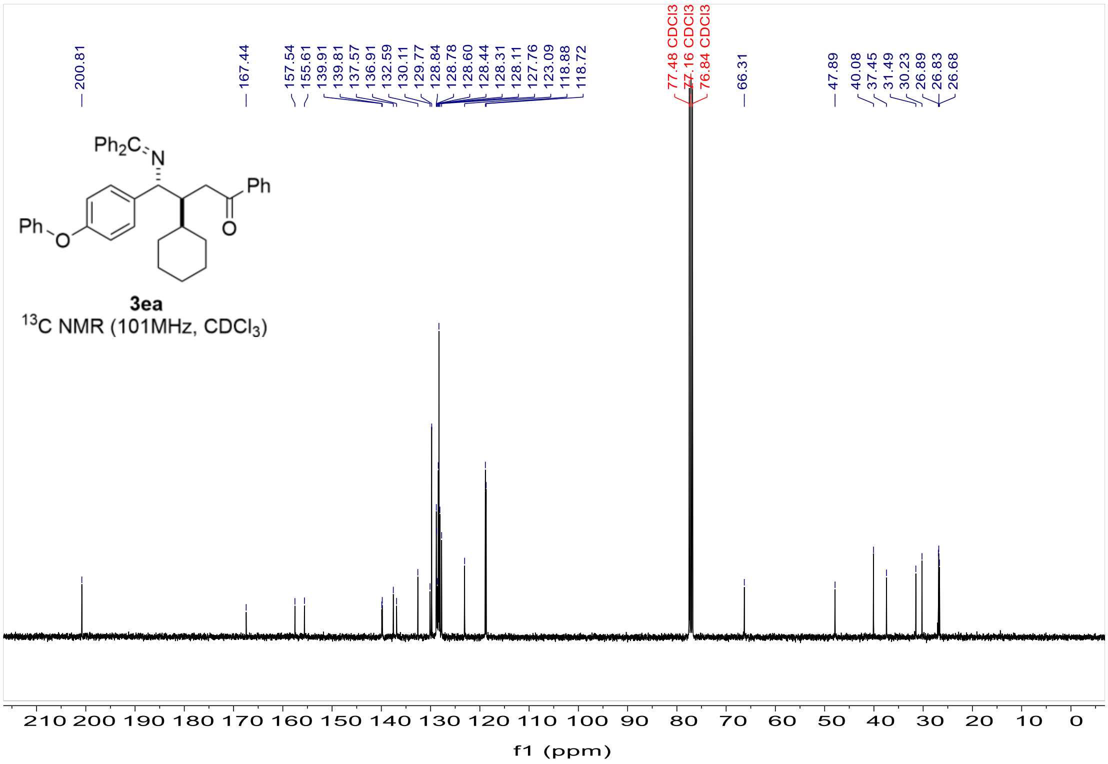


the crude of 3ea

^{1}H NMR (400MHz, CDCl$_3$)

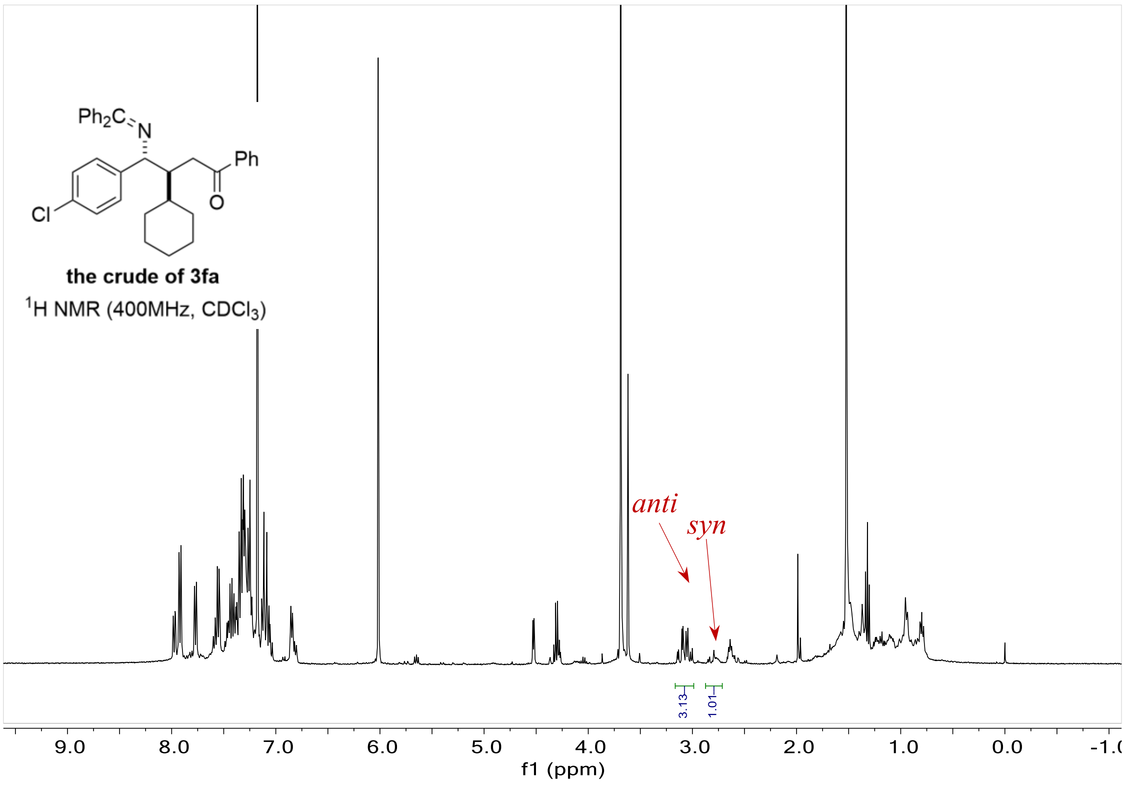

Ph2C=N
Ph
O
Ph
O
the crude of 3ea
1H NMR (400MHz, CDCl3)
anti
syn
5.07
1.00
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
f1 (ppm)


7.89
7.87
7.66
7.64
7.51
7.49
7.48
7.41
7.40
7.40
7.39
7.38
7.37
7.35
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.26 CDCl3
7.20
7.18
7.09
7.07
7.05
6.98
6.97
6.97
6.96
6.95
6.90
6.88
4.63
4.62
3.33
3.32
3.29
3.28
3.12
3.10
3.06
2.75
2.74
2.72
1.61
1.61
1.57
1.57
1.47
1.47
1.45
1.45
1.44
1.27
1.25
1.23
1.22
1.21
1.21
1.20
1.07
1.05
1.04
1.02
0.98
0.97
0.95
0.93
0.92
0.91
0.90
0.89
0.88
0.88
0.87
0.86
Ph2C=N
Ph
O
Ph
O
3ea
1H NMR (400MHz, CDCl3)
1.98
1.96
1.17
10.10
1.95
1.07
3.89
1.91
1.00
0.98
1.02
1.02
3.02
2.14
1.00
3.34
1.77
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)



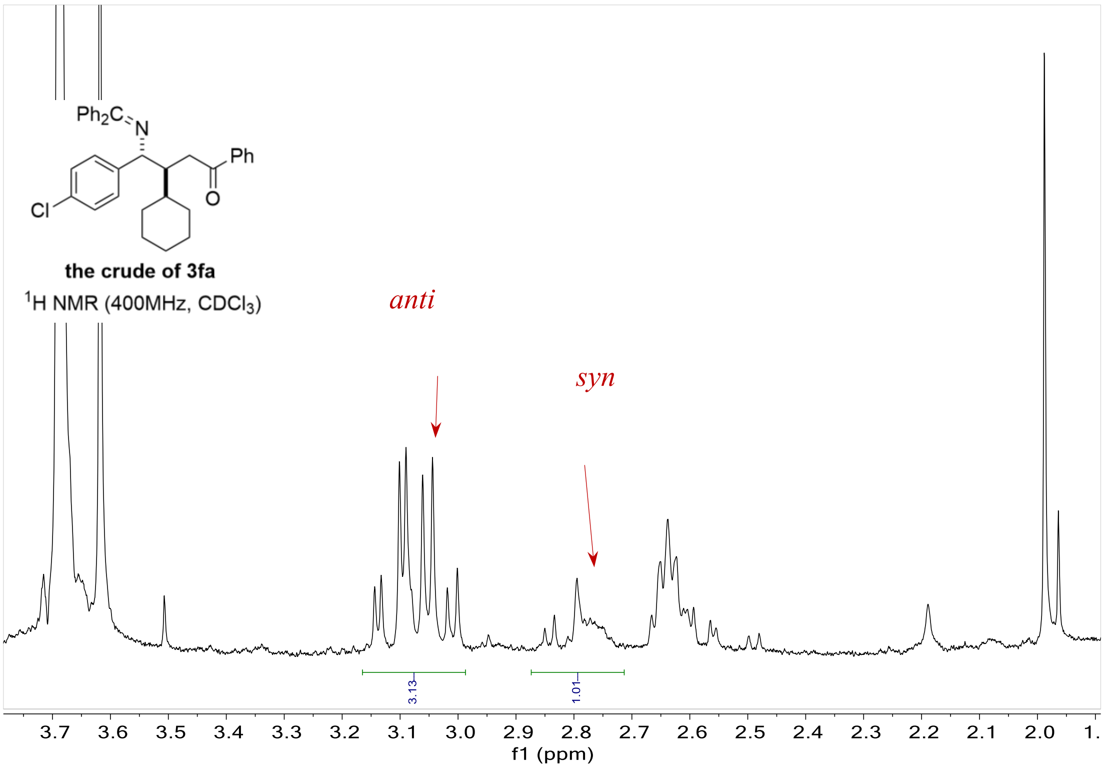
3ea

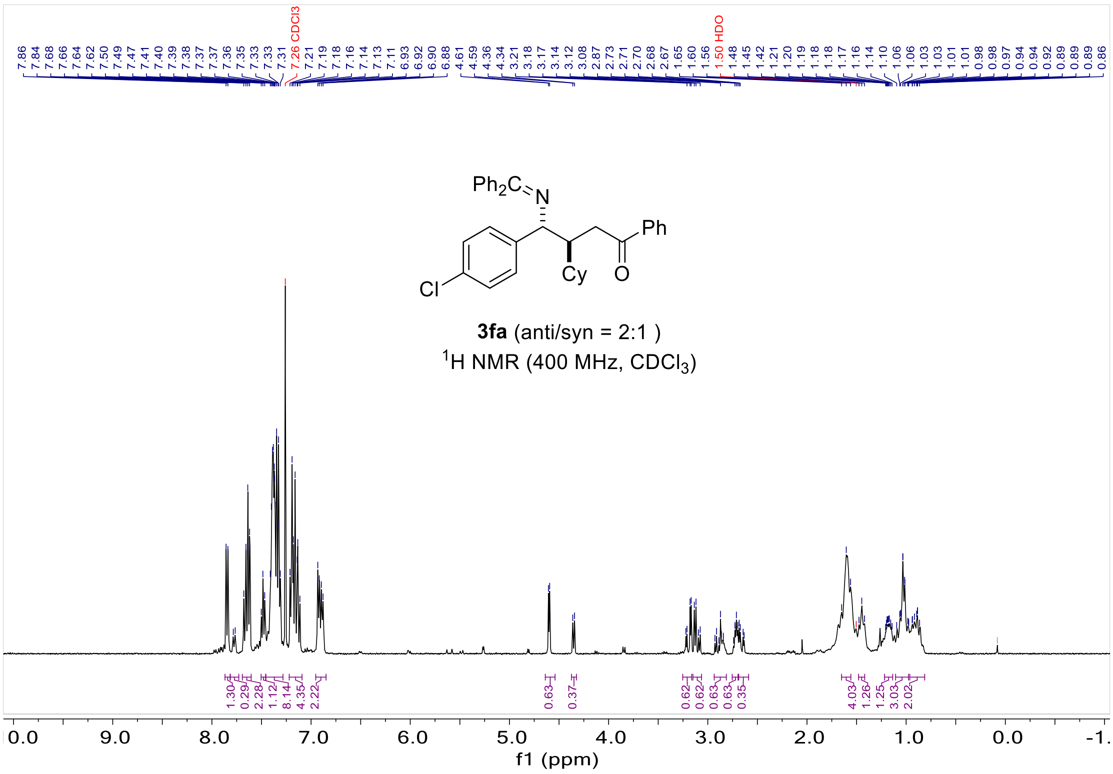
^{13}C NMR (101MHz, CDCl$_3$)

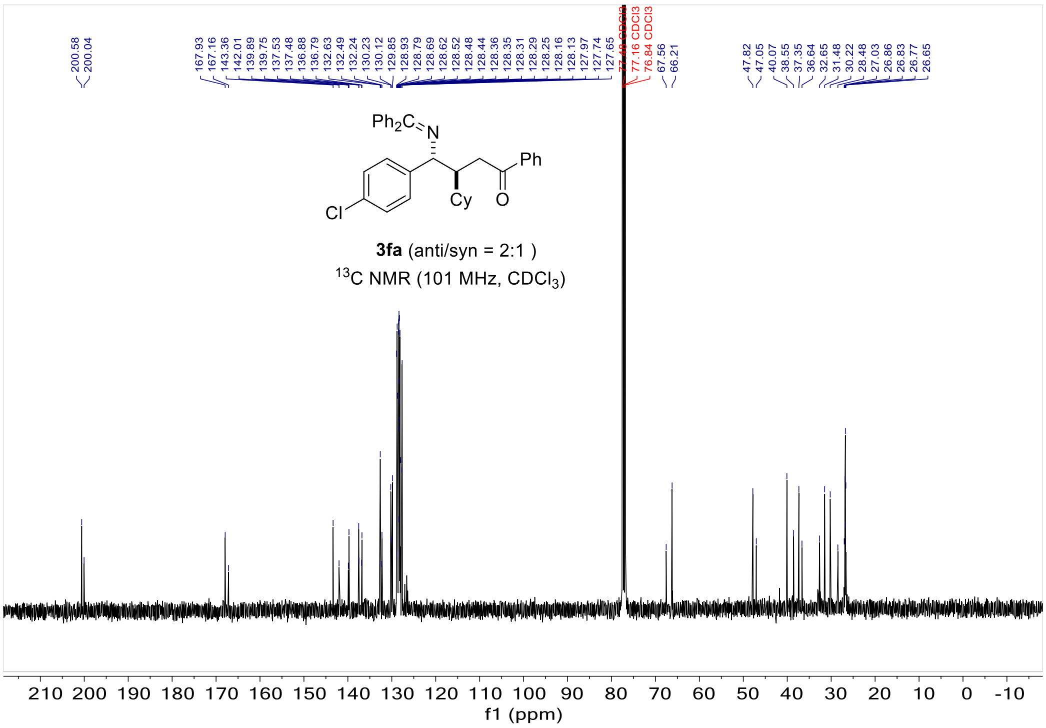


the crude of 3fa

^{1}H NMR (400MHz, CDCl$_3$)

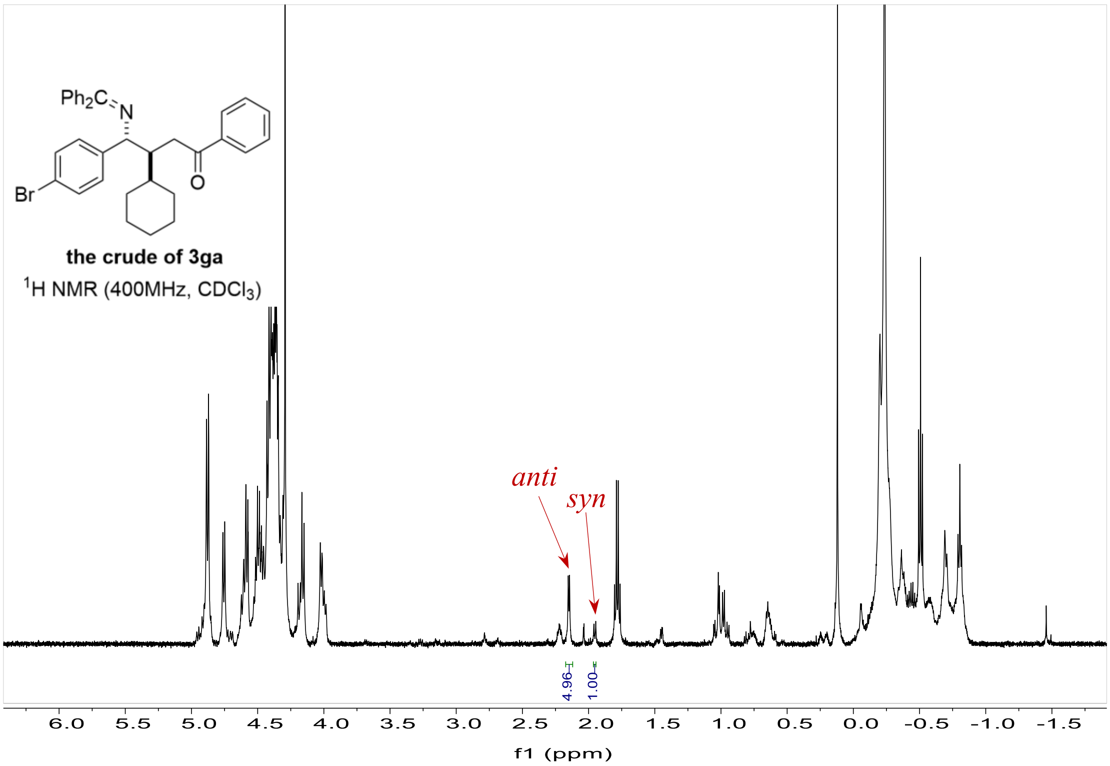

Ph$_2$C=N
Ph
Cl
O
the crude of 3fa
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
3.13
1.01
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.
f1 (ppm)


7.86
7.84
7.68
7.66
7.64
7.62
7.50
7.49
7.47
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.33
7.31
7.26 CDCl3
7.21
7.19
7.18
7.16
7.14
7.13
7.11
6.93
6.92
6.90
6.88
4.61
4.59
4.36
4.34
3.21
3.18
3.17
3.14
3.12
3.08
2.87
2.73
2.71
2.70
2.68
2.67
1.65
1.60
1.56
1.50 HDO
1.48
1.45
1.42
1.21
1.20
1.19
1.18
1.17
1.16
1.14
1.10
1.06
1.06
1.03
1.03
1.01
1.01
0.98
0.97
0.94
0.92
0.92
0.89
0.89
0.89
0.86
Ph$_2$C=N
Ph
Cl
Cy
O
3fa (anti/syn = 2:1)
^{1}H NMR (400 MHz, CDCl$_3$)
1.30
0.29
2.28
1.12
8.14
4.35
2.22
0.63
0.37
0.62
0.62
0.63
0.63
0.35
4.03
1.26
1.25
3.03
2.02
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.
f1 (ppm)



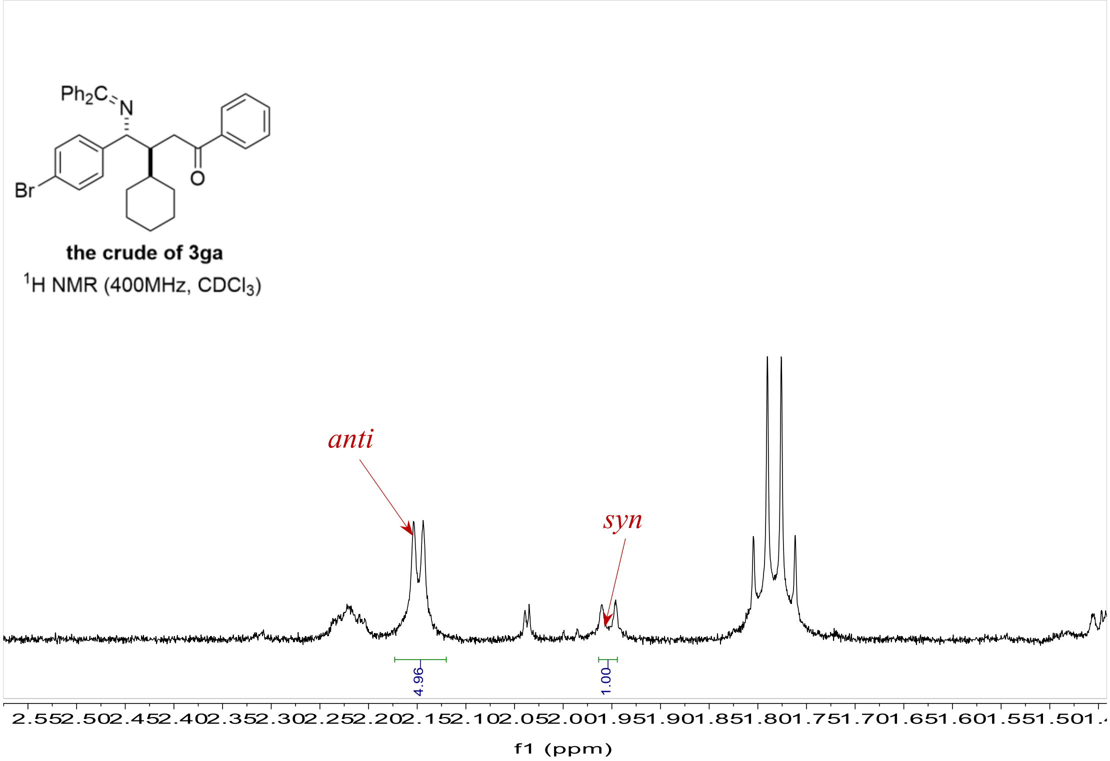
3fa (anti/syn = 2:1)

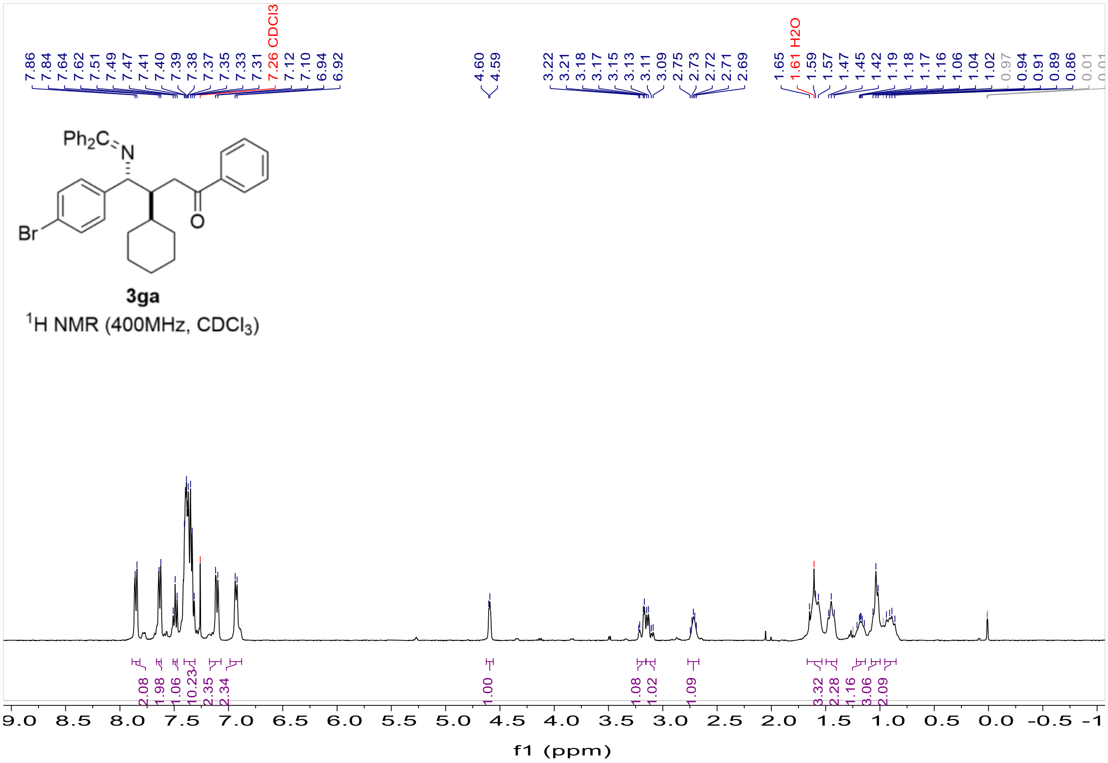
^{13}C NMR (101 MHz, CDCl$_3$)

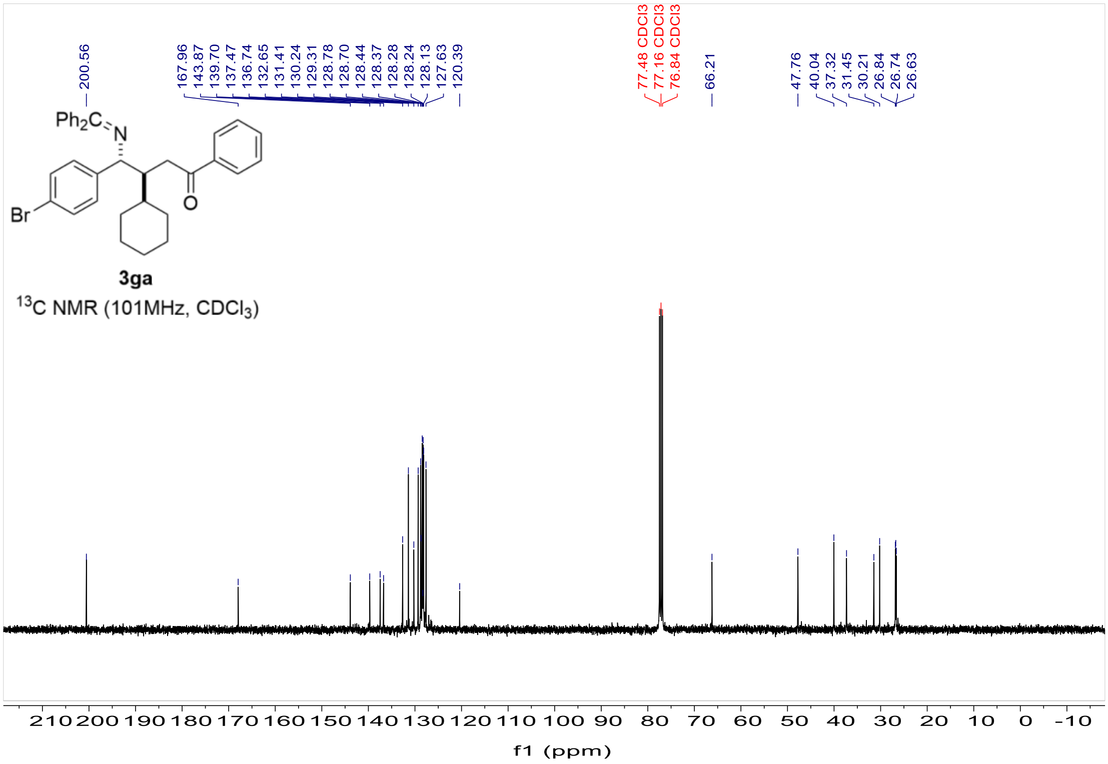


the crude of 3ga

^{1}H NMR (400MHz, CDCl$_3$)

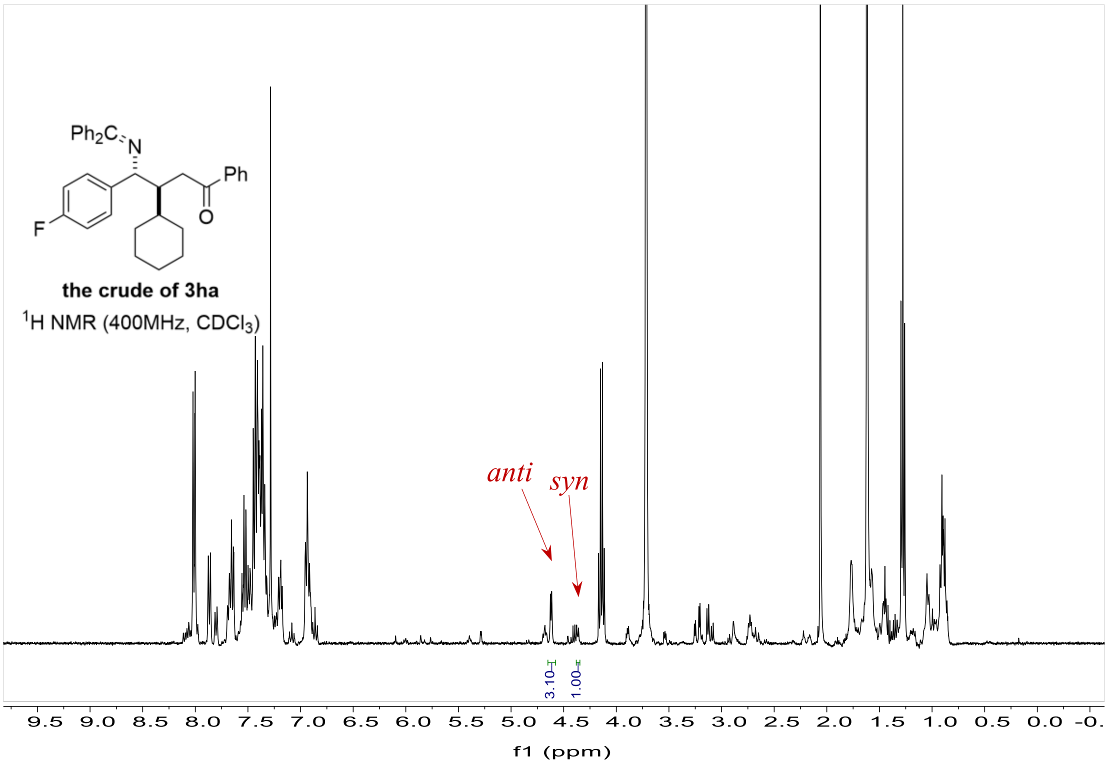

Ph2C=N
Br
O
the crude of 3ga
1H NMR (400MHz, CDCl3)
anti
syn
4.96
1.00
2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50
f1 (ppm)


7.86 7.84 7.62 7.51 7.49 7.47 7.41 7.40 7.39 7.38 7.37 7.35 7.33 7.31 7.26 CDCl3 7.12 7.10 6.94 6.92
4.60 4.59
3.22 3.21 3.18 3.17 3.15 3.13 3.11 3.09 2.75 2.73 2.72 2.71 2.69
1.65 1.61 H2O 1.59 1.57 1.47 1.45 1.42 1.19 1.18 1.17 1.16 1.06 1.04 1.02 0.97 0.94 0.91 0.89 0.86 0.01 0.01
Ph2C=N
Br
O
3ga
1H NMR (400MHz, CDCl3)
2.08 1.98 1.06 10.23 2.35 2.34
1.00
1.08 1.02
1.09
3.32 2.28 1.16 3.06 2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



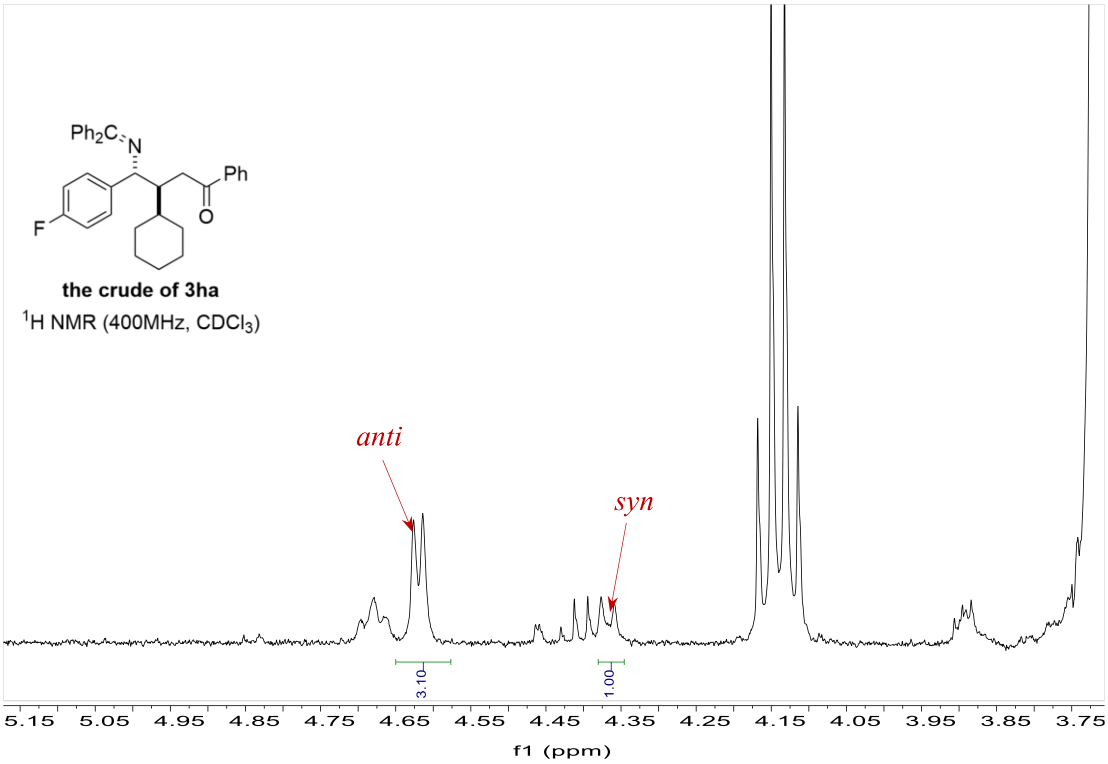
3ga

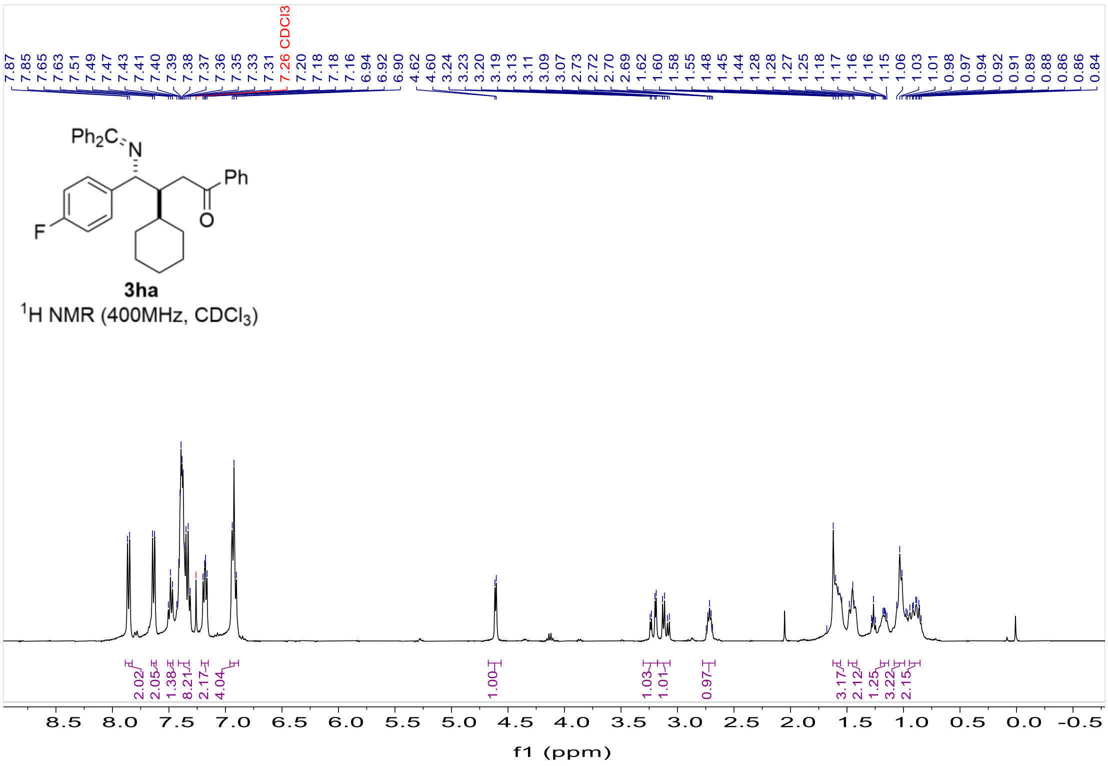
^{13}C NMR (101MHz, CDCl$_3$)

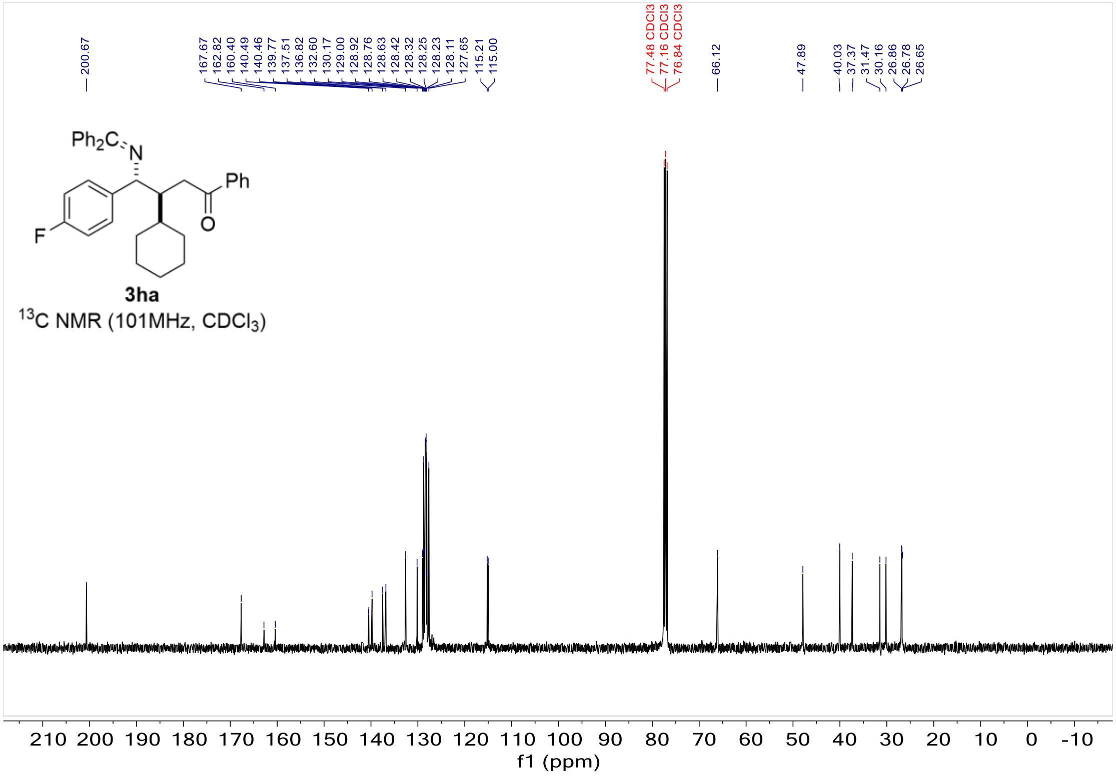


the crude of 3ha

^{1}H NMR (400MHz, CDCl$_3$)

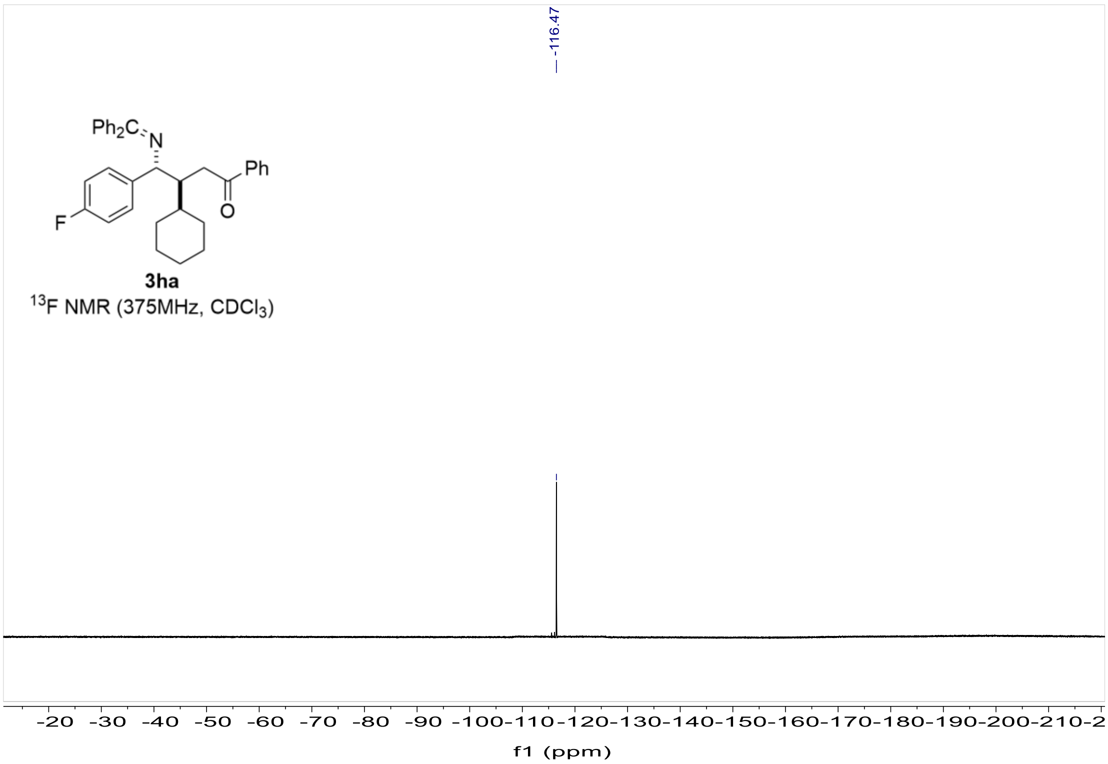

Ph2C
N
Ph
F
O
the crude of 3ha
1H NMR (400MHz, CDCl3)
anti
syn
3.10
1.00
5.15
5.05
4.95
4.85
4.75
4.65
4.55
4.45
4.35
4.25
4.15
4.05
3.95
3.85
3.75
f1 (ppm)


7.87
7.85
7.65
7.63
7.51
7.49
7.47
7.43
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.33
7.31
7.26 CDCl3
7.20
7.18
7.16
6.94
6.92
6.90
4.62
4.60
3.24
3.23
3.20
3.19
3.13
3.11
3.09
3.07
2.73
2.72
2.70
2.69
1.62
1.60
1.58
1.55
1.48
1.45
1.44
1.28
1.28
1.27
1.25
1.18
1.17
1.16
1.15
1.06
1.03
1.01
0.98
0.97
0.94
0.92
0.91
0.89
0.88
0.86
0.86
0.84
Ph2C
N
Ph
F
O
3ha
1H NMR (400MHz, CDCl3)
2.02
2.05
1.38
8.21
2.17
4.04
1.00
1.03
1.01
0.97
3.17
2.12
1.25
3.22
2.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



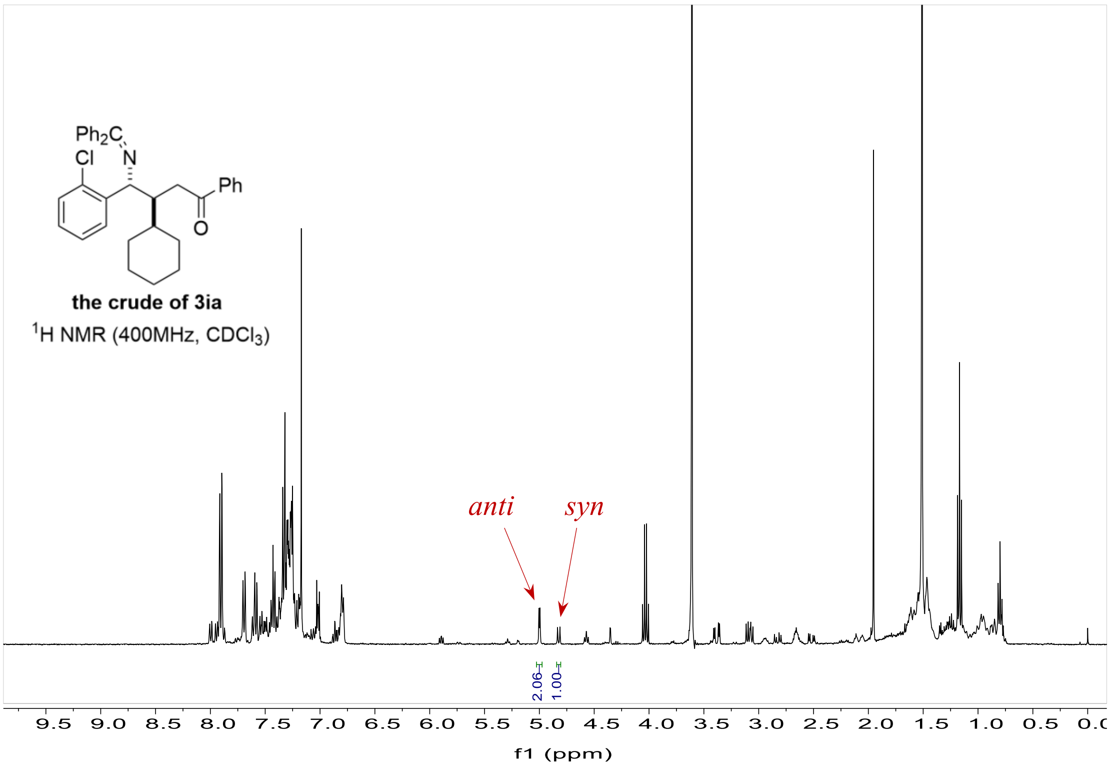
3ha

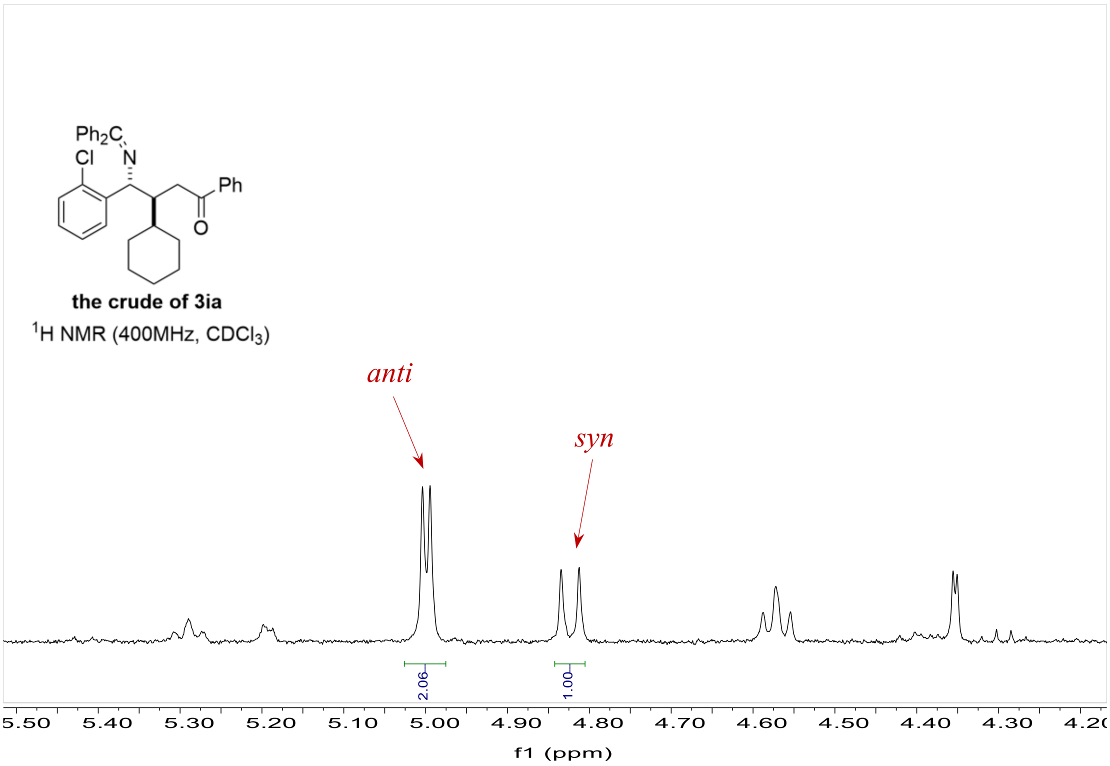
^{13}C NMR (101MHz, CDCl$_3$)

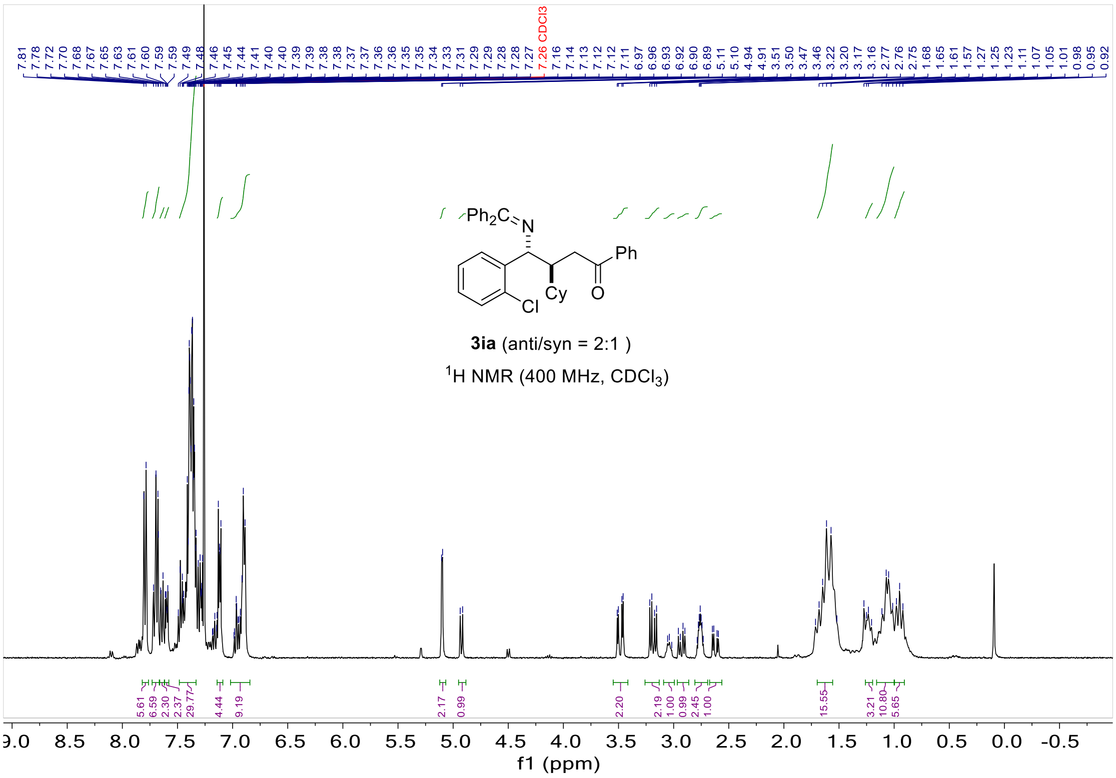


3ha

^{13}F NMR (375MHz, CDCl$_3$)

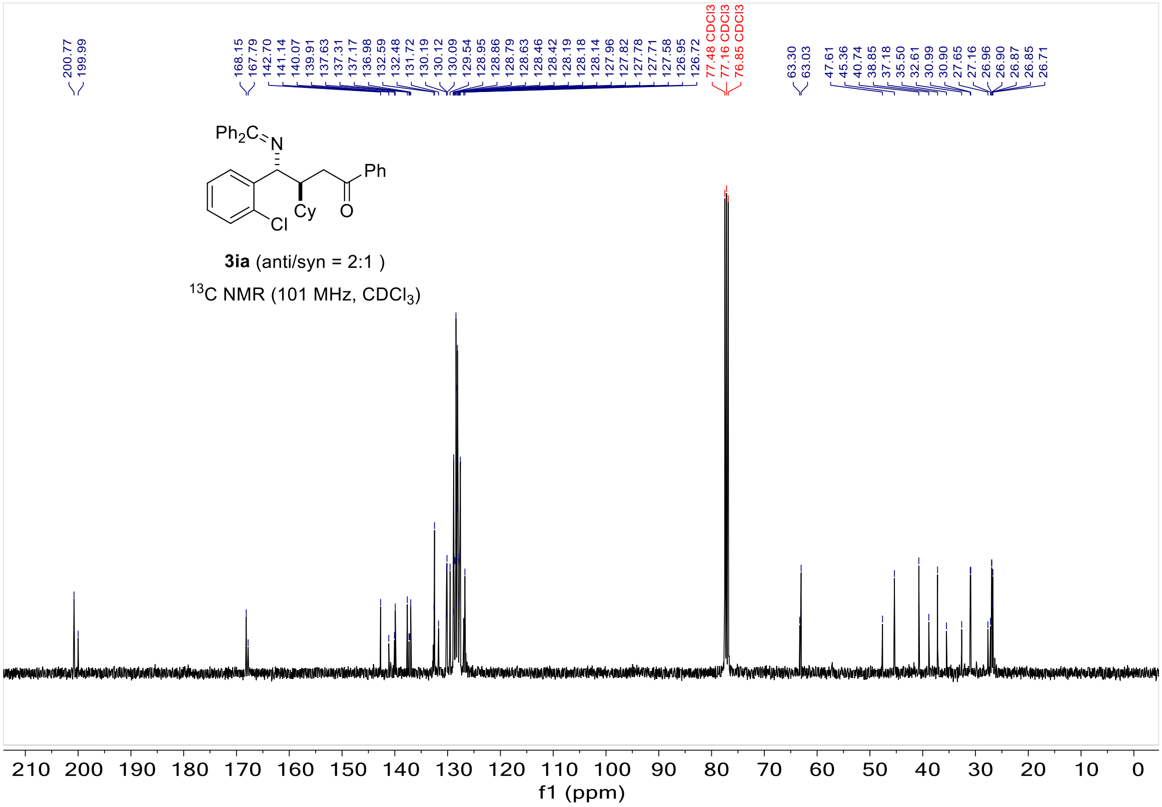

Ph$_2$C
N
Cl
Ph
O
the crude of 3ia
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.06
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph$_2$C
N
Cl
Ph
O
the crude of 3ia
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.06
1.00
5.50 5.40 5.30 5.20 5.10 5.00 4.90 4.80 4.70 4.60 4.50 4.40 4.30 4.20
f1 (ppm)



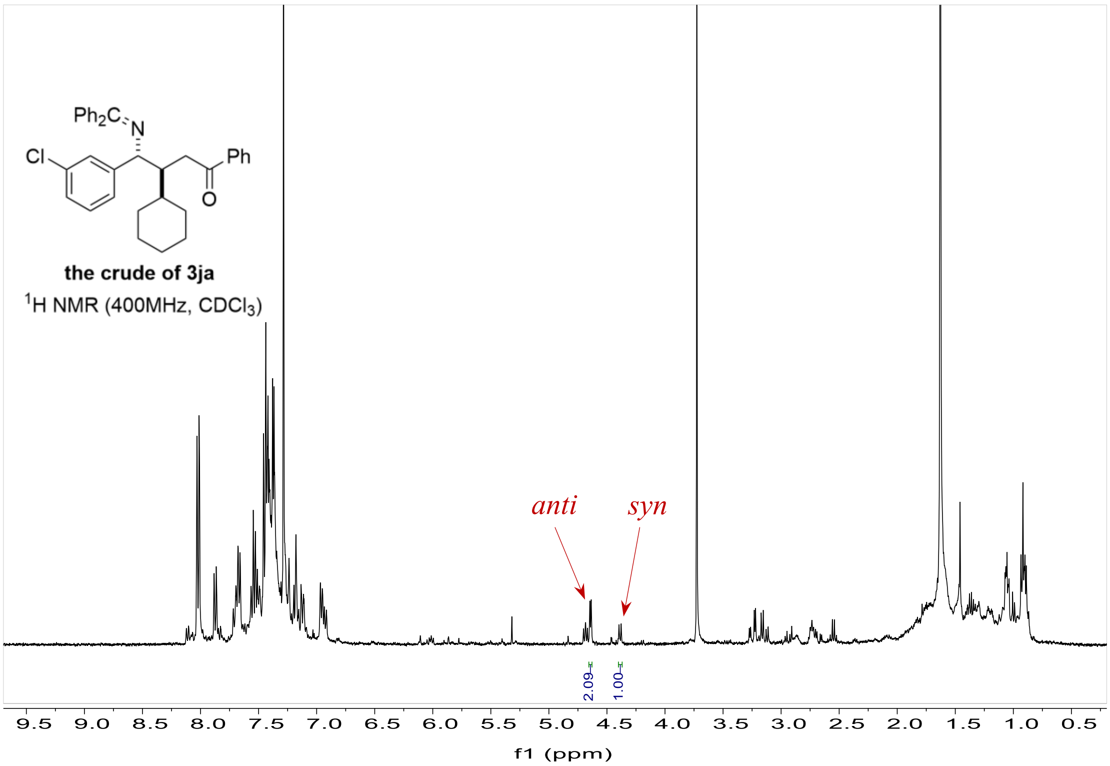
3ia (anti/syn = 2:1)

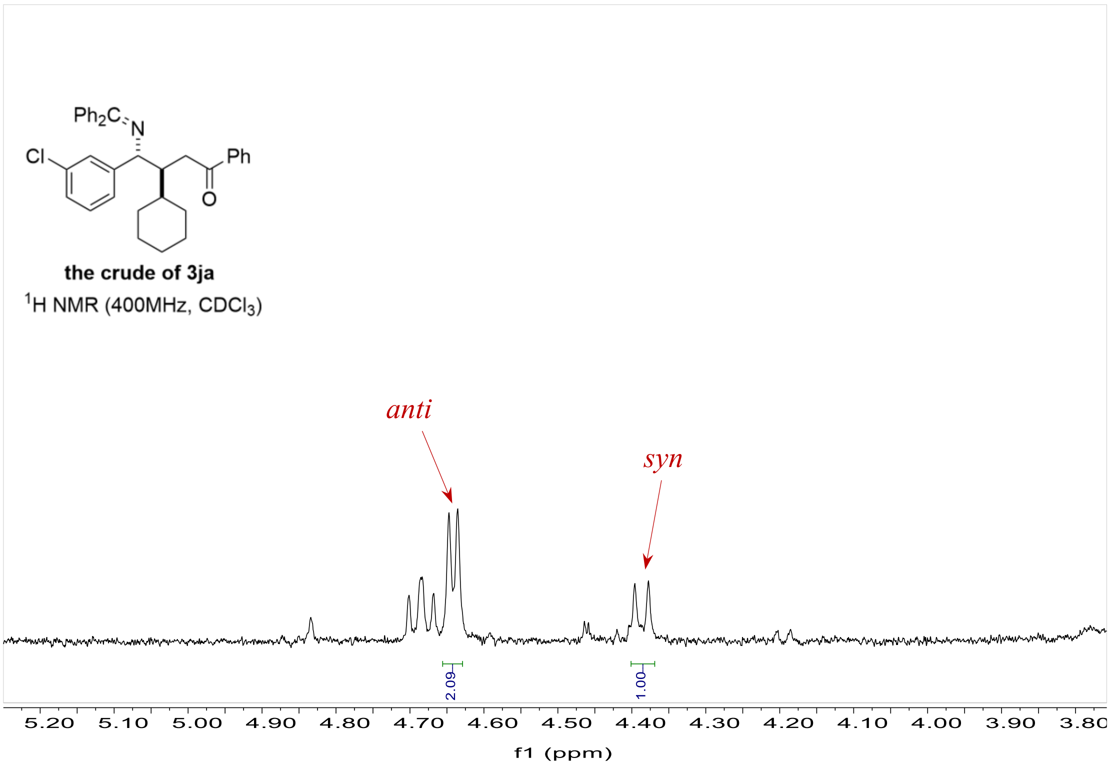
^{1}H NMR (400 MHz, CDCl$_3$)

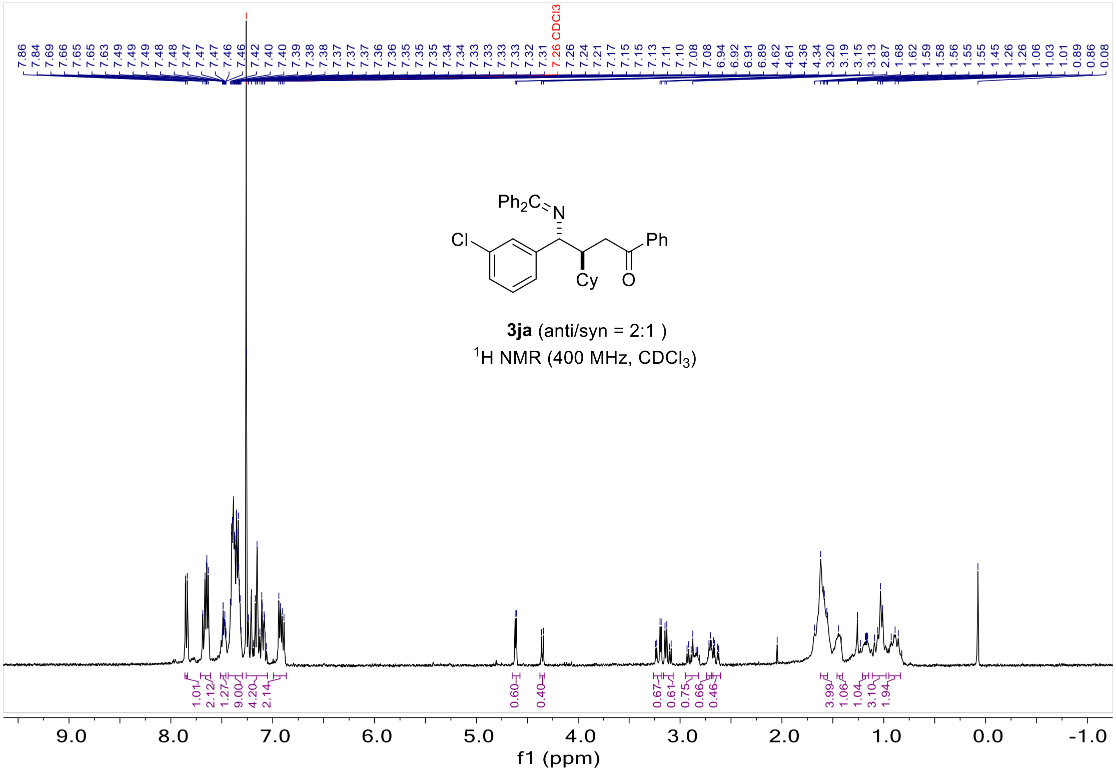


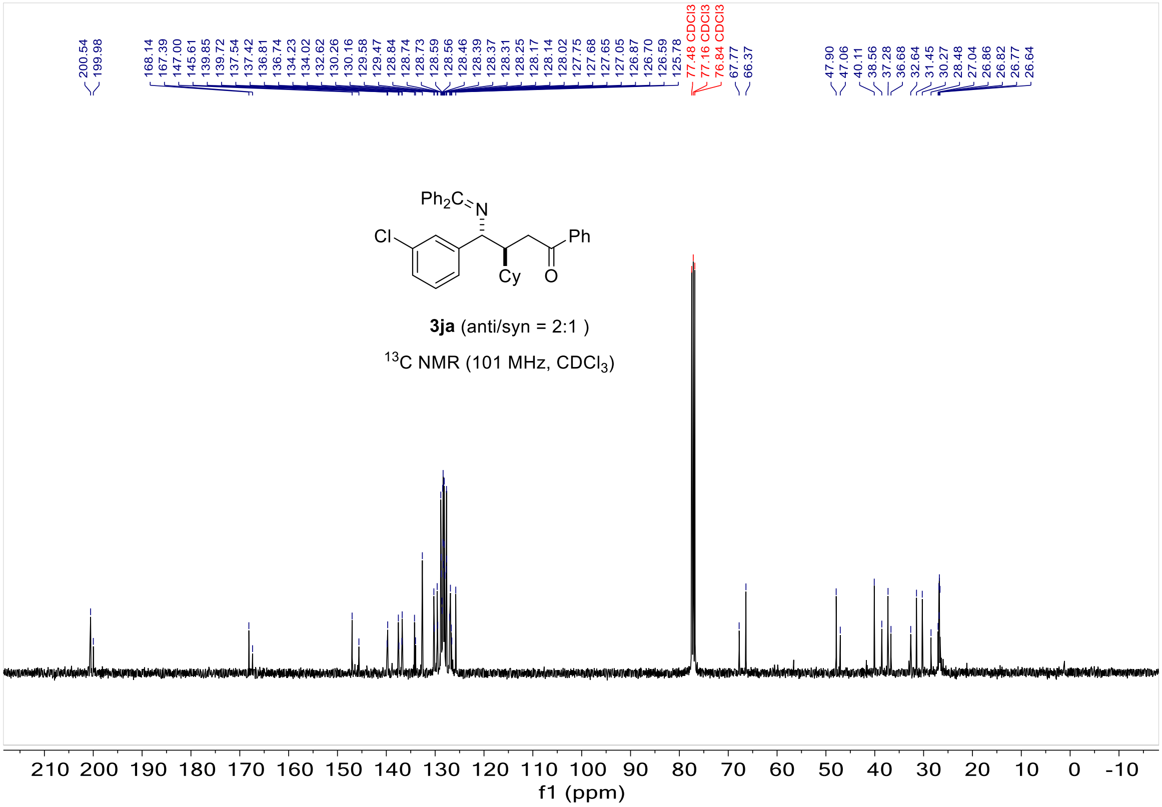
3ia (anti/syn = 2:1)

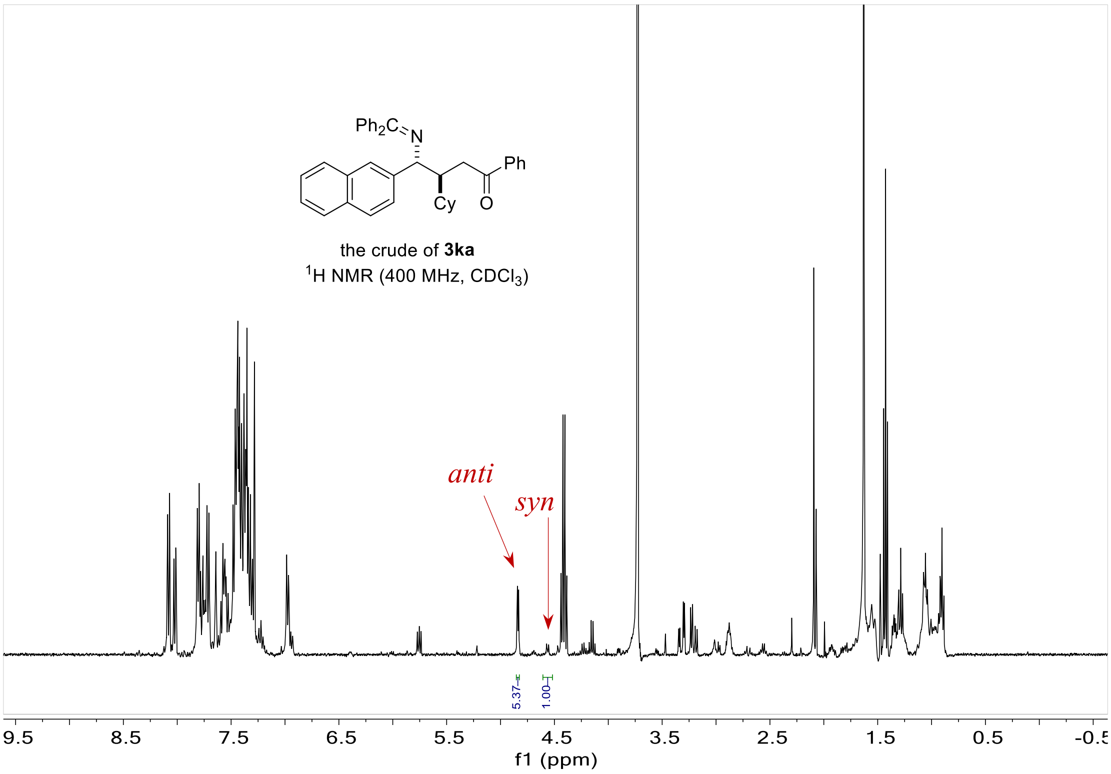
^{13}C NMR (101 MHz, CDCl$_3$)

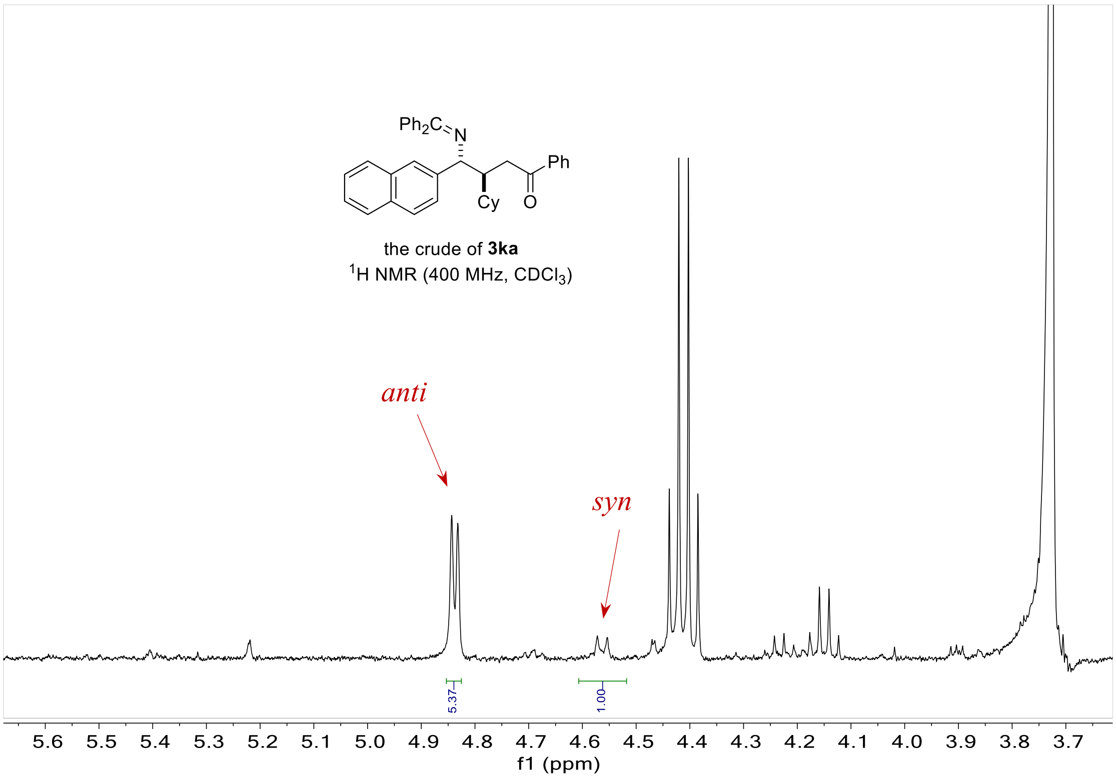

Ph2C
N
Cl
Ph
O
the crude of 3ja
1H NMR (400MHz, CDCl3)
anti
syn
2.09
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

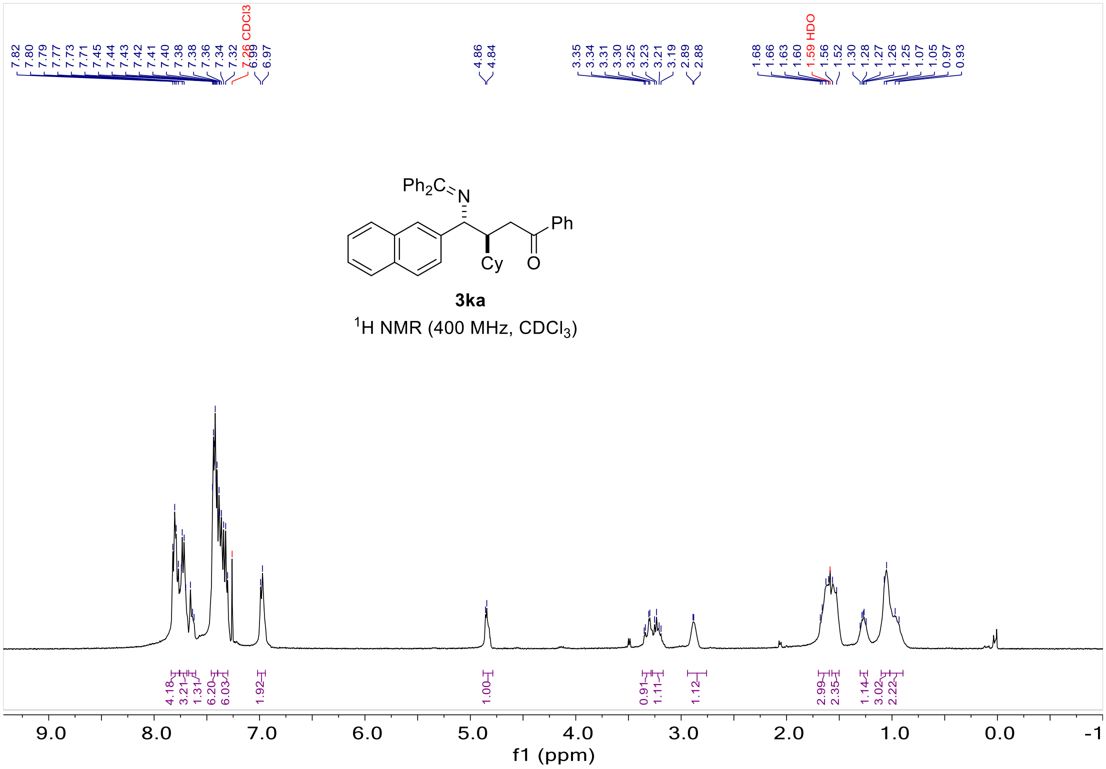

Ph2C
N
Cl
Ph
O
the crude of 3ja
1H NMR (400MHz, CDCl3)
anti
syn
2.09
1.00
5.20
5.10
5.00
4.90
4.80
4.70
4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
f1 (ppm)


7.86
7.84
7.69
7.66
7.65
7.65
7.63
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.31
7.26 CDCl3
7.26
7.24
7.21
7.17
7.15
7.15
7.13
7.11
7.10
7.08
7.08
6.94
6.92
6.91
6.89
4.62
4.61
4.36
4.34
3.20
3.19
3.15
3.13
2.87
1.68
1.62
1.59
1.58
1.56
1.55
1.55
1.45
1.26
1.26
1.06
1.03
1.01
0.89
0.86
0.08
Ph$_2$C=N
Cl
Ph
Cy
O
3ja (anti/syn = 2:1)
^{1}H NMR (400 MHz, CDCl$_3$)
1.01
2.12
1.27
9.00
4.20
2.14
0.60
0.40
0.67
0.61
0.75
0.66
0.46
3.99
1.06
1.04
3.10
1.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


200.54
199.98
168.14
167.39
147.00
145.61
139.85
139.72
137.54
137.42
136.81
136.74
134.23
134.02
132.62
130.26
130.16
129.58
129.47
128.84
128.74
128.73
128.59
128.56
128.46
128.39
128.37
128.31
128.25
128.17
128.14
128.02
127.75
127.68
127.65
127.05
126.87
126.70
126.59
125.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.77
66.37
47.90
47.06
40.11
38.56
37.28
36.68
32.64
31.45
30.27
28.48
27.04
26.86
26.82
26.77
26.64
Ph$_2$C=N
Cl
Ph
Cy
O
3ja (anti/syn = 2:1)
^{13}C NMR (101 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

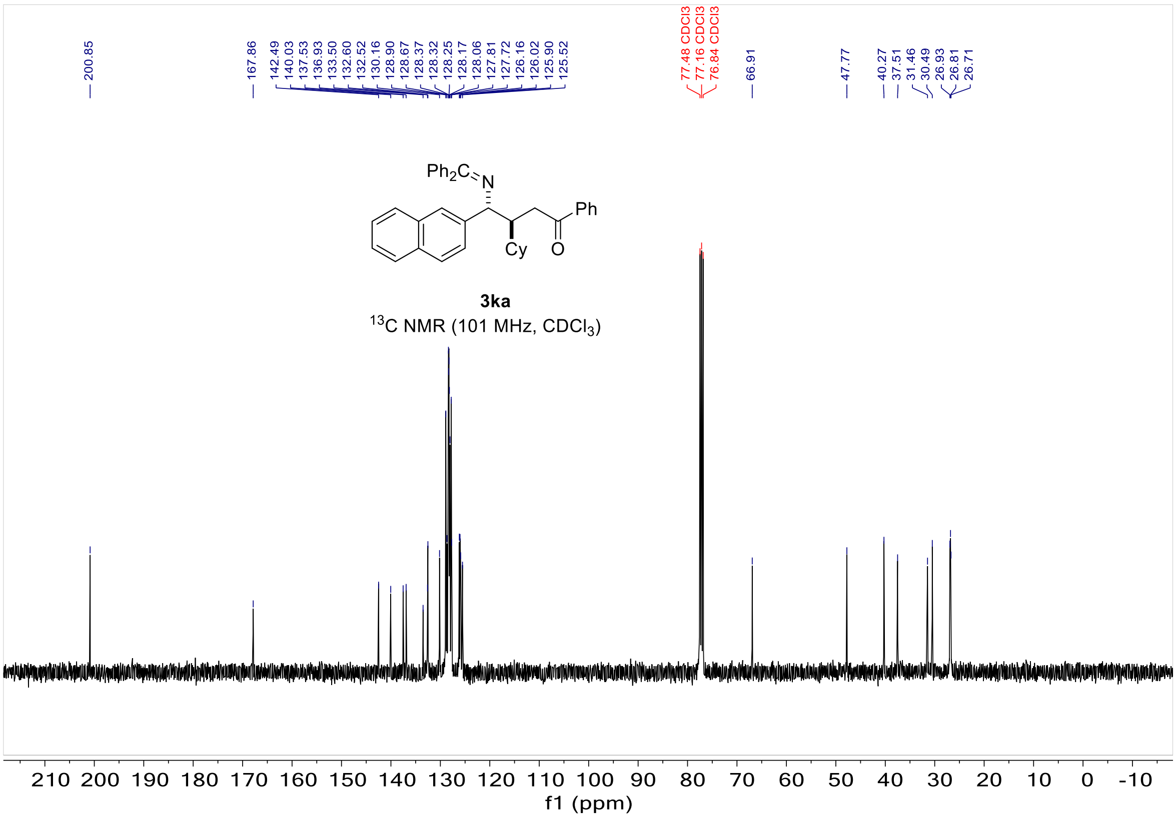

Ph2C=N
Ph
Cy
O
the crude of 3ka
1H NMR (400 MHz, CDCl3)
anti
syn
5.37
1.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


Ph2C=N
Ph
Cy
O
the crude of 3ka
1H NMR (400 MHz, CDCl3)
anti
syn
5.37
1.00
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
f1 (ppm)



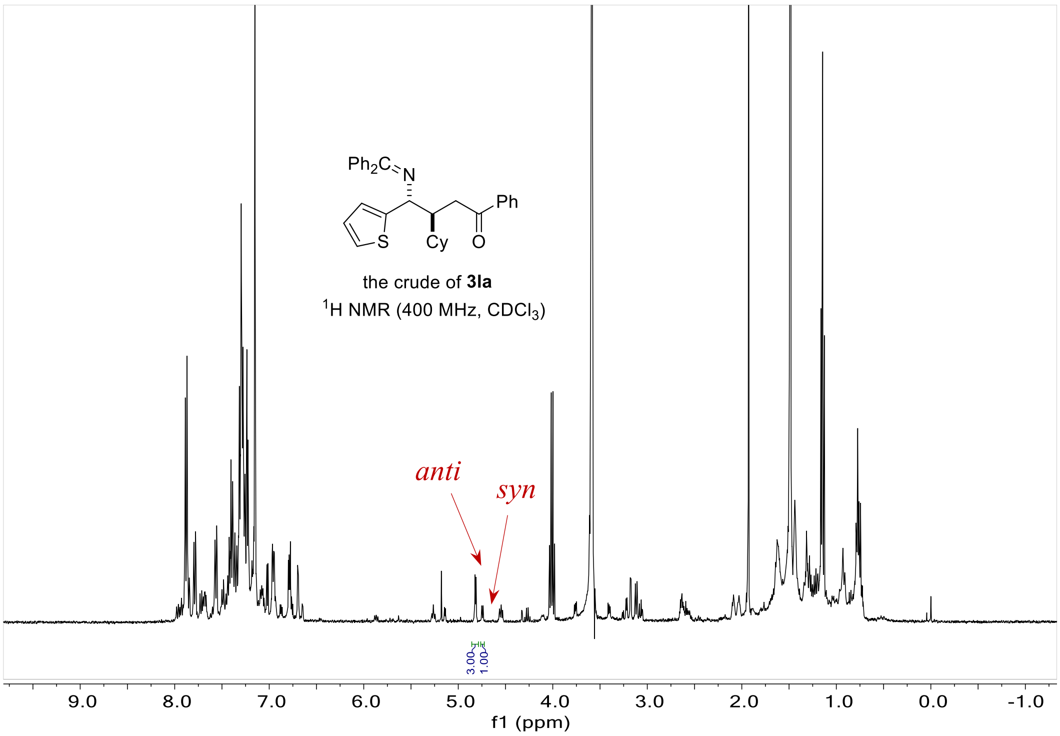
3ka

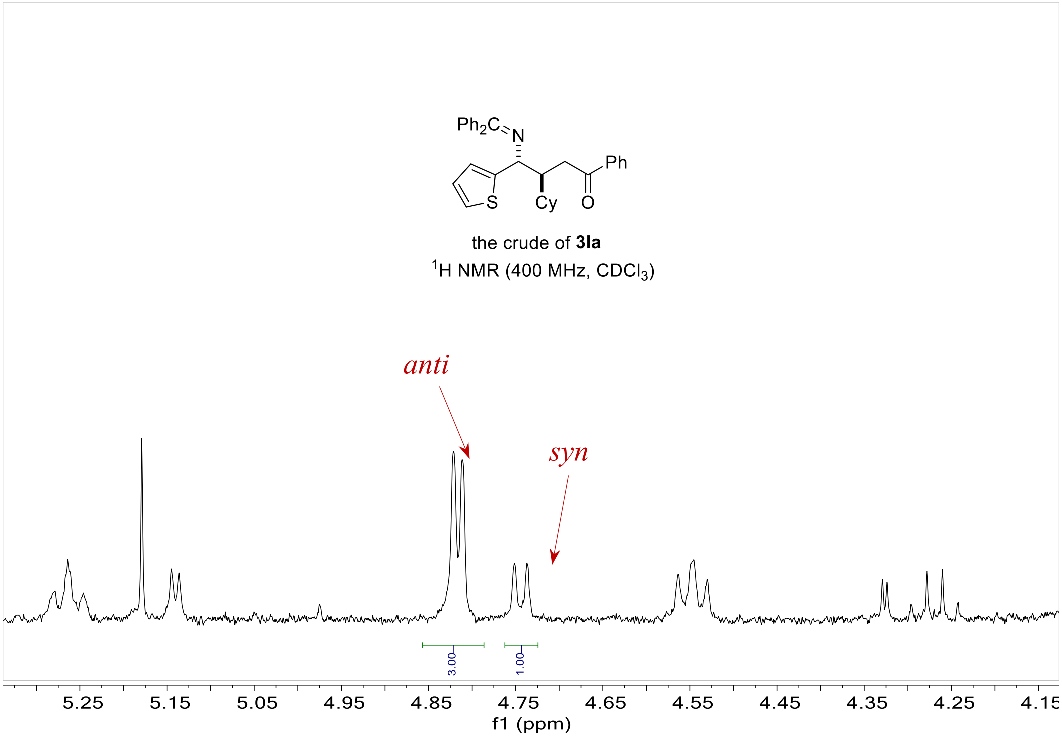
^{1}H NMR (400 MHz, $CDCl_3$)

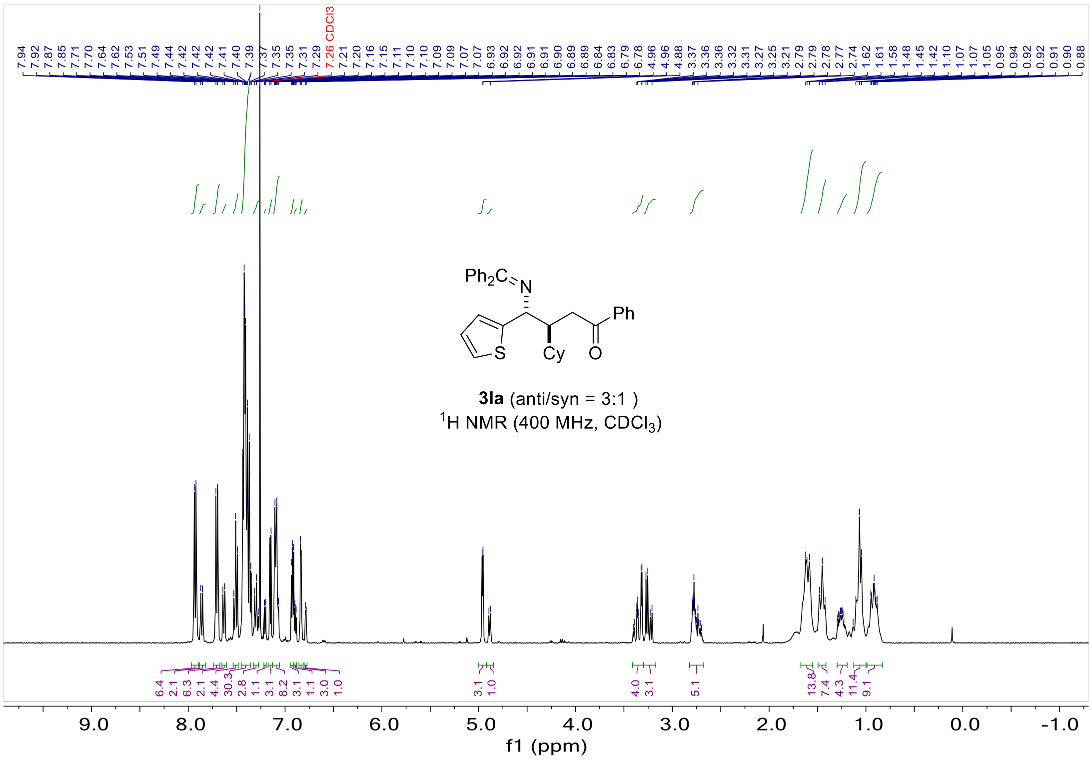


3ka

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

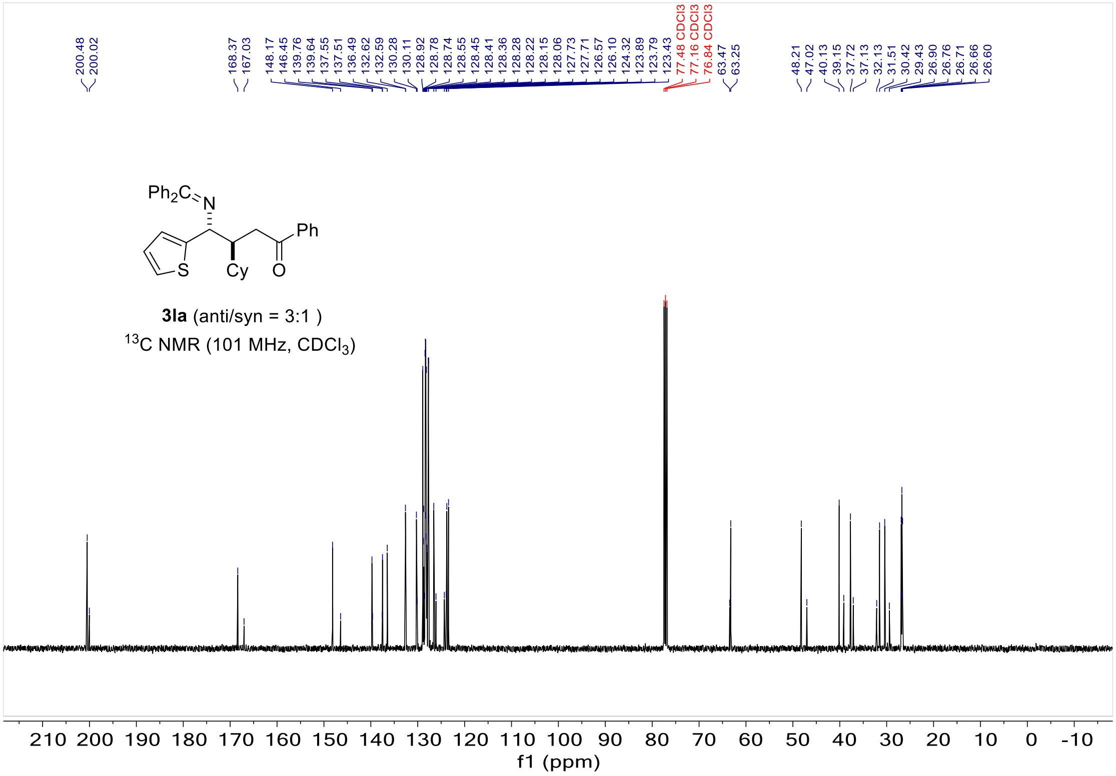

Ph$_2$C=N
Ph
S
Cy
O
the crude of **3la**
^{1}H NMR (400 MHz, CDCl$_3$)
anti
syn
3.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


Ph$_2$C=N
Ph
S
Cy
O
the crude of **3la**
^{1}H NMR (400 MHz, CDCl$_3$)
anti
syn
3.00
1.00
5.25
5.15
5.05
4.95
4.85
4.75
4.65
4.55
4.45
4.35
4.25
4.15
f1 (ppm)



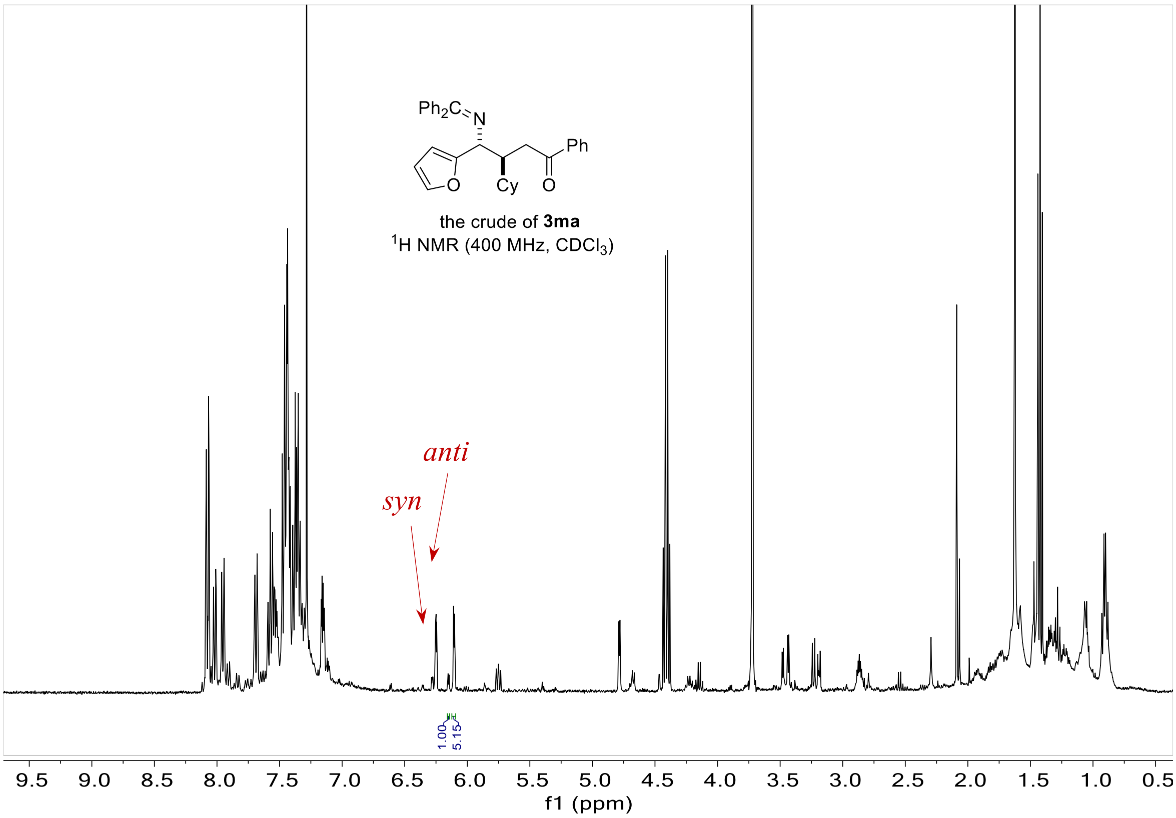
3la (anti/syn = 3:1)

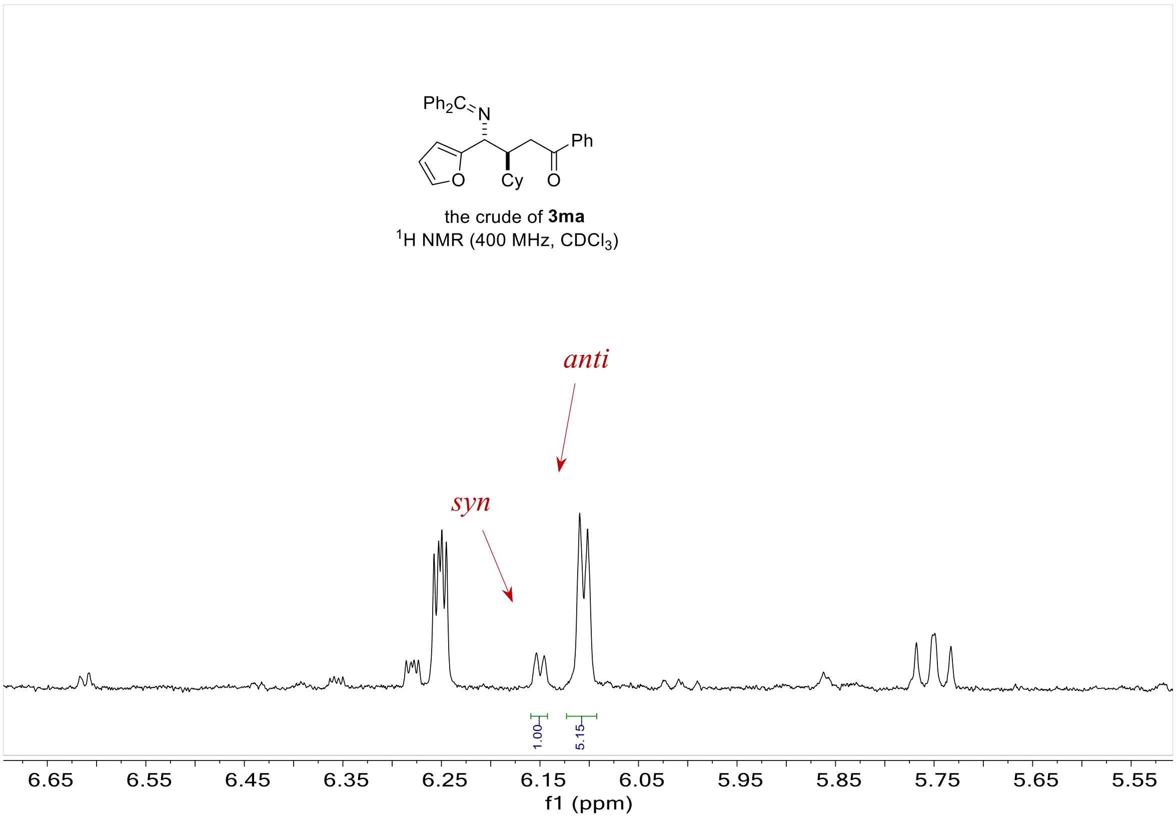
^{1}H NMR (400 MHz, CDCl$_3$)

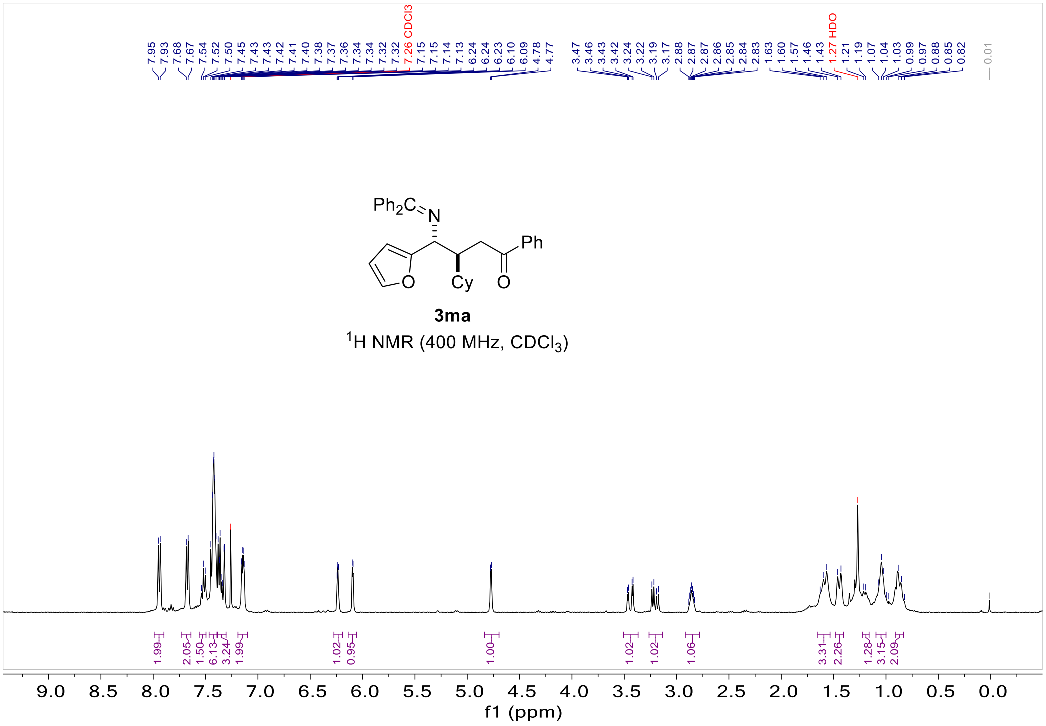


3la (anti/syn = 3:1)

^{13}C NMR (101 MHz, CDCl$_3$)

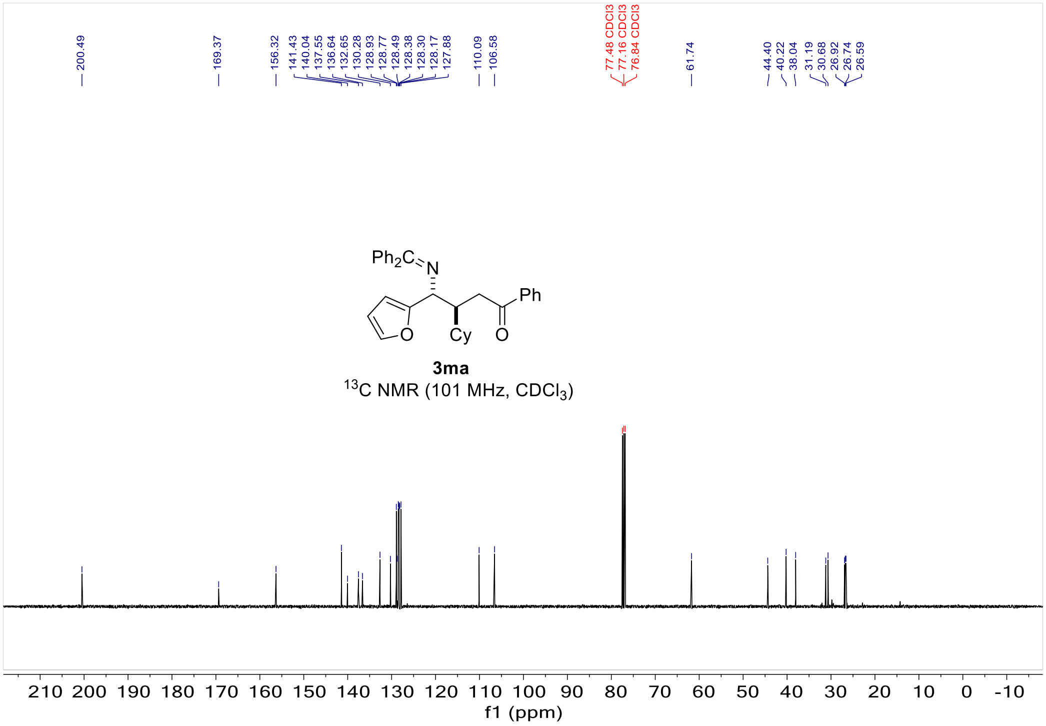

Ph2C=N
Ph
O
Cy
O
the crude of 3ma
1H NMR (400 MHz, CDCl3)
anti
syn
1.00
5.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph2C=N
Ph
O
Cy
O
the crude of 3ma
1H NMR (400 MHz, CDCl3)
anti
syn
1.00
5.15
6.65 6.55 6.45 6.35 6.25 6.15 6.05 5.95 5.85 5.75 5.65 5.55
f1 (ppm)



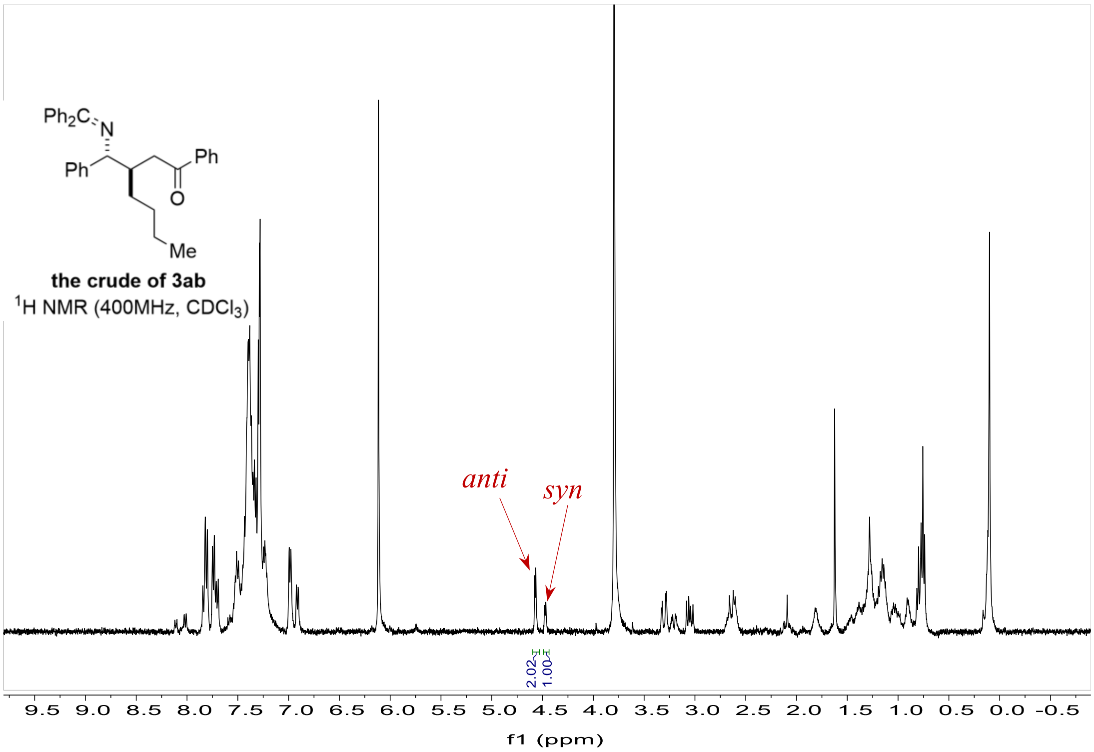
3ma

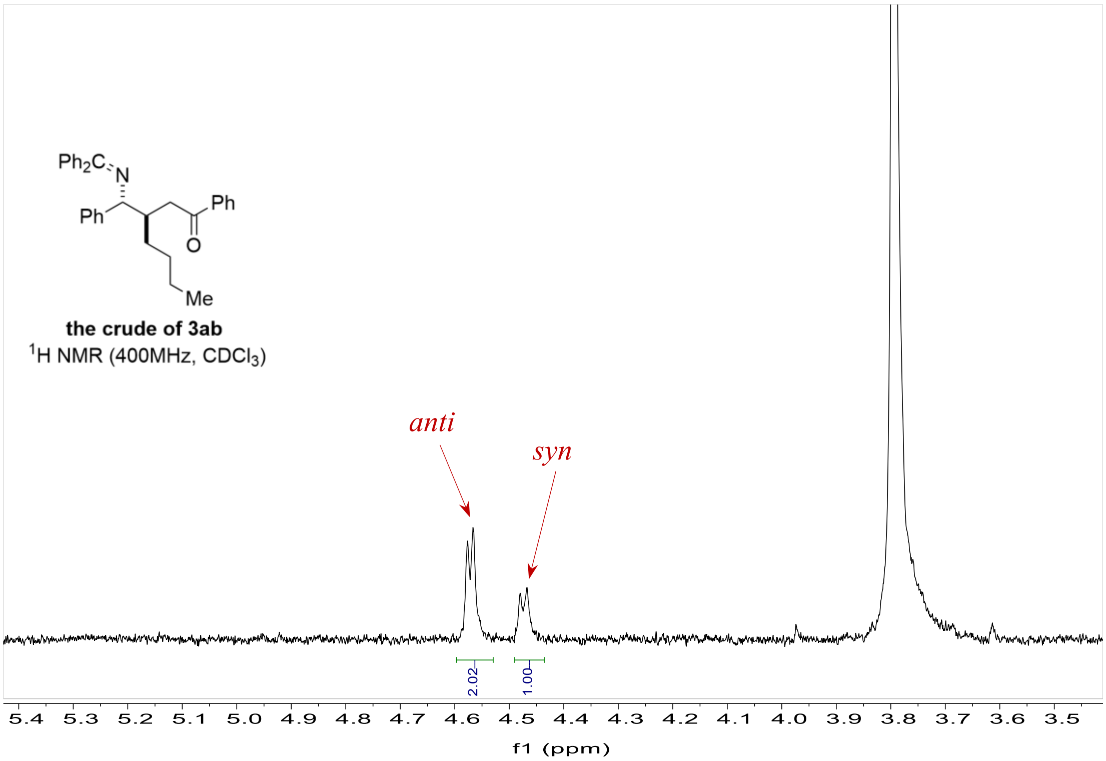
^{1}H NMR (400 MHz, $CDCl_3$)

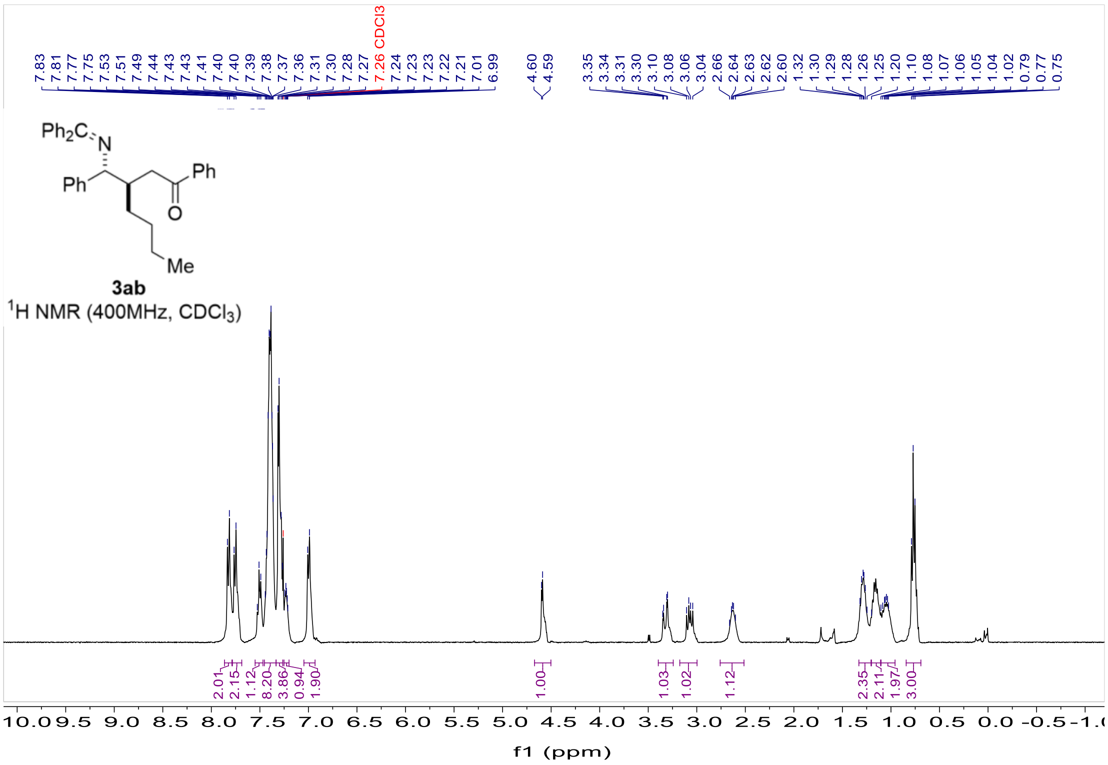


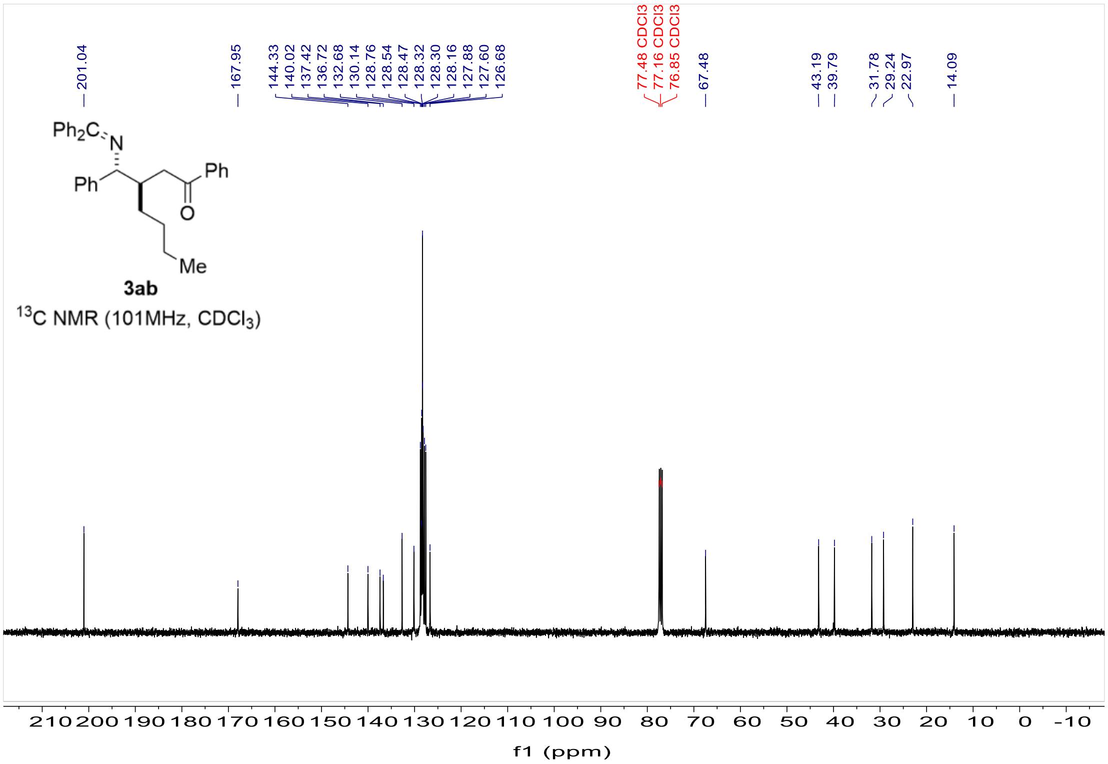
3ma

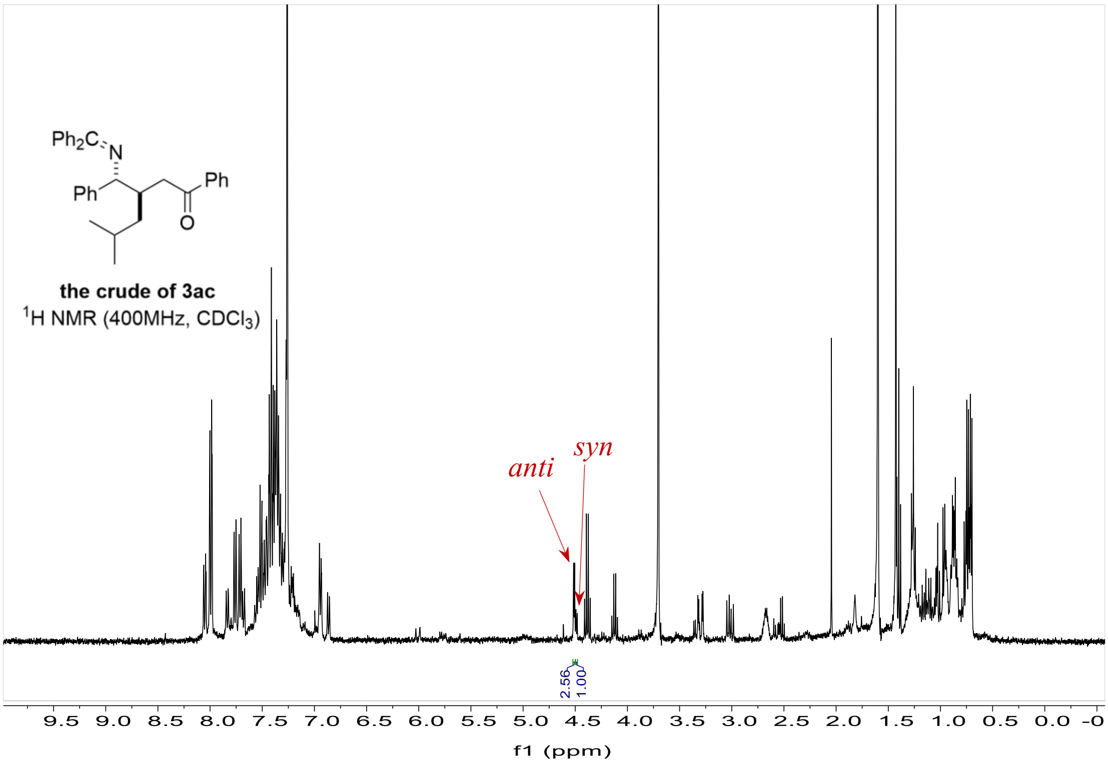
^{13}C NMR (101 MHz, $CDCl_3$)

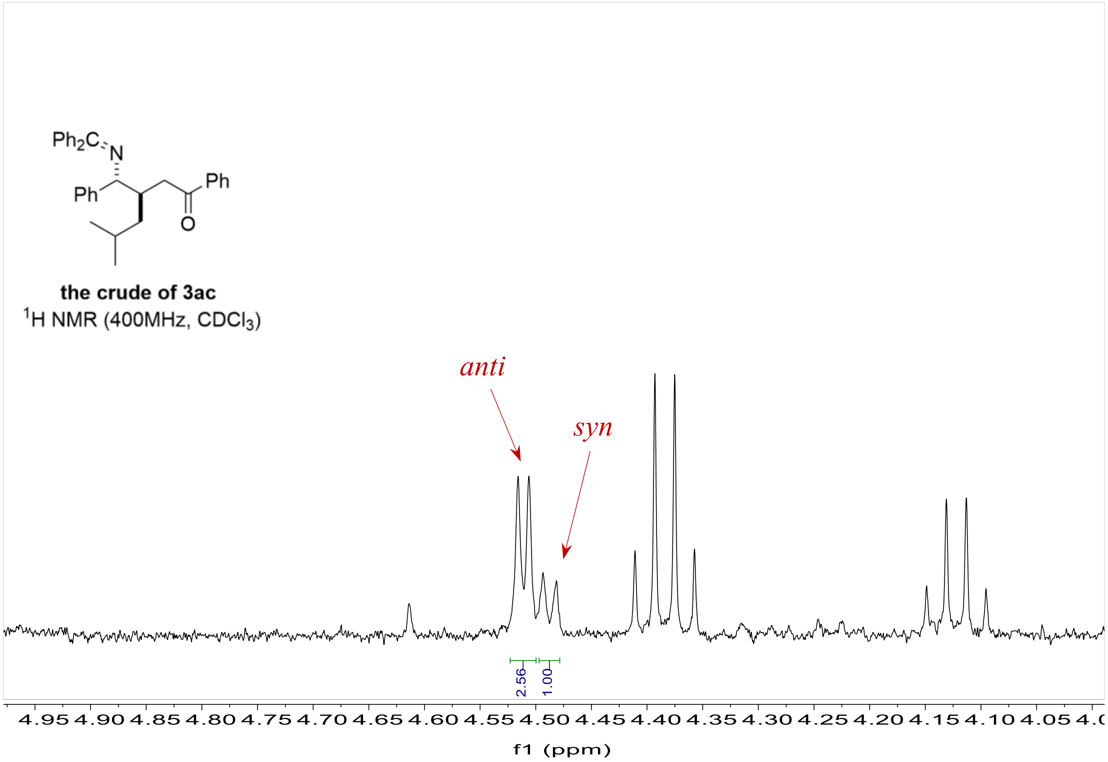

Ph2C
N
Ph
Ph
O
Me
the crude of 3ab
1H NMR (400MHz, CDCl3)
anti
syn
2.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

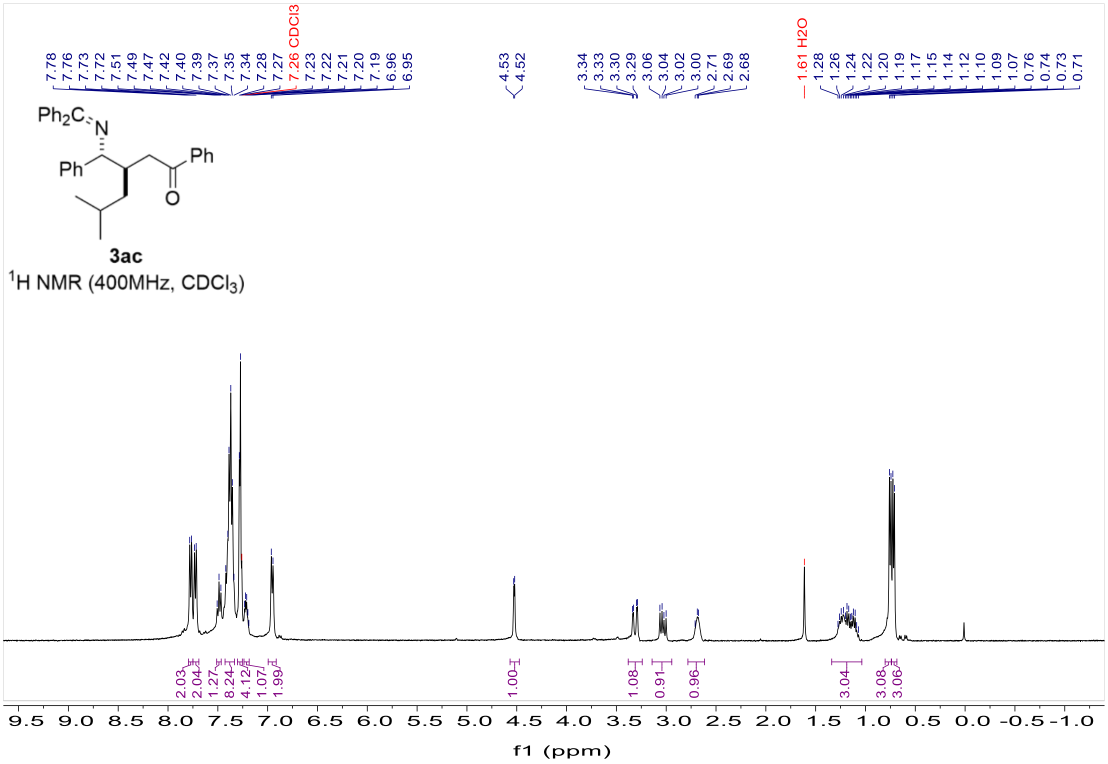

Ph2C
N
Ph
Ph
O
Me
the crude of 3ab
1H NMR (400MHz, CDCl3)
anti
syn
2.02
1.00
5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
f1 (ppm)

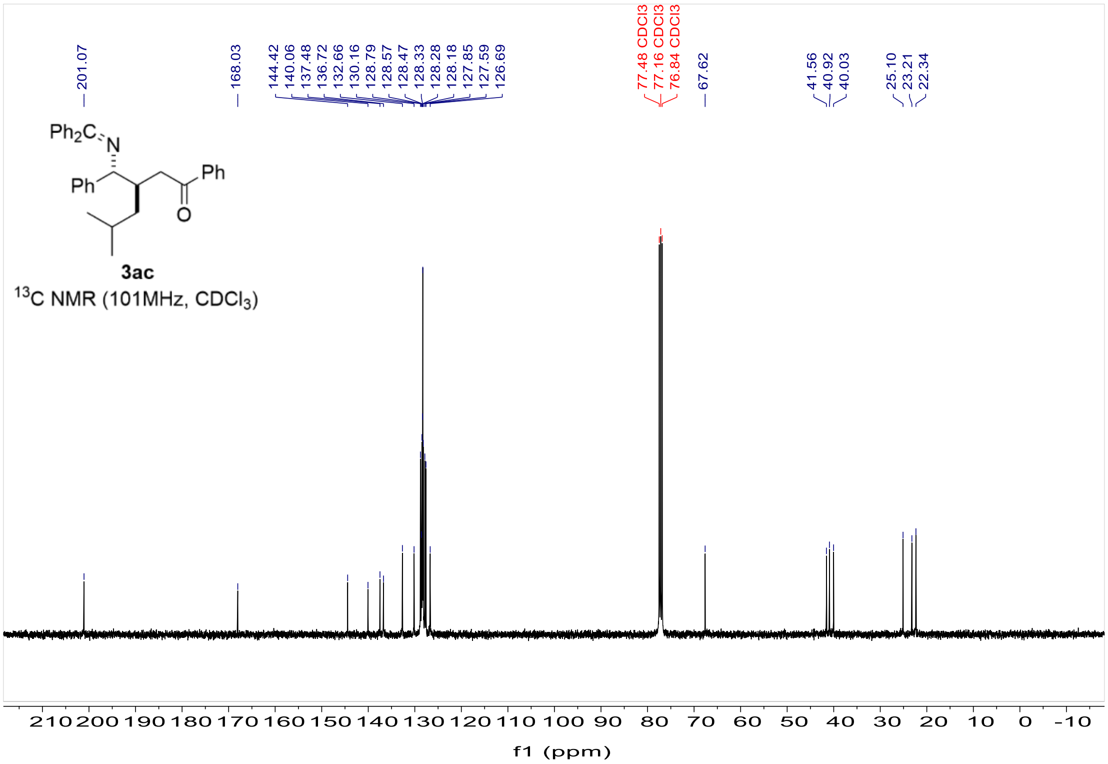

7.83
7.81
7.77
7.75
7.53
7.51
7.49
7.44
7.43
7.43
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.31
7.30
7.28
7.27
7.26 CDCl3
7.24
7.23
7.23
7.22
7.21
7.01
6.99
4.60
4.59
3.35
3.34
3.31
3.30
3.10
3.08
3.06
3.04
2.66
2.64
2.63
2.62
2.60
1.32
1.30
1.29
1.28
1.26
1.25
1.20
1.10
1.08
1.07
1.06
1.05
1.04
1.02
0.79
0.77
0.75
Ph2C
N
Ph
Ph
O
Me
3ab
1H NMR (400MHz, CDCl3)
2.01
2.15
1.12
8.20
3.86
0.94
1.90
1.00
1.03
1.02
1.12
2.35
2.11
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

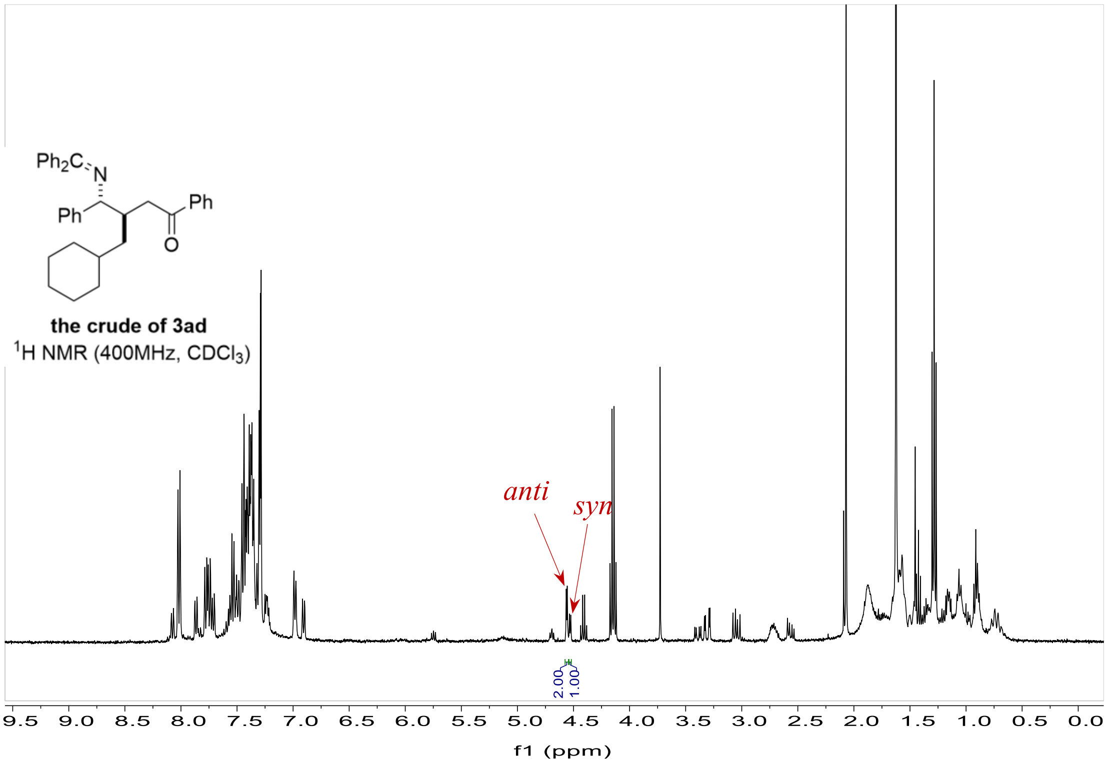

201.04
167.95
144.33
140.02
137.42
136.72
132.68
130.14
128.76
128.54
128.47
128.32
128.30
128.16
127.88
127.60
126.68
77.48 CDCl3
77.16 CDCl3
76.85 CDCl3
67.48
43.19
39.79
31.78
29.24
22.97
14.09
Ph2C
N
Ph
Ph
O
Me
3ab
13C NMR (101MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

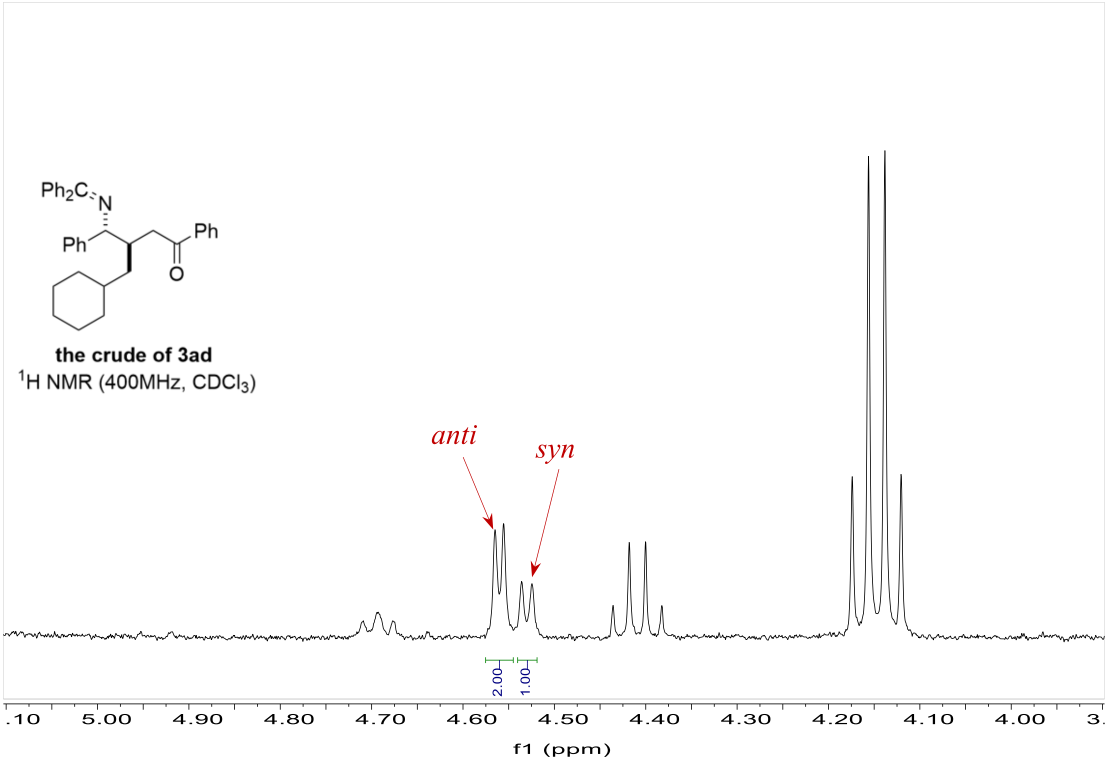

Ph$_2$C=N
Ph
Ph
O
the crude of 3ac
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.56
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

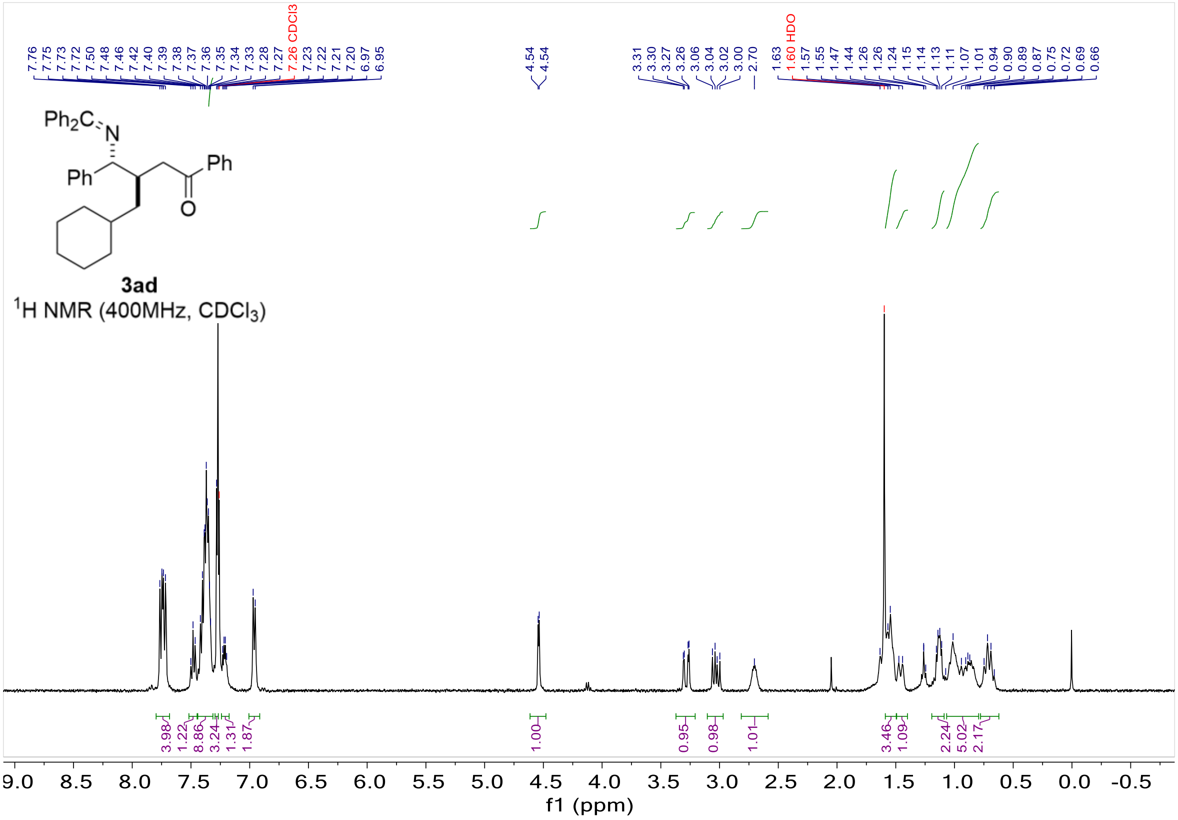

Ph$_2$C=N
Ph
Ph
O
the crude of 3ac
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.56
1.00
4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.0
f1 (ppm)

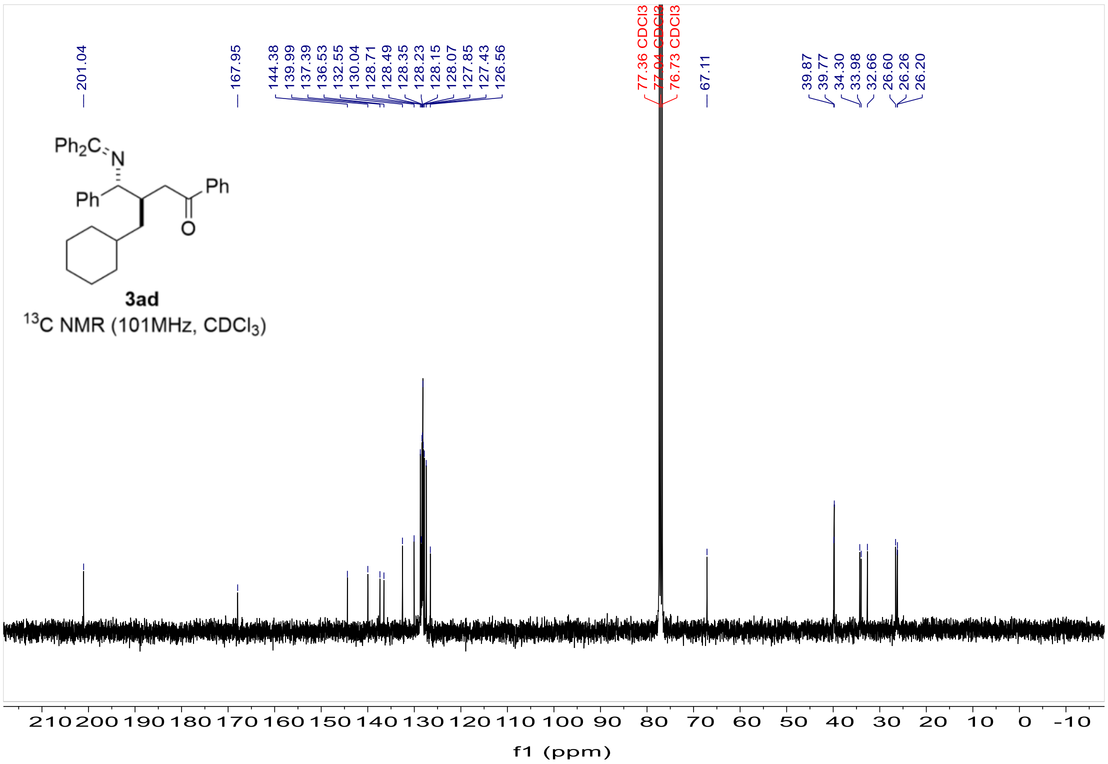

7.78 7.76 7.73 7.72 7.51 7.49 7.47 7.42 7.40 7.39 7.37 7.35 7.34 7.28 7.27 7.26 CDCl3 7.23 7.22 7.21 7.20 7.19 6.96 6.95
4.53 4.52
3.34 3.33 3.30 3.29 3.06 3.04 3.02 3.00 2.71 2.69 2.68
1.61 H2O
1.28 1.26 1.24 1.22 1.20 1.19 1.17 1.15 1.14 1.12 1.10 1.09 1.07 0.76 0.74 0.73 0.71
Ph$_2$C=N
Ph
Ph
O
3ac
^{1}H NMR (400MHz, CDCl$_3$)
2.03 2.04 1.27 8.24 4.12 1.07 1.99
1.00
1.08 0.91 0.96
3.04
3.08 3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

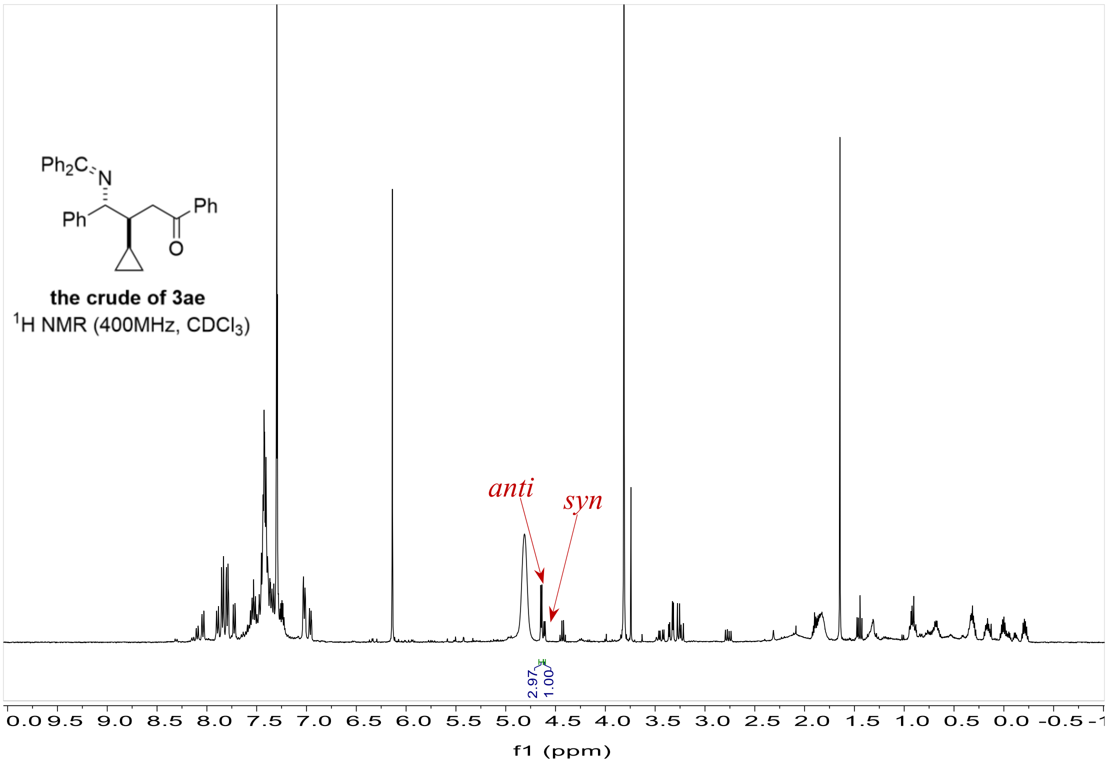

201.07
168.03
144.42 140.06 137.48 136.72 132.66 130.16 128.79 128.57 128.47 128.33 128.28 128.18 127.85 127.59 126.69
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
67.62
41.56 40.92 40.03
25.10 23.21 22.34
Ph$_2$C=N
Ph
Ph
O
3ac
^{13}C NMR (101MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph$_2$C=N
Ph
Ph
O
the crude of 3ad
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph$_2$C=N
Ph
Ph
O
the crude of 3ad
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.00
1.00
.10 5.00 4.90 4.80 4.70 4.60 4.50 4.40 4.30 4.20 4.10 4.00 3.
f1 (ppm)

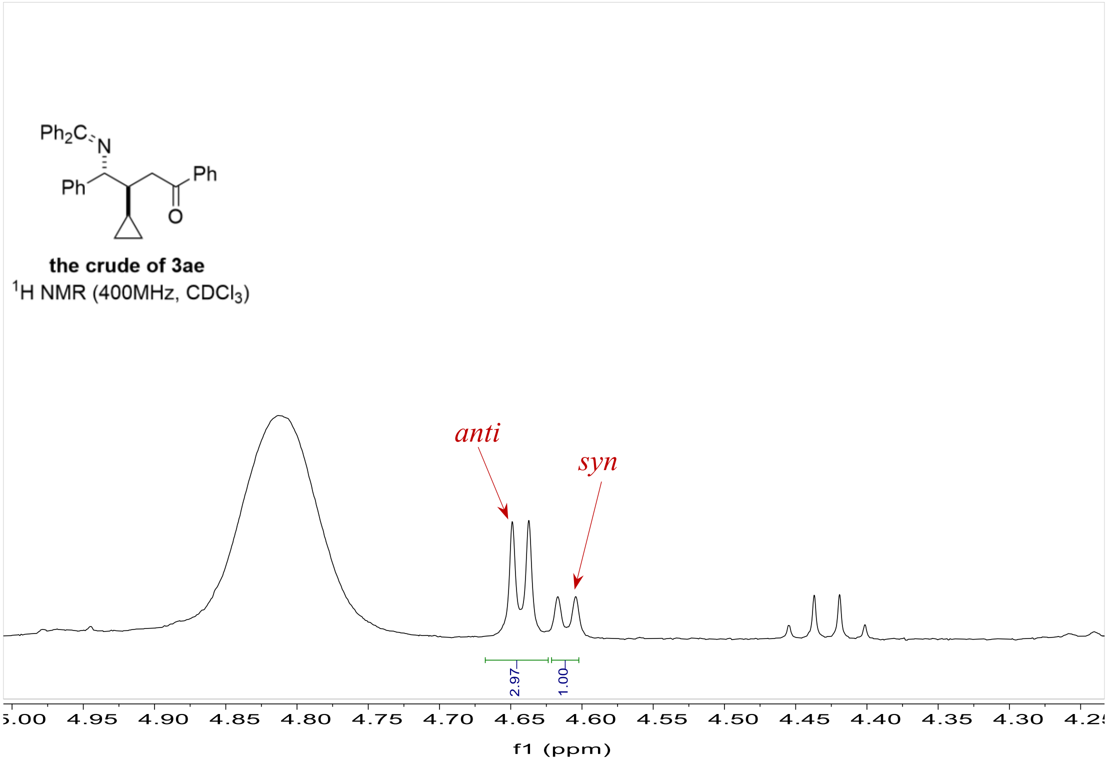

7.76 7.75 7.73 7.72 7.50 7.48 7.46 7.42 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.28 7.27 7.26 CDCl3 7.23 7.22 7.21 7.20 6.97 6.95
4.54 4.54
3.31 3.30 3.27 3.26 3.06 3.04 3.02 3.00 2.70
1.63 1.60 HDO 1.57 1.55 1.47 1.44 1.26 1.26 1.24 1.15 1.14 1.13 1.11 1.07 1.01 0.94 0.90 0.89 0.87 0.75 0.72 0.69 0.66
Ph2C=N
Ph
Ph
O
3ad
1H NMR (400MHz, CDCl3)
3.98 1.22 8.86 3.24 1.31 1.87
1.00
0.95 0.98 1.01
3.46 1.09 2.24 5.02 2.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


201.04
167.95
144.38 139.99 137.39 136.53 132.55 130.04 128.71 128.49 128.35 128.23 128.15 128.07 127.85 127.43 126.56
77.36 CDCl3 77.04 CDCl3 76.73 CDCl3
67.11
39.87 39.77 34.30 33.98 32.66 26.60 26.26 26.20
Ph2C=N
Ph
Ph
O
3ad
13C NMR (101MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



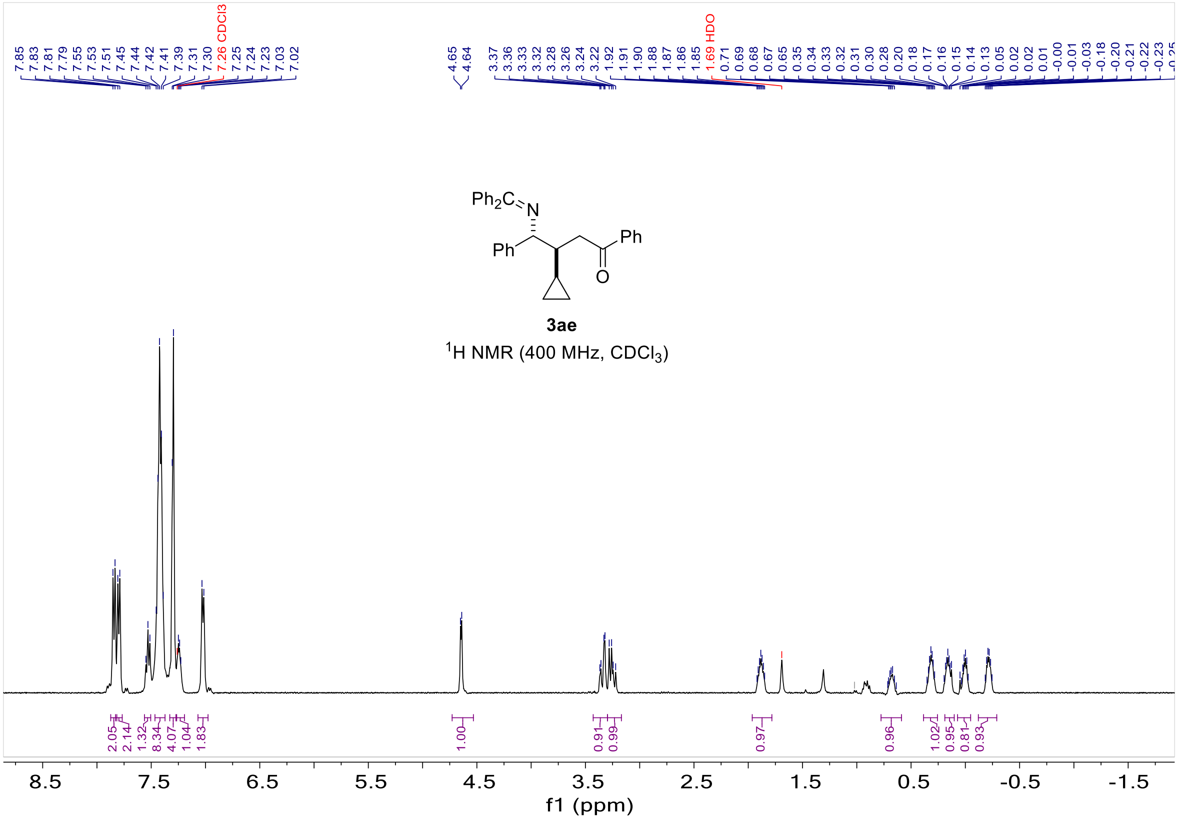
the crude of 3ae

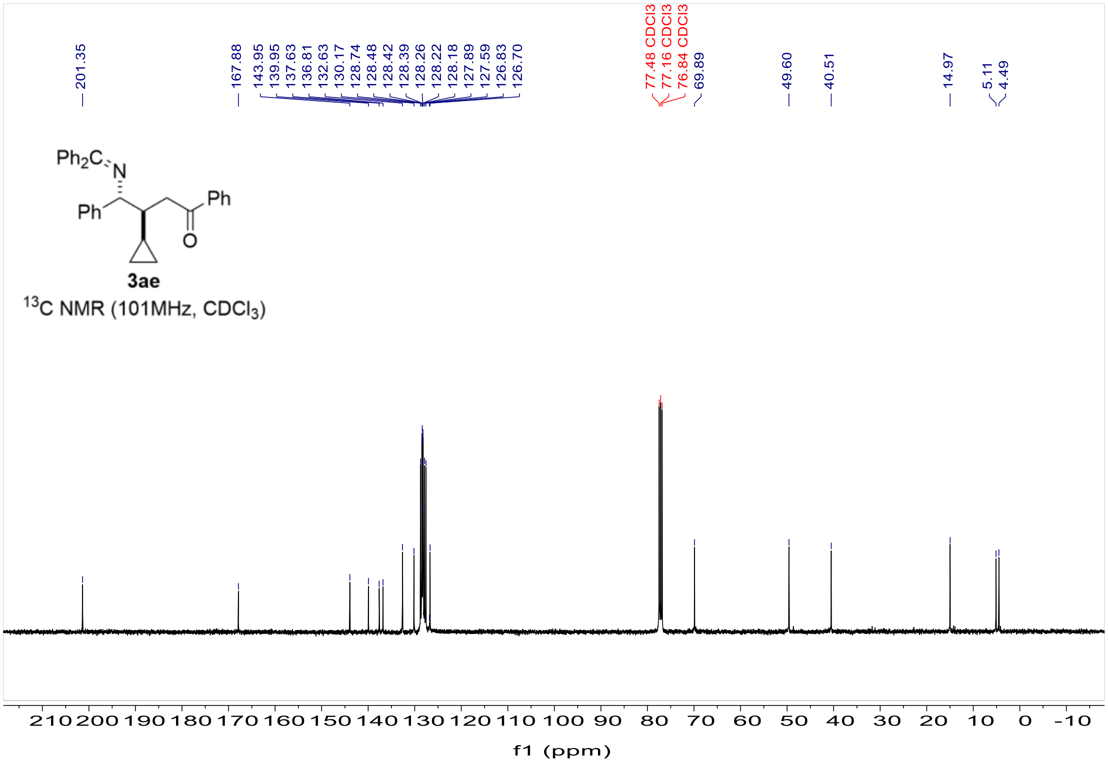
^1H NMR (400MHz, $CDCl_3$)

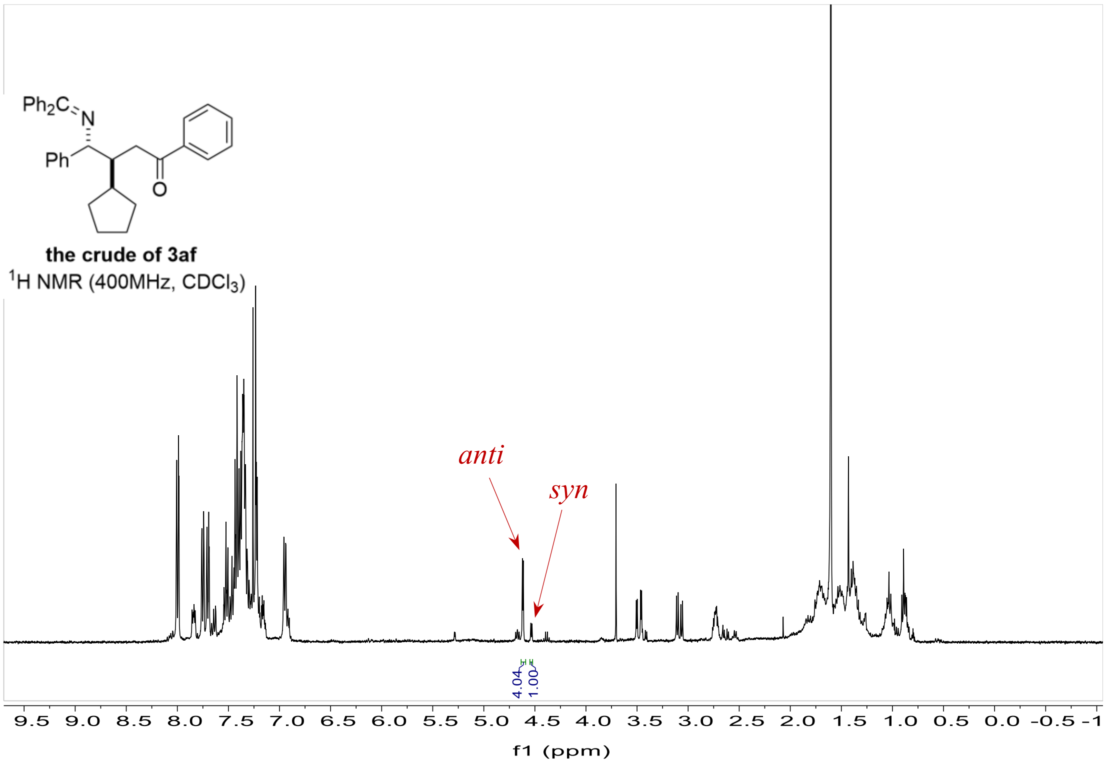


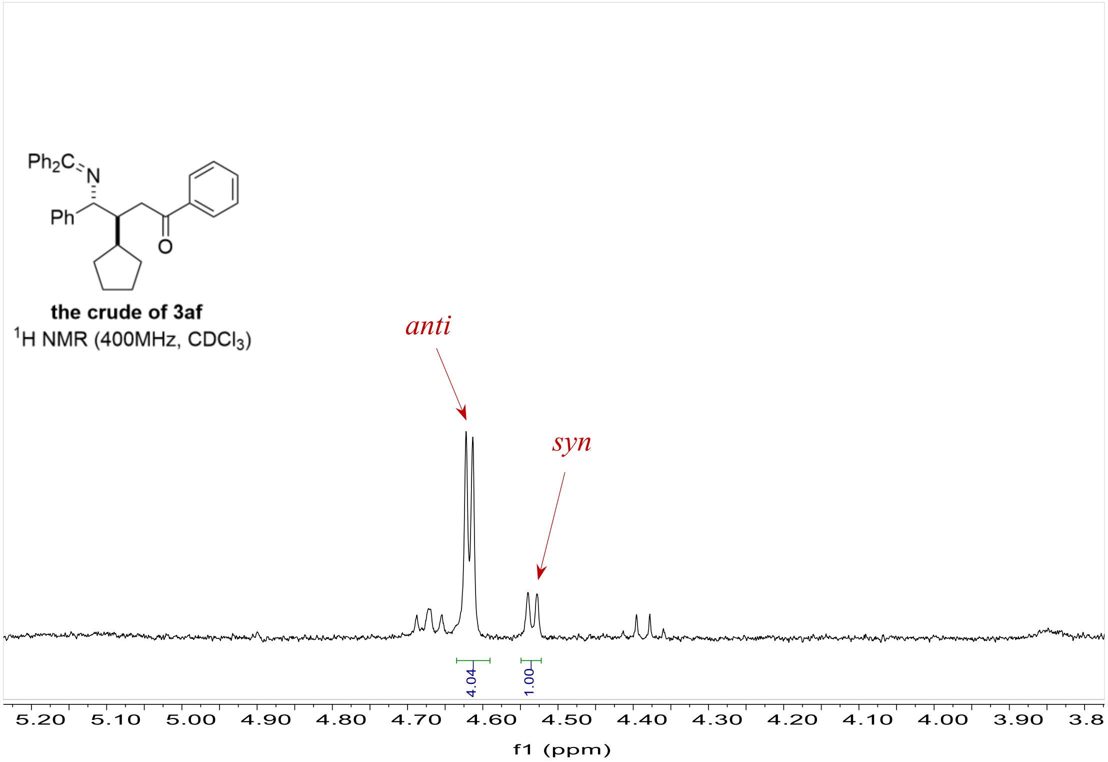
the crude of 3ae

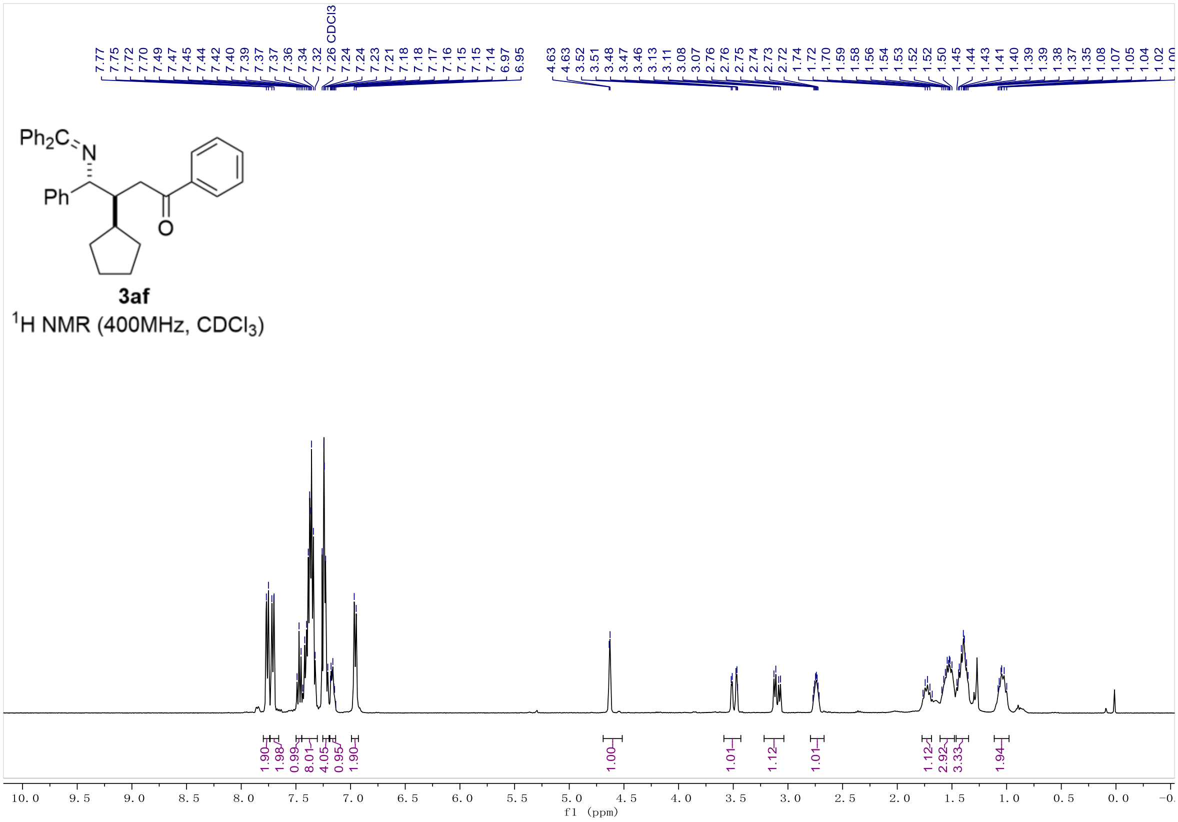
^1H NMR (400MHz, $CDCl_3$)

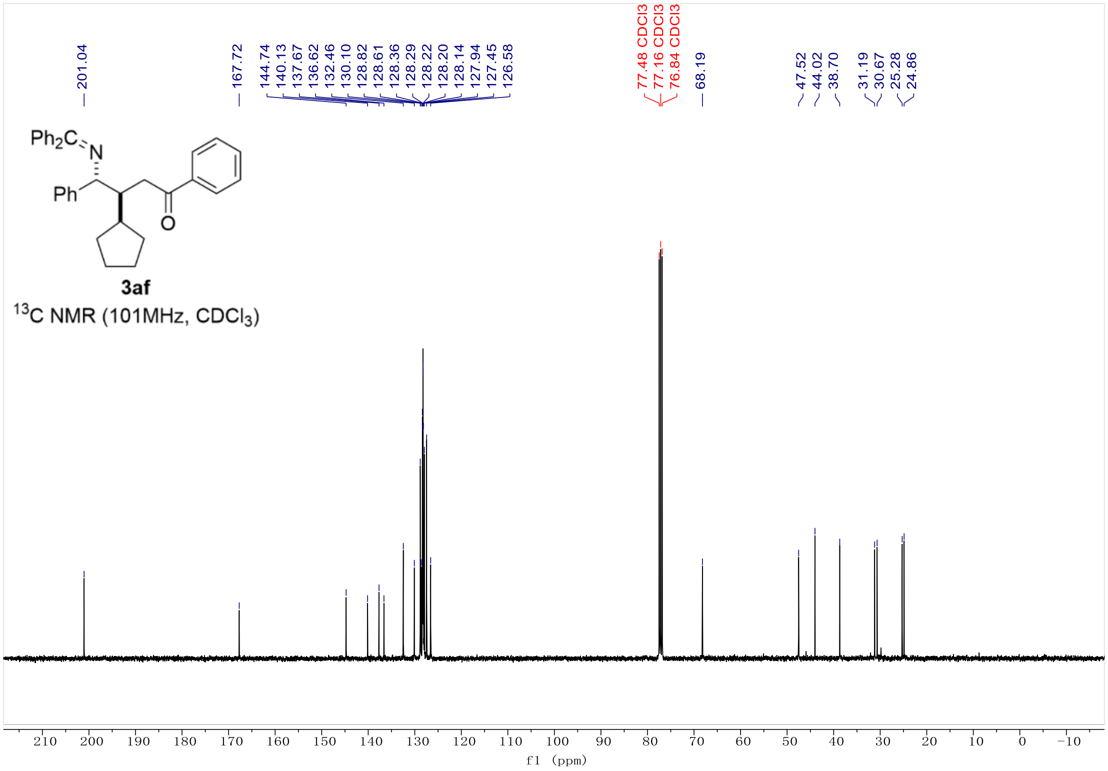

7.85
7.83
7.81
7.79
7.55
7.53
7.51
7.45
7.44
7.42
7.41
7.39
7.31
7.30
7.26 CDCl3
7.25
7.24
7.23
7.03
7.02
4.65
4.64
3.37
3.36
3.33
3.32
3.28
3.26
3.24
3.22
1.92
1.91
1.90
1.88
1.87
1.86
1.86
1.85
1.69 HDO
0.71
0.69
0.68
0.67
0.65
0.35
0.34
0.33
0.32
0.31
0.30
0.28
0.20
0.18
0.17
0.16
0.15
0.14
0.13
0.05
0.02
0.02
0.01
-0.00
-0.03
-0.18
-0.20
-0.21
-0.22
-0.23
Ph2C
N
Ph
Ph
O
3ae
1H NMR (400 MHz, CDCl3)
2.05
2.14
1.32
8.34
4.07
1.04
1.83
1.00
0.91
0.99
0.97
0.96
1.02
0.95
0.81
0.93
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

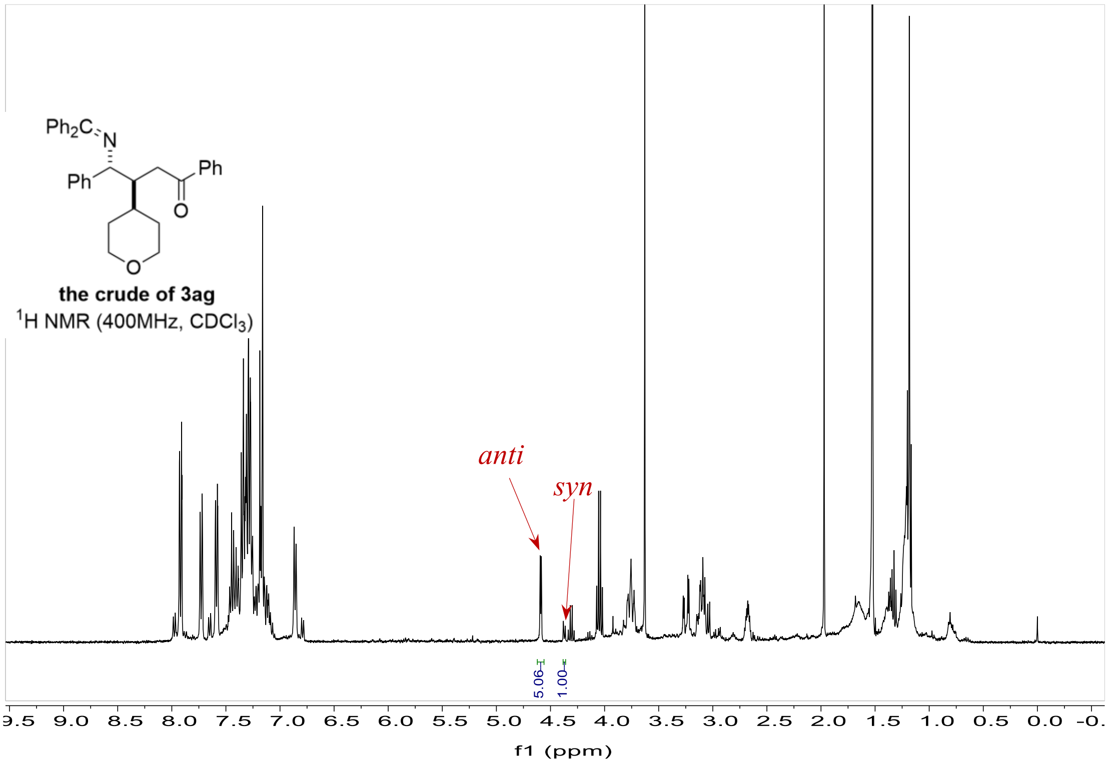

201.35
167.88
143.95
139.95
137.63
136.81
132.63
130.17
128.74
128.48
128.42
128.39
128.26
128.22
128.18
127.89
127.59
126.83
126.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.89
49.60
40.51
14.97
5.11
4.49
Ph2C
N
Ph
Ph
O
3ae
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

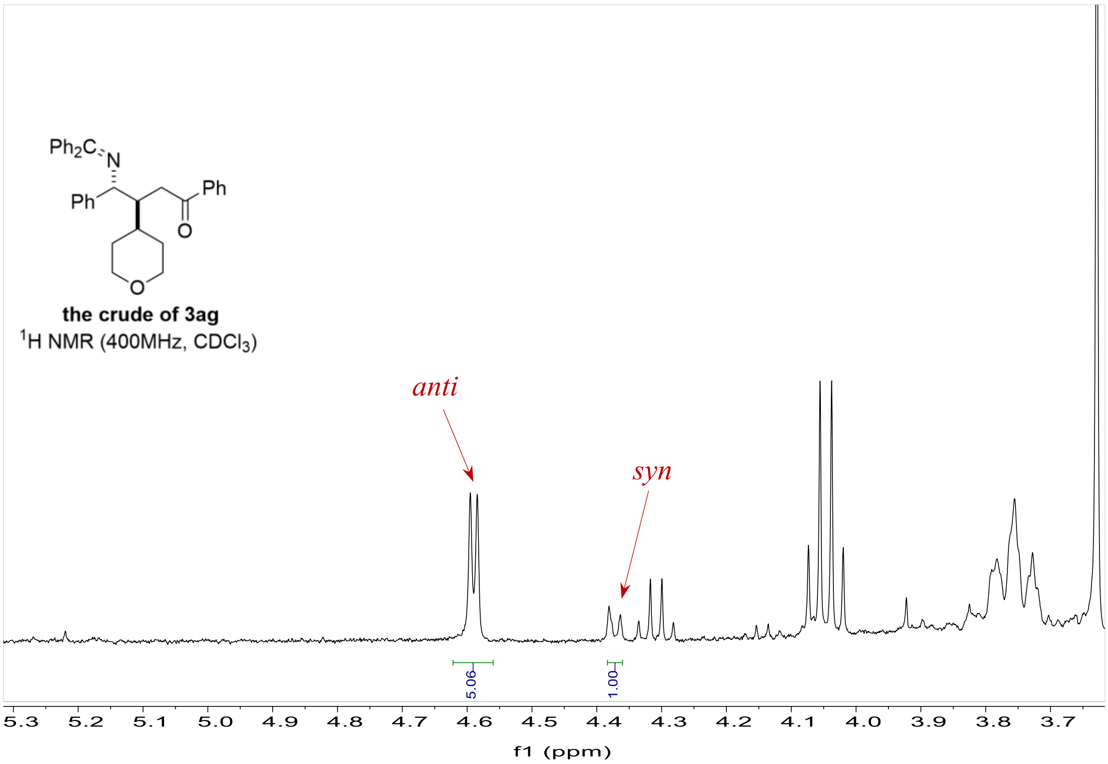

Ph$_2$C=N
Ph
O
the crude of 3af
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
4.04
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

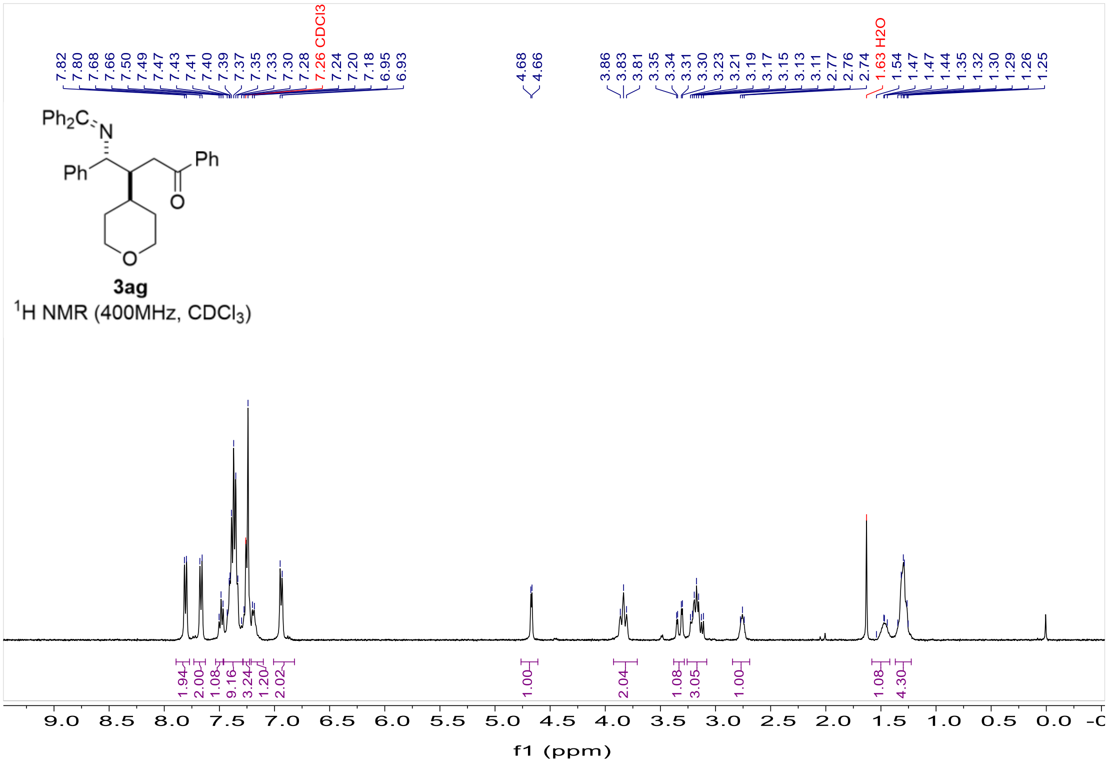

Ph$_2$C=N
Ph
O
the crude of 3af
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
4.04
1.00
5.20 5.10 5.00 4.90 4.80 4.70 4.60 4.50 4.40 4.30 4.20 4.10 4.00 3.90 3.8
f1 (ppm)


7.77
7.75
7.72
7.70
7.49
7.47
7.45
7.44
7.42
7.40
7.39
7.37
7.37
7.36
7.34
7.32
7.26 CDCl3
7.24
7.24
7.23
7.21
7.18
7.18
7.17
7.16
7.15
7.15
7.14
6.97
6.95
4.63
4.63
3.52
3.51
3.48
3.47
3.46
3.13
3.11
3.08
3.07
2.76
2.75
2.74
2.73
2.72
1.74
1.72
1.70
1.59
1.58
1.56
1.54
1.53
1.52
1.52
1.50
1.45
1.44
1.43
1.41
1.40
1.39
1.39
1.38
1.37
1.35
1.08
1.07
1.05
1.04
1.02
Ph2C
N
Ph
O
3af
1H NMR (400MHz, CDCl3)
1.90
1.98
0.99
8.01
4.05
0.95
1.90
1.00
1.01
1.12
1.01
1.12
2.92
3.33
1.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


201.04
167.72
144.74
140.13
137.67
136.62
132.46
130.10
128.82
128.61
128.36
128.29
128.22
128.20
128.14
127.94
127.45
126.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.19
47.52
44.02
38.70
31.19
30.67
25.28
24.86
Ph2C
N
Ph
O
3af
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

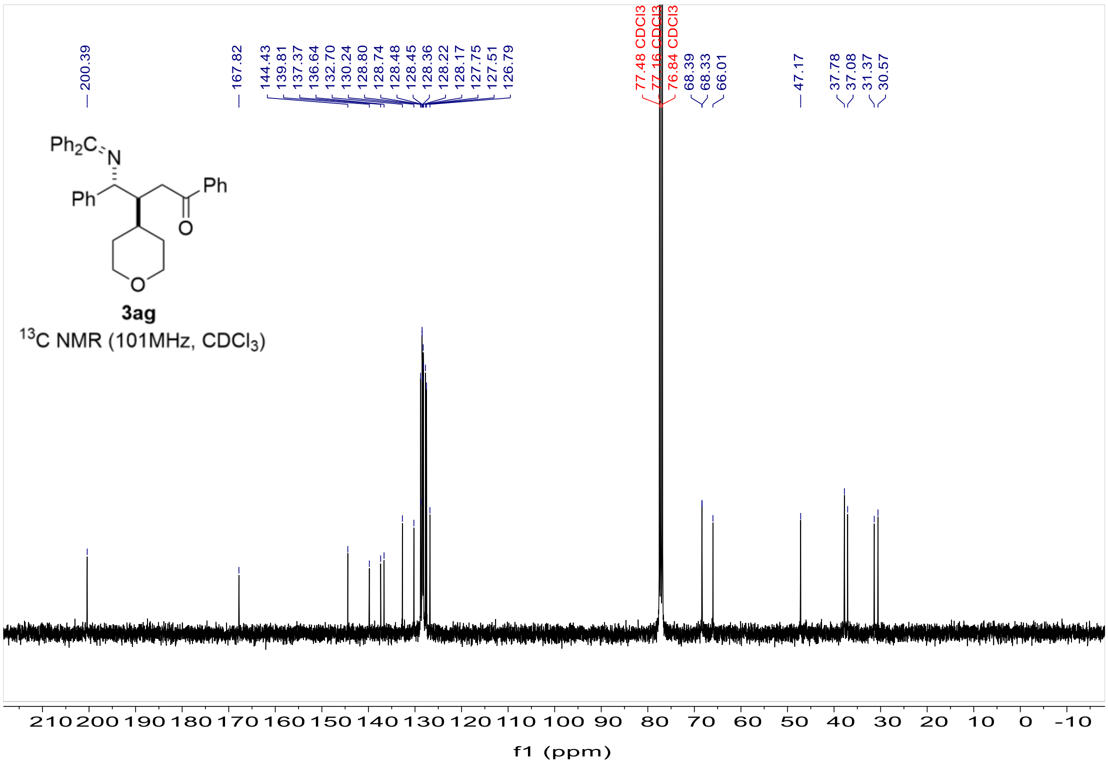

Ph2C=N
Ph
Ph
O
O
the crude of 3ag
1H NMR (400MHz, CDCl3)
anti
syn
5.06
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


Ph2C=N
Ph
Ph
O
O
the crude of 3ag
1H NMR (400MHz, CDCl3)
anti
syn
5.06
1.00
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7
f1 (ppm)



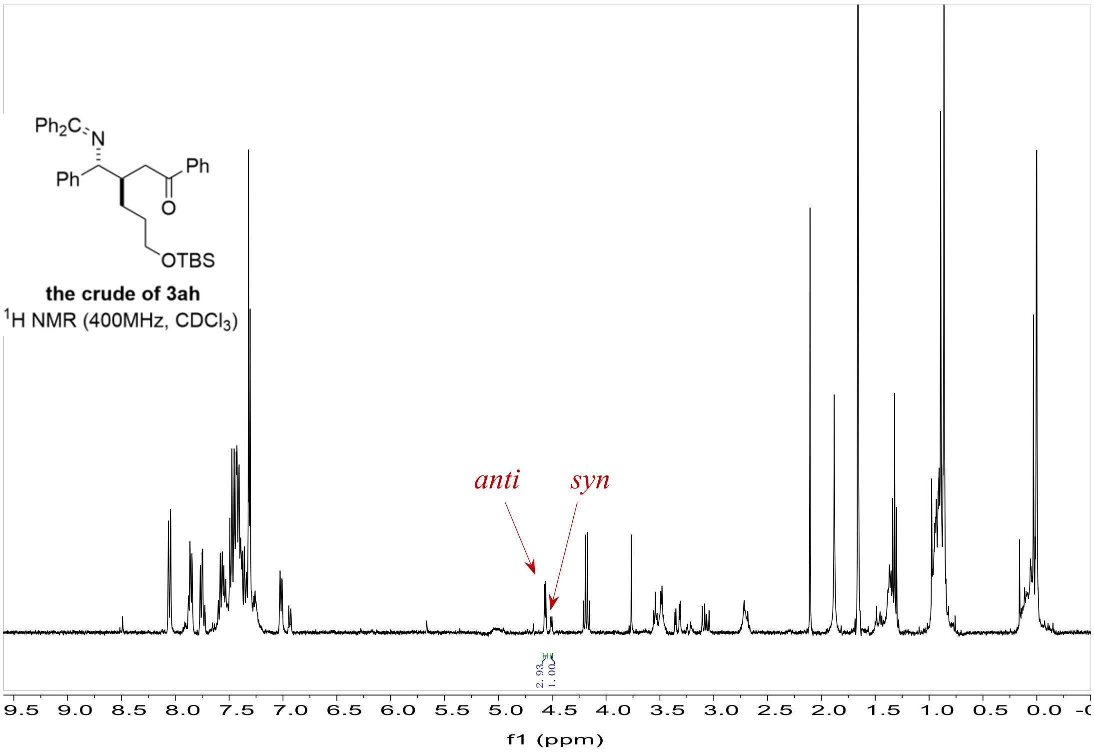
3ag

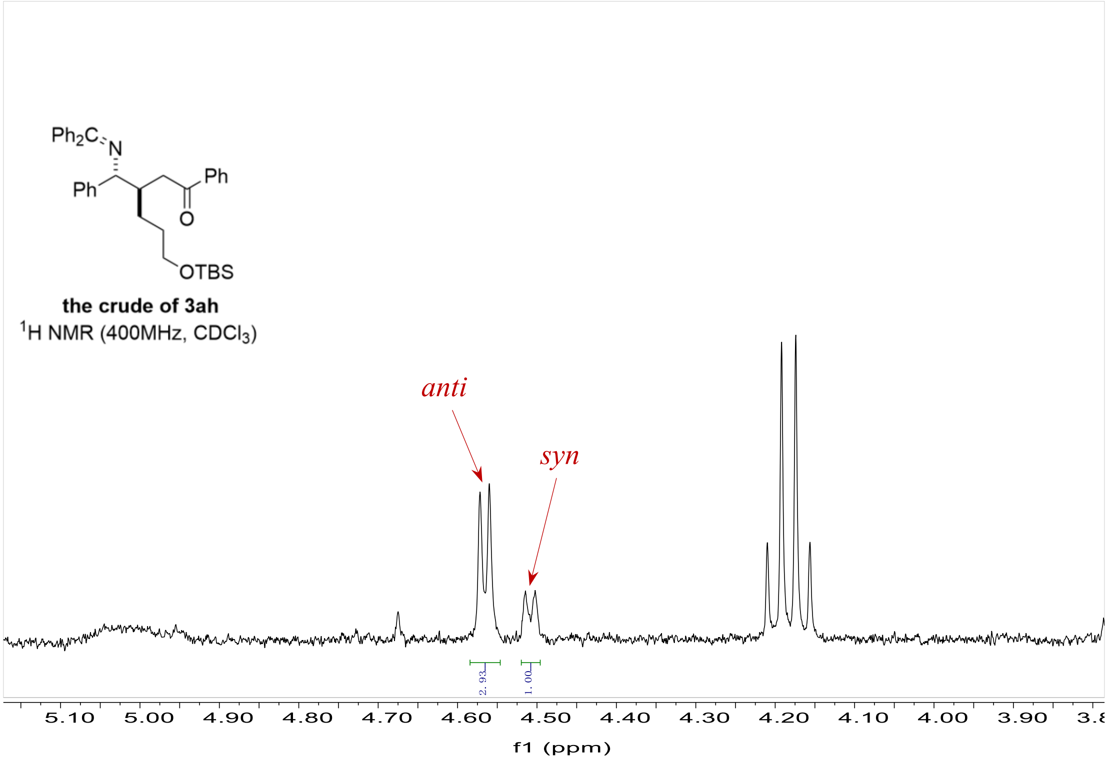
^{1}H NMR (400MHz, CDCl$_3$)

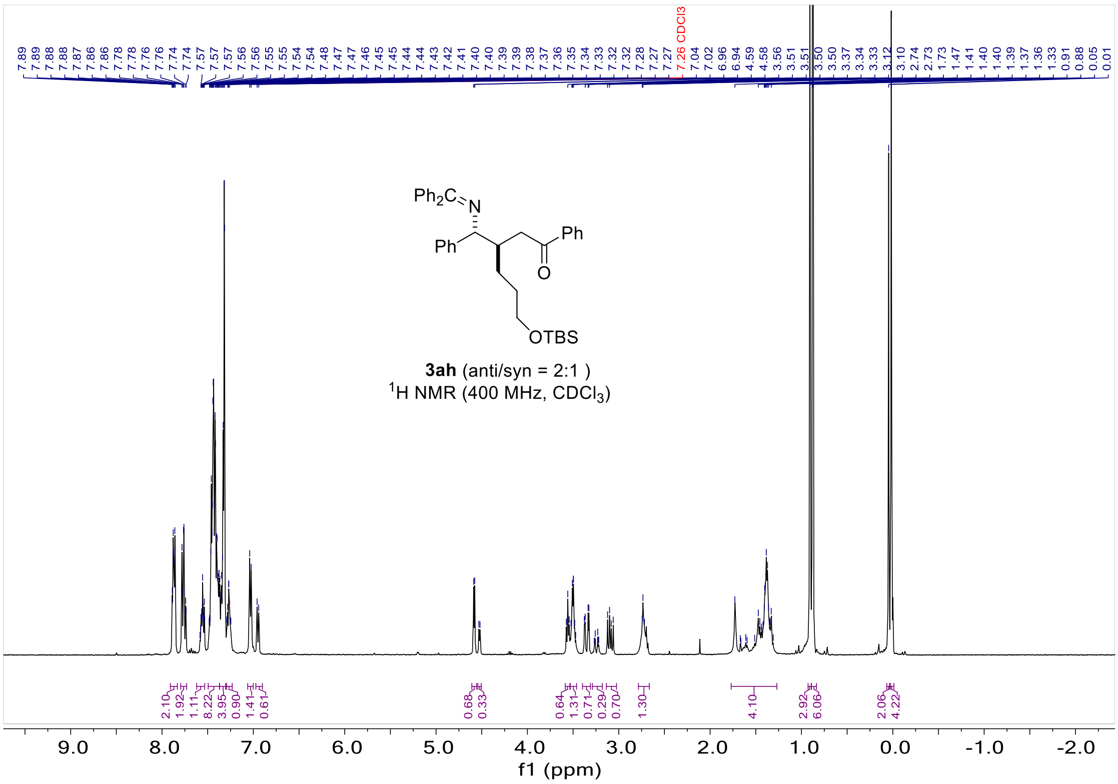


3ag

^{13}C NMR (101MHz, CDCl$_3$)

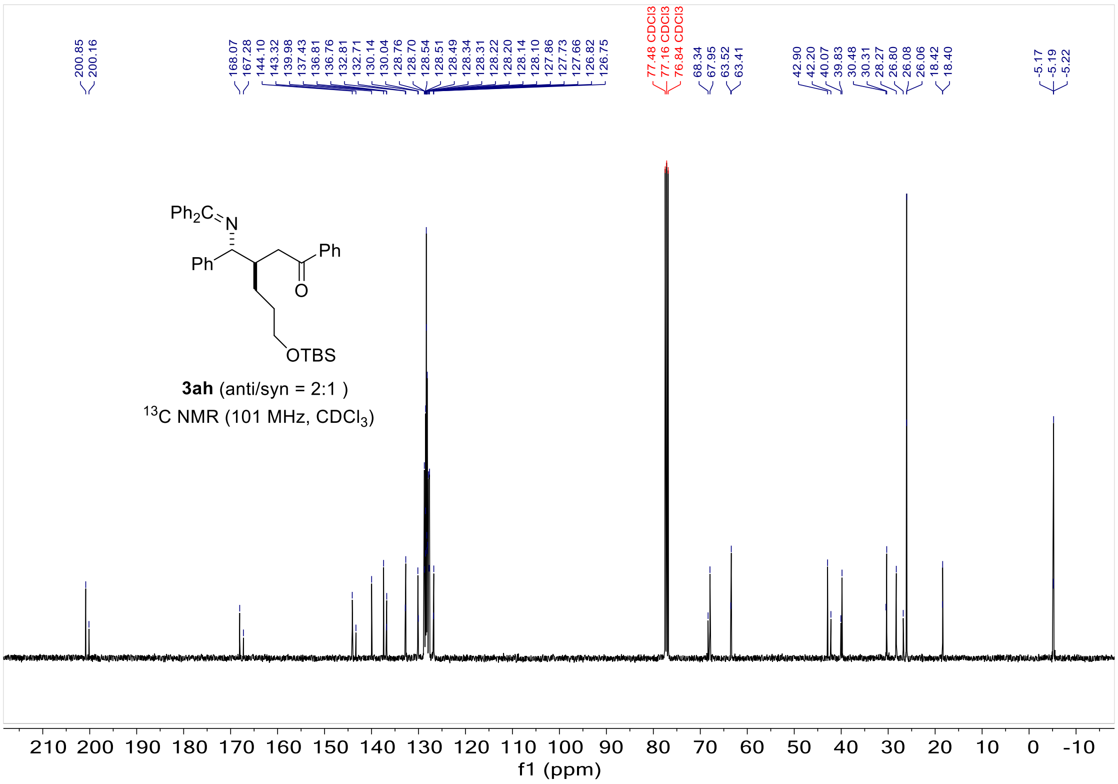

Ph2C
N
Ph
Ph
O
OTBS
the crude of 3ah
1H NMR (400MHz, CDCl3)
anti
syn
2.93
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph2C
N
Ph
Ph
O
OTBS
the crude of 3ah
1H NMR (400MHz, CDCl3)
anti
syn
2.93
1.00
5.10 5.00 4.90 4.80 4.70 4.60 4.50 4.40 4.30 4.20 4.10 4.00 3.90
f1 (ppm)



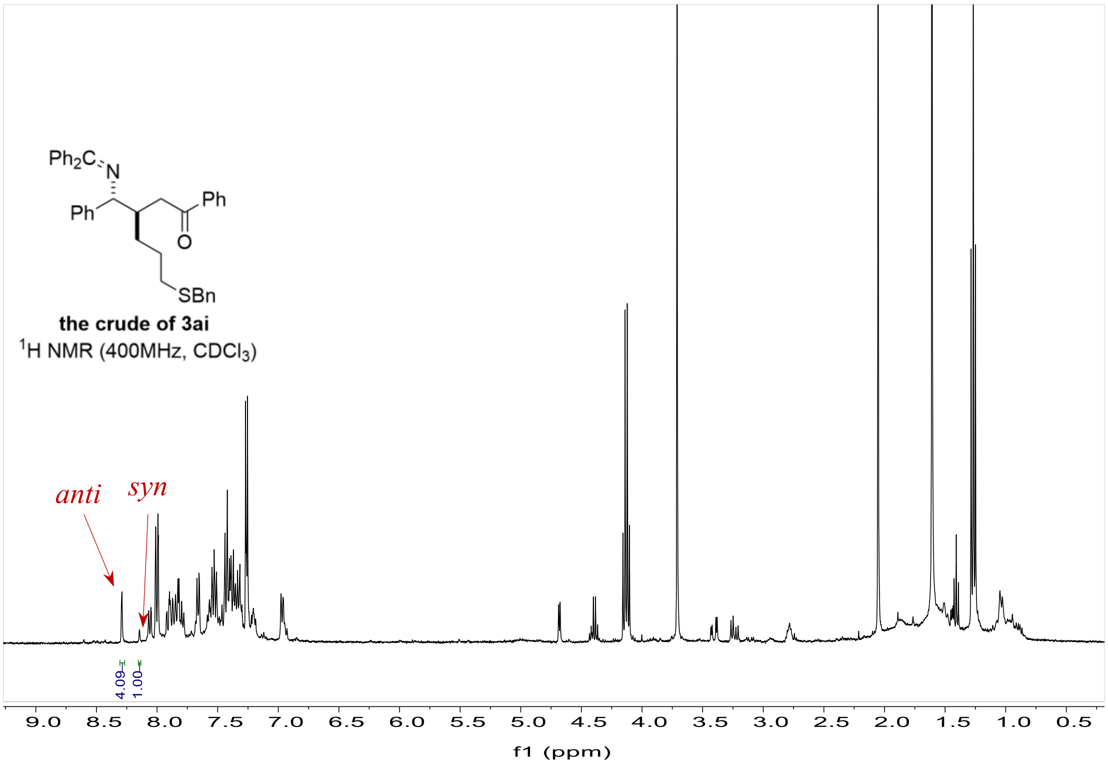
3ah (anti/syn = 2:1)

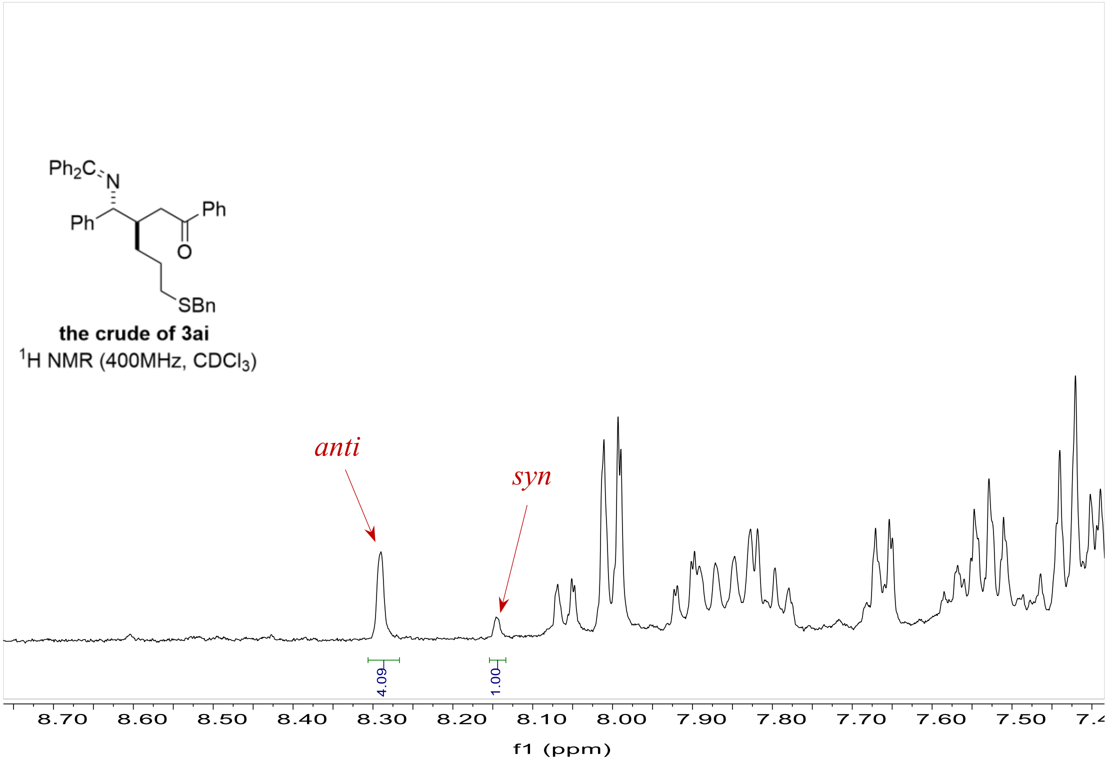
^{1}H NMR (400 MHz, CDCl$_3$)

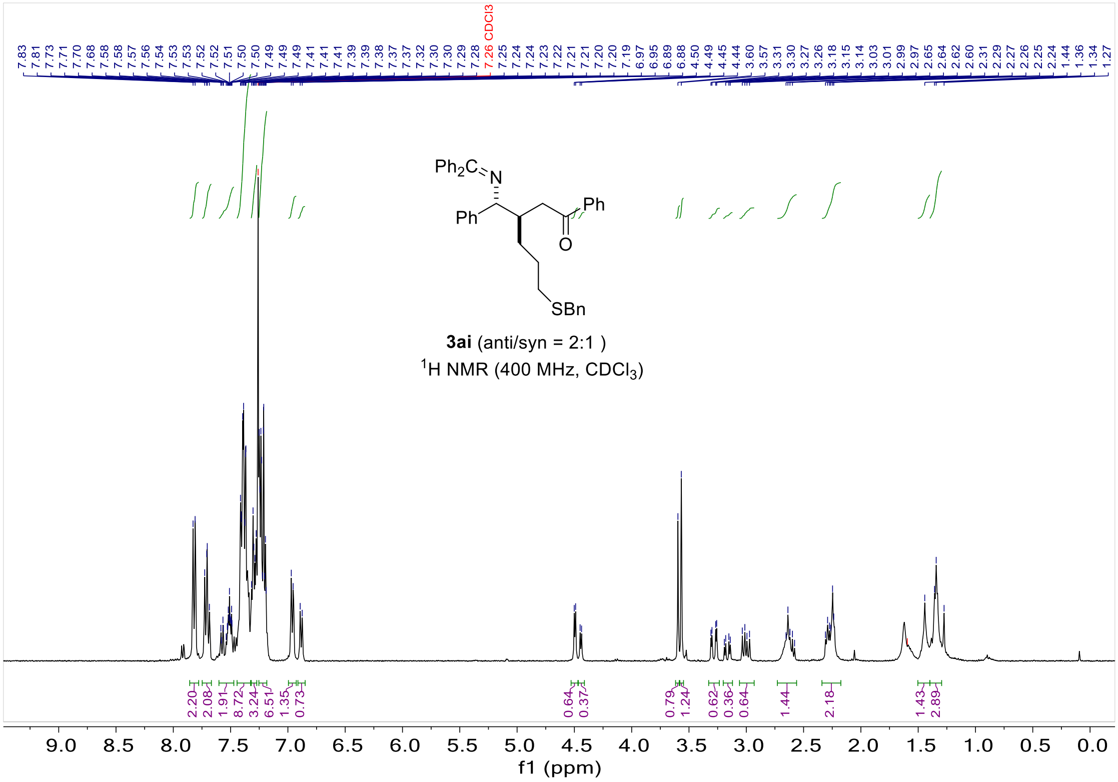


3ah (anti/syn = 2:1)

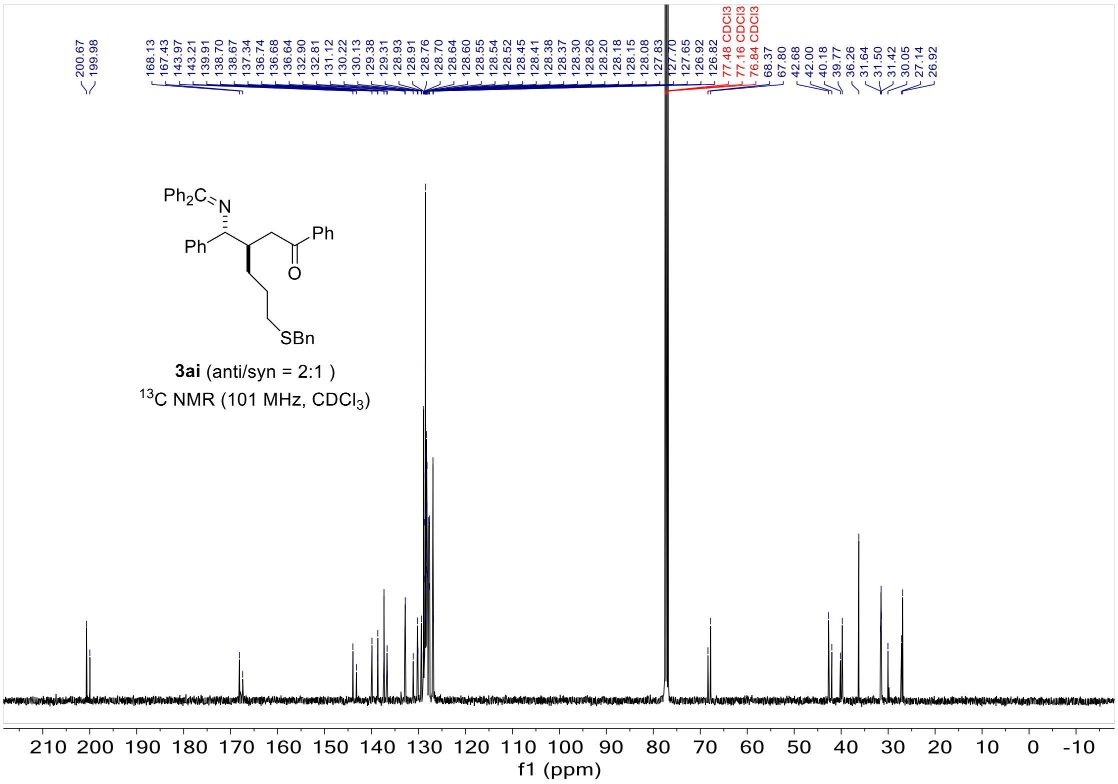
^{13}C NMR (101 MHz, CDCl$_3$)


Ph$_2$C=N
Ph
Ph
O
SBn
the crude of 3ai
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
4.09
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

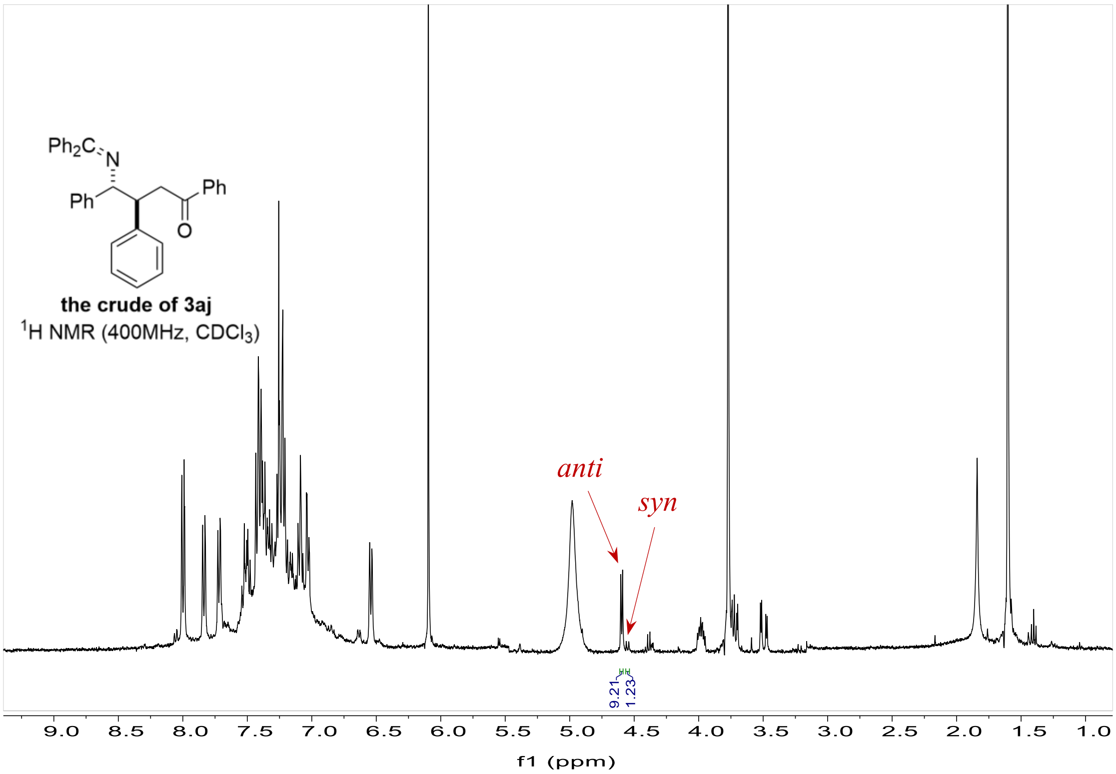

Ph$_2$C=N
Ph
Ph
O
SBn
the crude of 3ai
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
4.09
1.00
8.70
8.60
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.4
f1 (ppm)

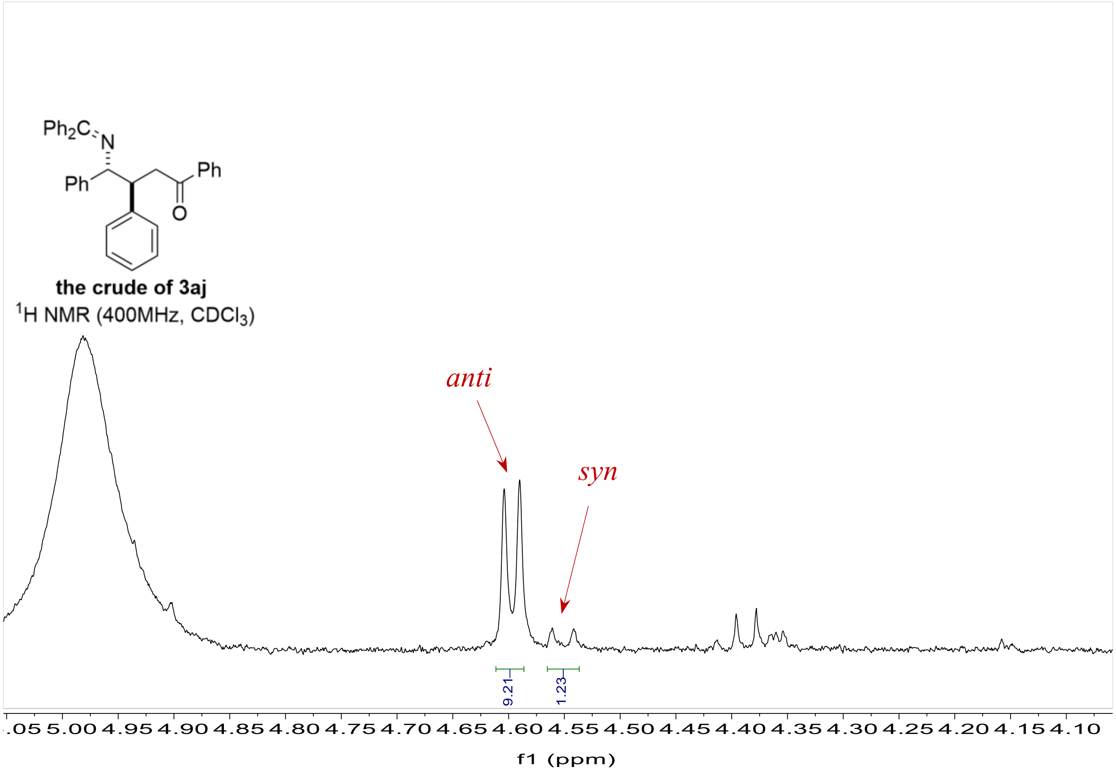


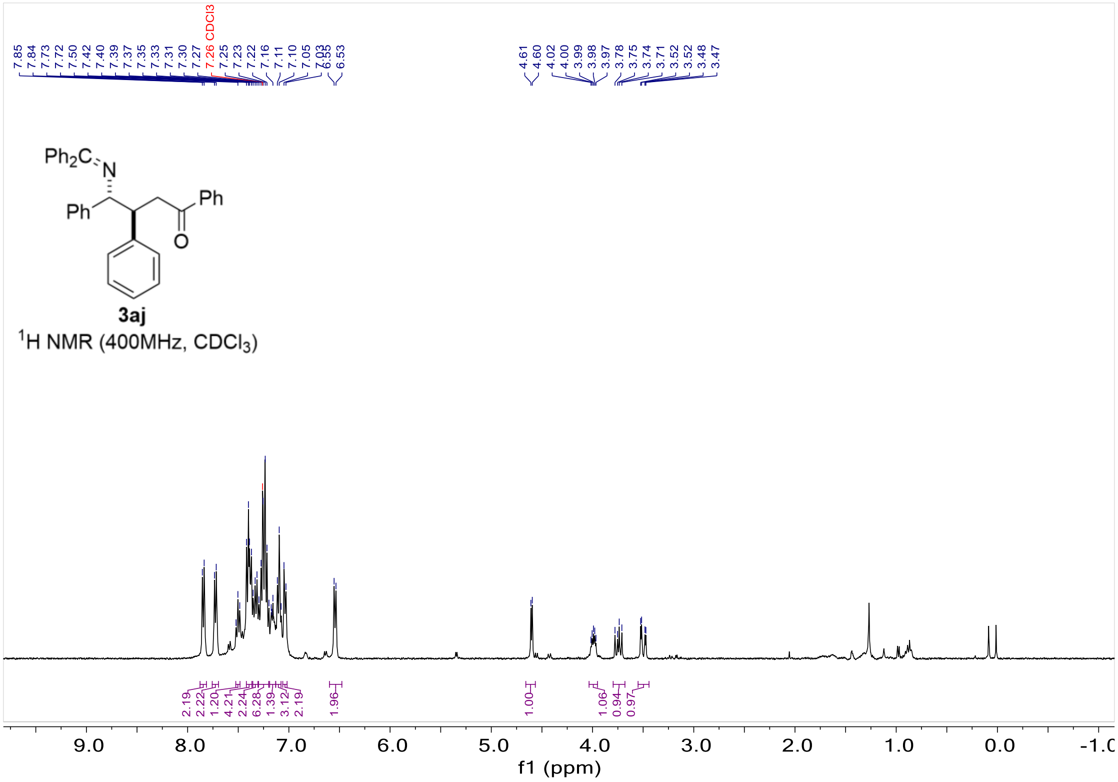
3ai (anti/syn = 2:1)
^{1}H NMR (400 MHz, $CDCl_3$)

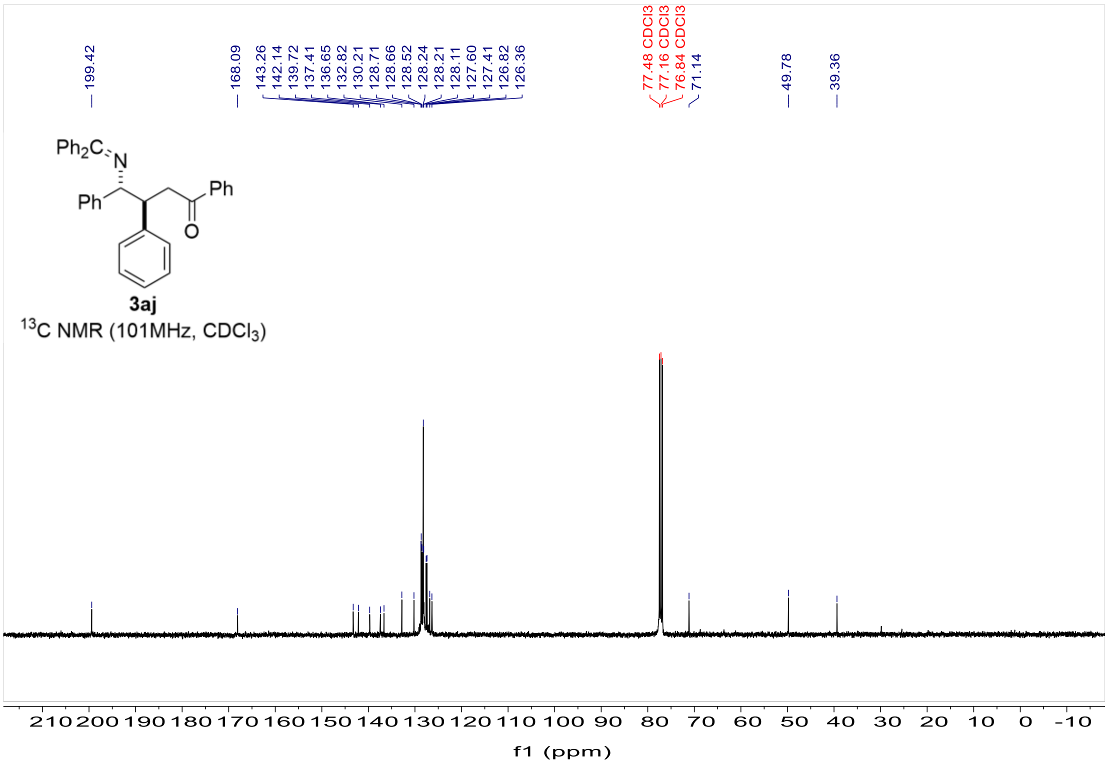


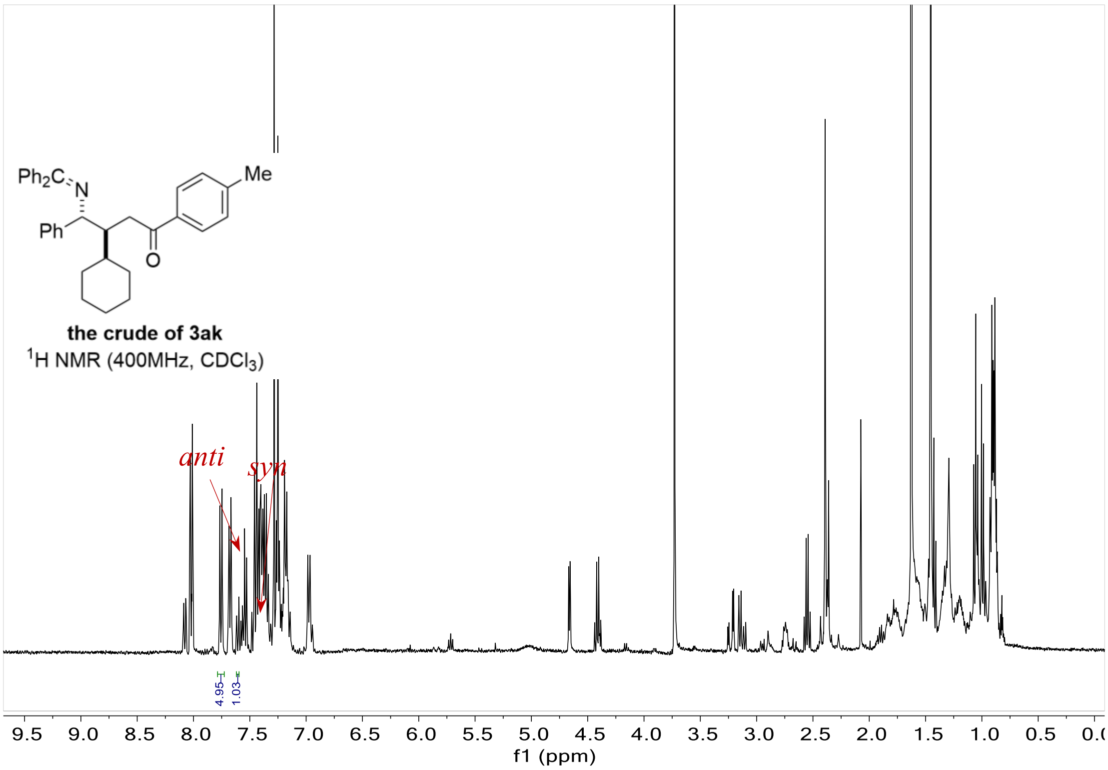
3ai (anti/syn = 2:1)
^{13}C NMR (101 MHz, $CDCl_3$)

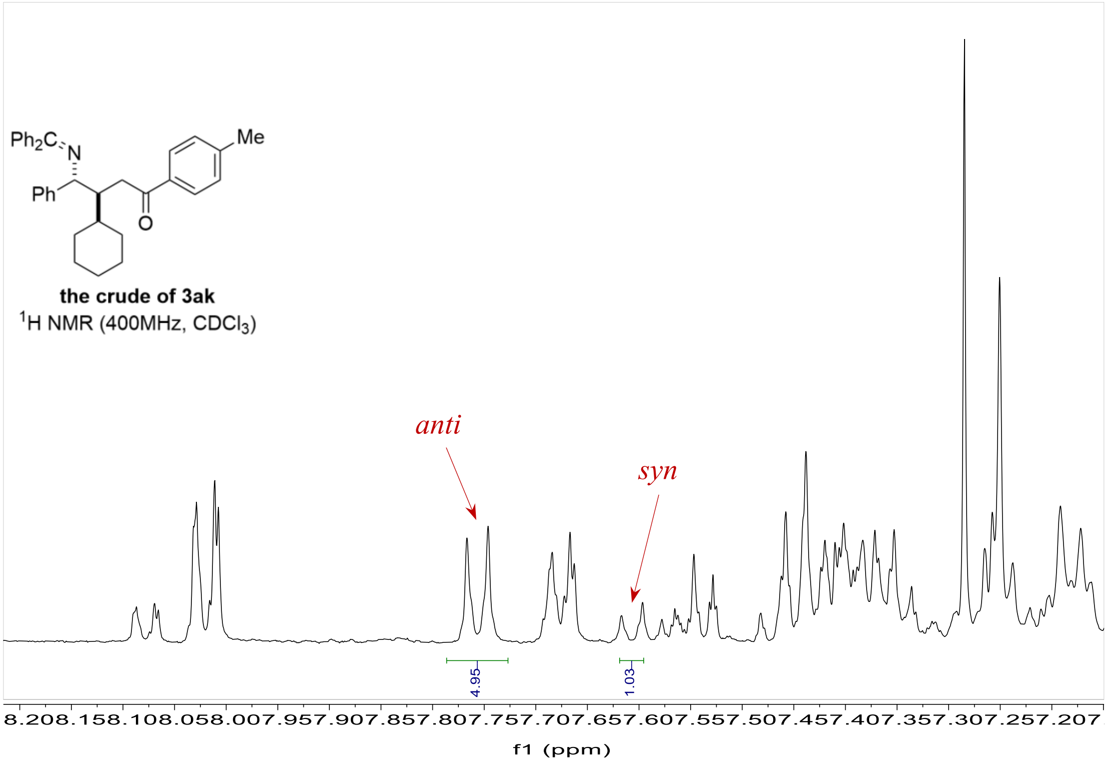

Ph2C=N
Ph
Ph
O
the crude of 3aj
1H NMR (400MHz, CDCl3)
anti
syn
9.21
1.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

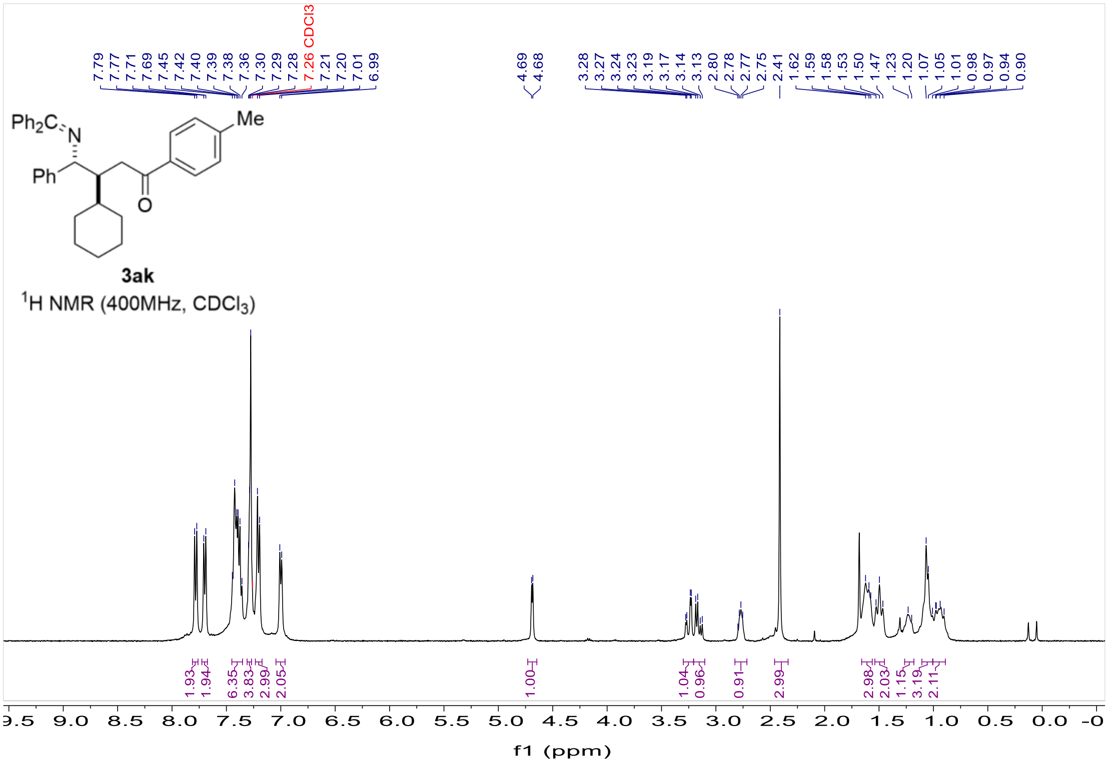

Ph2C=N
Ph
Ph
O
the crude of 3aj
1H NMR (400MHz, CDCl3)
anti
syn
9.21
1.23
.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10
f1 (ppm)


7.85
7.84
7.73
7.72
7.50
7.42
7.40
7.39
7.37
7.35
7.33
7.31
7.30
7.27
7.26 CDCl3
7.25
7.23
7.22
7.16
7.11
7.10
7.05
7.03
6.55
6.53
4.61
4.60
4.02
4.00
3.99
3.98
3.97
3.78
3.75
3.74
3.71
3.52
3.52
3.48
3.47
Ph2C
N
Ph
Ph
O
3aj
1H NMR (400MHz, CDCl3)
2.19
2.22
1.20
4.21
2.24
6.28
1.39
3.12
2.19
1.96
1.00
1.06
0.94
0.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


199.42
168.09
143.26
142.14
139.72
137.41
136.65
132.82
130.21
128.71
128.66
128.52
128.24
128.21
128.11
127.60
127.41
126.82
126.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.14
49.78
39.36
Ph2C
N
Ph
Ph
O
3aj
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

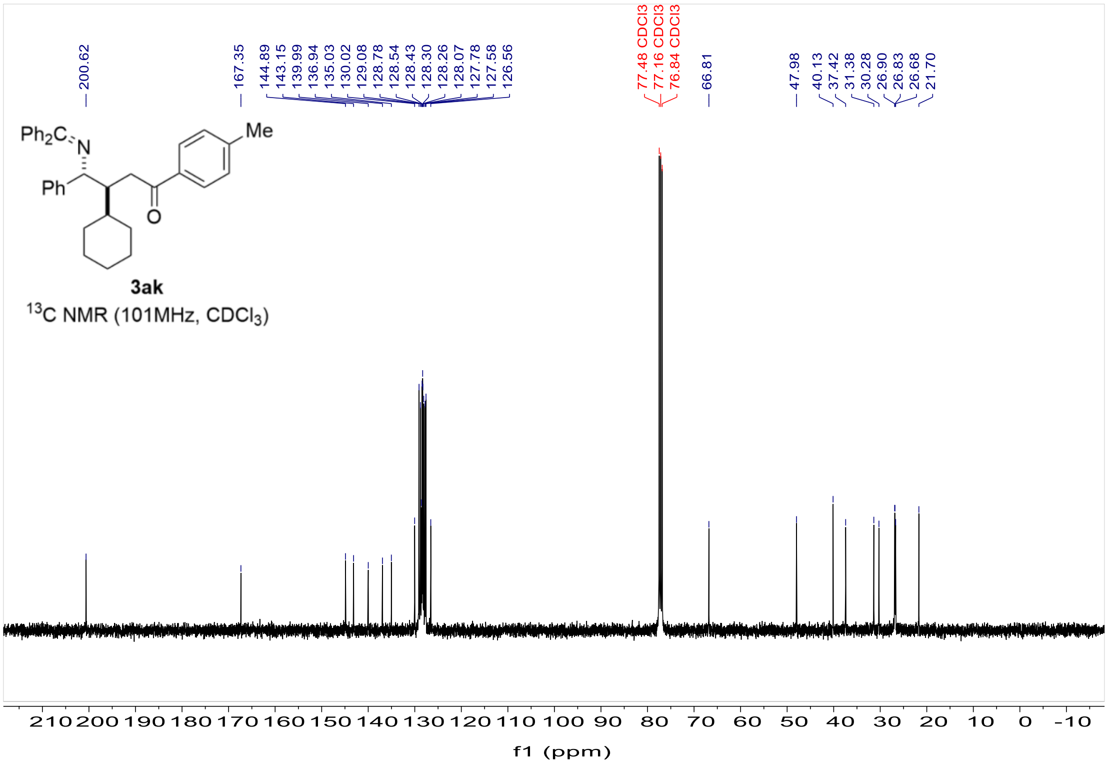

Ph2C N
Me
Ph
O
the crude of 3ak
1H NMR (400MHz, CDCl3)
anti
syn
4.95
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph2C N
Me
Ph
O
the crude of 3ak
1H NMR (400MHz, CDCl3)
anti
syn
4.95
1.03
8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)



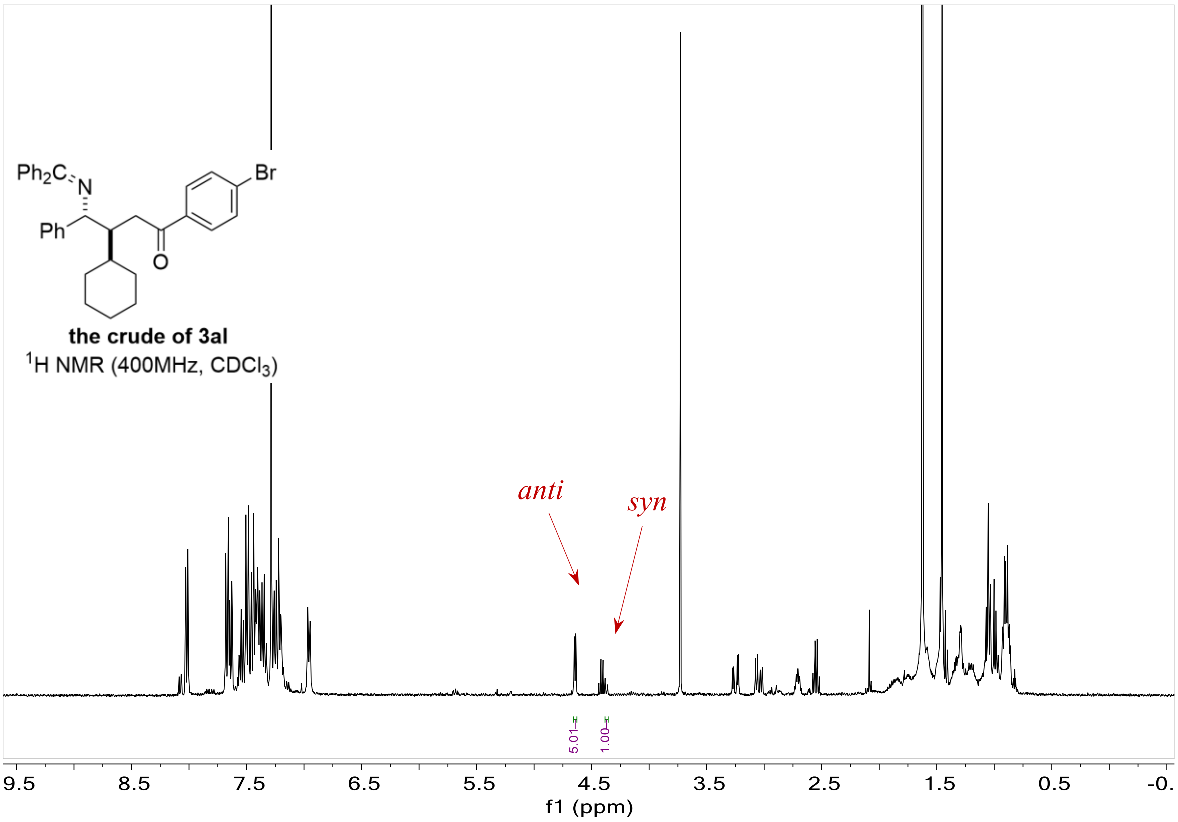
3ak

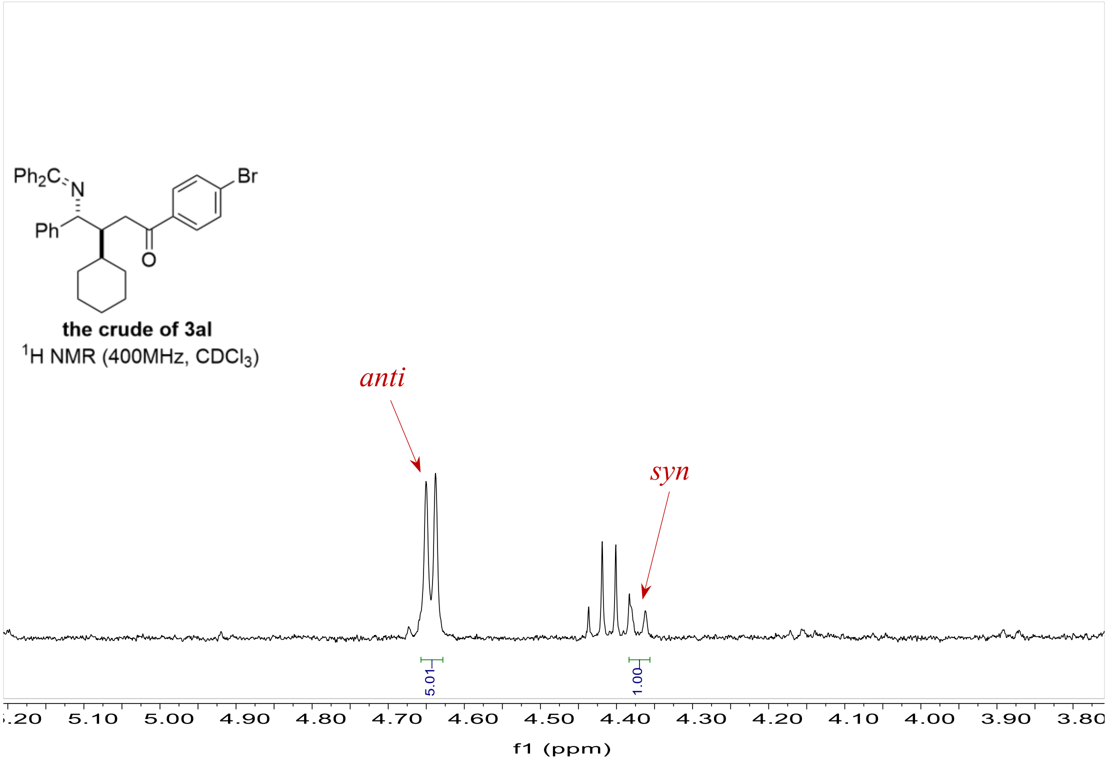
^{1}H NMR (400MHz, CDCl$_3$)

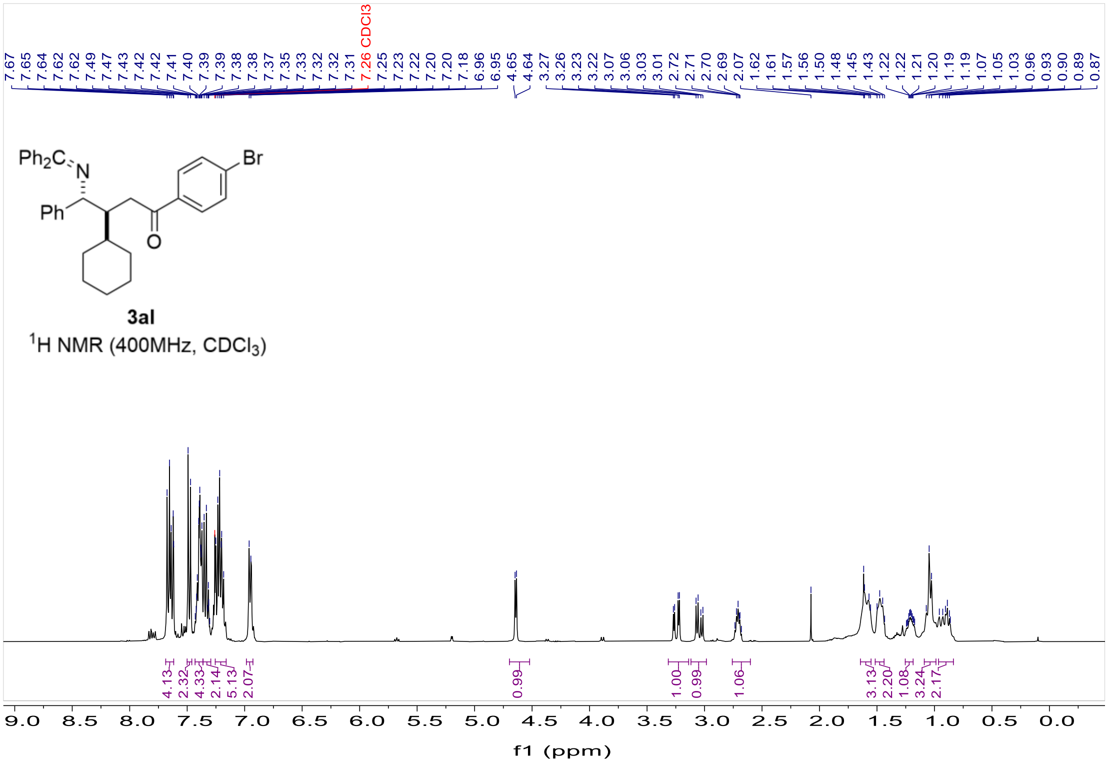


3ak

^{13}C NMR (101MHz, CDCl$_3$)

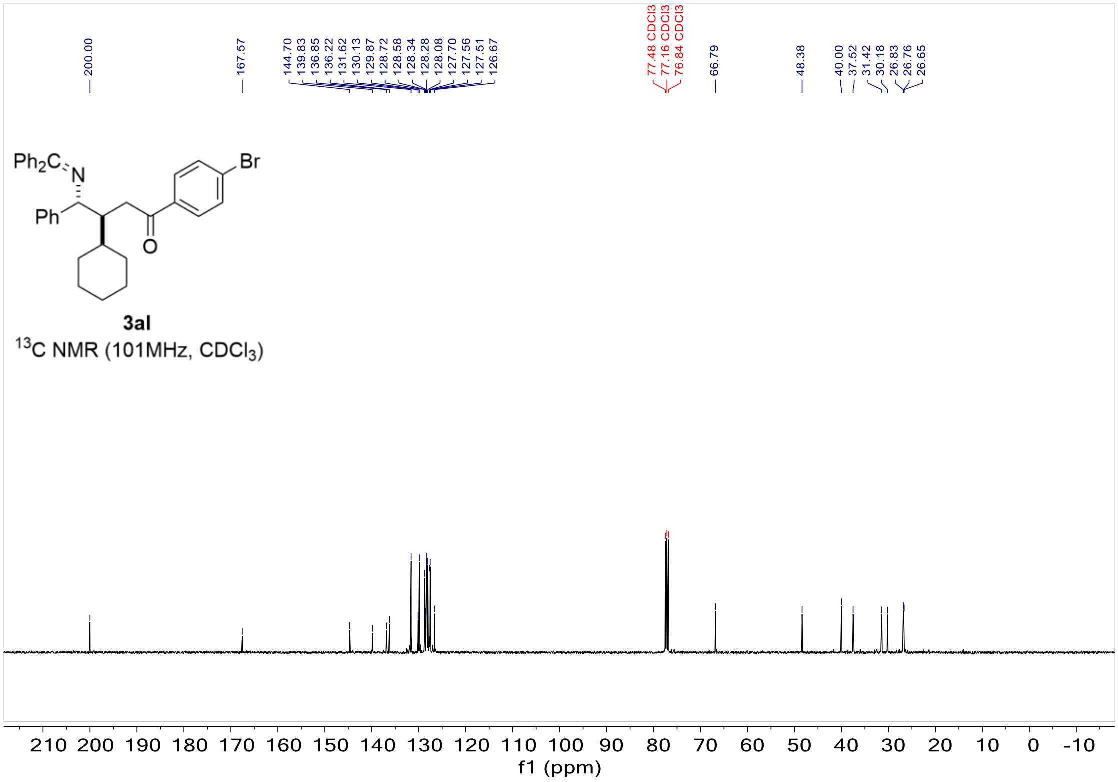

Ph2C
N
Br
Ph
O
the crude of 3al
1H NMR (400MHz, CDCl3)
anti
syn
5.01
1.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)


Ph2C
N
Br
Ph
O
the crude of 3al
1H NMR (400MHz, CDCl3)
anti
syn
5.01
1.00
.20
5.10
5.00
4.90
4.80
4.70
4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
f1 (ppm)



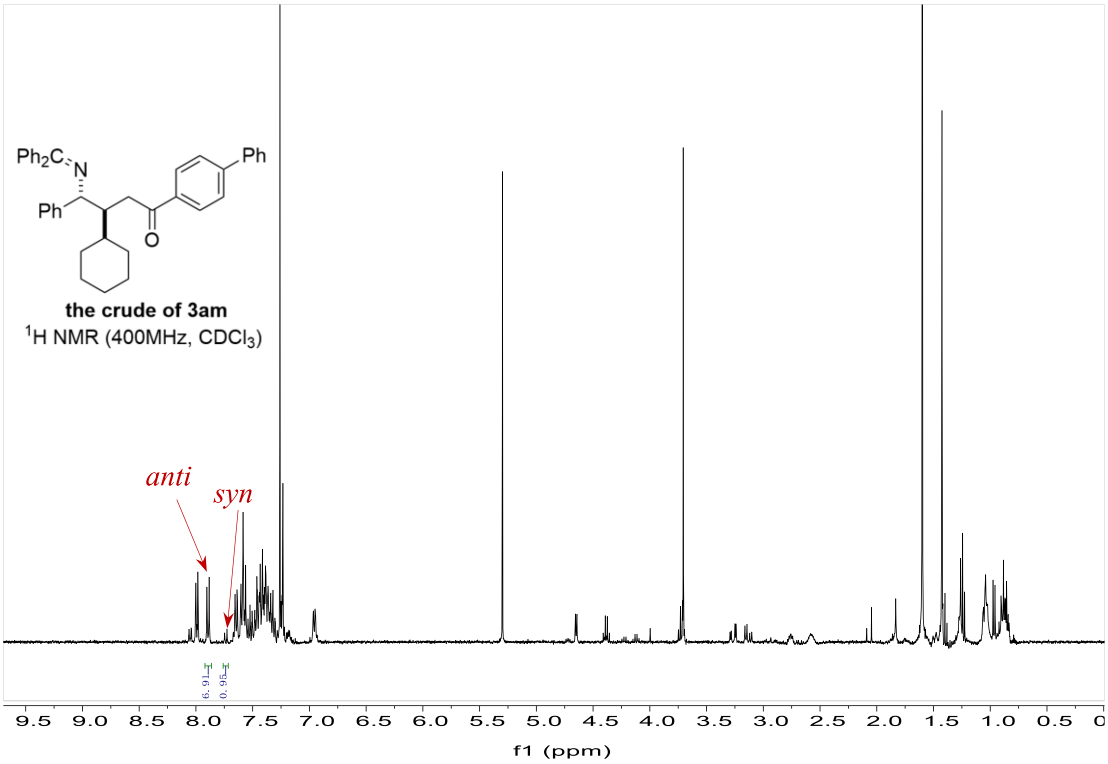
3al

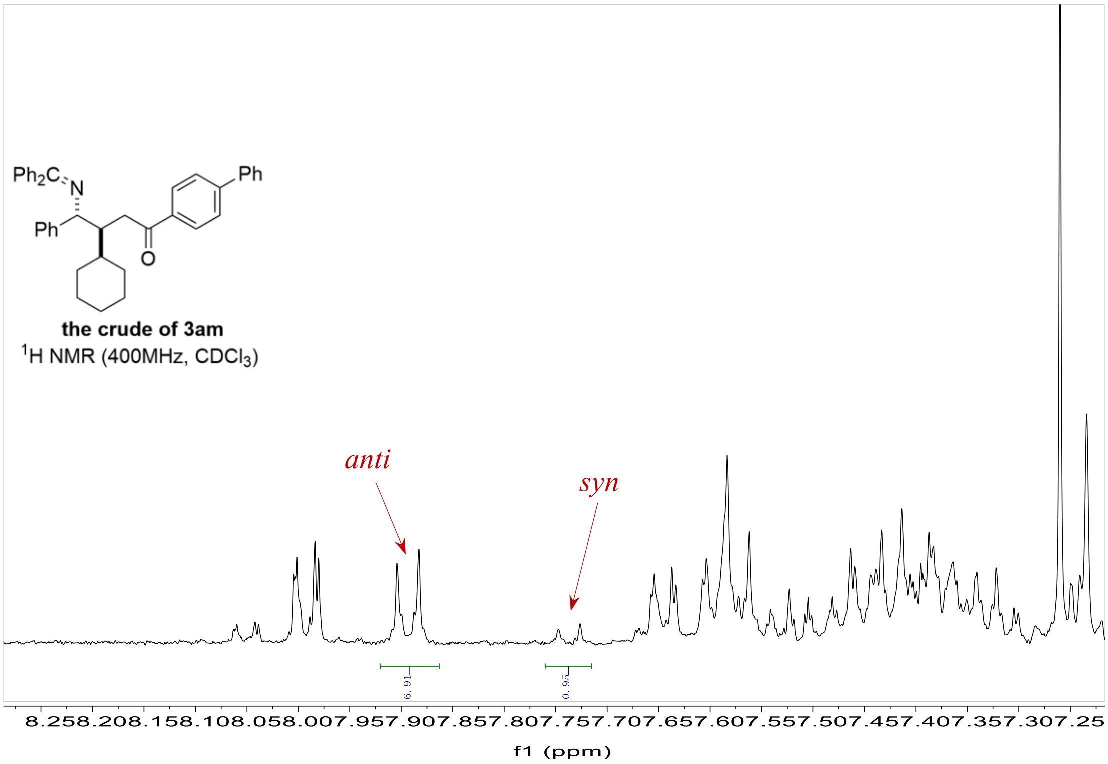
^{1}H NMR (400MHz, CDCl$_3$)

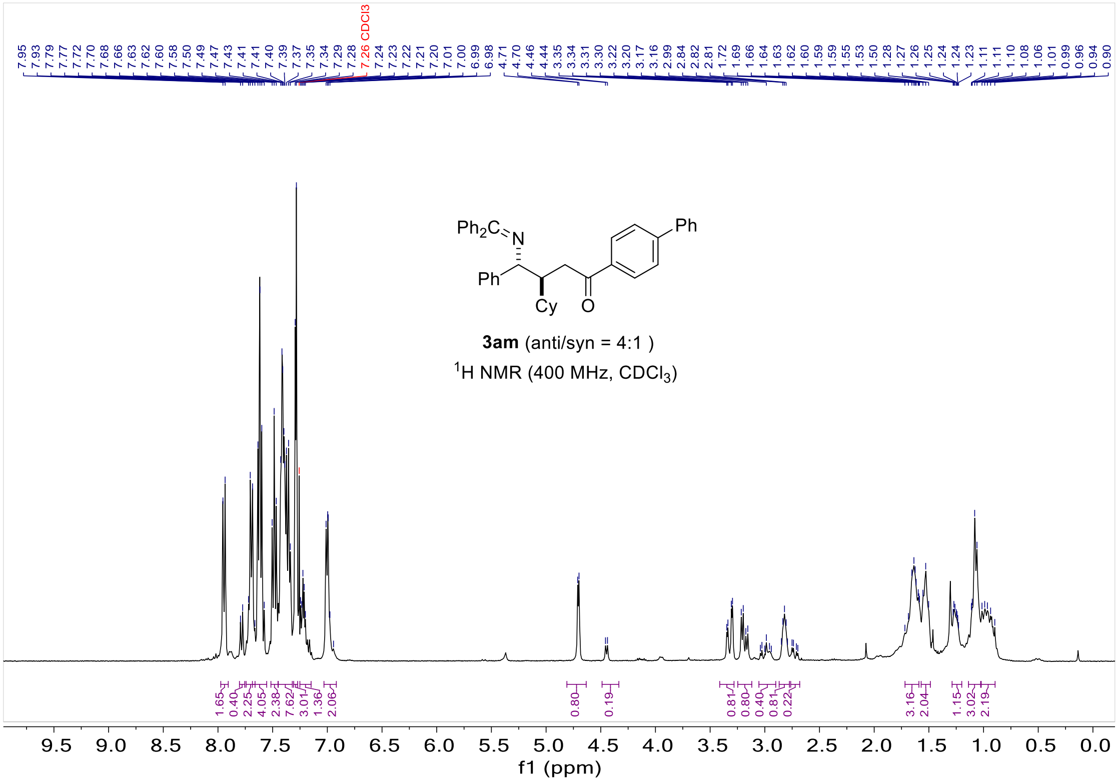


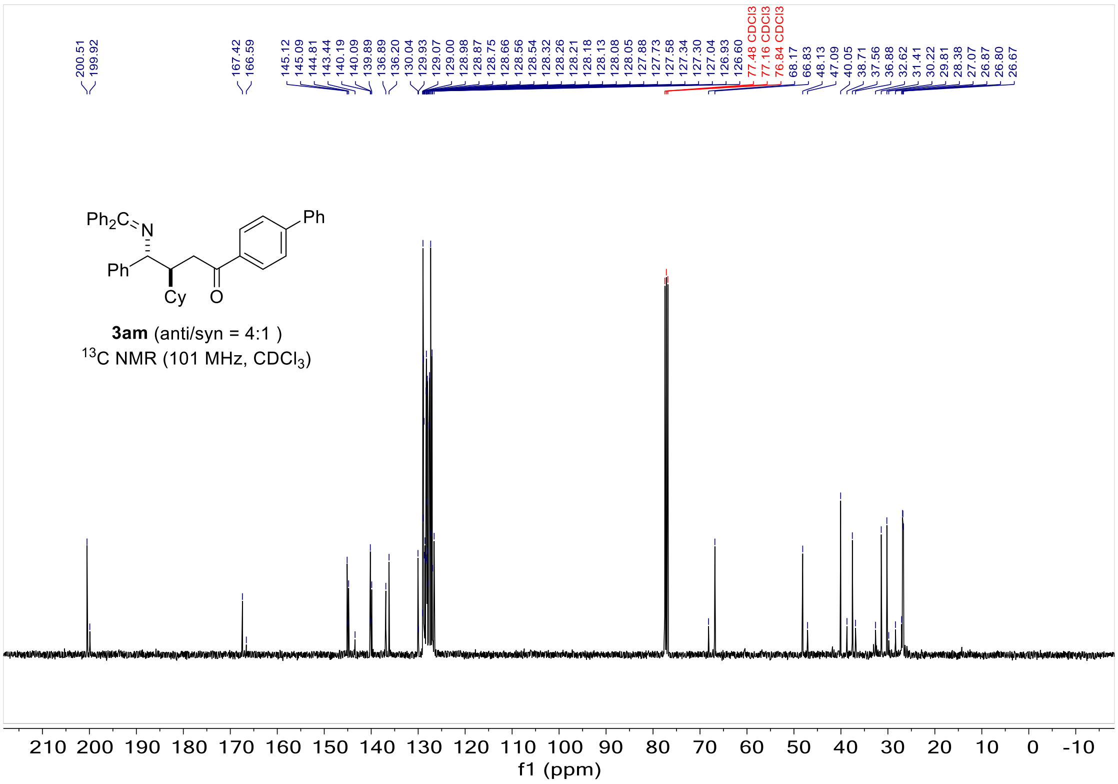
3al

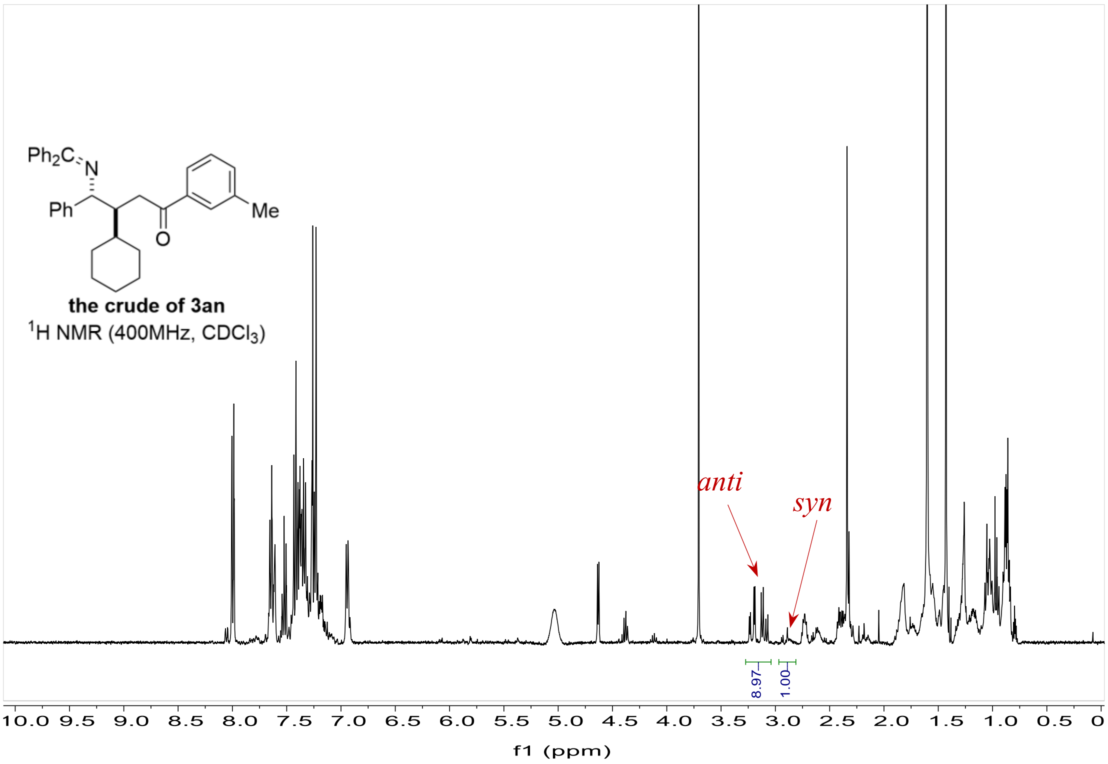
^{13}C NMR (101MHz, CDCl$_3$)

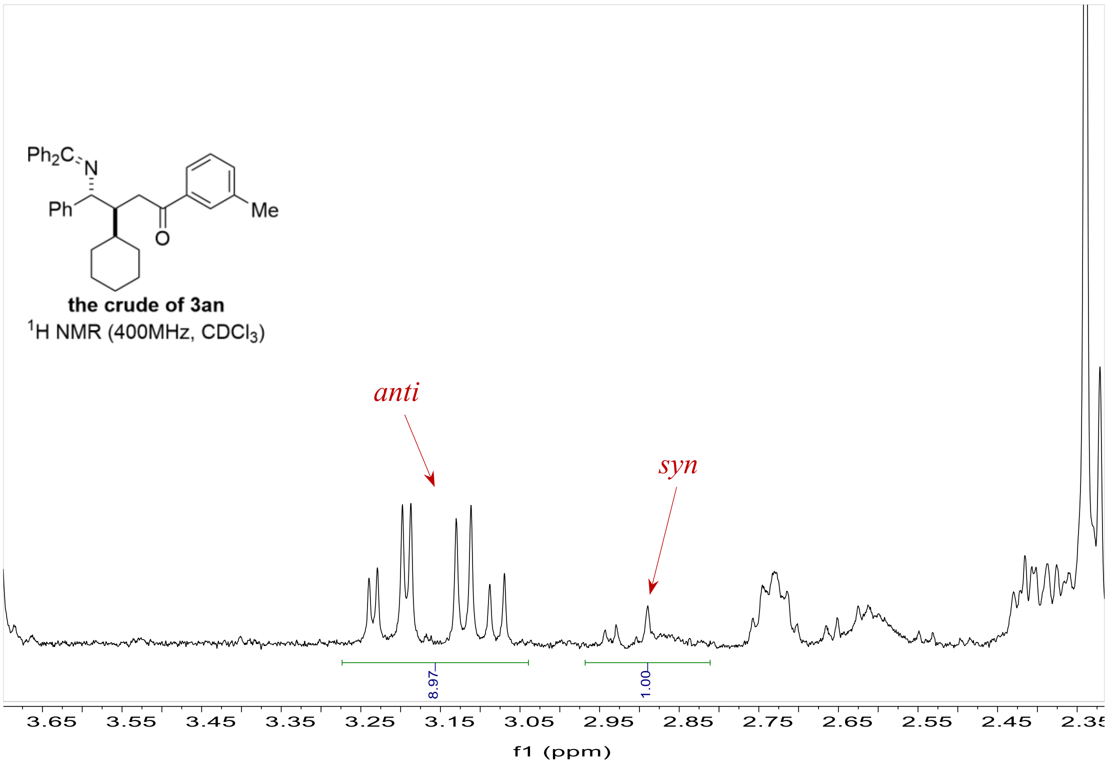

Ph2C=N
Ph
Ph
O
the crude of 3am
1H NMR (400MHz, CDCl3)
anti
syn
6.91
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

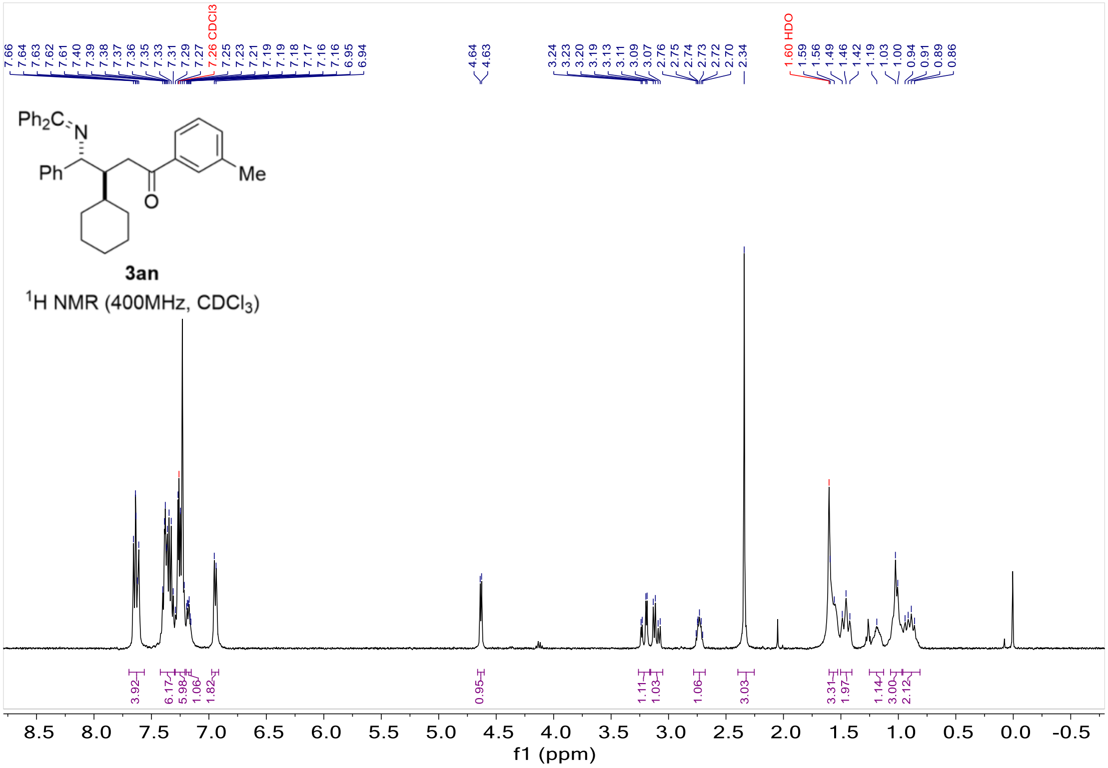

Ph2C=N
Ph
Ph
O
the crude of 3am
1H NMR (400MHz, CDCl3)
anti
syn
6.91
0.95
8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)


7.95
7.93
7.79
7.77
7.72
7.70
7.68
7.66
7.63
7.62
7.60
7.58
7.50
7.49
7.47
7.43
7.41
7.41
7.40
7.39
7.37
7.35
7.34
7.29
7.28
7.26 CDCl3
7.24
7.23
7.22
7.21
7.20
7.01
7.00
6.99
6.98
4.71
4.70
4.46
4.44
3.35
3.34
3.31
3.30
3.22
3.20
3.17
3.16
2.99
2.84
2.82
2.81
1.72
1.69
1.66
1.64
1.63
1.62
1.60
1.59
1.59
1.55
1.53
1.50
1.28
1.27
1.26
1.25
1.24
1.24
1.23
1.11
1.11
1.10
1.08
1.06
1.01
0.99
0.96
0.94
0.90
Ph2C
N
Ph
Cy
O
Ph
3am (anti/syn = 4:1)
1H NMR (400 MHz, CDCl3)
1.65
0.40
2.25
4.05
2.38
7.62
3.01
1.36
2.06
0.80
0.19
0.81
0.80
0.40
0.81
0.22
3.16
2.04
1.15
3.02
2.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.51
199.92
167.42
166.59
145.12
145.09
144.81
143.44
140.19
140.09
139.89
136.89
136.20
130.04
129.93
129.07
129.00
128.98
128.87
128.75
128.66
128.56
128.54
128.32
128.26
128.21
128.18
128.13
128.08
128.05
127.88
127.73
127.58
127.34
127.30
127.04
126.93
126.60
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.17
66.83
48.13
47.09
40.05
38.71
37.56
36.88
32.62
31.41
30.22
29.81
28.38
27.07
26.87
26.80
26.67
Ph2C
N
Ph
Cy
O
Ph
3am (anti/syn = 4:1)
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

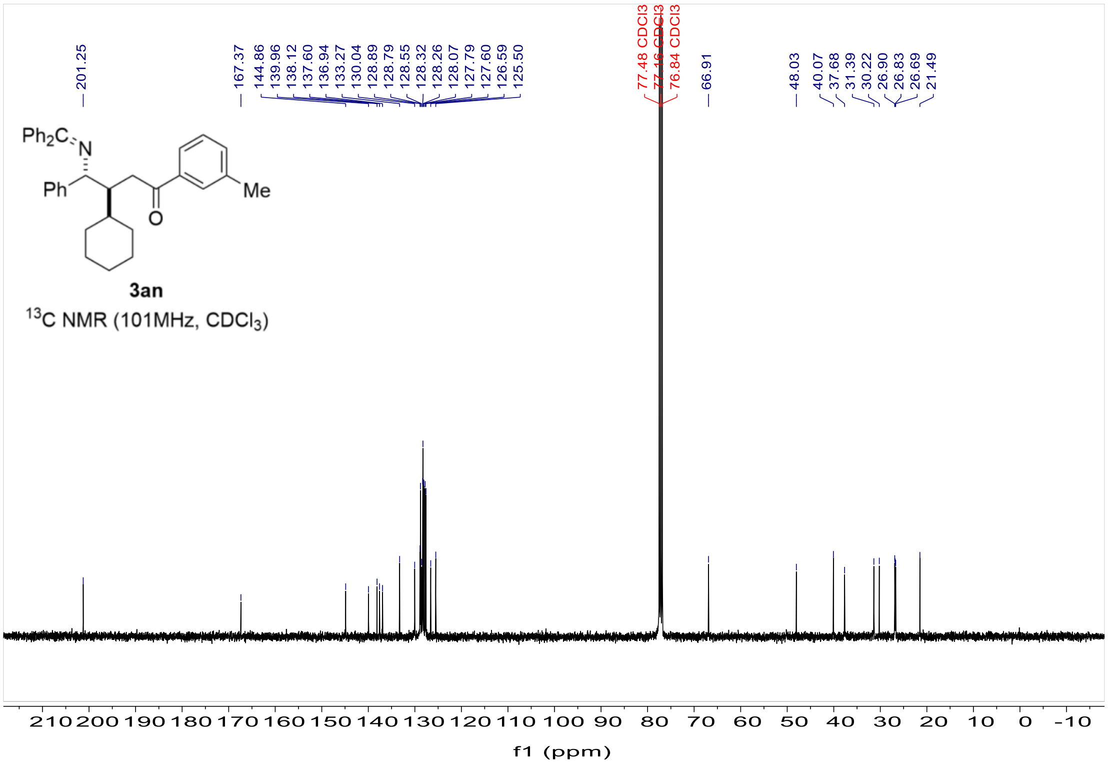

Ph2C
N
Ph
O
Me
the crude of 3an
1H NMR (400MHz, CDCl3)
anti
syn
8.97
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


Ph2C
N
Ph
O
Me
the crude of 3an
1H NMR (400MHz, CDCl3)
anti
syn
8.97
1.00
3.65 3.55 3.45 3.35 3.25 3.15 3.05 2.95 2.85 2.75 2.65 2.55 2.45 2.35
f1 (ppm)



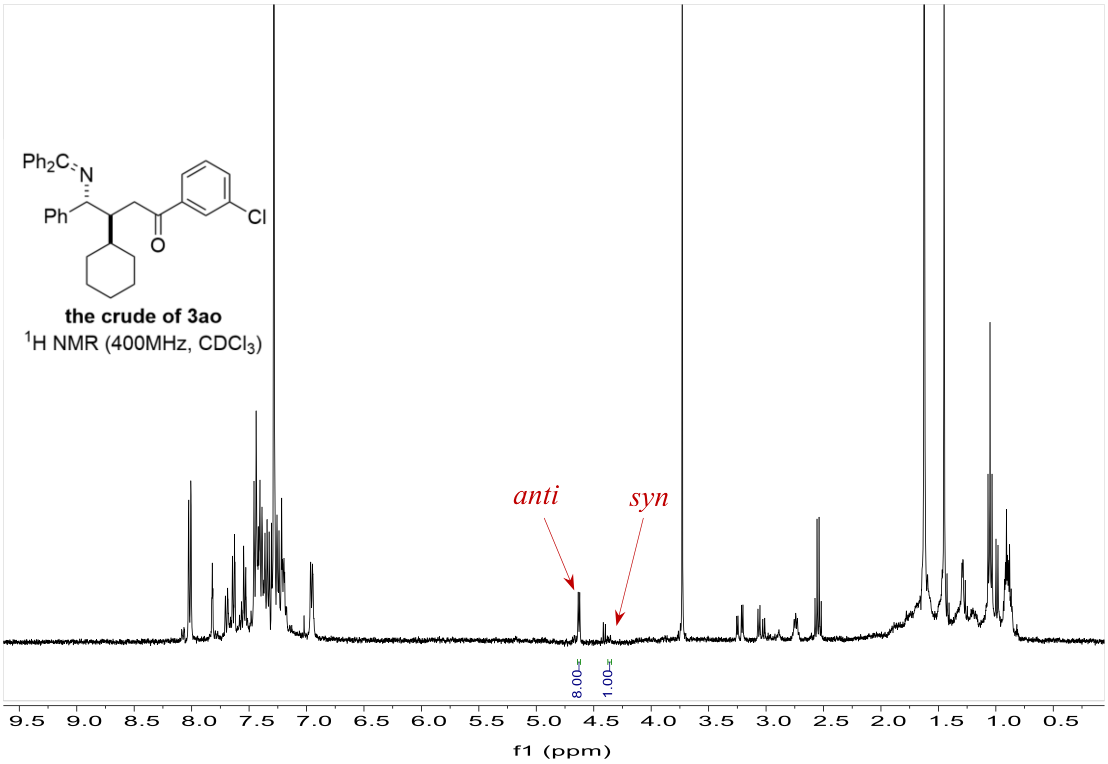
3an

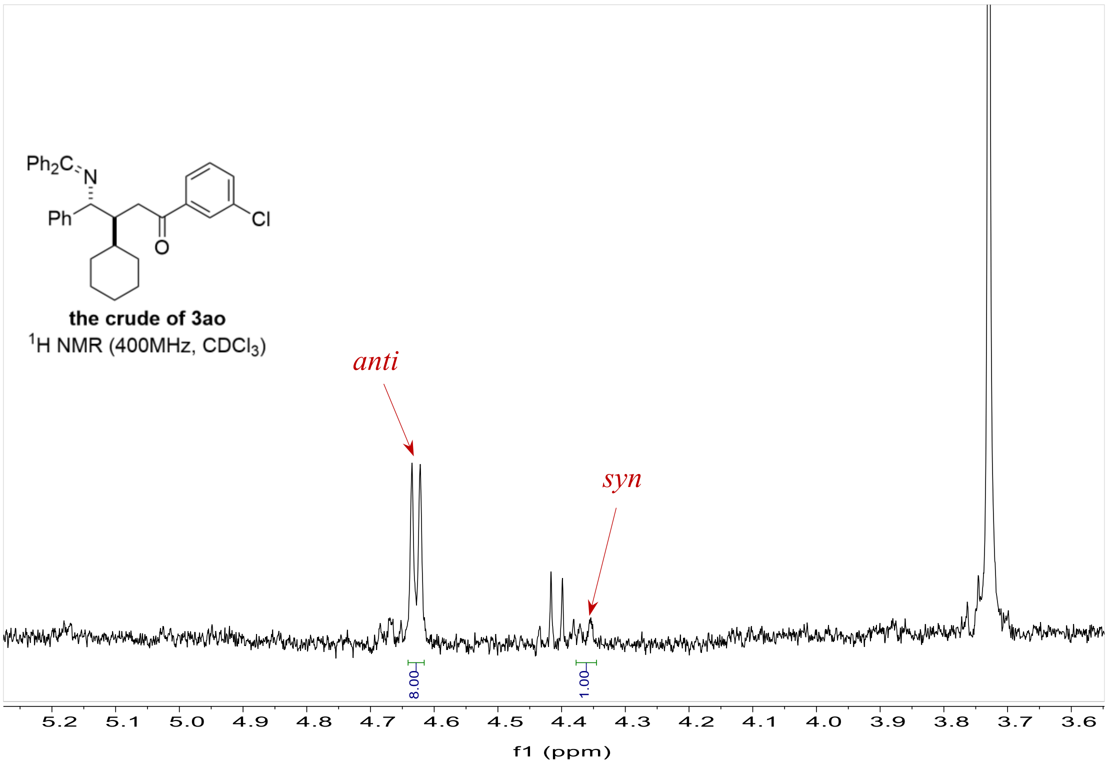
^{1}H NMR (400MHz, CDCl$_3$)

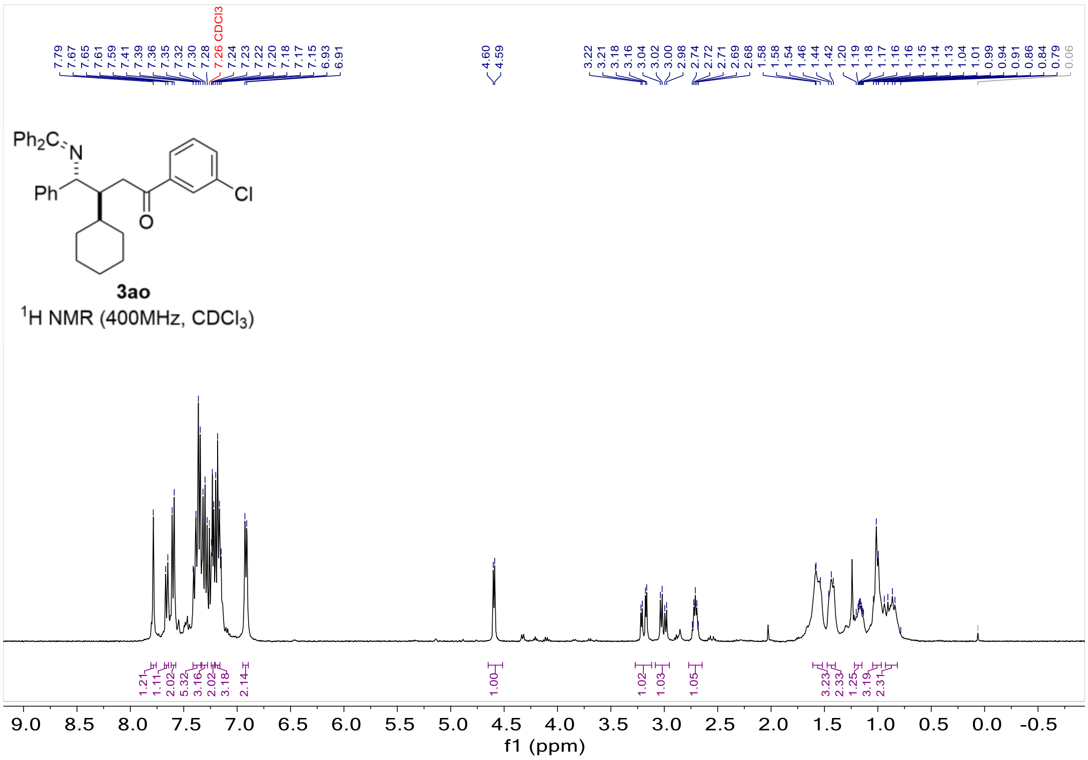


3an

^{13}C NMR (101MHz, CDCl$_3$)

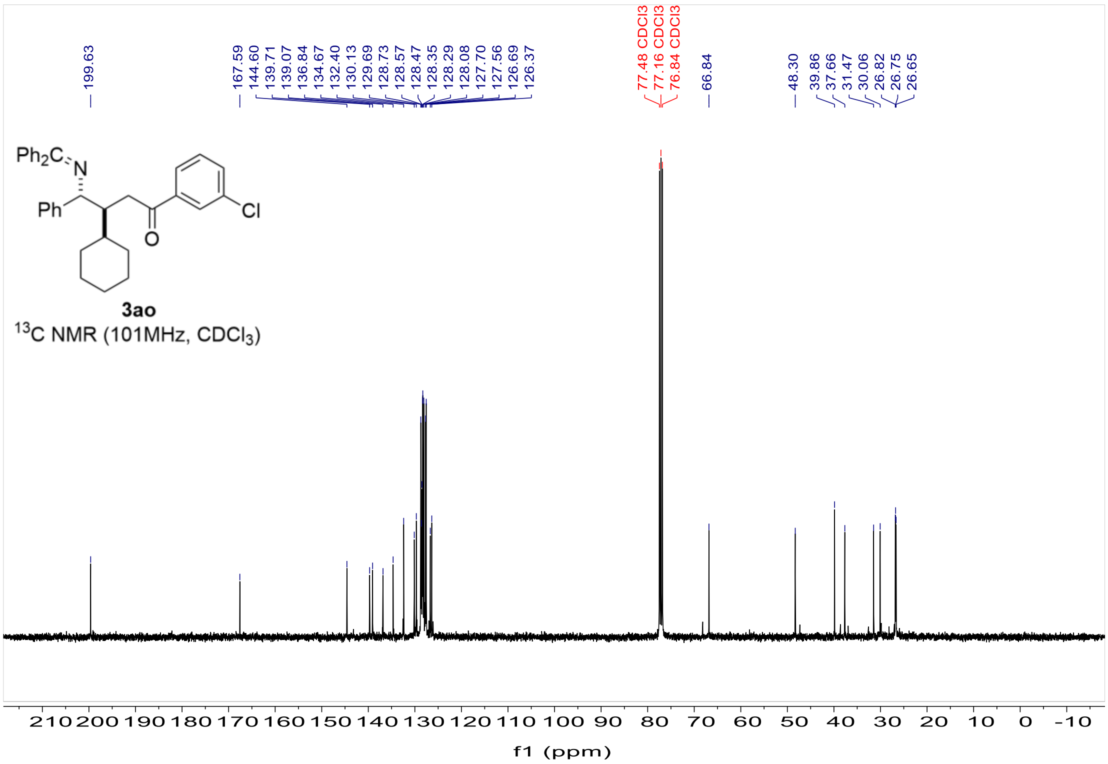

Ph$_2$C=N
Ph
Cl
O
the crude of 3ao
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
8.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph$_2$C=N
Ph
Cl
O
the crude of 3ao
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
8.00
1.00
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6
f1 (ppm)



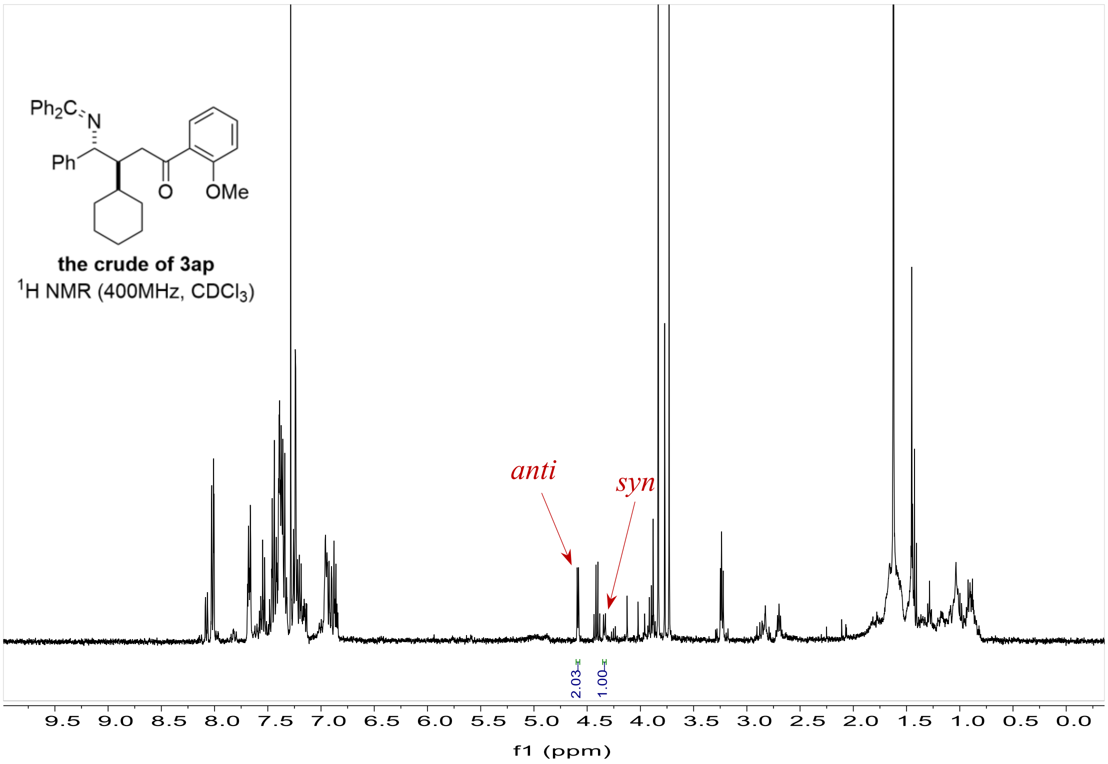
3ao

^{1}H NMR (400MHz, CDCl$_3$)

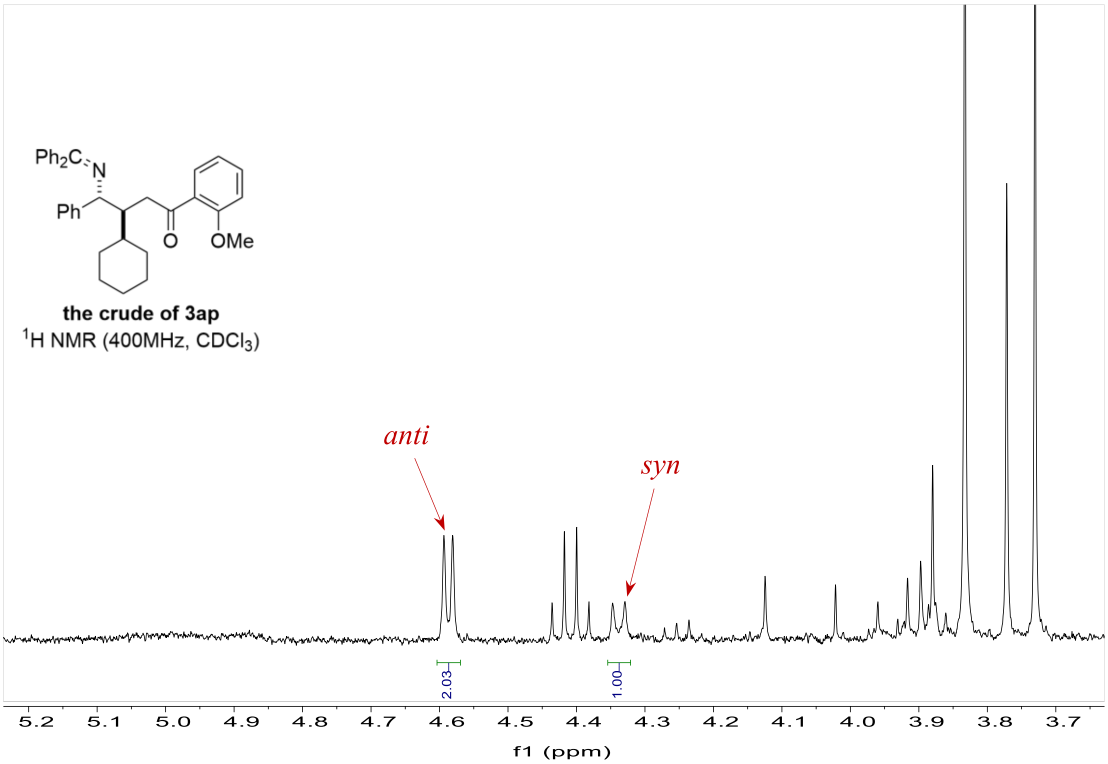


3ao

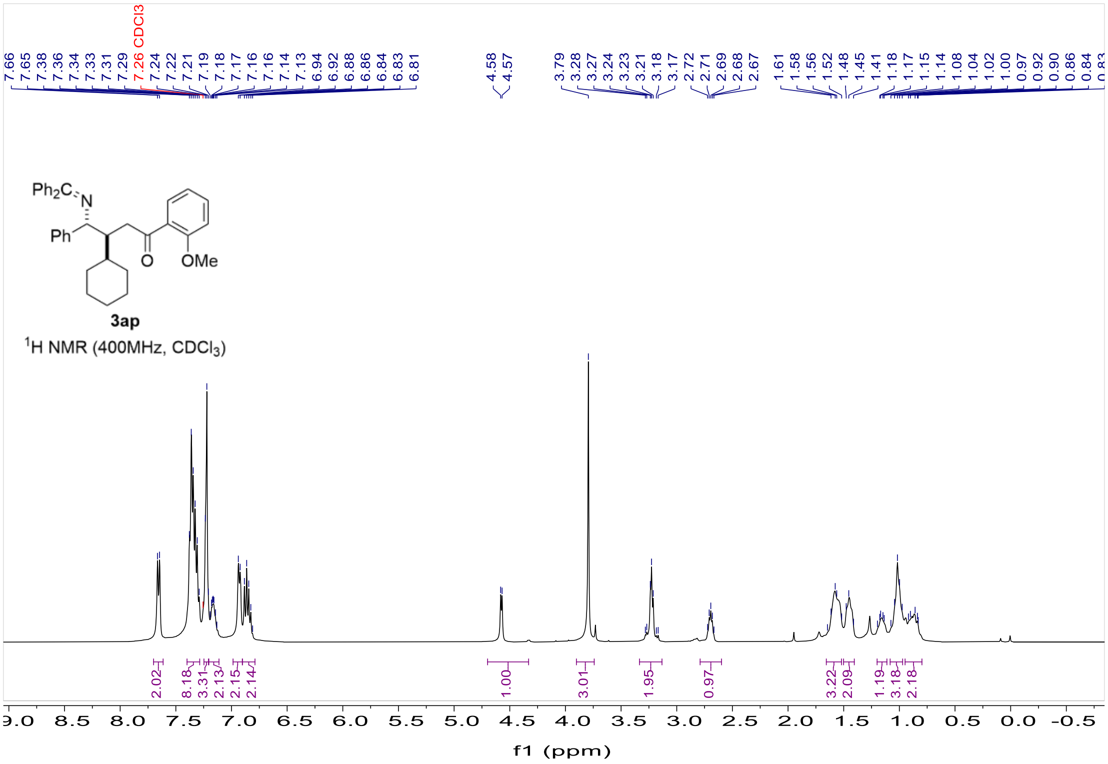
^{13}C NMR (101MHz, CDCl$_3$)

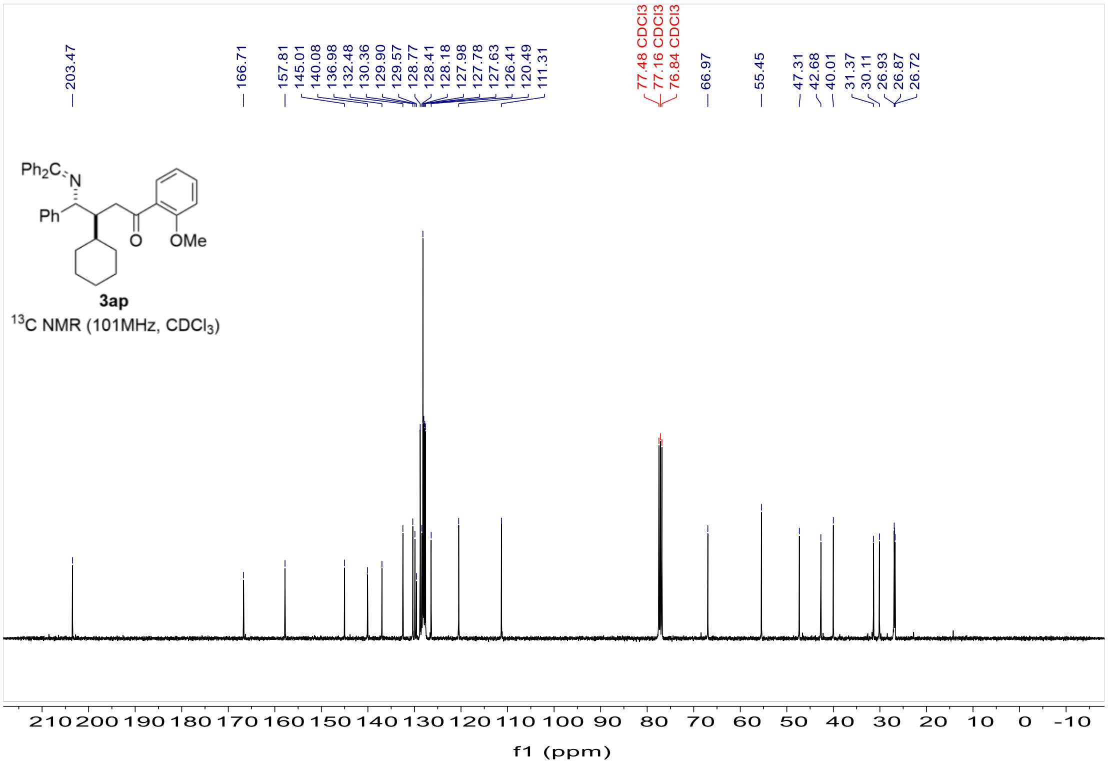


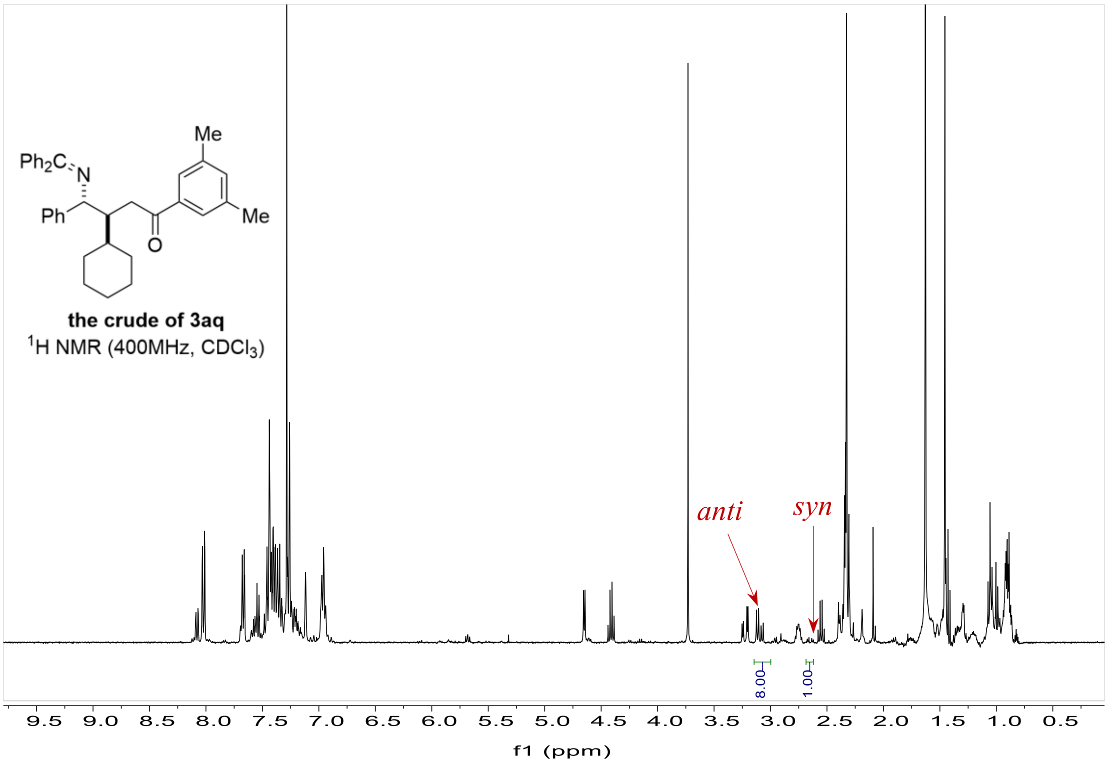
Ph$_2$C
N
Ph
O
OMe
the crude of 3ap
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

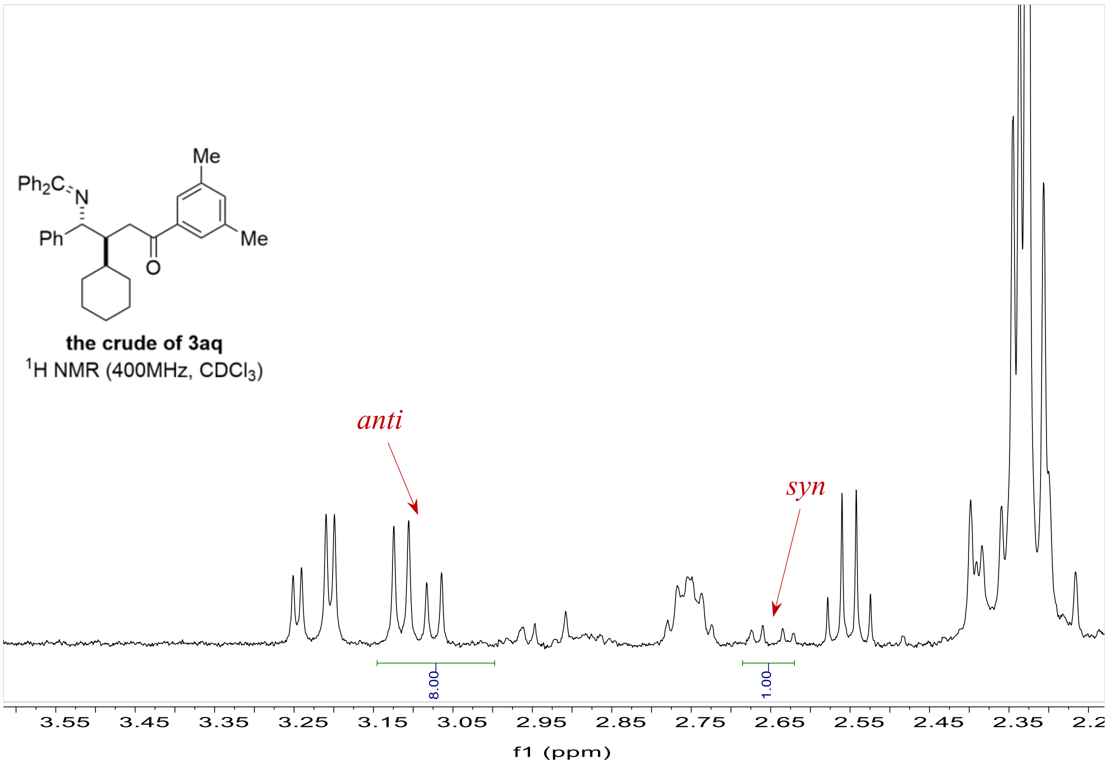


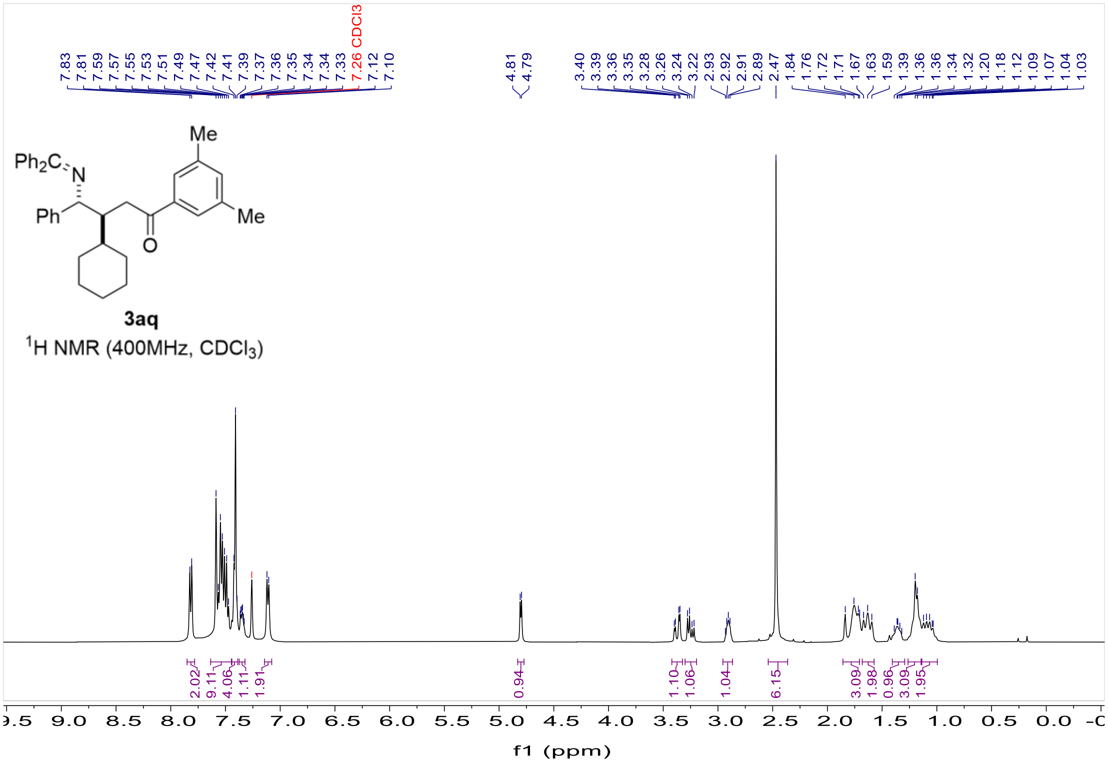
Ph$_2$C
N
Ph
O
OMe
the crude of 3ap
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
2.03
1.00
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7
f1 (ppm)


7.66
7.65
7.38
7.36
7.34
7.33
7.31
7.29
7.26 CDCl3
7.24
7.22
7.21
7.19
7.18
7.17
7.16
7.16
7.14
7.13
6.94
6.92
6.88
6.86
6.84
6.83
6.81
4.58
4.57
3.79
3.28
3.27
3.24
3.23
3.21
3.18
3.17
2.72
2.71
2.69
2.68
2.67
1.61
1.58
1.56
1.52
1.48
1.45
1.41
1.18
1.17
1.15
1.14
1.08
1.04
1.02
1.00
0.97
0.92
0.90
0.86
0.84
Ph2C N
Ph
O
OMe
3ap
1H NMR (400MHz, CDCl3)
2.02
8.18
3.31
2.13
2.15
2.14
1.00
3.01
1.95
0.97
3.22
2.09
1.19
3.18
2.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


203.47
166.71
157.81
145.01
140.08
136.98
132.48
130.36
129.90
129.57
128.77
128.41
128.18
127.98
127.78
127.63
126.41
120.49
111.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.97
55.45
47.31
42.68
40.01
31.37
30.11
26.93
26.87
26.72
Ph2C N
Ph
O
OMe
3ap
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

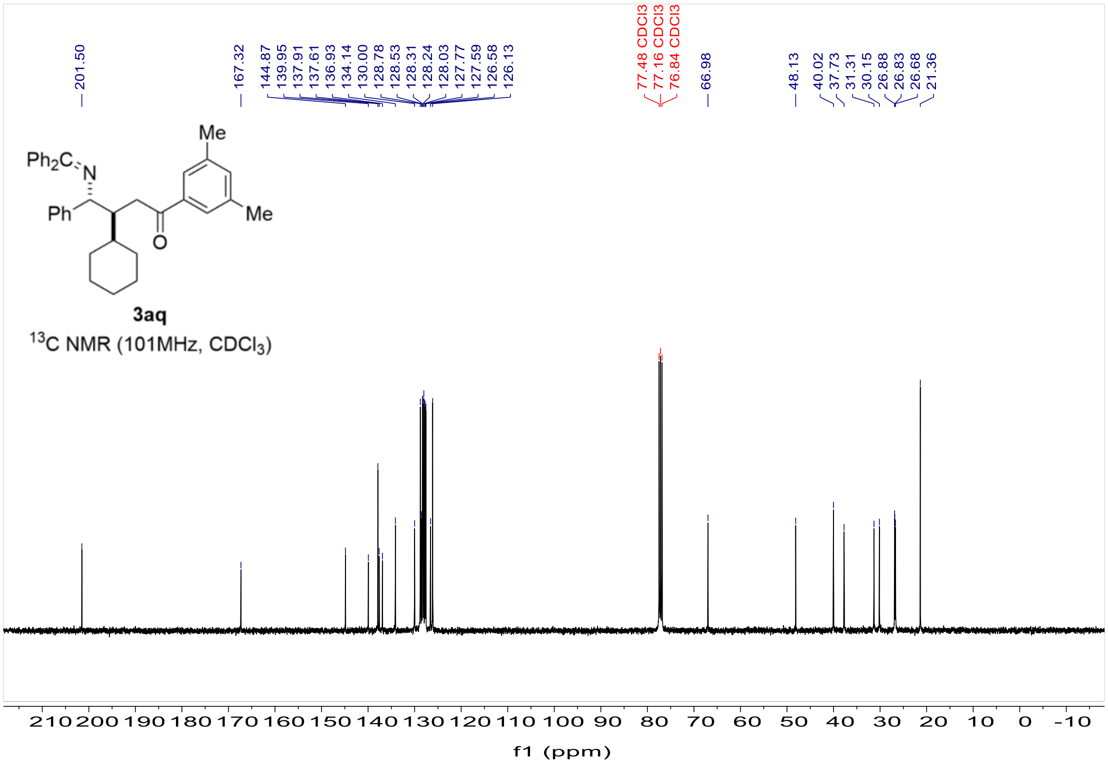

Ph$_2$C=N
Ph
Me
Me
O
the crude of 3aq
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
8.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph$_2$C=N
Ph
Me
Me
O
the crude of 3aq
^{1}H NMR (400MHz, CDCl$_3$)
anti
syn
8.00
1.00
3.55 3.45 3.35 3.25 3.15 3.05 2.95 2.85 2.75 2.65 2.55 2.45 2.35 2.2
f1 (ppm)



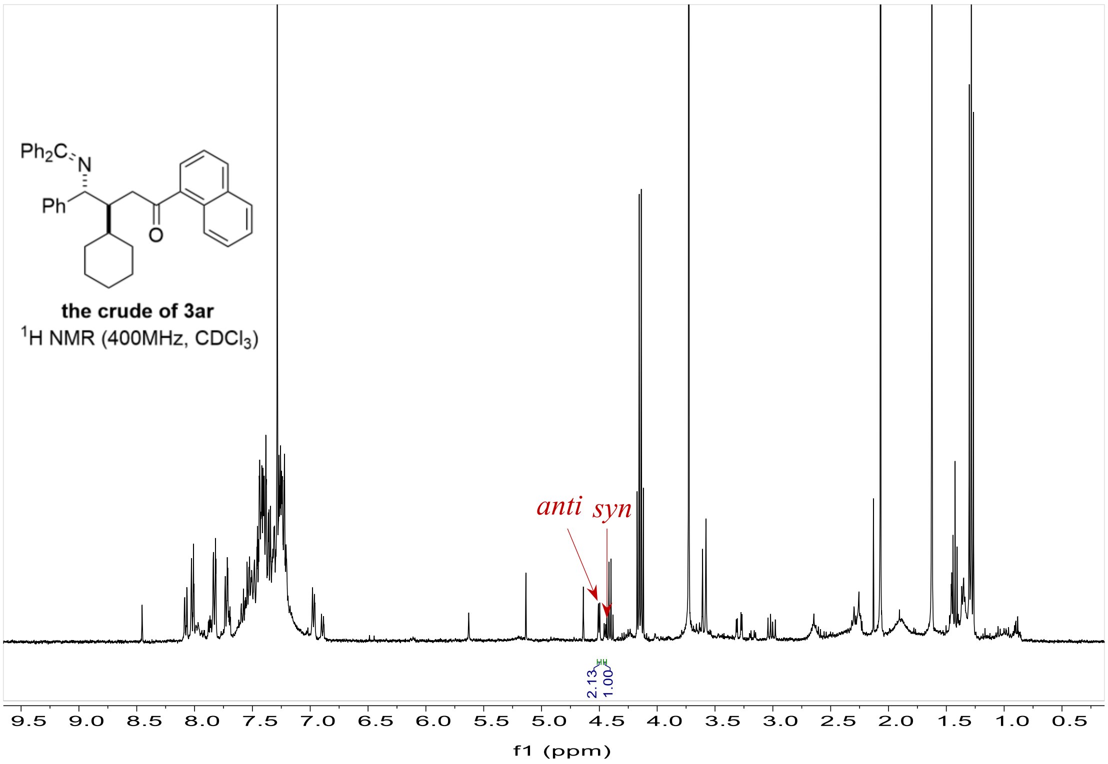
3aq

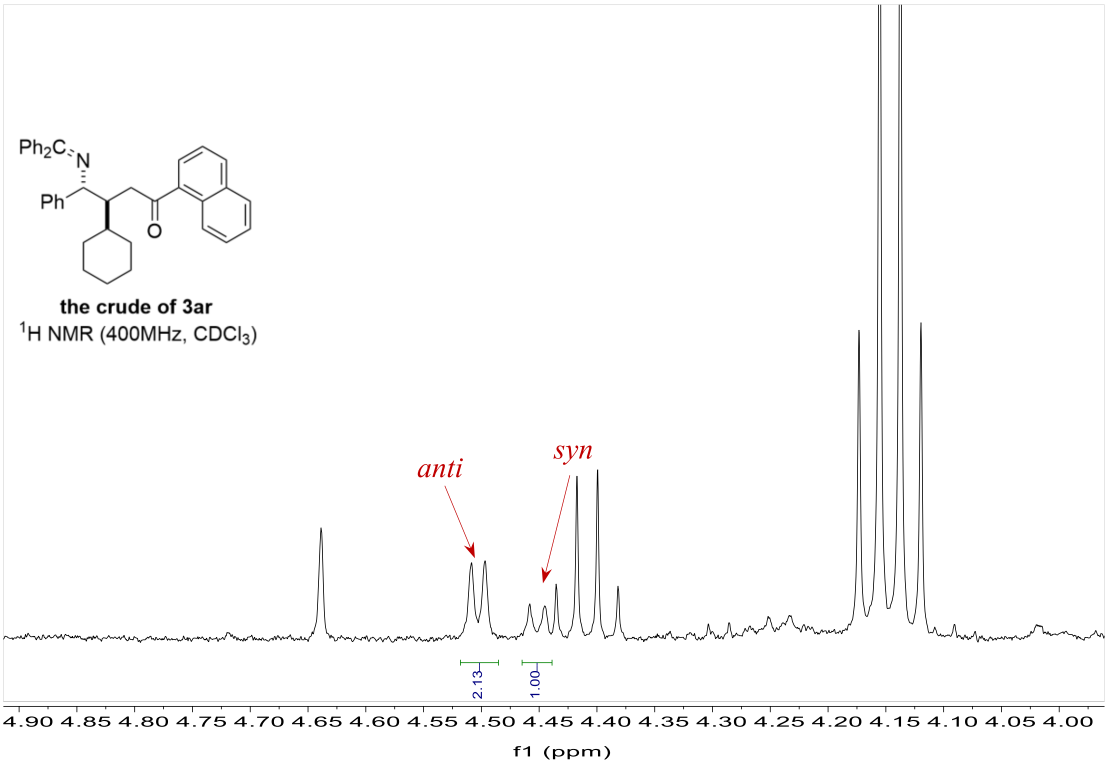
^{1}H NMR (400MHz, CDCl$_3$)

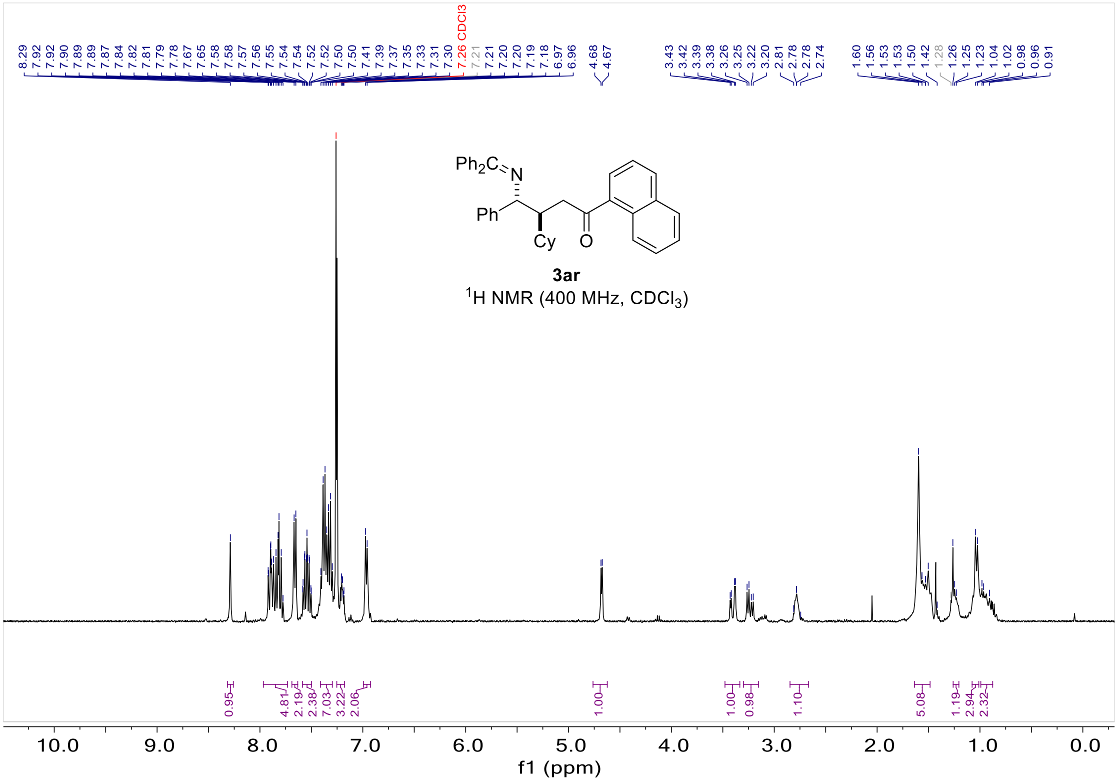


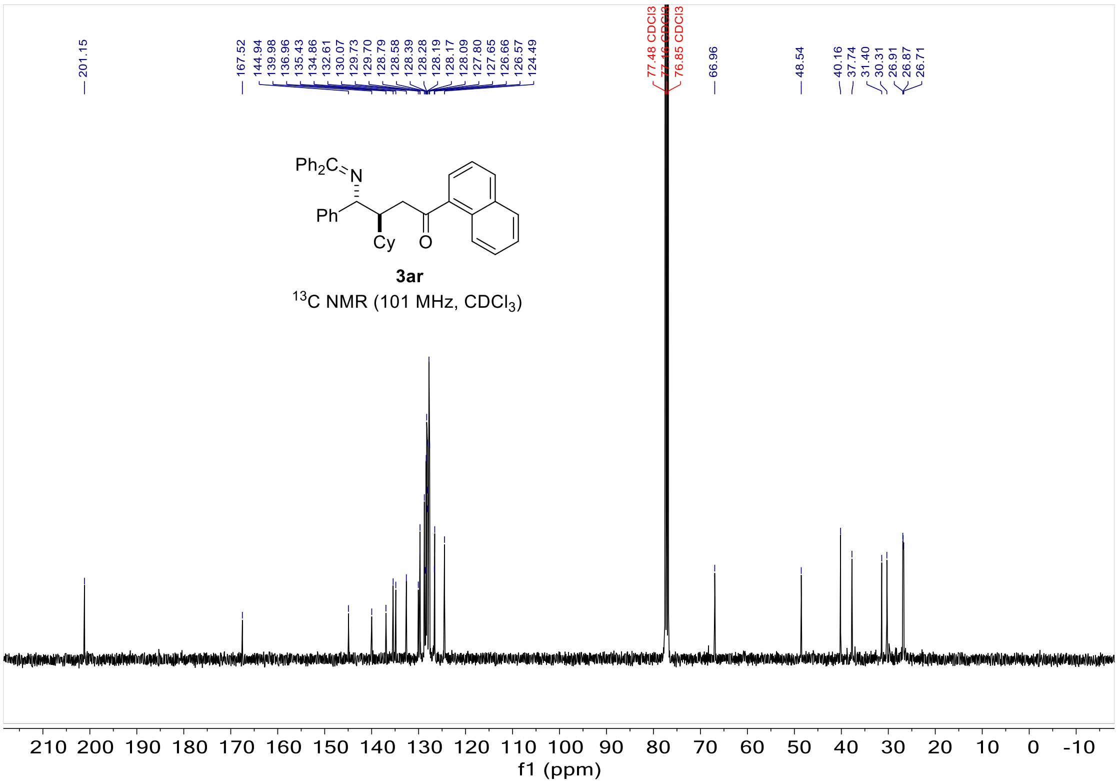
3aq

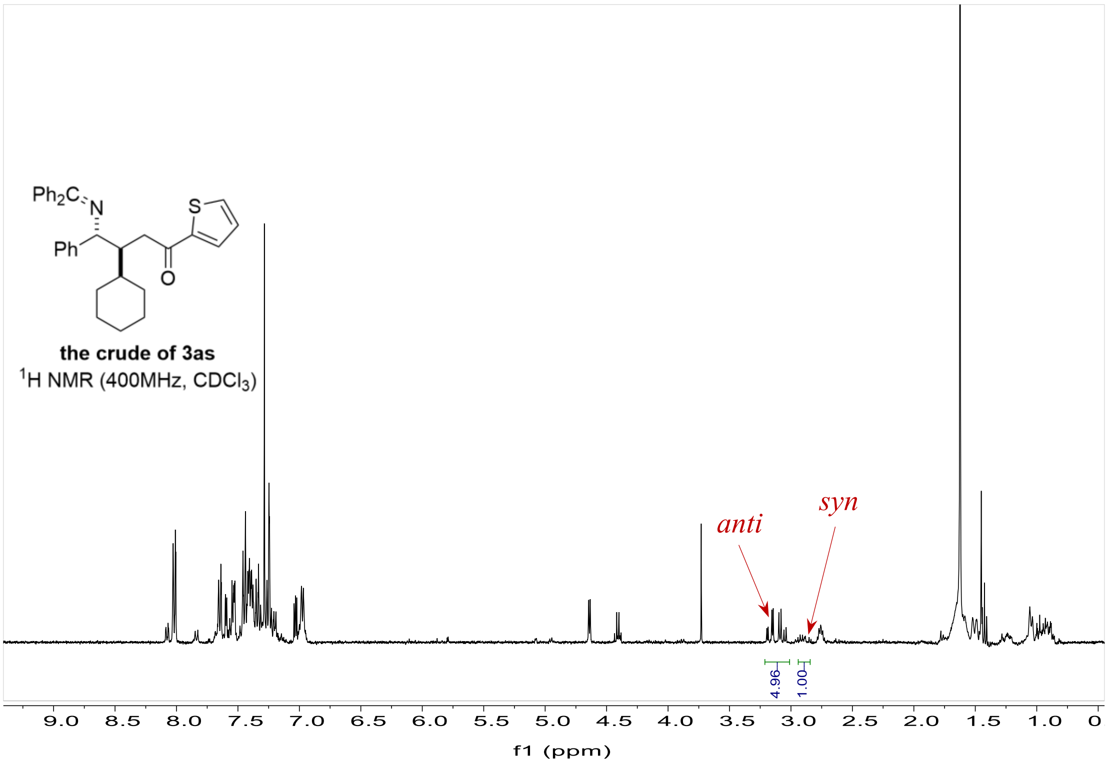
^{13}C NMR (101MHz, CDCl$_3$)

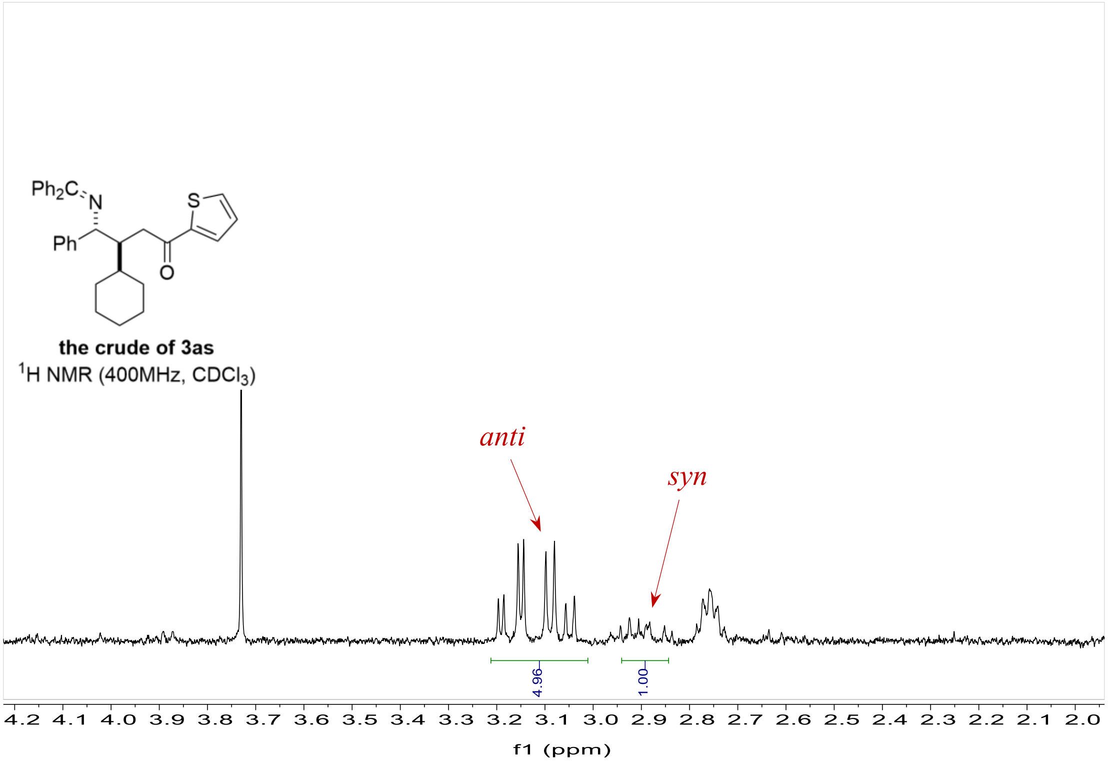

Ph2C
N
Ph
O
the crude of 3ar
1H NMR (400MHz, CDCl3)
anti
syn
2.13
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

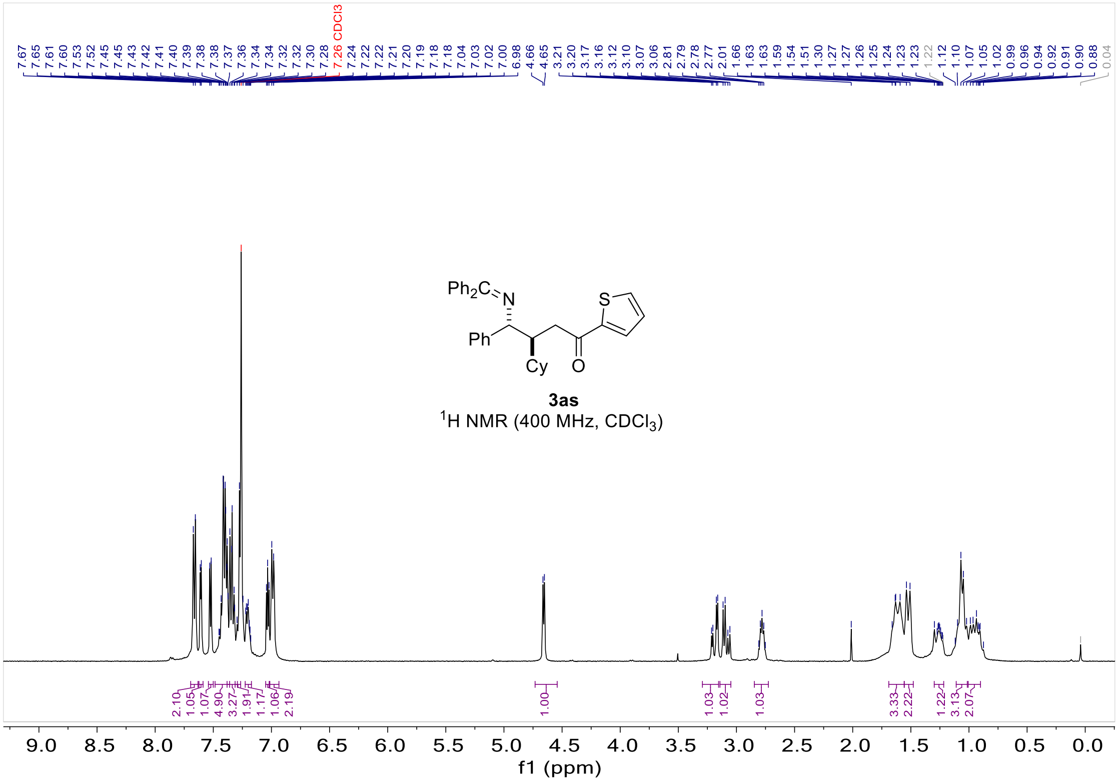

Ph2C
N
Ph
O
the crude of 3ar
1H NMR (400MHz, CDCl3)
anti
syn
2.13
1.00
4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00
f1 (ppm)


8.29 7.92 7.92 7.90 7.89 7.89 7.87 7.84 7.82 7.81 7.79 7.78 7.67 7.65 7.58 7.58 7.57 7.56 7.55 7.54 7.54 7.52 7.52 7.50 7.50 7.41 7.39 7.37 7.35 7.33 7.31 7.30 7.26 CDCl3 7.21 7.21 7.20 7.20 7.19 7.18 6.97 6.96
4.68 4.67
3.43 3.42 3.39 3.38 3.26 3.25 3.22 3.20 2.81 2.78 2.78 2.74
1.60 1.56 1.53 1.53 1.50 1.42 1.28 1.26 1.25 1.23 1.04 1.02 0.98 0.96 0.91
Ph2C=N
Ph
Cy
O
3ar
1H NMR (400 MHz, CDCl3)
0.95 4.81 2.19 2.38 7.03 3.22 2.06 1.00 1.00 0.98 1.10 5.08 1.19 2.94 2.32
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


201.15
167.52 144.94 139.98 136.96 135.43 134.86 132.61 130.07 129.73 129.70 128.79 128.58 128.39 128.28 128.19 128.17 128.09 127.80 127.65 126.66 126.57 124.49
77.48 CDCl3 77.16 CDCl3 76.85 CDCl3
66.96
48.54
40.16 37.74 31.40 30.31 26.91 26.87 26.71
Ph2C=N
Ph
Cy
O
3ar
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

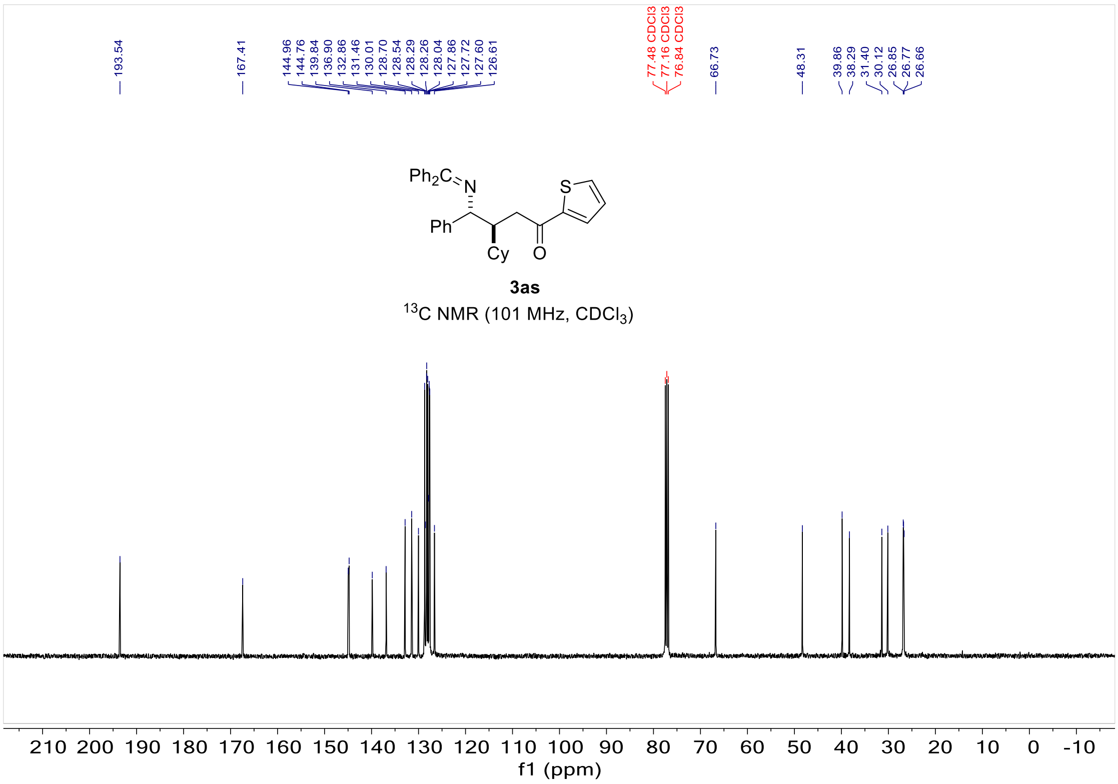

Ph2C=N
S
Ph
O
the crude of 3as
1H NMR (400MHz, CDCl3)
anti
syn
4.96
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
f1 (ppm)


Ph2C=N
S
Ph
O
the crude of 3as
1H NMR (400MHz, CDCl3)
anti
syn
4.96
1.00
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
f1 (ppm)



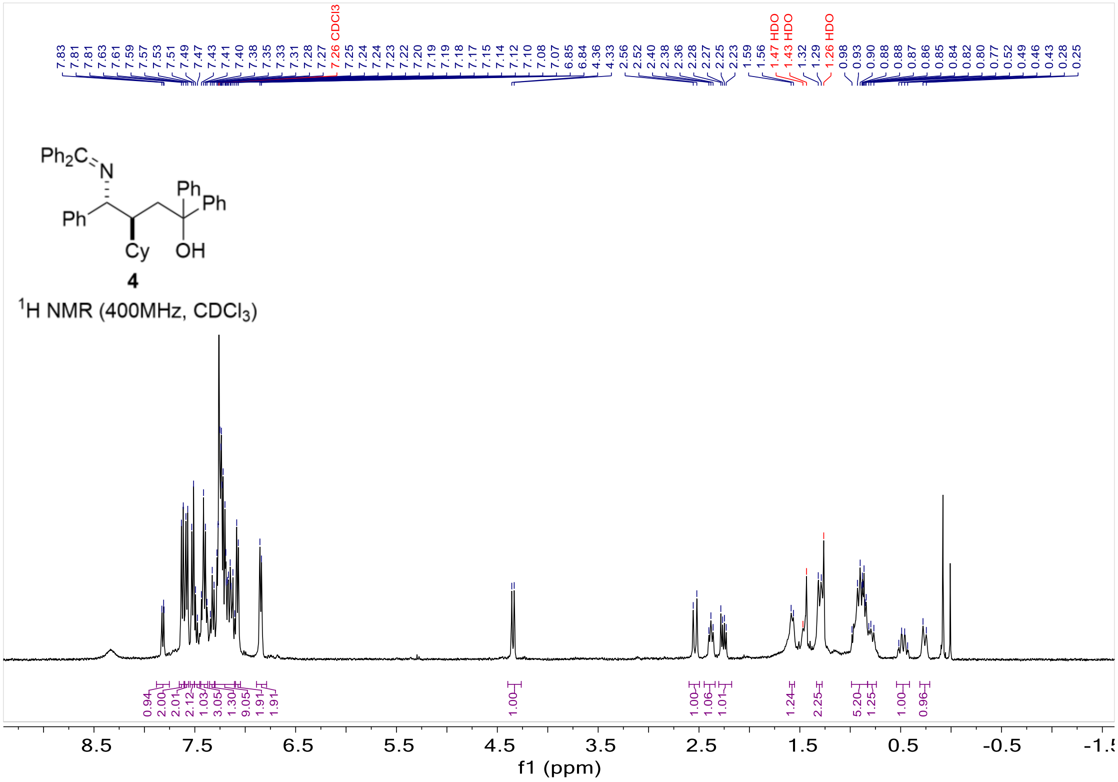
3as

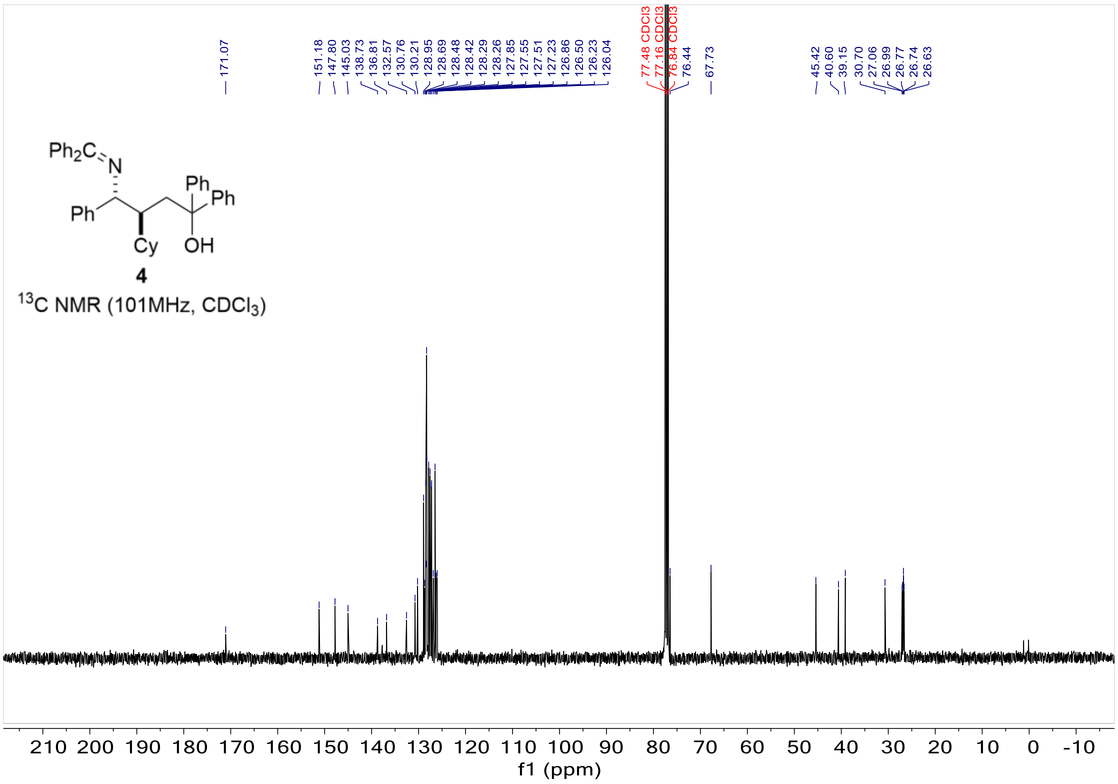
^{1}H NMR (400 MHz, CDCl$_3$)

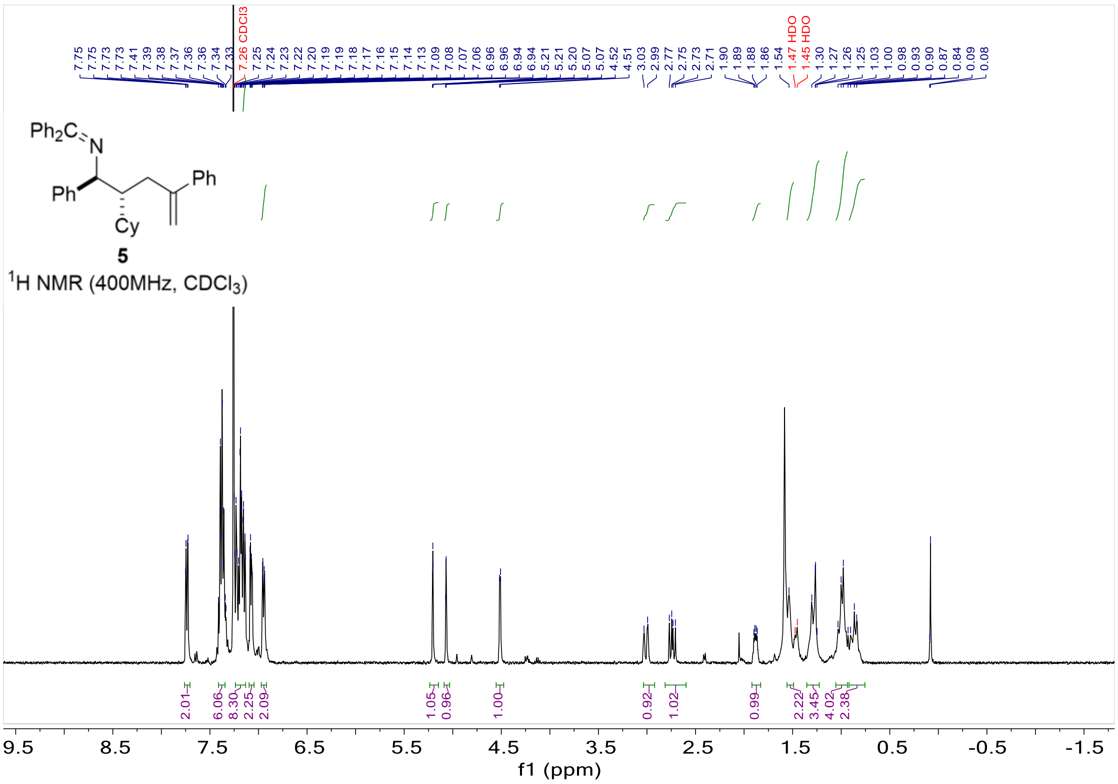


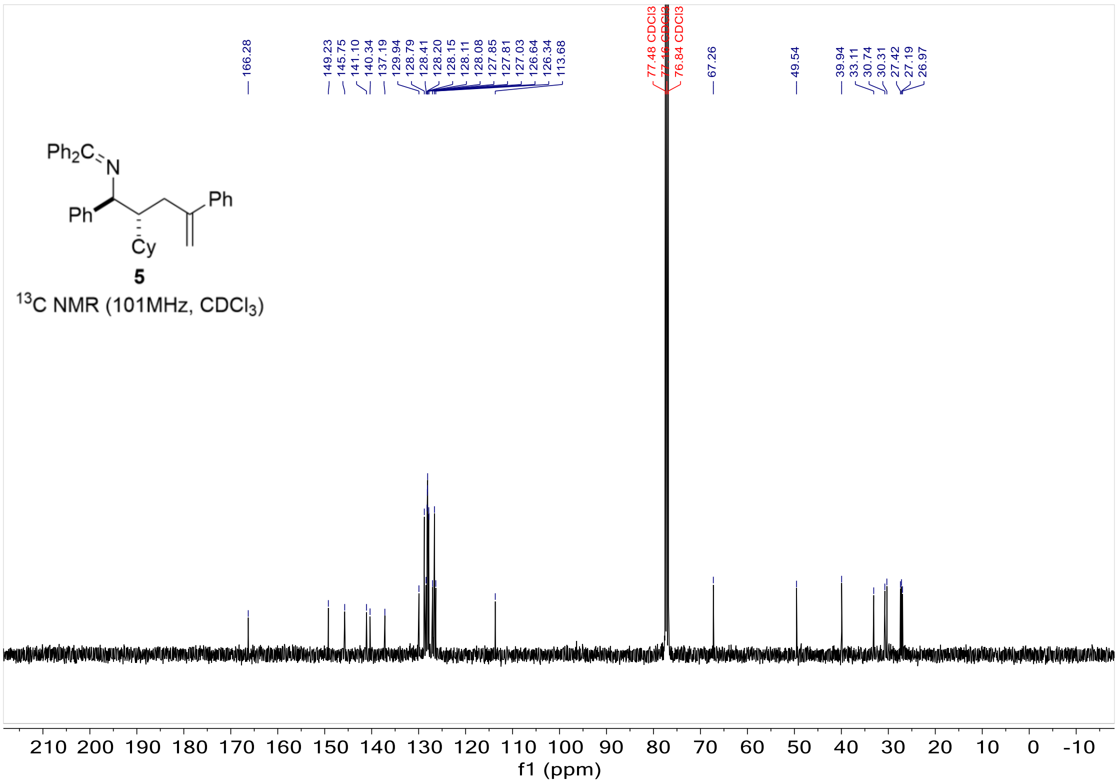
3as

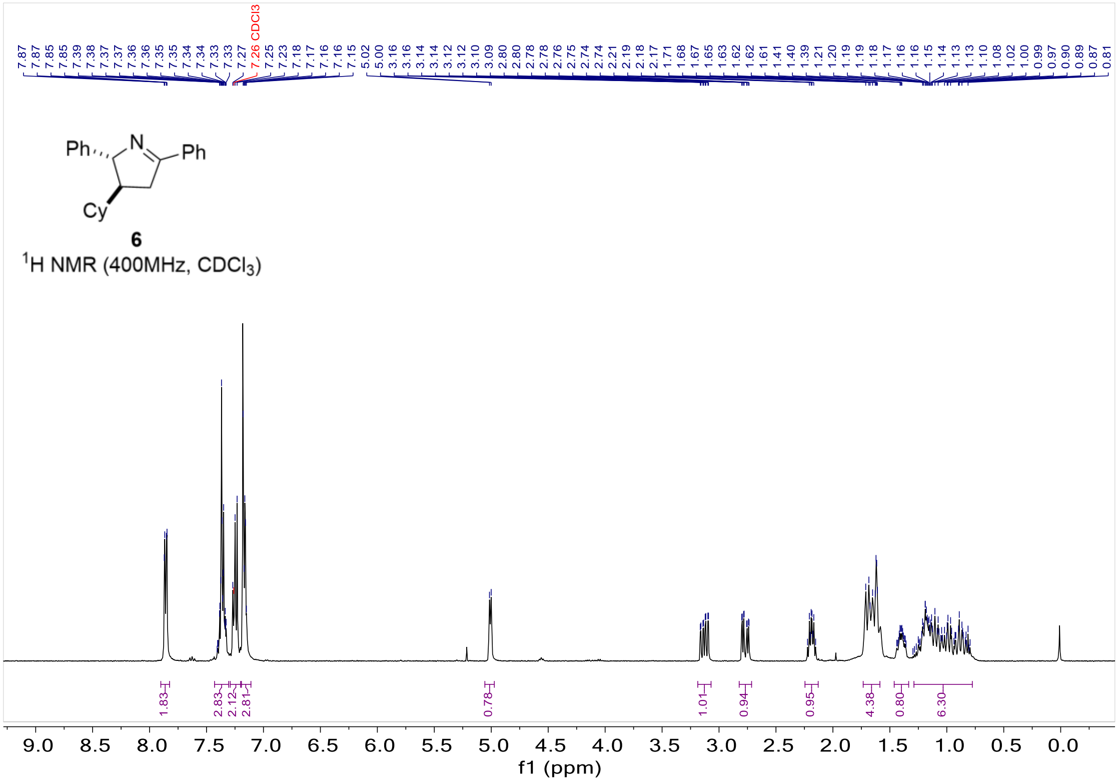
^{13}C NMR (101 MHz, CDCl$_3$)


7.83
7.81
7.63
7.61
7.59
7.57
7.53
7.51
7.49
7.47
7.43
7.41
7.40
7.38
7.35
7.33
7.31
7.28
7.27
7.26 CDCl3
7.25
7.24
7.24
7.23
7.22
7.20
7.19
7.19
7.18
7.17
7.15
7.14
7.12
7.10
7.08
7.07
6.85
6.84
4.36
4.33
2.56
2.52
2.40
2.38
2.36
2.28
2.27
2.25
2.23
1.59
1.56
1.47 HDO
1.43 HDO
1.32
1.29
1.26 HDO
0.98
0.93
0.90
0.88
0.88
0.87
0.86
0.85
0.84
0.82
0.80
0.77
0.52
0.49
0.46
0.43
0.28
0.25
Ph2C=N
Ph
Ph
Ph
Cy
OH
4
1H NMR (400MHz, CDCl3)
0.94
2.00
2.01
2.12
1.03
3.05
1.30
9.05
1.91
1.91
1.00
1.00
1.06
1.01
1.24
2.25
5.20
1.25
1.00
0.96
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.
f1 (ppm)


171.07
151.18
147.80
145.03
138.73
136.81
132.57
130.76
130.21
128.95
128.69
128.48
128.42
128.29
128.26
127.85
127.55
127.51
127.23
126.86
126.50
126.23
126.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.44
67.73
45.42
40.60
39.15
30.70
27.06
26.99
26.77
26.74
26.63
Ph2C=N
Ph
Ph
Ph
Cy
OH
4
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

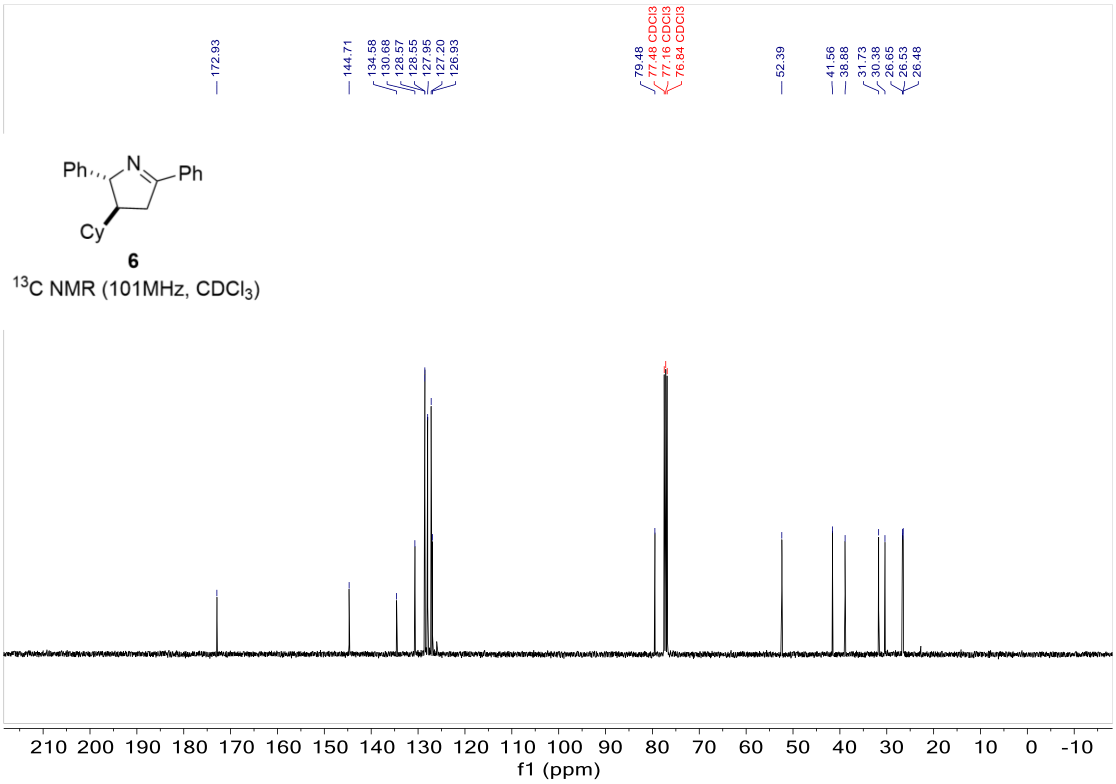

7.75
7.75
7.73
7.73
7.41
7.39
7.38
7.37
7.36
7.36
7.34
7.33
7.26 CDCl3
7.25
7.24
7.23
7.22
7.20
7.19
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.09
7.08
7.07
7.06
6.96
6.96
6.94
6.94
5.21
5.21
5.20
5.07
5.07
4.52
4.51
3.03
2.99
2.77
2.75
2.73
2.71
1.90
1.89
1.88
1.86
1.54
1.47 HDO
1.45 HDO
1.30
1.27
1.26
1.25
1.03
1.00
0.98
0.93
0.90
0.87
0.84
0.09
0.08
Ph2C=N
Ph
Ph
Cy
5
1H NMR (400MHz, CDCl3)
2.01
6.06
8.30
2.25
2.09
1.05
0.96
1.00
0.92
1.02
0.99
2.22
3.45
4.02
2.38
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


166.28
149.23
145.75
141.10
140.34
137.19
129.94
128.79
128.41
128.20
128.15
128.11
128.08
127.85
127.81
127.03
126.64
126.34
113.68
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.26
49.54
39.94
33.11
30.74
30.31
27.42
27.19
26.97
Ph2C=N
Ph
Ph
Cy
5
13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



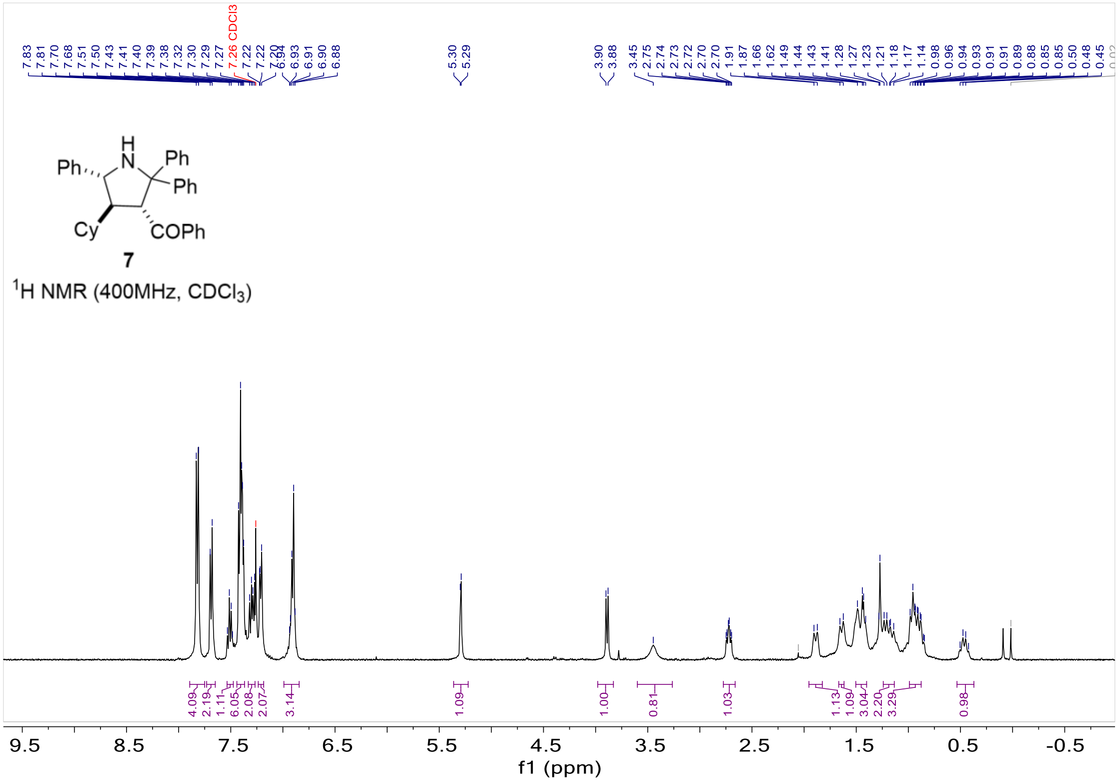
6

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



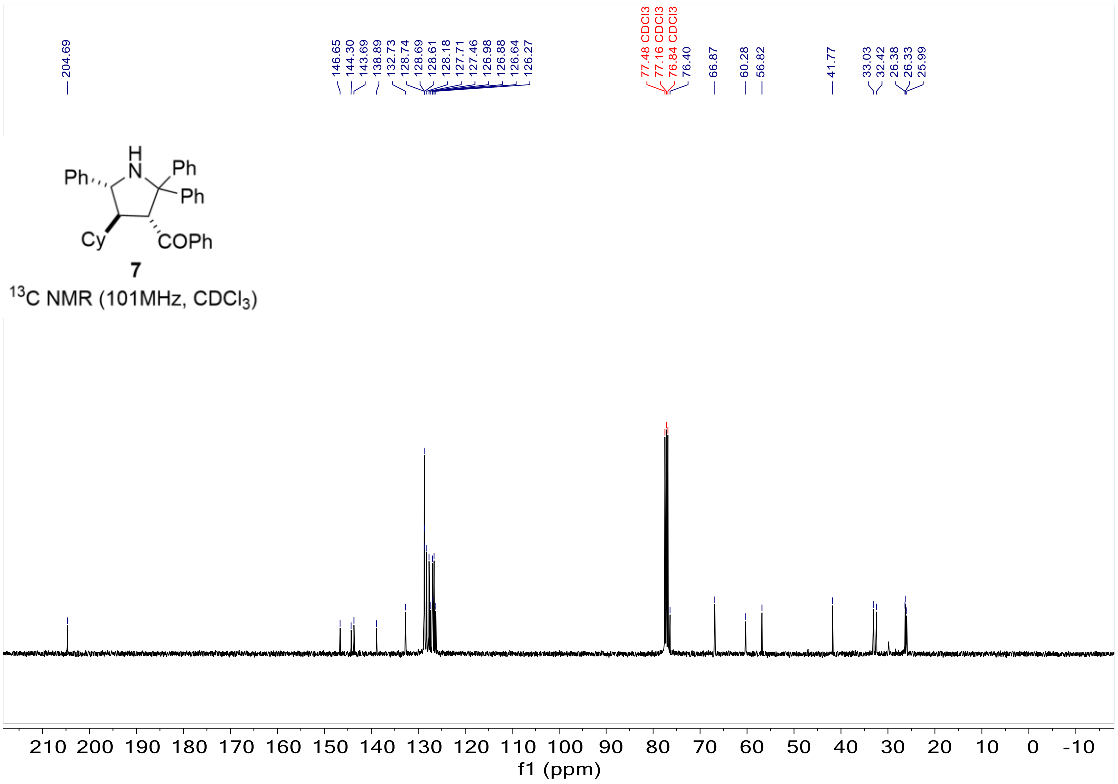
6

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



7

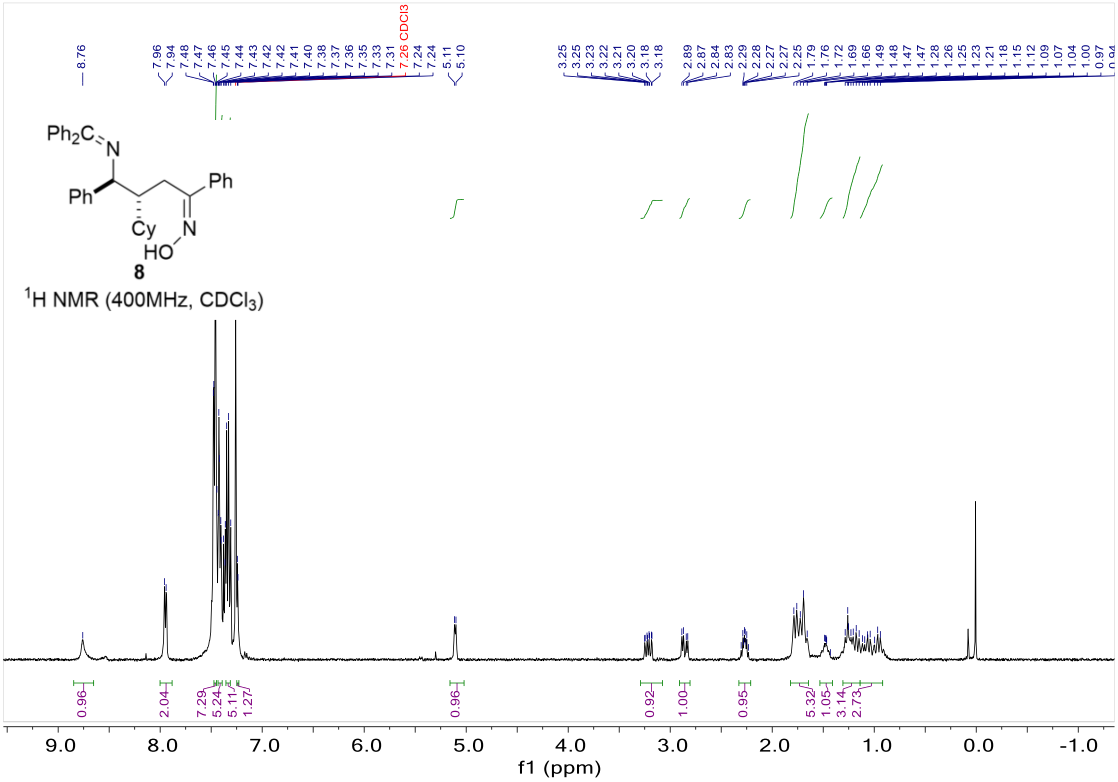
^{1}H NMR (400MHz, CDCl$_3$)



7

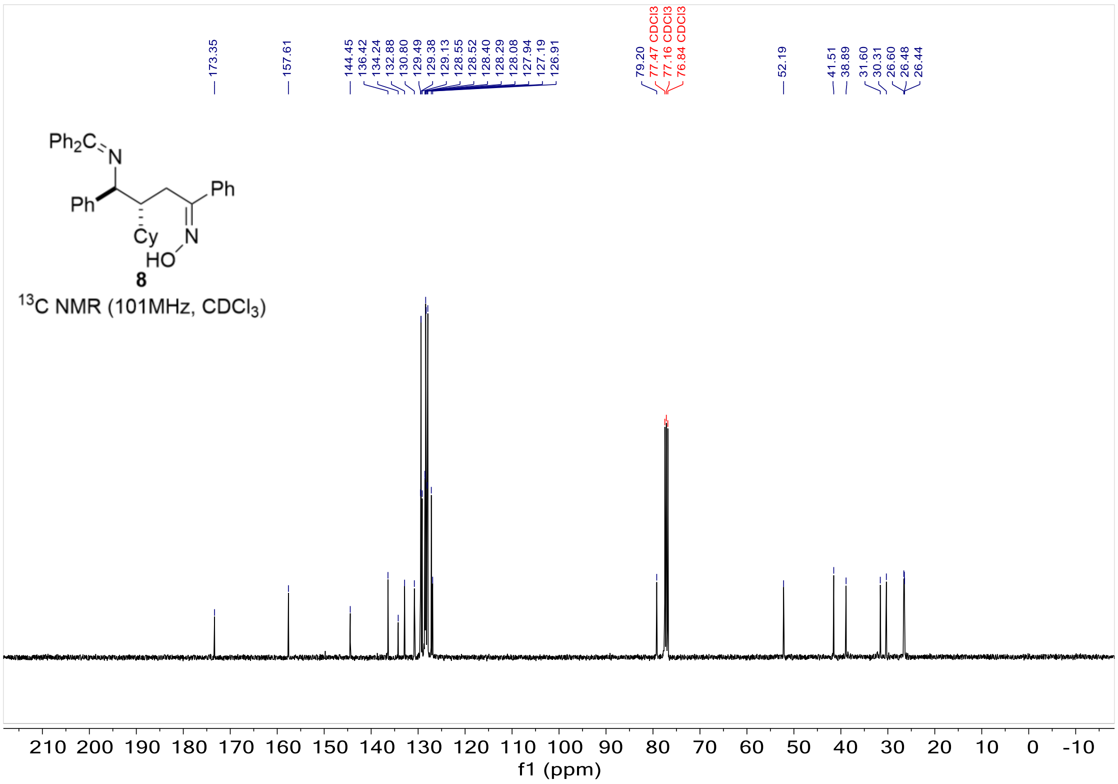
^{13}C NMR (101MHz, CDCl$_3$)

anti



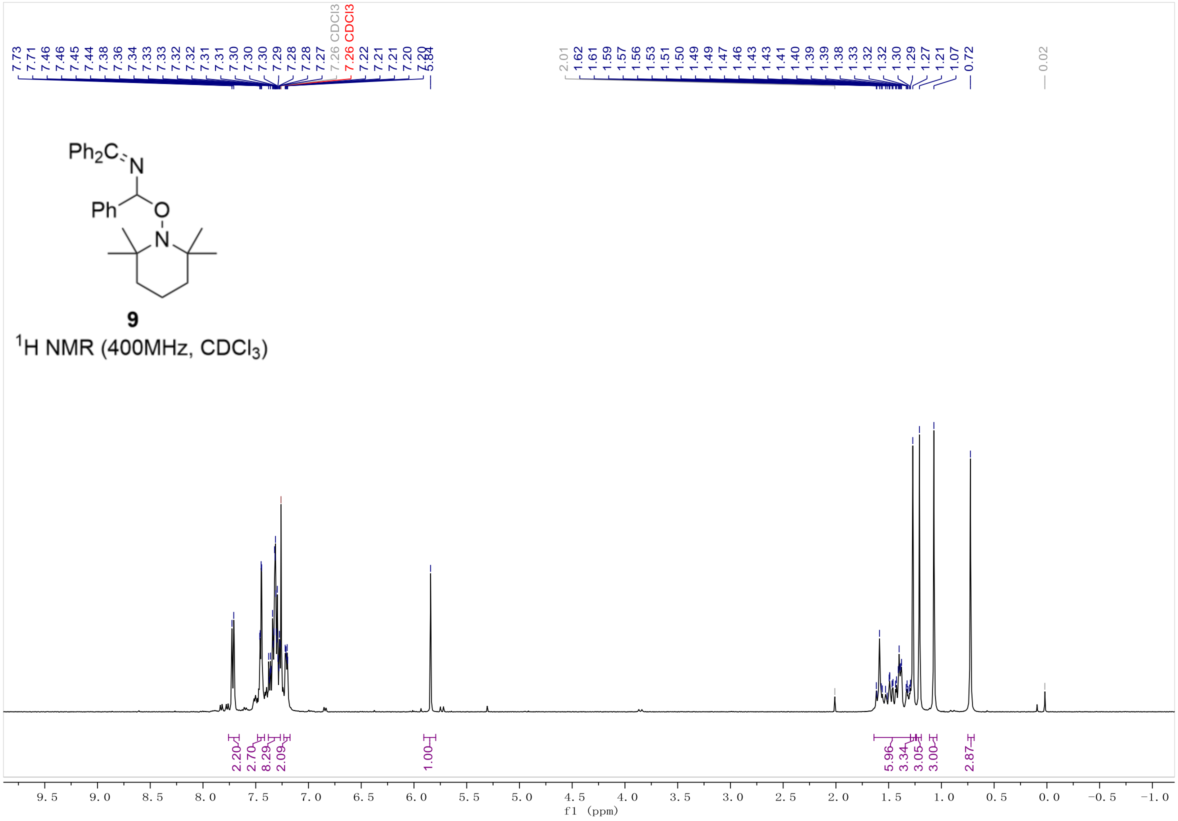
8

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



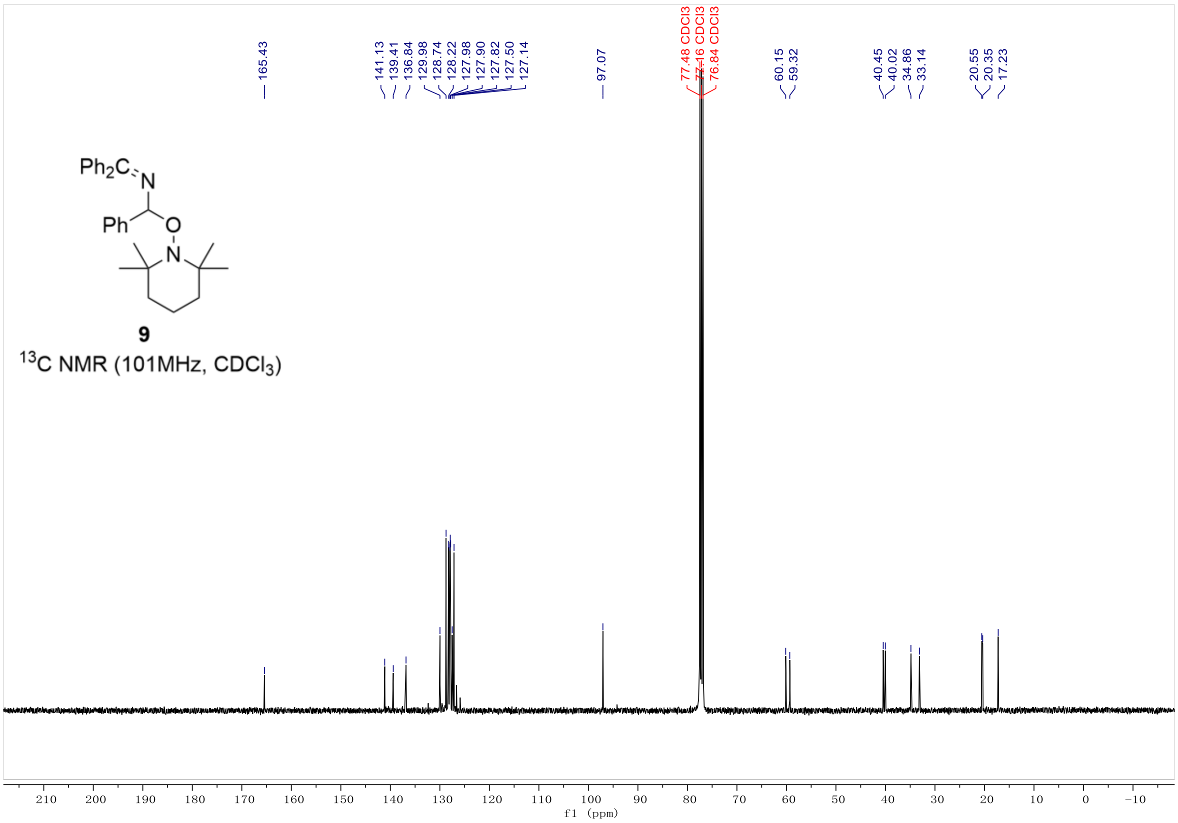
8

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



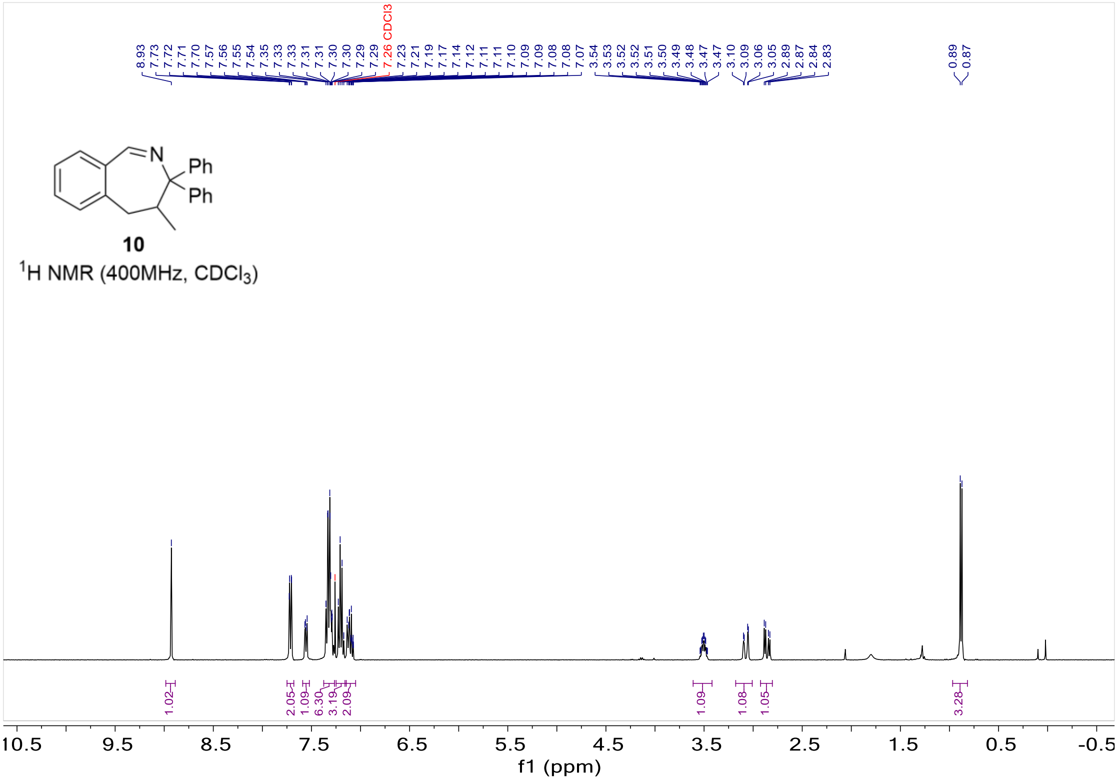
9

^{1}H NMR (400MHz, CDCl$_3$)



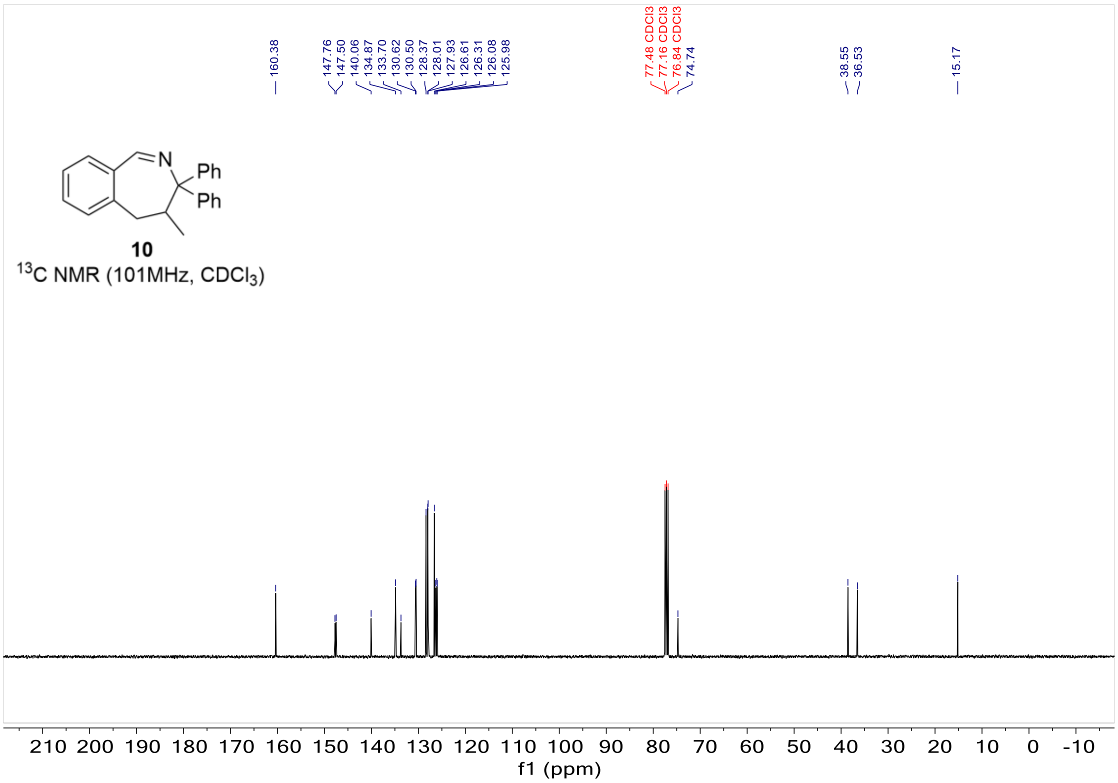
9

^{13}C NMR (101MHz, CDCl$_3$)



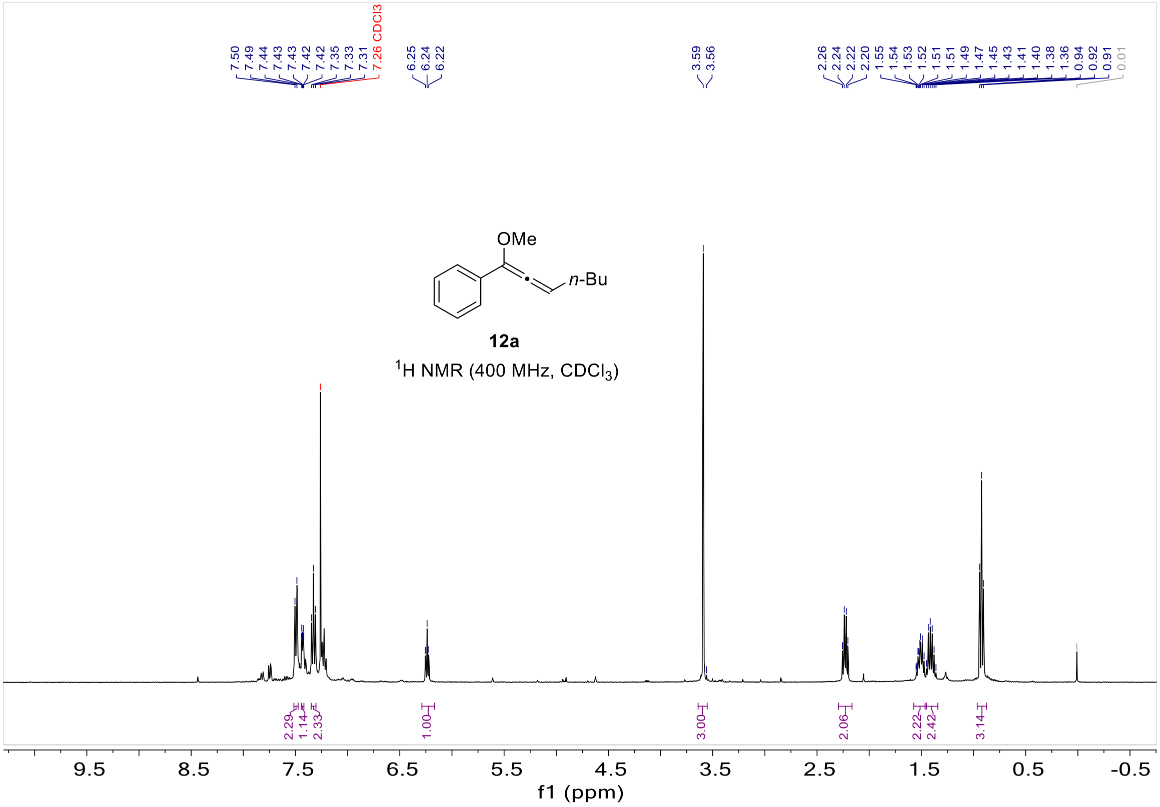
10

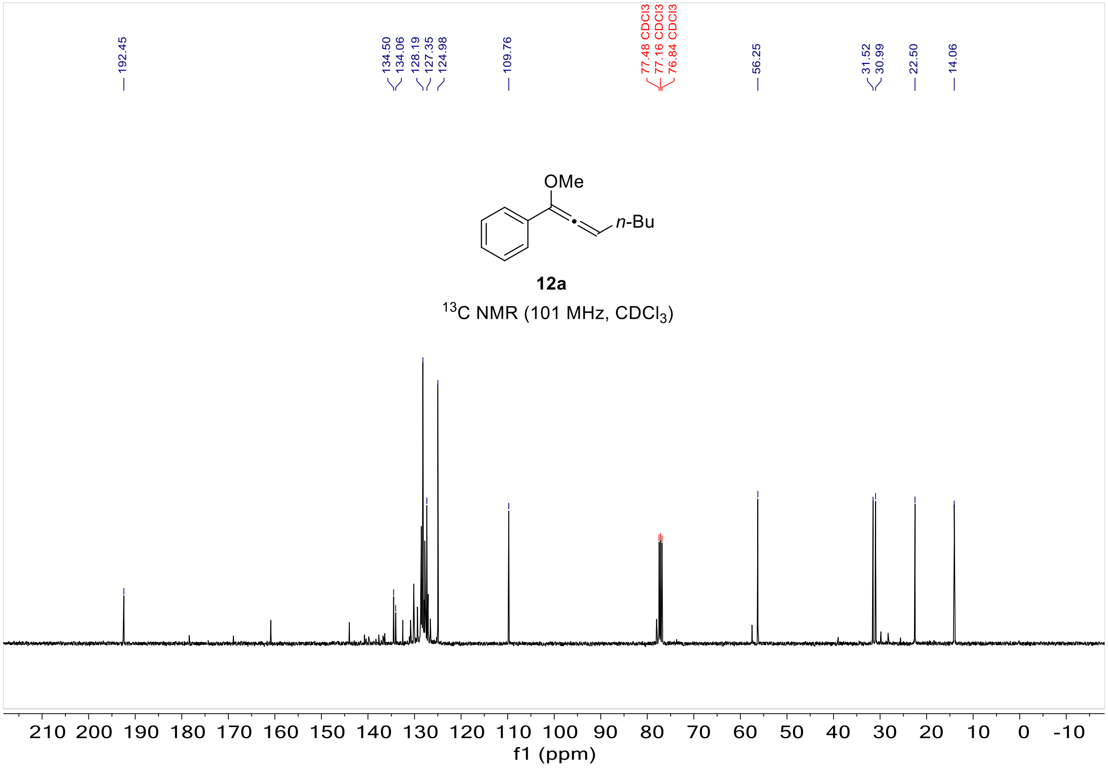
^{1}H NMR (400MHz, $CDCl_3$)

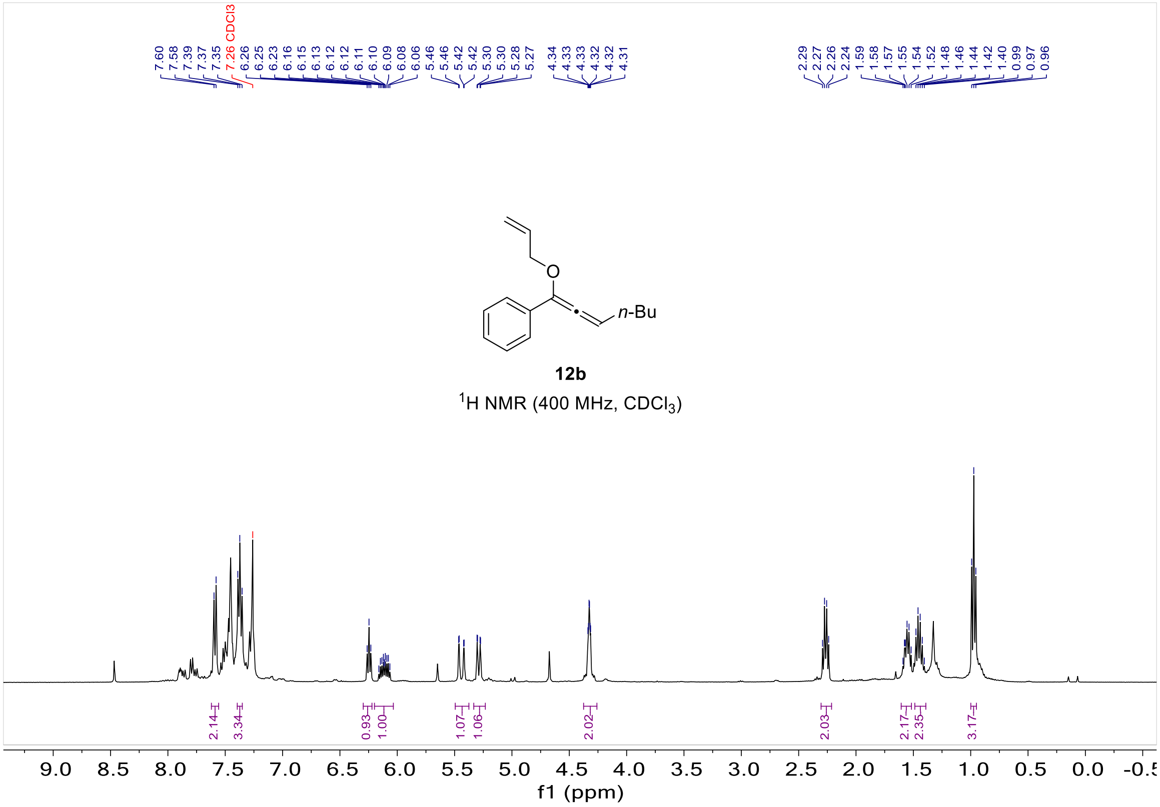


10

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

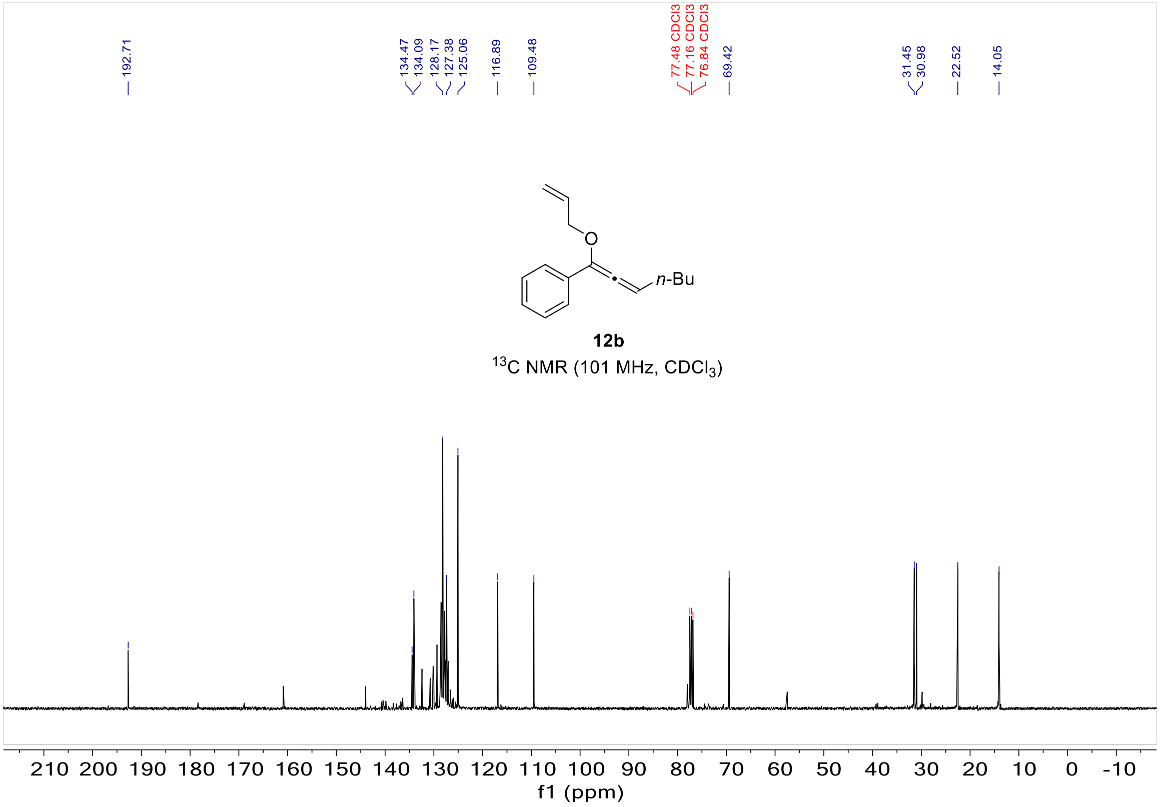

7.50
7.49
7.44
7.43
7.43
7.42
7.35
7.33
7.31
7.26 CDCl3
6.25
6.24
6.22
3.59
3.56
2.26
2.24
2.22
2.20
1.55
1.54
1.53
1.52
1.51
1.49
1.47
1.45
1.43
1.41
1.40
1.38
1.36
0.94
0.92
0.91
0.01
OMe
n-Bu
12a
¹H NMR (400 MHz, CDCl₃)
2.29
1.14
2.33
1.00
3.00
2.06
2.22
2.42
3.14
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


192.45
134.50
134.06
128.19
127.35
124.98
109.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.25
31.52
30.99
22.50
14.06
OMe
n-Bu
12a
¹³C NMR (101 MHz, CDCl₃)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



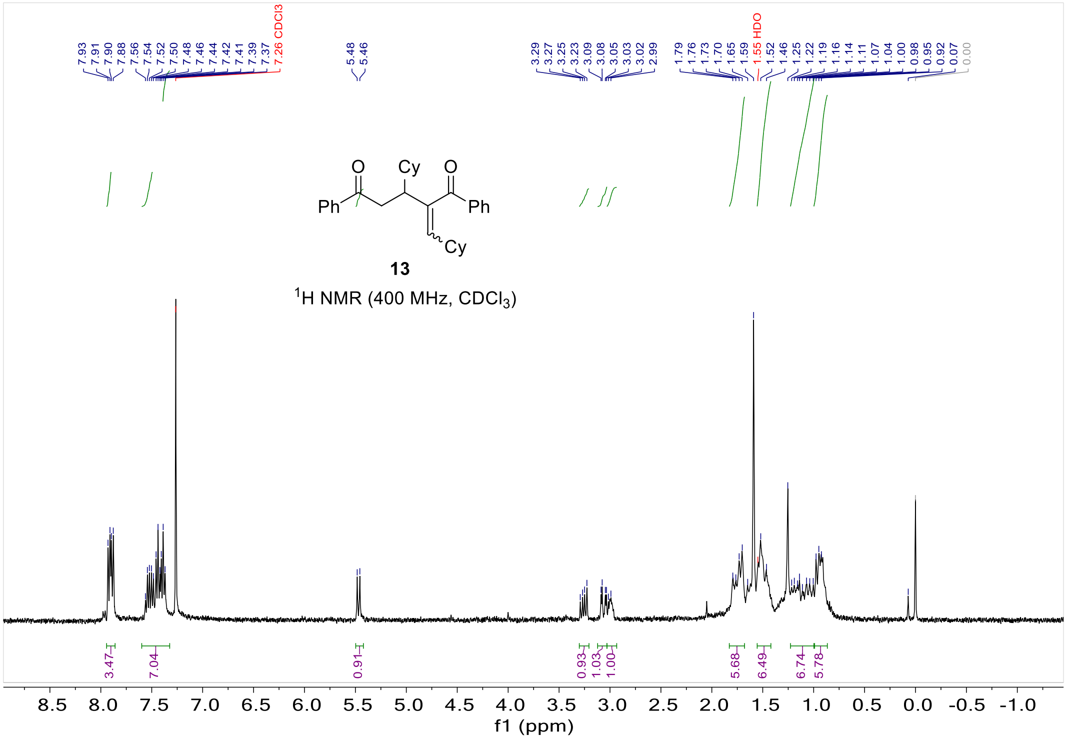
12b

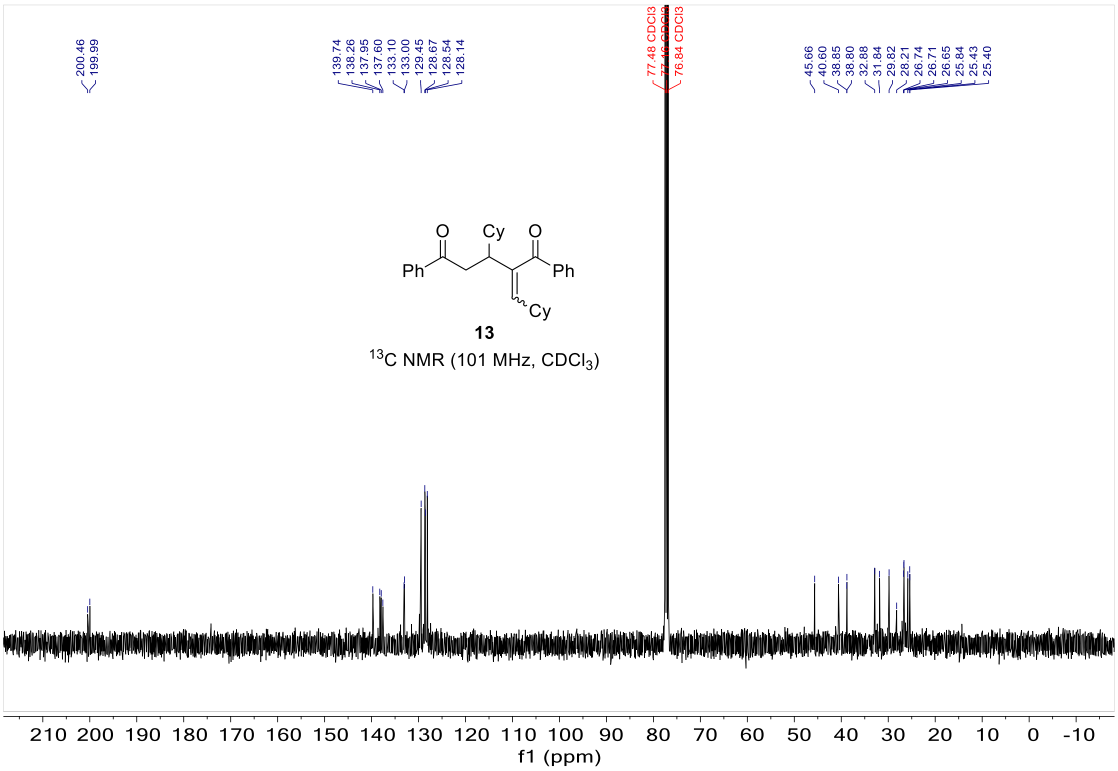
^{1}H NMR (400 MHz, $CDCl_3$)



12b

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


7.93
7.91
7.90
7.88
7.56
7.54
7.52
7.50
7.48
7.46
7.44
7.42
7.41
7.39
7.37
7.26 CDCl3
5.48
5.46
3.29
3.27
3.25
3.23
3.09
3.08
3.05
3.03
3.02
2.99
1.79
1.76
1.73
1.70
1.65
1.59
1.55 HDO
1.52
1.46
1.25
1.22
1.19
1.16
1.14
1.11
1.07
1.04
1.00
0.98
0.95
0.92
0.07
0.00
O
Cy
O
Ph
Ph
Cy
13
1H NMR (400 MHz, CDCl3)
3.47
7.04
0.91
0.93
1.03
1.00
5.68
6.49
6.74
5.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


200.46
199.99
139.74
138.26
137.95
137.60
133.10
133.00
129.45
128.67
128.54
128.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.66
40.60
38.85
38.80
32.88
31.84
29.82
28.21
26.74
26.71
26.65
25.84
25.43
25.40
O
Cy
O
Ph
Ph
Cy
13
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6. References

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[3] M. J. McGill, A. X. Wayment, C. R. Schull, K. A. Scheidt, *Adv. Synth. Catal*. **2024**, *367*. e202401207.

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[6] N. Okamoto, T. Sueda, H. Minami, Y. Miwa, and R. Yanada, *Ogr. Lett.* **2015,** *17*, 1336-1339.

[7] J. Wang, G. Deng, C. Liu, Z. Chen, K. Yu, W. Chen, H. Zhang, X. Yang, *Adv. Synth. Catal.* **2020**, *362*, 2268.

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