Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Heterogeneous Ru/TiO_2 for hydroaminomethylation of olefins: multicomponent synthesis of amines

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Materials

All chemicals and reagents are of analytical grade and used as purchased without further purification. The detail list of the used chemicals and reagents are shown in Table S1.

Table S1. The detail list of the used chemicals and reagents.

Chemicals	Purity	Corporation
$RuCl_3 \cdot nH_2O$	36.0-38.0% metal basis	The Non Ferrous Metal Institute of Shenyang, China
$RhCl_3 \cdot nH_2O$	> 39%	The Non Ferrous Metal Institute of Shenyang, China
$PdCl_2$	> 99%	The Non Ferrous Metal Institute of Shenyang, China
TiO_2 (P25)	99.8%	Aladdin
TiO_2-A (Anatase)	99.8%	Aladdin
TiO_2-R (Rutile)	99.8%	Aladdin
ZnO	AR	Aladdin
WO_3	99.9%	Aladdin
MgO	99.9%	Aladdin
Tetrahydrofuran	AR	Macklin
Ethyl acetate	AR	TianDa Chemical Reagent Co., Ltd, China
Petroleum ether	AR	Tianjin Fuyu Fine Chemical Co., Ltd, China
Aniline	99.5%	Sinopharm Chemical Reagent Co., Ltd
Cyclohexylamine	98.5%	
p-Methylaniline	99.0%	ACROS ORGANICS
p-Chloroaniline	98.0%	Energy chemical
p-Tertbutylaniline	98.0%	
p-Methoxyaniline	97.0%	Aladdin
p-Fluoroaniline	99.0%	
o-Toluidine	99.0%	
o-Chloroaniline	CP	
o-Methoxyaniline	98.0%	
2-ethylaniline	99.0%	
2, 6-diethylaniline	99.0%	
m-Toluidine	99.0%	
2, 6-Dimethylaniline	99.0%	
2,6-Dimethoxyaniline	99.0%	

Furfurylamine	99.0%	
1-Naphthylamine	99.0%	
Benzylamine	99.0%	
n-Hexylamine	99.0%	
N-Methylaniline	98.0%	
N-Ethylaniline	99.0%	
Diphenylamine	99.0%	
Dibenzylamine	98.0%	
Di-n-propylamine	99.0%	
Piperidine	99.0%	
p-Methoxystyrene	95.0%	
p-Fluorostyrene	97.0%	
p-Chlorostyrene	97.0%	
Alpha-methylstyrene	AR	
Cyclopentene	96%	Aladdin
ındoline	99.0%	Macklin
Morpholine	98.0%	Macklin
Styrene	98.0%	TCI
p-Methylstyrene	98.0%	
1-Penten	98%	
Cyclohexene	99.0%	ACROS ORGANICS
p-Methylaniline	99.0%	
DMSO-D_6	99.8 atom % D, contains 0.03% (v/v) TMS	Sigma-Aldrich, America
$CDCl_3$		
Ethylene	99.9%	Dalian Guangming Special Gas Products Co., Ltd, China
Propylene		
CO	99.9999%	Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China
Millipore-purified water	18 MΩ·cm	

General procedure for calculation of the initial rates

Hydroformylation reaction of cyclohexene

Catalyst (Ru/TiO_2, 0.1 g), cyclohexene (0.5 mmol), solvent (THF, 2.0 mL) and a magnetic stir bar were added into the autoclave reactor of 15 mL, respectively. The reactor was purged with CO for three times. After that, CO and H_2 were charged into the reactor to 1.0 MPa. Finally, the reactor was sealed and placed in a preheated mantle at 160 °C for 30 min. After reaction, the autoclave reactor was cooled with ice water. The crude reaction mixture was analyzed by gas

chromatography with *n*-dodecane as internal standard to give cyclohexane formaldehyde in 16% yields.

Condensation reaction of cyclohexane formaldehyde and aniline

The reaction occurred spontaneously and rapidly when adding cyclohexane formaldehyde (0.4 mmol) to aniline (0.5 mmol) in THF (2.0 mL) even in the absence of Ru/TiO_2.

Hydrogenation reaction of imine

Catalyst (Ru/TiO_2, 0.1 g), imine (0.4 mmol), solvent (THF, 2.0 mL), and a magnetic stir bar were added into the autoclave reactor of 15 mL, respectively. The reactor was purged with H_2 for three times. After that, H_2 were charged into the reactor to 1.0 MPa. Finally, the reactor was sealed and placed in a preheated mantle at 160 °C for 5 min. After reaction, the autoclave reactor was cooled with ice water. The crude reaction mixture was analyzed by gas chromatography with *n*-dodecane as internal standard to give **1**. The reaction occurred rapidly when exposing imine to H_2 in THF at 160 °C in the presence of Ru/TiO_2.

General procedure for the reusability of Ru/TiO_2

To examine the reusability of the Ru/TiO_2, the Ru/TiO_2 was recovered by centrifugation and washed with ethanol (3×6 mL). After that, the recovered catalyst was dried under 80 °C overnight and reused for the next run.

General procedure for the effect of removal of catalyst in Figure S1(b)

Catalyst (Ru/TiO_2, 0.1 g), aniline (0.4 mmol), cyclohexene (1.0 mmol), solvent (THF, 2.0 mL), and magnetic stir bar were added into the autoclave reactor of 15 mL, respectively. The reactor was purged with CO for three times. After that, CO and H_2 were charged into the reactor to a certain pressure. Finally, the reactor was sealed and placed in a preheated mantle at 160 °C. After reaction for 2 h, the filtrate was obtained after separating catalyst through

centrifugation. And the obtained filtrate was collected and analyzed by GC. After analyzation, the resulting filtrate was placed into the autoclave reactor to continue react for another 1 h under the same conditions with the original reaction. Then, repeating the above steps.

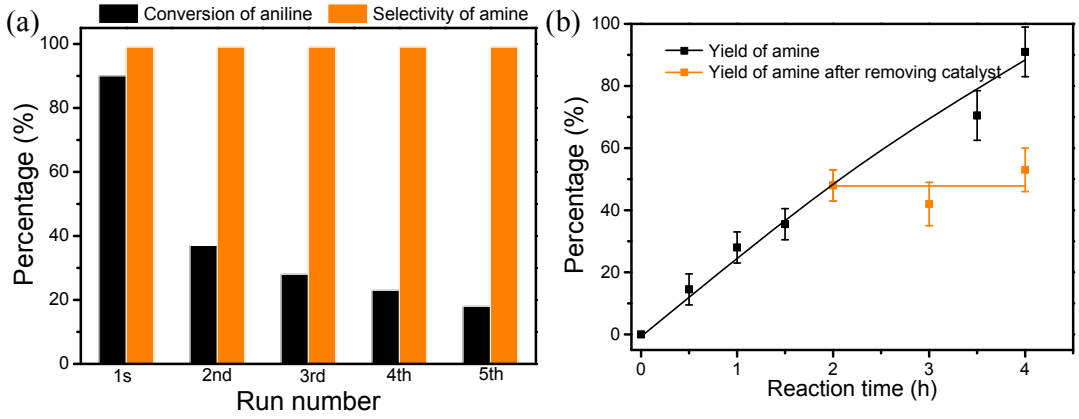


Figure S1. (a) The reused experiment of Ru/TiO_2. Reaction conditions: Ru/TiO_2 (0.1 g), aniline (0.4 mmol), cyclohexene (1.0 mmol), CO (0.5 MPa), H_2 (0.5 MPa), THF (2.0 mL), 160 °C, 4 h. (b) Effect of removal of catalyst Ru/TiO_2. Reaction conditions: Ru/TiO_2 (0.1 g), aniline (0.4 mmol), cyclohexene (1.0 mmol), CO (0.5 MPa), H_2 (0.5 MPa), THF (2.0 mL), 160 °C.

In order to further investigate the reason for the deactivation of the catalyst, TEM, XRD, and IR characterization of the catalyst after reaction was conducted and shown in Figure S2. The TEM characterization of the catalyst after reaction was given in Figure S2A. The resulting data indicate that the Ru particle size increases slightly from 1.8 nm to 2.0 nm after reaction. In addition, XRD characterization was conducted for the catalyst after reaction and no peaks related to Ru species were observed (Figure S2B), indicating that Ru species are highly dispersed on TiO_2, which is in accordance with the TEM characterization result. Hereinafter, Ru/TiO_2 catalyst was quite stable after reaction.

The IR characterization of the catalyst after reaction was conducted and shown in Figure S2B. Three remarkable peaks at 2074, 2002 and 1884 cm^{-1} were observed on Ru/TiO_2 after reaction. According to the references,[1] the peak at 2074 cm^{-1} was assigned to the multicarbonyl species on the partially oxidized Ru sites [$Ru^{\delta+}(CO)_x$], although there is no consensus regarding the oxidation state of Ru (δ) and the number of carbonyl groups (*x*). The peak at 2002 and 1884 cm^{-1} were usually assigned to the metallic Ru particles. The

appearance of the peak at 1884 cm^{-1} was due to the slight increase of the Ru particle size after reaction.[2] The IR result indicates that the excess amount of CO can absorbed on Ru/TiO_2 surface, which might have negative effect on the absorption of other substrates in the next reaction recycle.

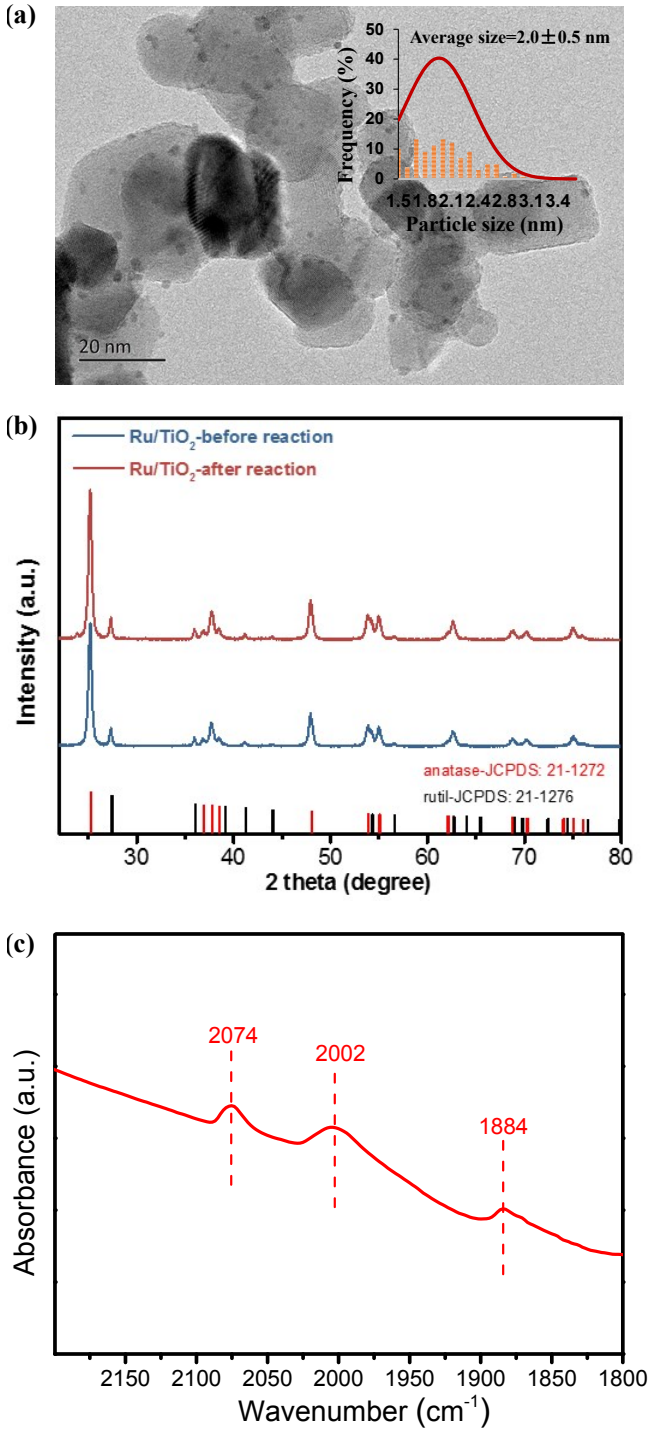


Figure S2. TEM (A), XRD (B) and IR (C) of Ru/TiO_2 after reaction.

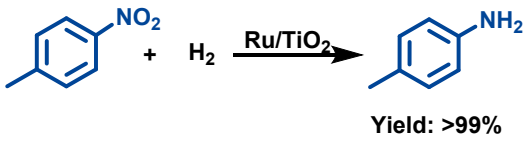


Figure S3. The hydrogenation of *p*-nitrotoluene. Reaction conditions: Ru/TiO_2 (0.1 g), *p*-nitrotoluene (0.2 mmol), H_2 (0.5 MPa), CO (0.5 MPa), 160 °C, 8 h.

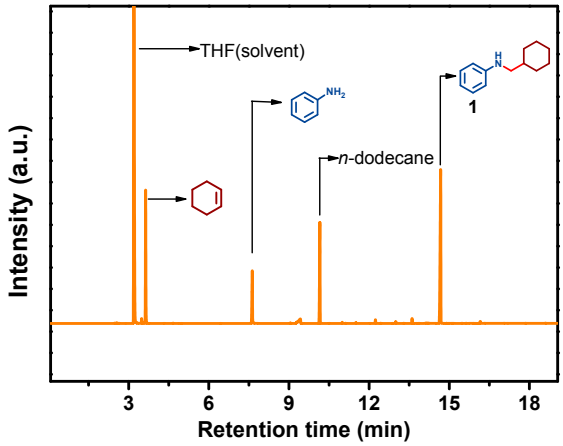


Figure S4. The product distribution of the reaction to synthesize amine (**1**) from aniline, cyclohexene, CO, and H_2. Reaction conditions: catalyst (0.1 g), aniline (0.4 mmol), cyclohexene (1.0 mmol), 160 °C, 3 h.

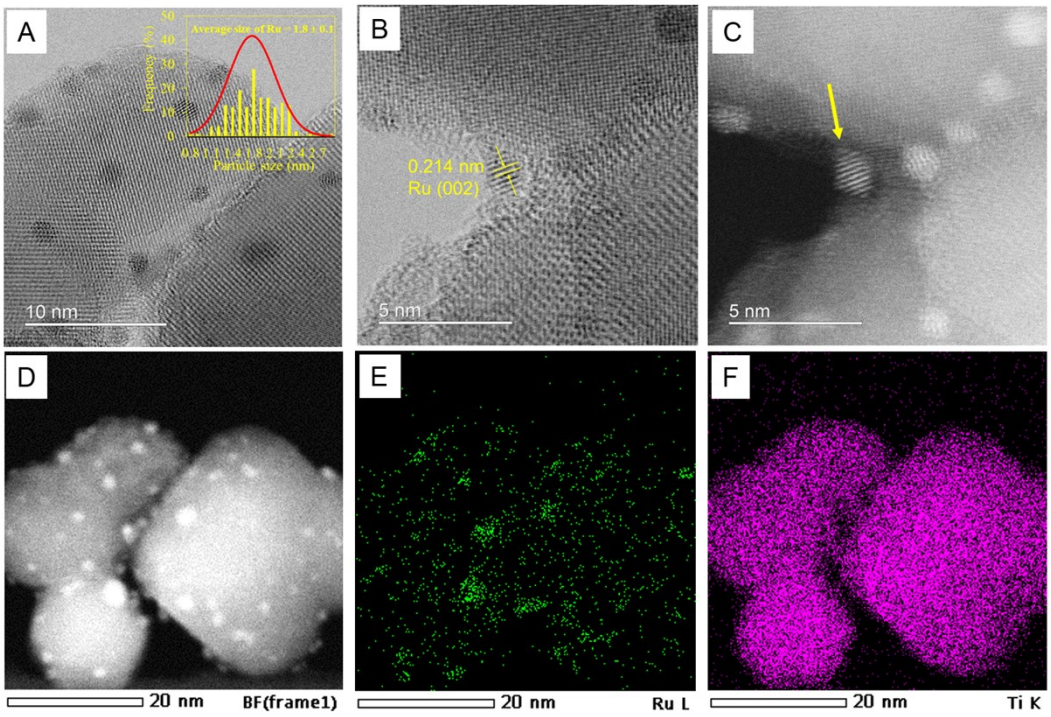


Figure S5. (A) STEM image of Ru/TiO_2. (B) The HRTEM image of Ru/TiO_2. (B) and (C) HAADF-STEM image of Ru/TiO_2. (E) Elemental mapping image of Ru. (F) Elemental mapping image of Ti.

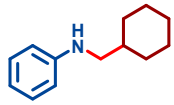
Table S2. Summary of various catalytic systems for the synthesis of amines via hydroaminomethylation of olefins.

Entry	Catalysts	Reaction systems	*T*/°C	P_{CO}/ MPa	P_{H2}/ MPa	Yield of products /%	Ref.[a]	Published year
1	Ru/TiO_2	heterogeneous	165	0.5	0.5	91	This work	-
2	Rhodium exchanged titanosilicates (ETS-10 and ETS-4)	heterogeneous	100	1.35	5.4	>95	10	2014
3	$[Rh(cod)_2]BF_4$ (0.1 mol%); IPHOS (0.4 mol%)	homogeneous	120	1.0	2.0	>99	6a	2002
4	$[Rh(cod)_2]BF_4$	homogeneous	125	0.7	3.3	98	6b	2003
5	$Ru_3(CO)_{12}$	homogeneous	130	1.0	5.0	93	7a	2013
6	$Ru_3(CO)_{12}$(0.5 mol%); K_2CO_3 (20%)	homogeneous	130	4.0	-	81	7b	2014
7	$Rh(acac)(CO)_2$	homogeneous	50	0.2	0.2	89	8	2017
8	$[Rh(COD)_2]BF_4$; pH = 4.8 HCO_2Na buffer	homogeneous	80	H_2:CO (1:1, 0.34 MPa)		91	9	2018

[a] The number were in accordance with the reference numbers in the manuscript.

Characterization of products

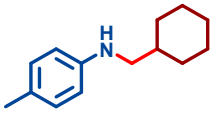
Product **1**.



1

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **1** as a light yellow liquid in 84% yield.[3] ^{1}H NMR (400 MHz, DMSO) δ = 7.03 (t, *J* = 7.9, 2H), 6.58 – 6.43 (m, 3H), 5.53 (s, 1H), 2.02 (t, *J* = 5.9, 2H), 1.69 (ddd, *J* = 24.0, 19.3, 8.5, 5H), 1.31 – 0.73 (m, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 149.66, 129.26, 115.50, 112.22, 49.94, 37.28, 31.29, 26.66, 26.03.

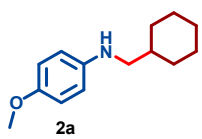
Product **1a**.



1a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **1a** as a light yellow liquid in 85% yield. Spectral data were in accordance with those previously reported.[4] ^{1}H NMR (400 MHz, DMSO) δ = 6.85 (d, *J* = 8.2, 2H), 6.45 (d, *J* = 8.4, 2H), 5.30 (t, *J* = 5.8, 1H), 2.79 (t, *J* = 6.3, 2H), 2.12 (s, 3H), 1.69 (ddd, *J* = 30.1, 24.2, 11.5, 5H), 1.32 – 0.79 (m, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 147.45, 129.71, 129.71, 123.80, 112.39, 112.39, 50.27, 37.30, 31.31, 31.31, 26.68, 26.04, 26.04, 20.52.

Product **2a**.

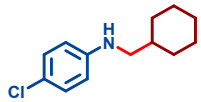


2a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **2a** as a

light yellow liquid in 72% yield.[5] Spectral data were in accordance with those previously reported. ^{1}H NMR (400 MHz, DMSO) δ = 6.75 – 6.62 (m, 2H), 6.56 – 6.42 (m, 2H), 5.09 (s, 1H), 3.62 (s, 3H), 2.77 (d, *J* = 6.2, 2H), 1.73 – 1.43 (m, 4H), 1.26 – 0.77 (m, 7H). ^{13}C NMR (101 MHz, DMSO) δ = 150.78, 144.03, 115.04, 115.04, 113.25, 113.25, 50.88, 50.88, 37.35, 31.35, 31.35, 26.69, 26.06, 26.06.

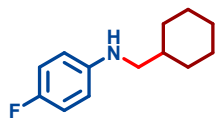
Product **3a**.



3a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **3a** as a light yellow liquid in 97% yield.[6] Following was the ^{1}H NMR spectrum of **3a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.05 (t, *J* = 6.0, 2H), 6.54 (t, *J* = 6.0, 2H), 5.79 (t, *J* = 5.6, 1H), 2.81 (t, *J* = 6.2, 2H), 1.82 – 1.56 (m, 5H), 1.02 (dddd, *J* = 26.2, 18.7, 17.0, 8.8, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 148.56, 128.94, 128.94, 118.65, 113.50, 113.50, 49.92, 37.18, 31.20, 31.20, 26.61, 25.98, 25.98.

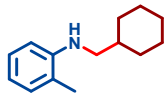
Product **4a**.



4a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **4a** as a light yellow liquid in 97% yield.[7] Following was the ^{1}H NMR and ^{13}C NMR spectrum of **4a**. ^{1}H NMR (400 MHz, CD3CN) δ = 6.92 – 6.80 (m, 12H), 6.66 – 6.47 (m, 2H), 4.32 (s, 1H), 2.86 (d, *J* = 6.7, 2H), 1.85 – 1.12 (m, 11H). ^{13}C NMR (101 MHz, CD_3CN) δ = 156.64, 146.51, 115.86, 115.64, 113.49, 113.42, 51.14, 37.81, 31.53, 31.53, 26.96, 26.36, 26.36.

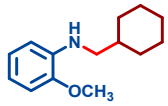
Product **5a**.



5a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **5a** as a light yellow liquid in 96% yield. Following was the ^{1}H NMR spectrum of **5a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.04 – 6.88 (m, 2H), 6.45 (t, *J* = 7.4, 2H), 4.69 (s, *J* = 5.2, 1H), 2.90 (t, *J* = 6.2, 2H), 2.06 (s, 3H), 1.83 – 1.50 (m, 6H), 1.19 (dd, J = 21.9, 8.5, 5H). ^{13}C NMR (101 MHz, DMSO) δ = 147.06, 130.14, 127.16, 121.85, 115.63, 109.32, 50.03, 36.82, 31.36, 31.36, 26.73, 26.05, 26.05, 18.13.

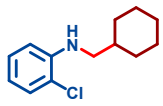
Product **6a**.



6a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **6a** as a light yellow liquid in 60% yield.[8] Following were the ^{1}H NMR and ^{13}C NMR spectra of **6a**. ^{1}H NMR (400 MHz, DMSO) δ = 6.80 (tt, *J* = 13.7, 6.7, 2H), 6.60 – 6.35 (m, 2H), 3.76 (s, 3H), 2.89 (t, *J* = 6.4, 2H), 1.84 – 1.44 (m, 5H), 1.36 – 0.70 (m, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 146.67, 138.75, 121.52, 115.55, 110.12, 109.40, 55.73, 49.72, 37.10, 31.22, 31.22, 26.66, 25.97, 25.97.

Product **7a**.

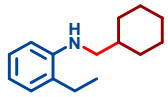


7a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **7a** as a light yellow liquid in 97% yield. Following was the ^{1}H NMR spectrum of **7a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.29 – 6.95 (m, 2H), 6.76 – 6.35 (m, 2H), 5.19 (s,

1H), 2.97 (t, *J* = 6.2, 2H), 1.65 (ddd, *J* = 22.9, 14.5, 10.0, 5H), 1.06 (dt, *J* = 22.6, 18.4, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 144.69, 129.37, 128.43, 118.04, 116.44, 111.58, 49.46, 36.79, 31.06, 26.63, 25.93.

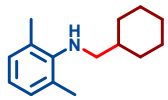
Product **8a**.



8a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **8a** as a light yellow liquid in 82% yield. Following was the ^{1}H NMR spectrum of **8a**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.01 (dd, *J* = 14.9, 7.5 Hz, 2H), 6.56 (dd, *J* = 7.6, 5.1 Hz, 2H), 4.05 (s, 1H), 2.97 (d, *J* = 6.7 Hz, 2H), 2.46 (q, *J* = 7.5 Hz, 2H), 1.96 – 1.57 (m, 7H), 1.32 – 1.19 (m, 4H), 1.17 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ = 146.64, 128.52, 127.99, 127.35, 117.87, 116.59, 110.19, 50.52, 37.55, 31.66, 31.66, 27.01, 26.40, 26.40, 24.23, 13.18

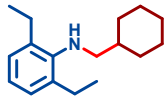
Product **9a**.



9a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **9a** as a light yellow liquid in 96% yield. Following were the ^{1}H NMR and ^{13}C NMR of **9a**. ^{1}H NMR (400 MHz, DMSO) δ = 6.90 (d, *J* = 7.4, 2H), 6.69 (t, *J* = 7.4, 1H), 3.58 (s, 1H), 2.71 (d, *J* = 6.5, 2H), 2.20 (s, 6H), 1.81 (d, *J* = 12.9, 2H), 1.72 – 1.57 (m, 3H), 1.55 – 1.32 (m, 2H), 1.28 – 1.06 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ = 147.01, 129.43, 129.43, 128.92, 128.92, 121.34, 54.90, 38.93, 38.93, 31.26, 26.70, 26.09, 26.09, 18.80, 18.80.

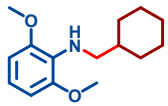
Product **10a**.



10a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **10a** as a light yellow liquid in 75% yield. Following were the ^{1}H NMR and ^{13}C NMR of **10a**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.00 (d, *J* = 7.5, 2H), 6.87 (t, *J* = 7.5, 1H), 3.11 (s, 1H), 2.72 (d, *J* = 6.5, 2H), 2.63 (q, *J* = 7.5, 4H), 1.99 – 1.62 (m, 7H), 1.29 (dd, *J* = 25.0, 12.0, 4H), 1.18 (t, *J* = 7.5, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ = 146.29, 137.10, 127.24, 127.24, 122.91, 117.87, 57.37, 39.63, 31.65, 31.65, 27.01, 26.46, 26.46, 24.59, 24.59, 15.02, 15.02.

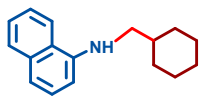
Product **11a**



11a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **11a** as a light yellow liquid in 41% yield. Following was the ^{1}H NMR and ^{13}C NMR spectrum of **11a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.69 (d, *J* = 7.4, 1H), 6.67 (dd, *J* = 8.9, 7.4, 1H), 6.59 – 6.53 (m, 2H), 3.74 (s, 6H), 3.01 (d, *J* = 6.6, 2H), 1.73 – 1.57 (m, 6H), 1.28 (dd, *J* = 17.7, 11.3, 5H). ^{13}C NMR (101 MHz, DMSO) δ = 150.04, 150.04, 128.00, 118.62, 105.91, 105.91, 56.40, 56.40, 53.08, 38.45, 30.98, 30.98, 26.71, 25.99, 25.99.

Product **13a**.

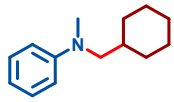


13a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1: 100 as eluent to get pure product 1**3a** as a red liquid in 99% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of

13a. ^{1}H NMR (400 MHz, DMSO) δ = 8.18 (d, *J* = 8.2, 1H), 7.73 (d, *J* = 8.1, 1H), 7.47 – 7.35 (m, 2H), 7.26 (dd, *J* = 14.5, 6.7, 1H), 7.05 (d, *J* = 8.1, 1H), 6.45 (d, *J* = 7.6, 1H), 6.12 (t, *J* = 5.4, 1H), 3.05 (t, *J* = 6.1, 2H), 1.90 – 1.55 (m, 7H), 1.29 – 1.06 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ = 144.75, 134.56, 128.35, 127.33, 125.98, 124.22, 123.39, 122.13, 115.26, 103.12, 50.22, 36.50, 31.51, 31.51, 26.70, 26.06, 26.06.

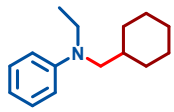
Product **17a**.



17a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **17a** as a light yellow liquid in 99% yield.[9] Following were the ^{1}H NMR and ^{13}C NMR spectra of **17a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.13 (dd, *J* = 8.6, 7.3, 2H), 6.71 – 6.28 (m, 3H), 3.12 (d, *J* = 6.8, 2H), 2.89 (s, 3H), 1.67 (t, *J* = 18.4, 6H), 1.20 – 0.84 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ = 149.67, 129.37, 115.47, 111.89, 55.89, 42.50, 36.71, 31.03, 26.57, 25.98.

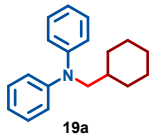
Product **18a**



18a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **18a** as a light yellow liquid in 85% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **18a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.12 (t, *J* = 7.9, 2H), 6.62 (d, *J* = 8.5, 2H), 6.52 (t, *J* = 7.2, 1H), 3.41 – 3.27 (m, 2H), 3.04 (d, J=7.0, 2H), 1.84 – 1.09 (m, 11H), 1.03 (t, *J* = 6.9, 4H). ^{13}C NMR (101 MHz, DMSO) δ = 148.39, 129.48, 129.48, 115.17, 112.07, 112.07, 56.67, 45.54, 36.77, 31.06, 31.06. 26.62, 26.05, 26.05, 11.93.

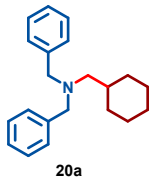
Product **19a**.



19a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:10 as eluent to get pure product **19a** as a light yellow liquid in 45% yield.[10] Following were the ^{1}H NMR and ^{13}C NMR spectra of **19a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.25 (t, *J* = 7.8, 4H), 7.00 – 6.84 (m, 6H), 3.53 (d, *J* = 7.1, 2H), 1.81 – 1.57 (m, 6H), 1.38 – 0.98 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ = 148.79, 148.79, 129.70, 129.70, 129.70, 129.70, 121.37, 121.37, 121.15, 121.15, 121.15, 121.15, 58.54, 36.73, 31.06, 31.06, 26.55, 26.00, 26.00.

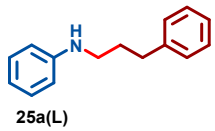
Product **20a**



20a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **20a** as a light yellow liquid in 96% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **20a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.45 – 7.16 (m, 10H), 3.47 (s, 4H), 2.14 (d, *J* = 7.2, 2H), 1.79 (d, *J* = 11.4, 2H), 1.68 – 1.36 (m, 4H), 1.36 – 0.85 (m, 7H). ^{13}C NMR (101 MHz, DMSO) δ = 140.08, 140.08, 128.92, 128.92, 128.92, 128.92, 128.61, 128.61, 128.61, 128.61, 127.28, 127.28, 60.57, 58.62, 58.62, 35.35, 31.64, 31.64, 26.79, 25.96, 25.96.

Product **25a**.

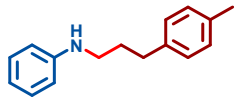


25a(L)

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **25a** as a

light yellow liquid in 80% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **25a(L)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.35 – 7.03 (m, 7H), 6.63 – 6.53 (m, 3H), 4.33 (s, 1H), 3.08 (dd, *J* = 12.4, 6.7, 2H), 2.76 – 2.67 (m, 2H), 1.87 (dd, *J* = 14.7, 7.6, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ = 142.89, 141.18, 129.61, 129.61, 128.96, 128.93, 126.34, 126.34, 116.87, 112.84, 112.84, 43.40, 33.48, 31.46.

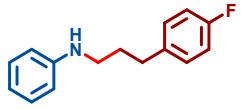
Product **26a**.



26a(L)

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **26a** as a light yellow liquid in 78% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **26a(L)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.23 – 6.99 (m, 6H), 6.64 – 6.51 (m, 3H), 4.33 (s, 1H), 3.06 (t, *J* = 7.0, 2H), 2.71 – 2.62 (m, 2H), 2.29 (s, 3H), 1.90 – 1.80 (m, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ = 149.68, 139.70, 135.78, 129.61, 129.61, 129.52, 129.52, 128.86, 128.86, 116.85, 112.83, 112.83, 43.40, 33.04, 31.52, 20.59.

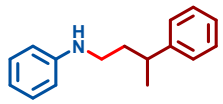
Product **27a**.



27a(L)

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **27a** as a light yellow liquid in 80% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **27a(L)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.35 – 7.17 (m, 2H), 7.17 – 6.95 (m, 4H), 6.63 – 6.34 (m, 3H), 4.33 (s, 1H), 3.06 (t, *J* = 6.9, 2H), 2.74 – 2.65 (m, 2H), 1.86 (td, *J* = 14.2, 7.1, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ = 160.54, 149.64, 138.86, 130.60, 130.53, 129.62, 117.88, 117.88, 116.90, 115.51, 115.30, 112.85, 43.28, 32.60, 31.50.

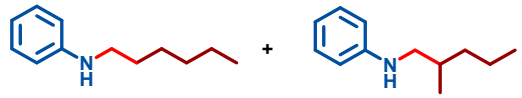
Product **28a**.



28a(L)

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **28a** as a light yellow liquid in 30% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **28a(L)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.38 – 7.16 (m, 5H), 7.12 – 7.03 (m, 2H), 6.53 (ddd, *J* = 9.6, 7.9, 1.0, 3H), 4.23 (s, 1H), 2.91 (ddd, *J* = 21.6, 12.9, 7.2, 3H), 1.86 (q, *J* = 7.3, 2H), 1.26 (d, *J* = 7.0, 3H).

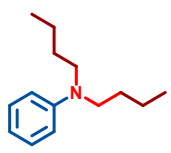
Product **29a**.



29a(L) major (about 68%)　　29a(B) minor (about 32%)

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **29a** as a light yellow liquid in 76% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **29a(L+B)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.30 – 6.84 (m, 4H), 6.75 – 6.33 (m, 6H), 4.27 (s, 2H), 3.06 (dt, *J* = 14.1, 7.2, 3H), 3.01 – 2.95 (m, 0.5H), 2.89 – 2.80 (m, 0.5H), 1.62 – 1.52 (m, 3H), 1.35 (dddd, *J* = 18.4, 14.6, 9.9, 5.3, 14H), 0.95 – 0.75 (m, 9H). ^{13}C NMR (101 MHz, CD_3CN) δ = 149.85, 149.78, 149.78, 129.59, 129.59, 116.74, 116.62, 112.81, 112.81, 112.77, 112.77, 50.31, 43.93, 37.33, 32.90, 32.01, 29.60, 27.16, 22.97, 20.40, 17.81, 14.26, 13.94.

Product **30a**.

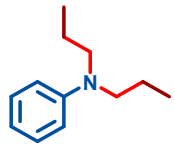


30a(L)

The crude product was purified by silicagel column chromatography using

ethyl acetate: petroleum ether = 1:200 as eluent to get pure product **30a** as a light yellow liquid in 97% yield. Following were the ^{1}H NMR and ^{13}C NMR spectra of **30a(L)**. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.19 – 7.06 (m, 2H), 6.66 (t, *J* = 6.9, 2H), 6.55 (t, *J* = 7.2, 1H), 3.34 – 3.15 (m, 4H), 1.64 – 1.43 (m, 4H), 1.39 – 1.26 (m, 4H), 0.92 (dt, *J* = 6.1, 4.6, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ = 148.88, 129.64, 129.64, 115.49, 112.32, 112.32, 50.82, 50.82, 29.69, 29.69, 20.54, 20.54, 13.86, 13.86.

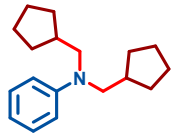
Product **31a**.



31a

The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **31a** as a light yellow liquid in 98% yield.[11] Following were the ^{1}H NMR and ^{13}C NMR spectra of **31a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.12 (t, *J* = 8.0, 2H), 6.61 (d, *J* = 8.2, 2H), 6.52 (t, *J* = 7.2, 1H), 3.26 – 3.14 (m, 4H), 1.62 – 1.34 (m, 4H), 0.87 (t, J=7.4, 6H). ^{13}C NMR (101 MHz, DMSO) δ = 148.28, 129.51, 129.51, 115.19, 111.86, 111.86, 52.39, 52.39, 20.41, 20.41, 11.68, 11.68.

Product **32a**.

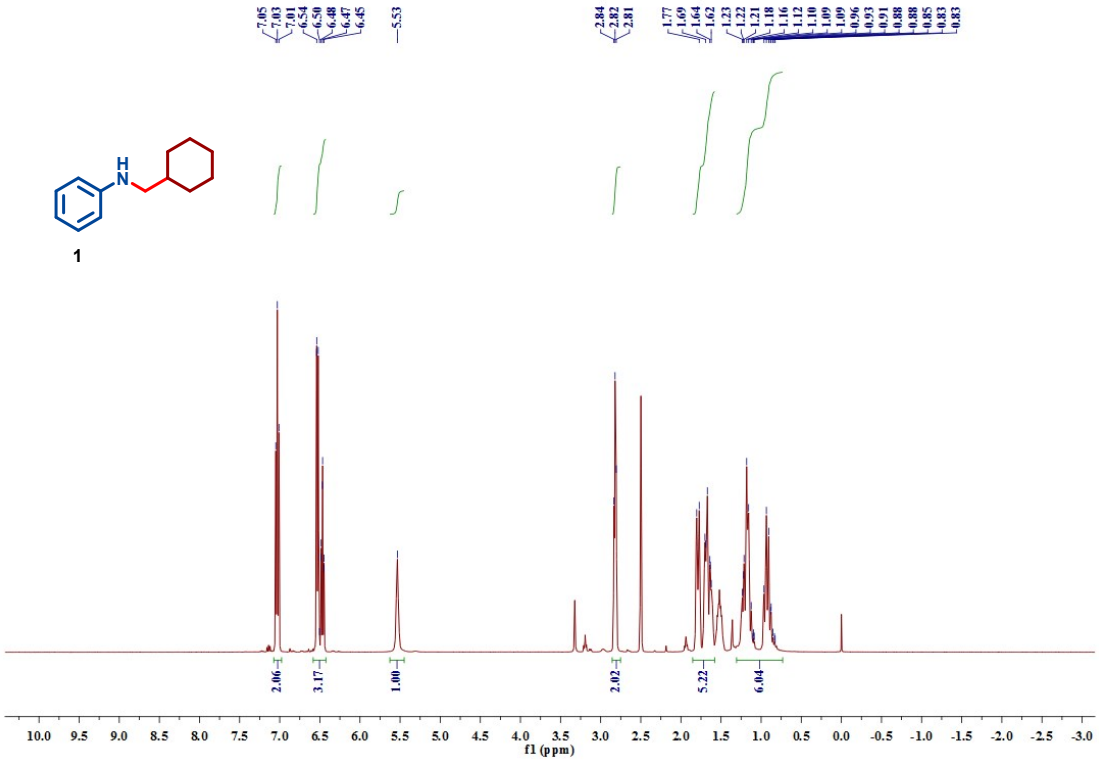


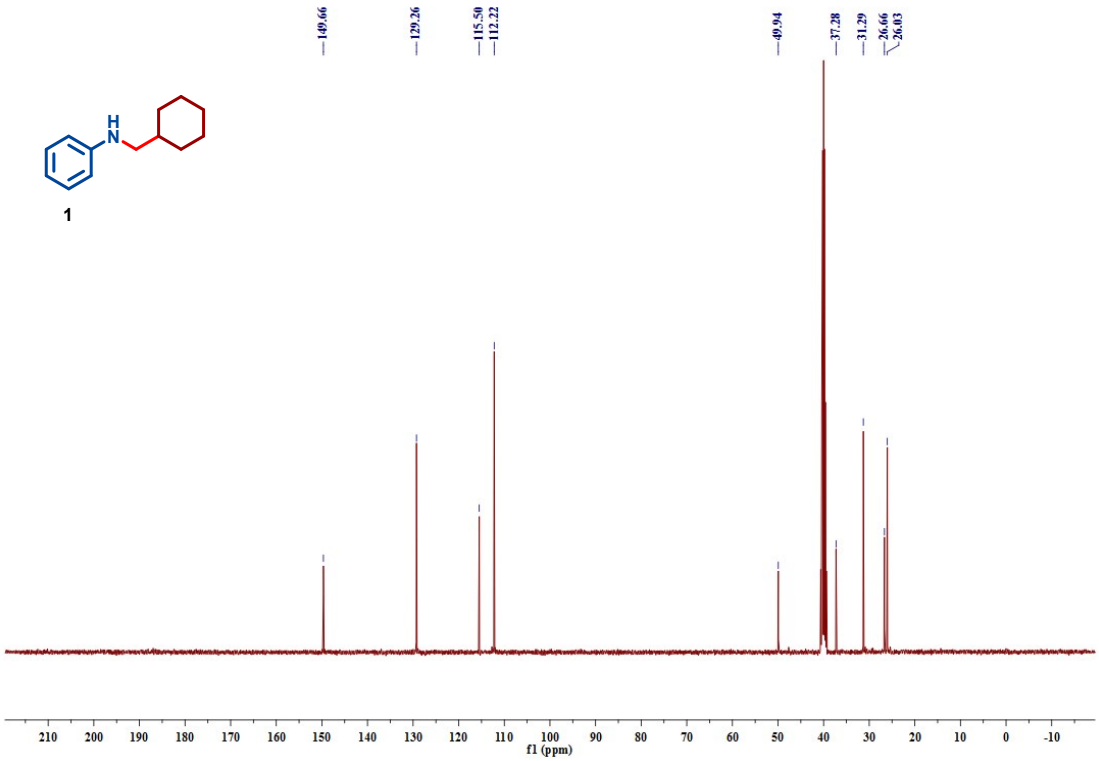
32a

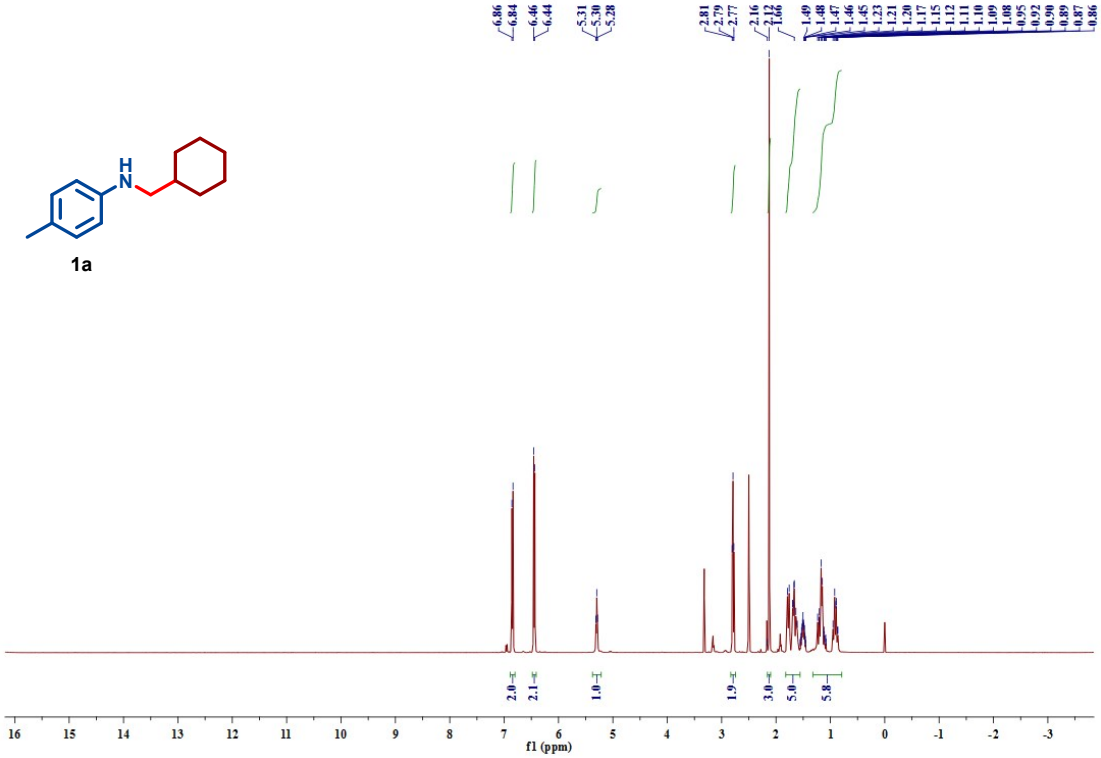
The crude product was purified by silicagel column chromatography using ethyl acetate: petroleum ether = 1:100 as eluent to get pure product **32a** as a light yellow liquid in 96% yield.[12] Following were the ^{1}H NMR and ^{13}C NMR spectra of **32a**. ^{1}H NMR (400 MHz, DMSO) δ = 7.12 (t, *J* = 7.9, 2H), 6.72 – 6.48 (m, 3H), 3.23 (d, *J* = 7.3, 4H), 1.77 – 1.00 (m, 18H). ^{13}C NMR (101 MHz, DMSO) δ = 148.70, 129.38, 129.38, 115.52, 112.93, 112.93, 56.25, 56.25, 38.28, 38.28,

30.57, 30.57, 30.57, 30.57, 24.96, 24.96, 24.96, 24.96.

^{1}H NMR and ^{13}C NMR spectra of products



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5.30
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2.79
2.77
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1.49
1.48
1.47
1.46
1.45
1.23
1.21
1.20
1.17
1.15
1.12
1.11
1.10
1.09
1.08
0.95
0.92
0.90
0.89
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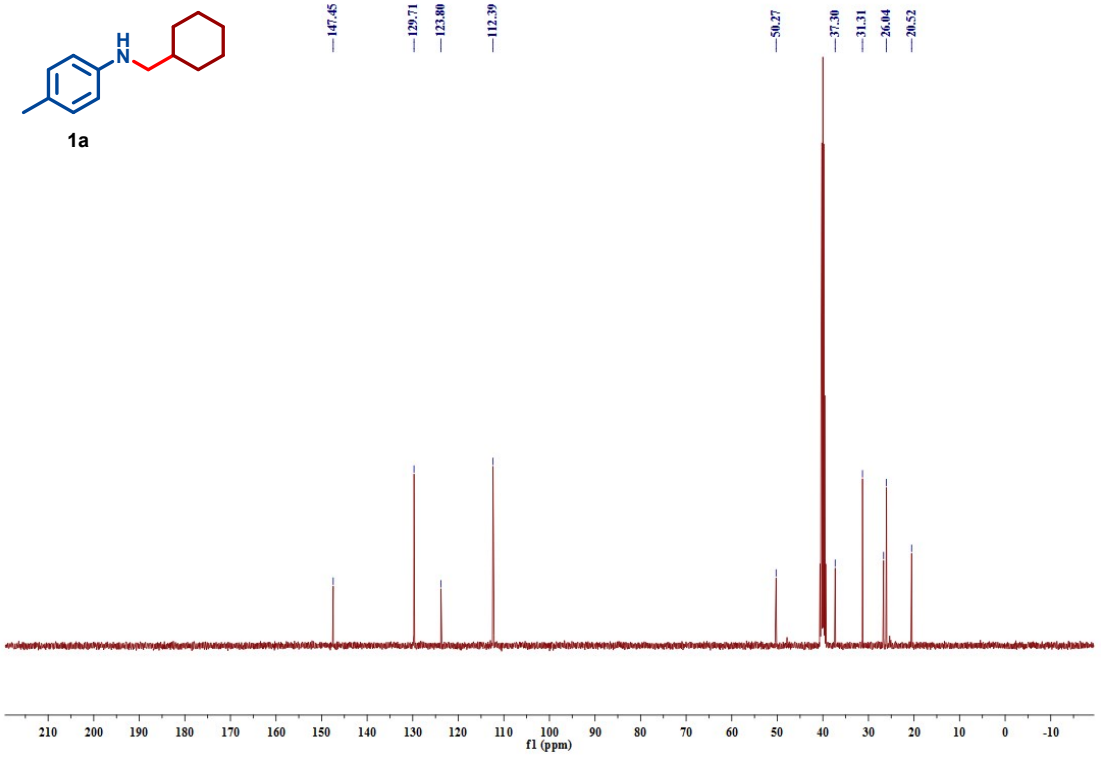
5.8
f1 (ppm)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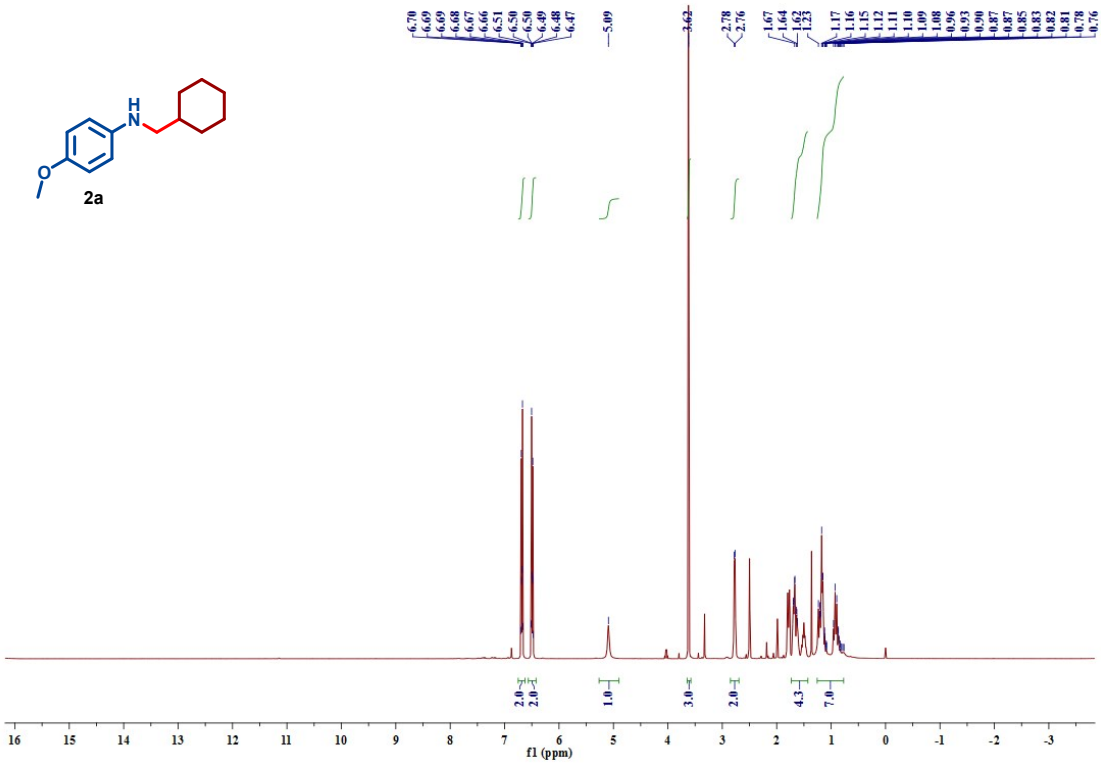
50.27
37.30
31.31
26.04
20.52
f1 (ppm)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1.62
1.23
1.17
1.16
1.15
1.12
1.11
1.10
1.09
1.08
0.96
0.93
0.90
0.87
0.87
0.85
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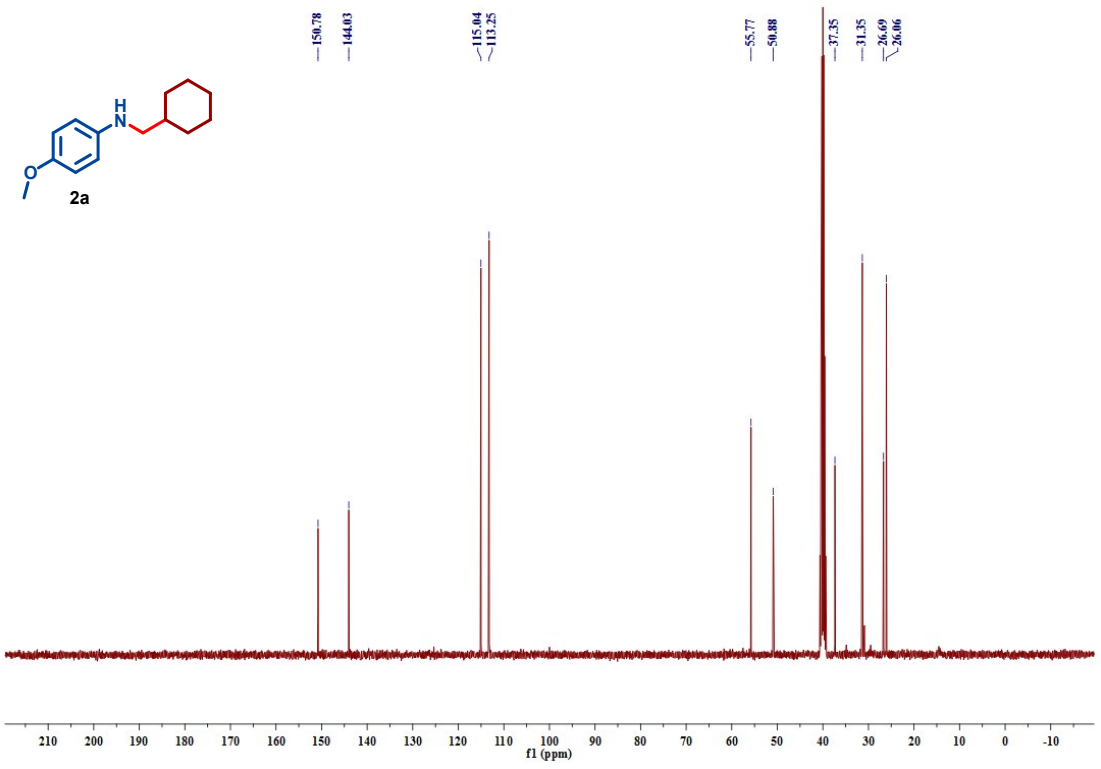
7.0
f1 (ppm)


2a
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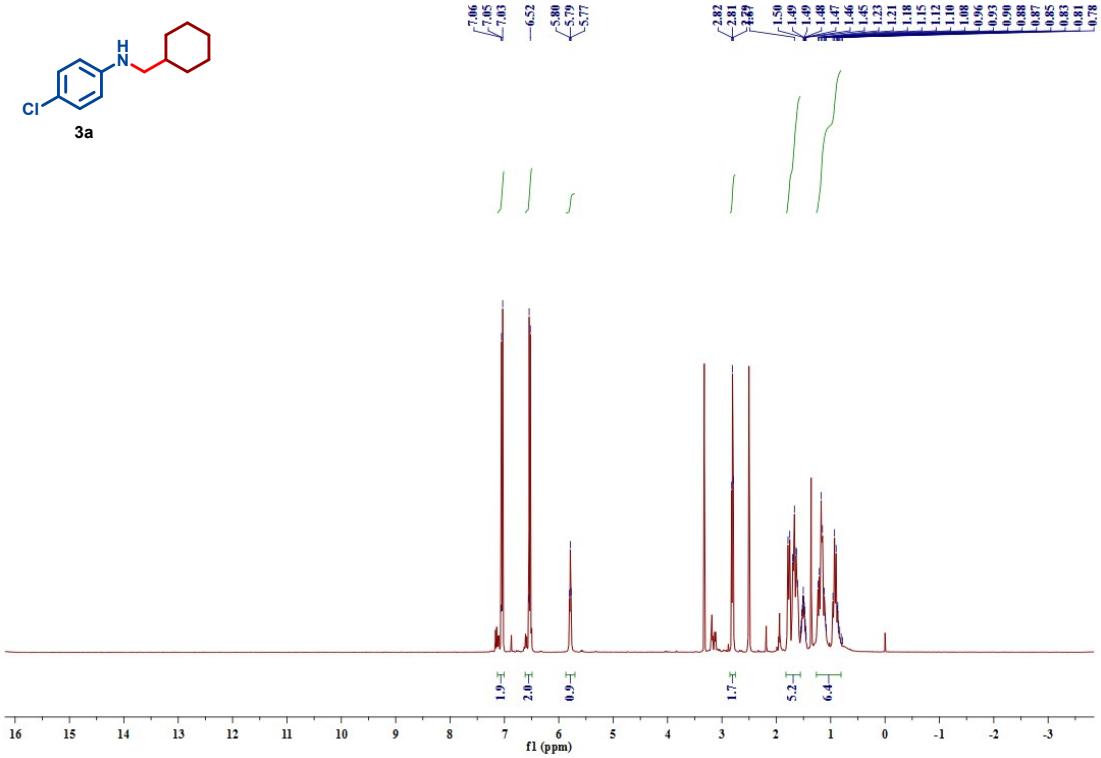
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1.23
1.21
1.18
1.15
1.12
1.10
1.08
0.96
0.93
0.90
0.88
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1.9
2.0
0.9
1.7
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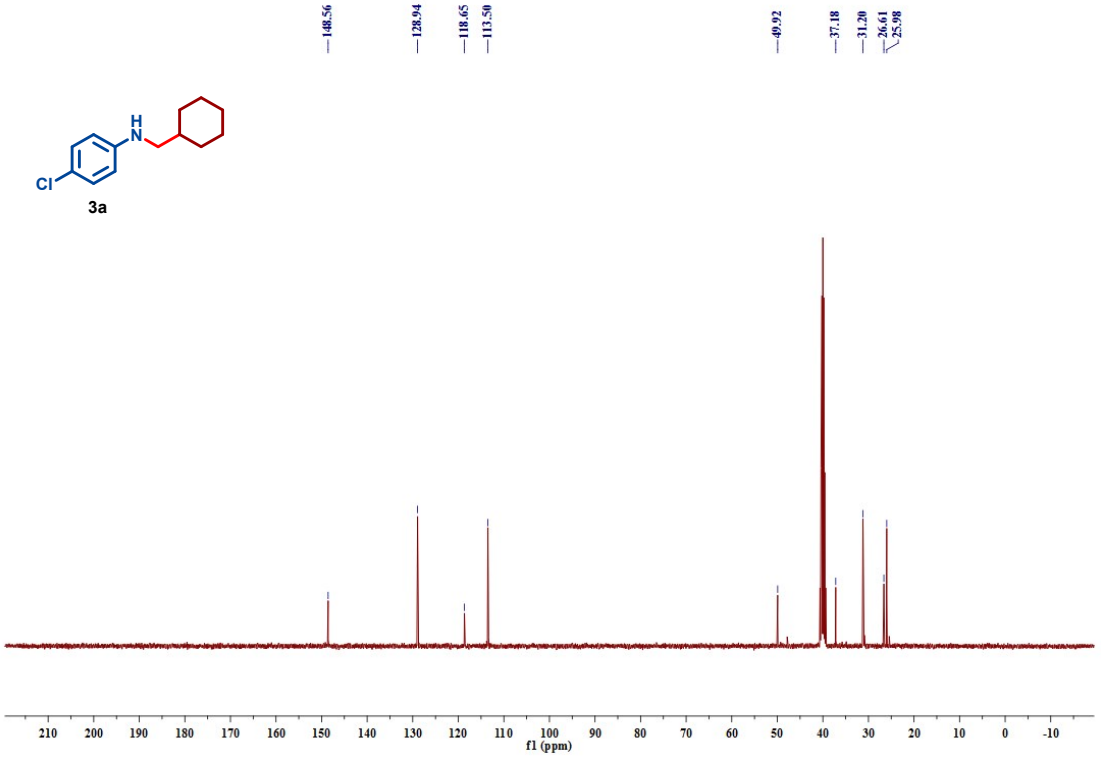
6.4
f1 (ppm)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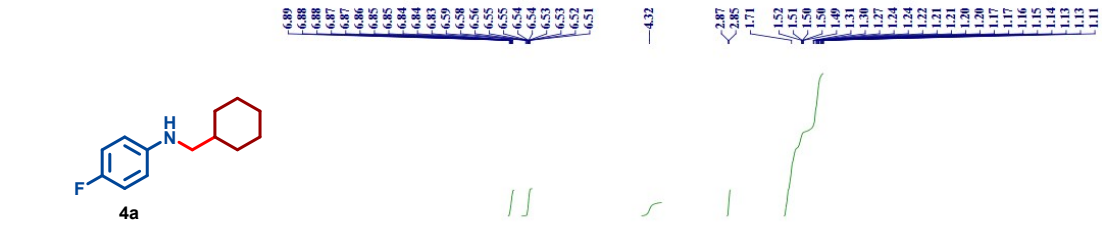
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1.50
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1.49
1.31
1.30
1.27
1.24
1.24
1.22
1.21
1.21
1.20
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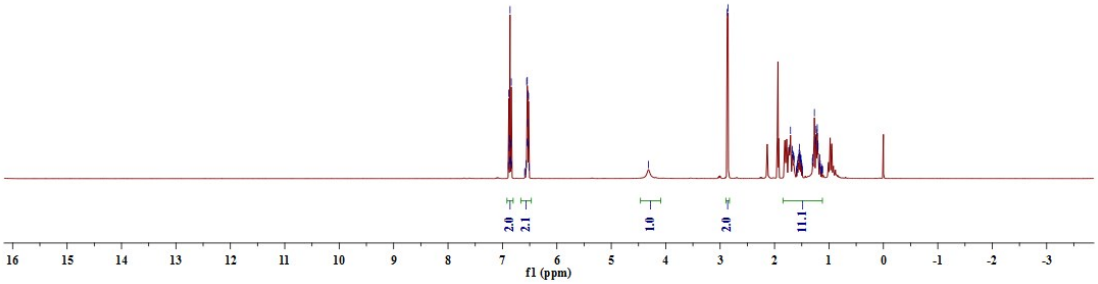
1.15
1.14
1.13
1.13
1.11

H
N
F

4a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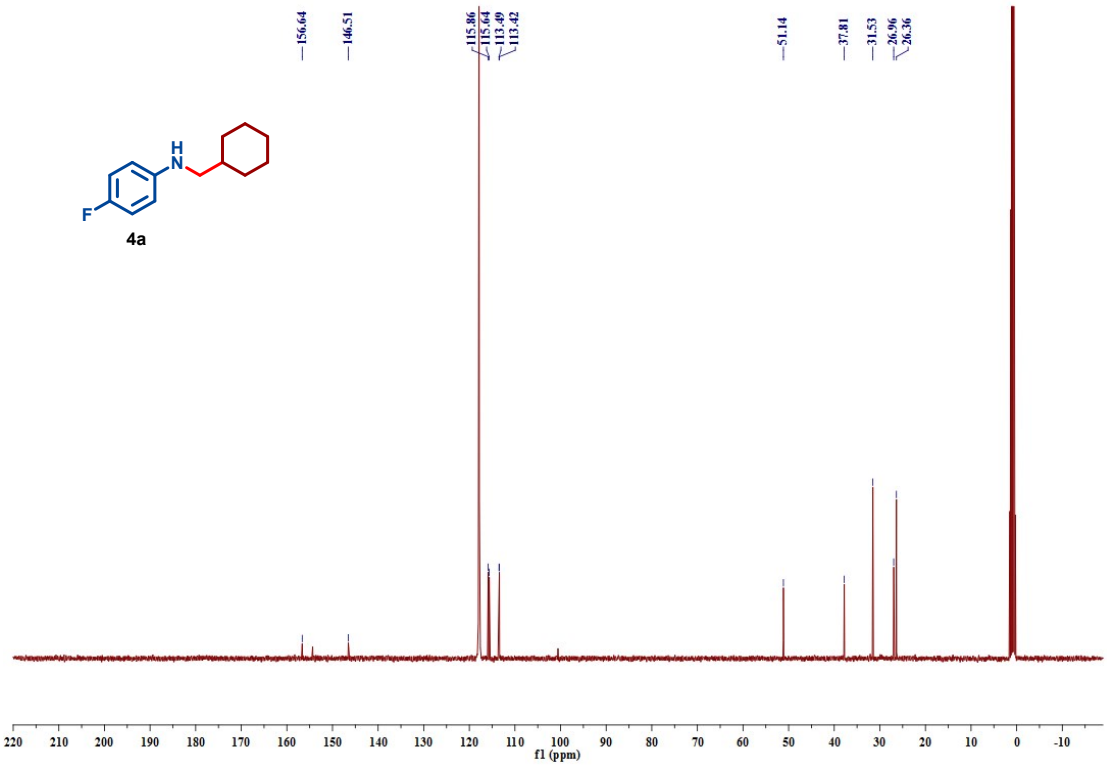
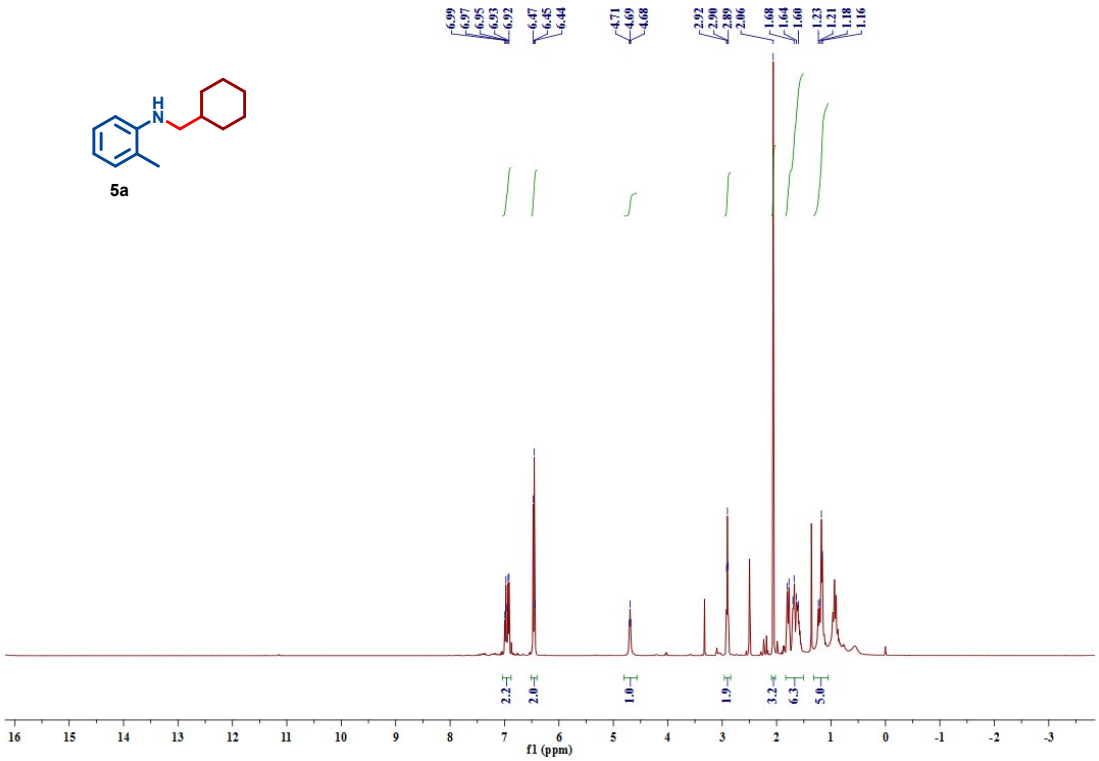
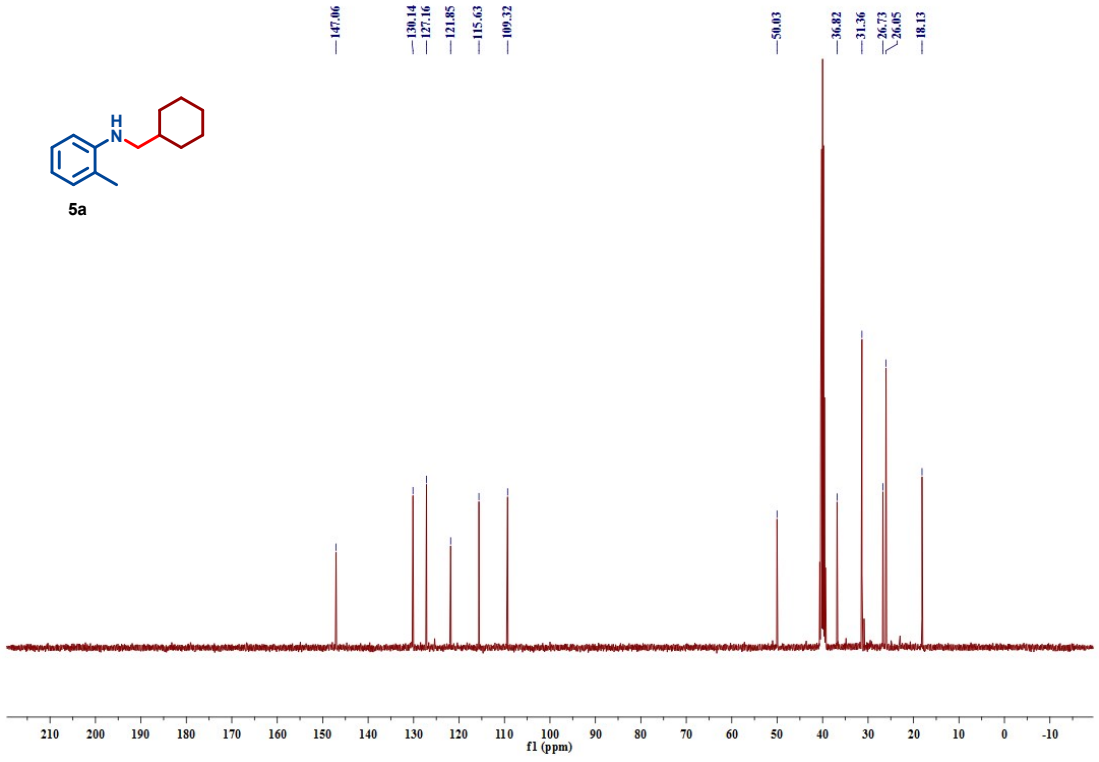
2.0
11.1
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

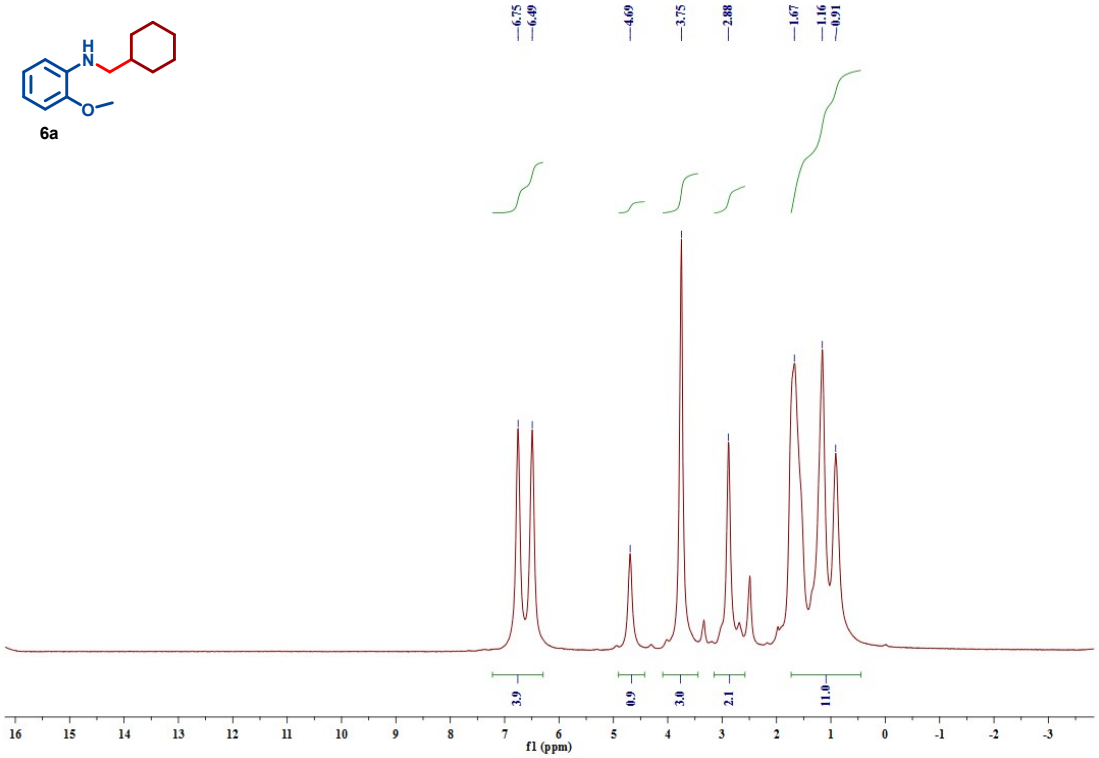

156.64
146.51
115.86
115.64
113.49
113.42
51.14
37.81
31.53
26.96
26.36
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

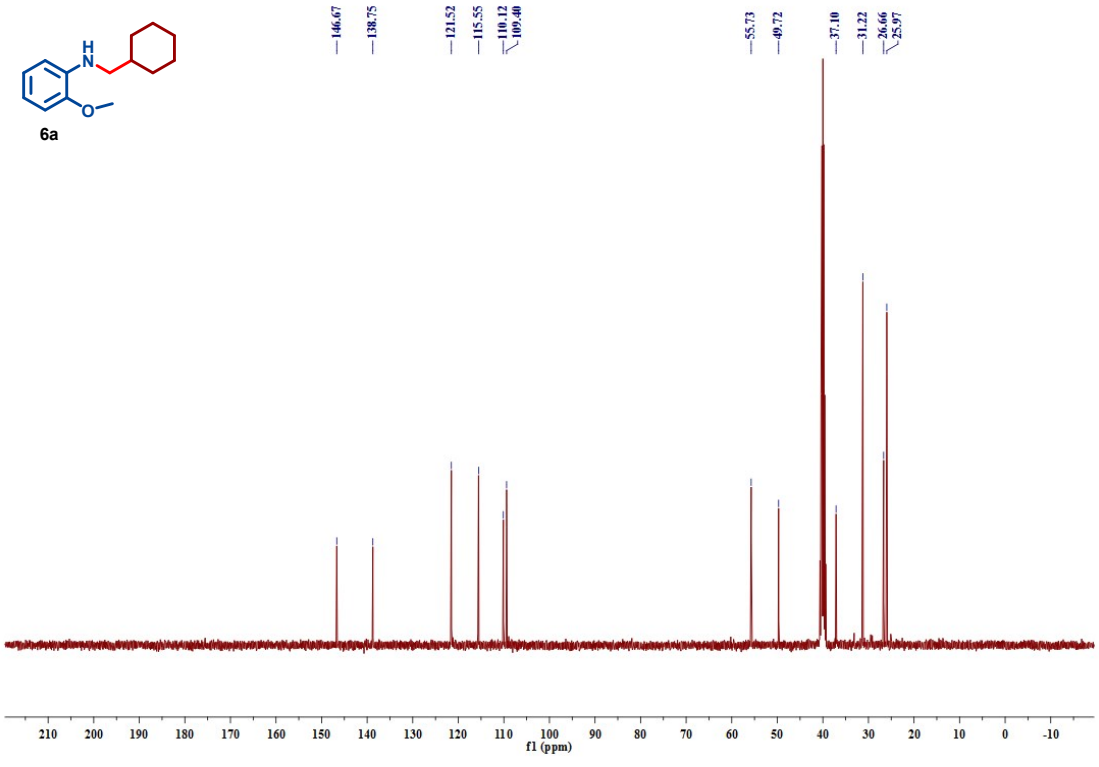
H
N
F

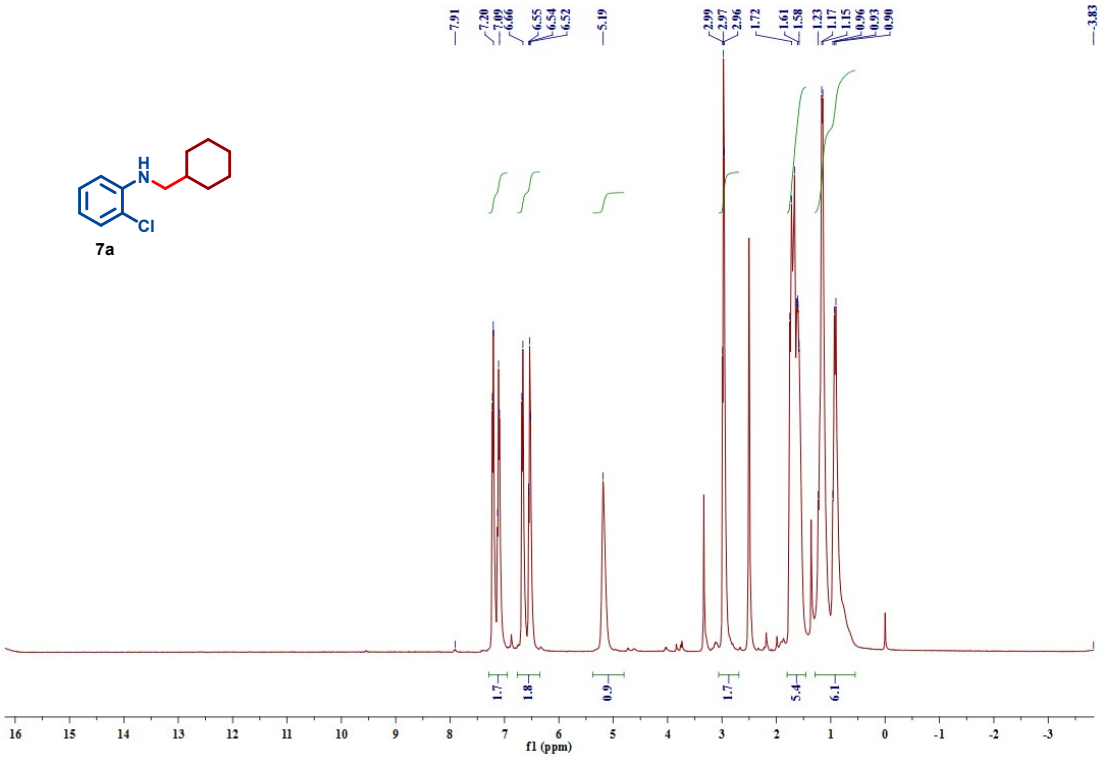
4a

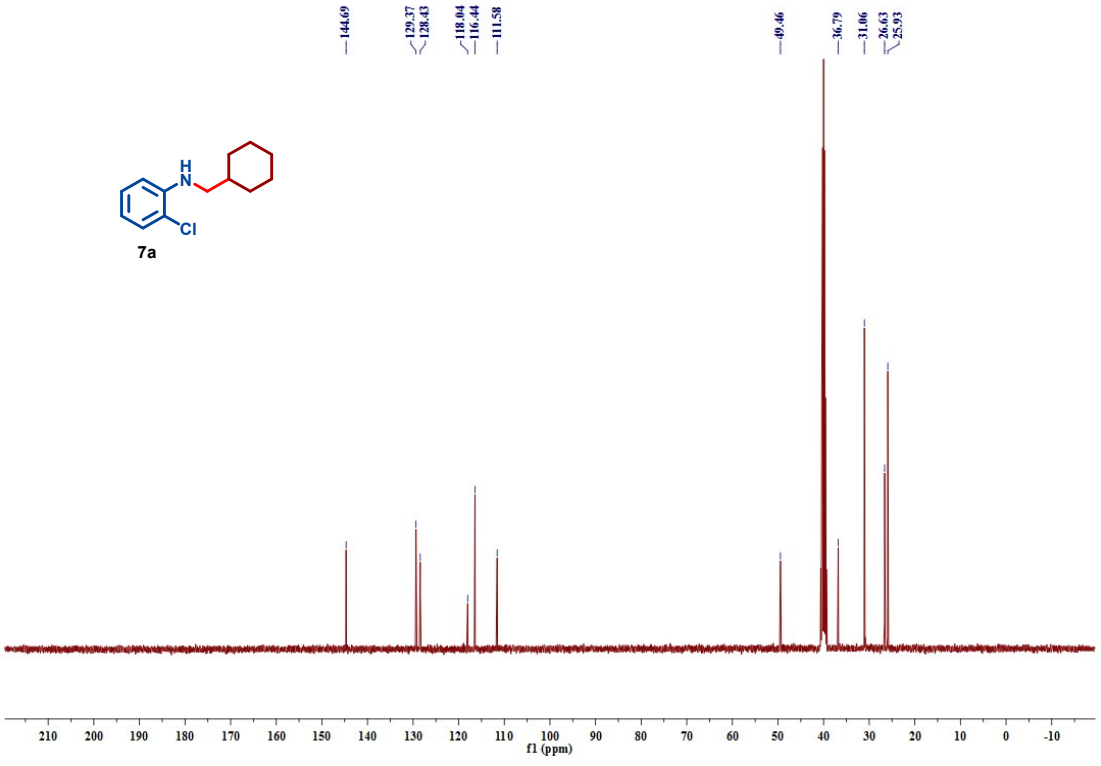

5a
6.99
6.97
6.95
6.93
6.92
6.47
6.45
6.44
4.71
4.69
4.68
2.92
2.90
2.89
2.06
1.68
1.64
1.60
1.23
1.21
1.18
1.16
2.2
2.0
1.0
1.9
3.2
6.3
5.0
f1 (ppm)

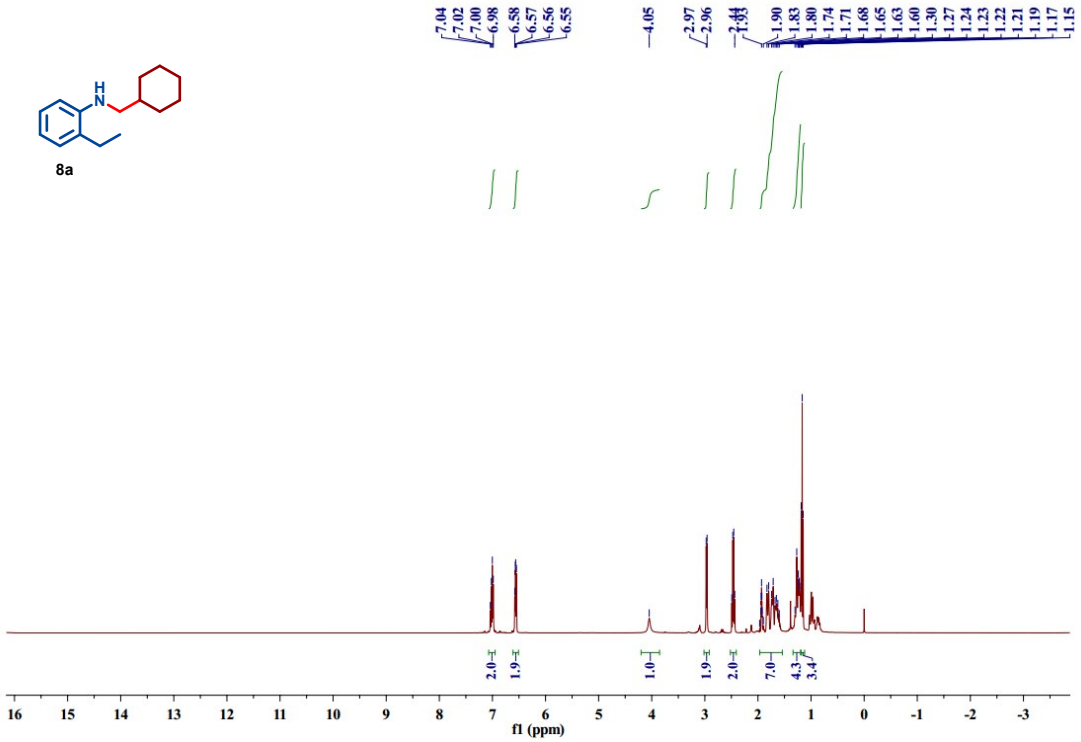

5a
147.06
130.14
127.16
121.85
115.63
109.32
50.03
36.82
31.36
26.73
26.05
18.13
f1 (ppm)

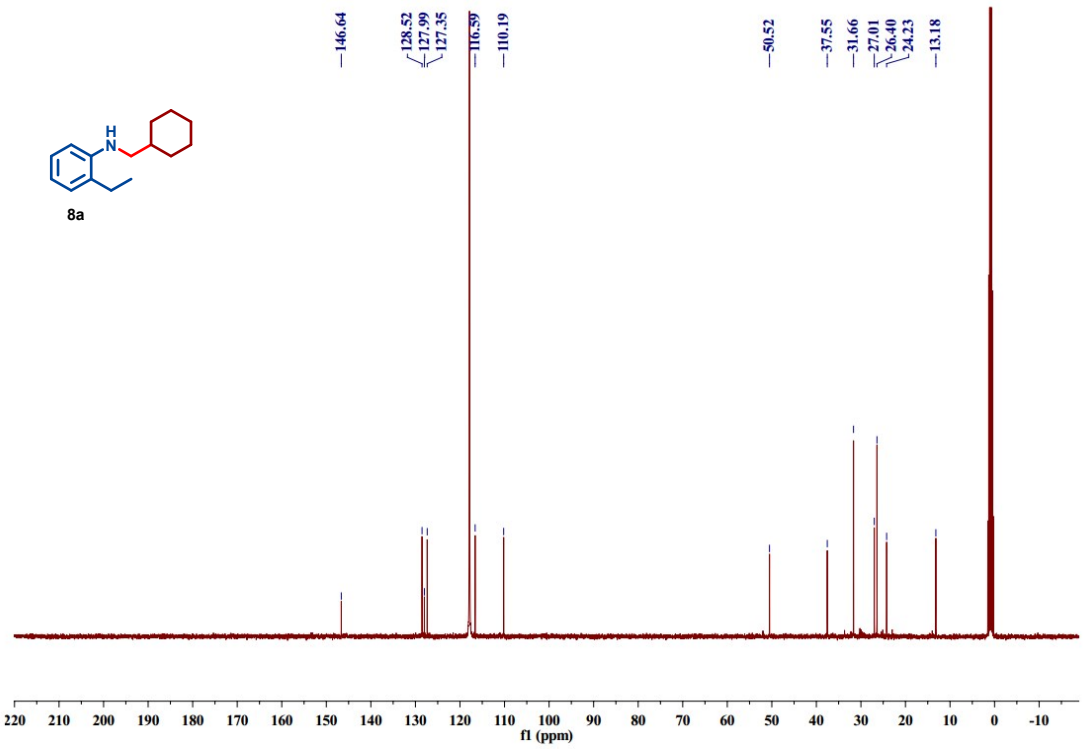

6a
6.75
6.49
4.69
3.75
2.88
1.67
1.16
0.91
3.9
0.9
3.0
2.1
11.0
f1 (ppm)

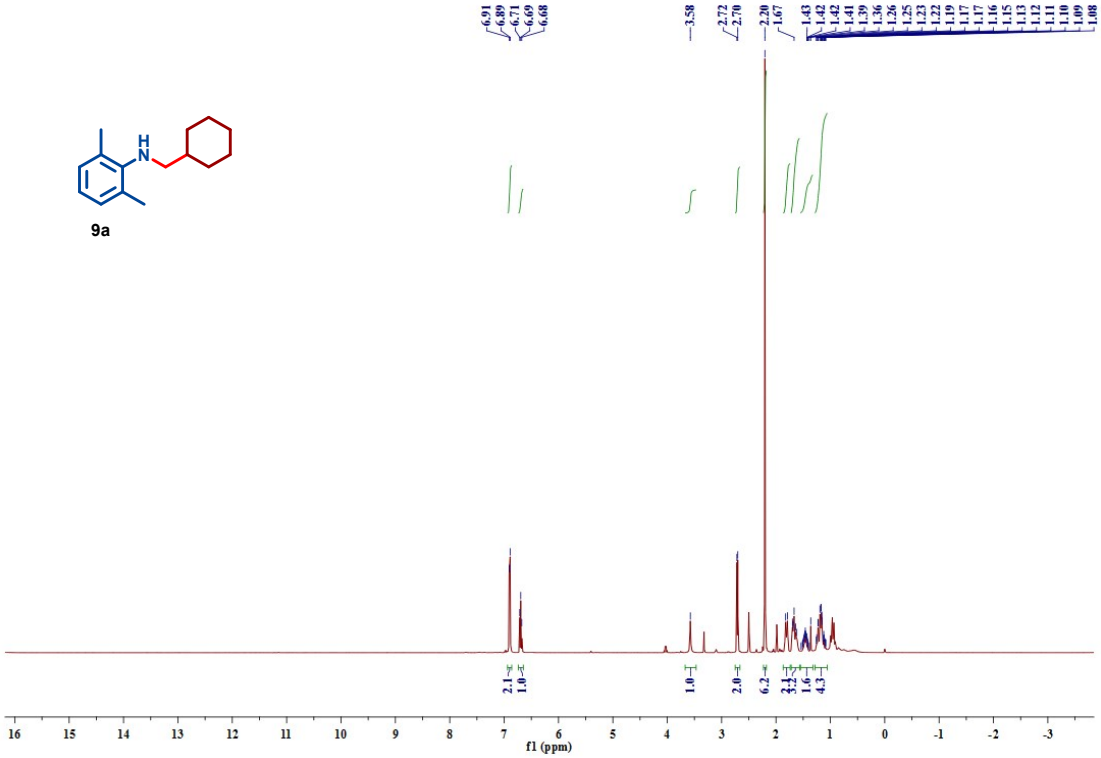

6a
146.67
138.75
121.52
115.55
110.12
109.40
55.73
49.72
37.10
31.22
26.66
25.97
f1 (ppm)

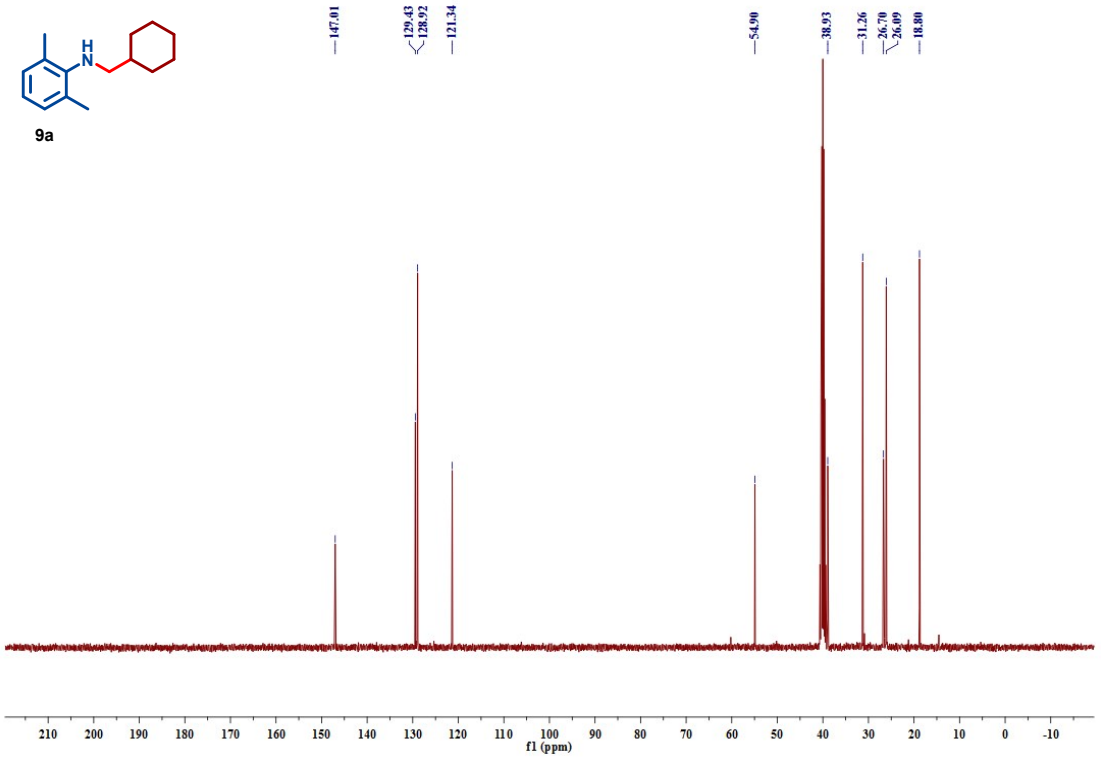

7.91
7.20
7.00
6.66
6.55
6.54
6.52
5.19
2.99
2.97
2.96
1.72
1.61
1.58
1.23
1.17
1.15
0.96
0.93
0.90
3.83
1.7
1.8
0.9
1.7
5.4
6.1
f1 (ppm)
H
N
Cl
7a

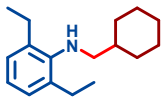

144.69
129.37
128.43
118.04
116.44
111.58
49.46
36.79
31.06
26.63
25.93
f1 (ppm)
H
N
Cl
7a


8a
7.04
7.02
7.00
6.98
6.58
6.57
6.56
6.55
4.05
2.97
2.96
1.90
1.83
1.80
1.74
1.71
1.68
1.65
1.63
1.60
1.30
1.27
1.24
1.23
1.22
1.21
1.19
1.17
1.15
2.0
1.9
1.0
1.9
2.0
7.0
4.3
3.4
f1 (ppm)

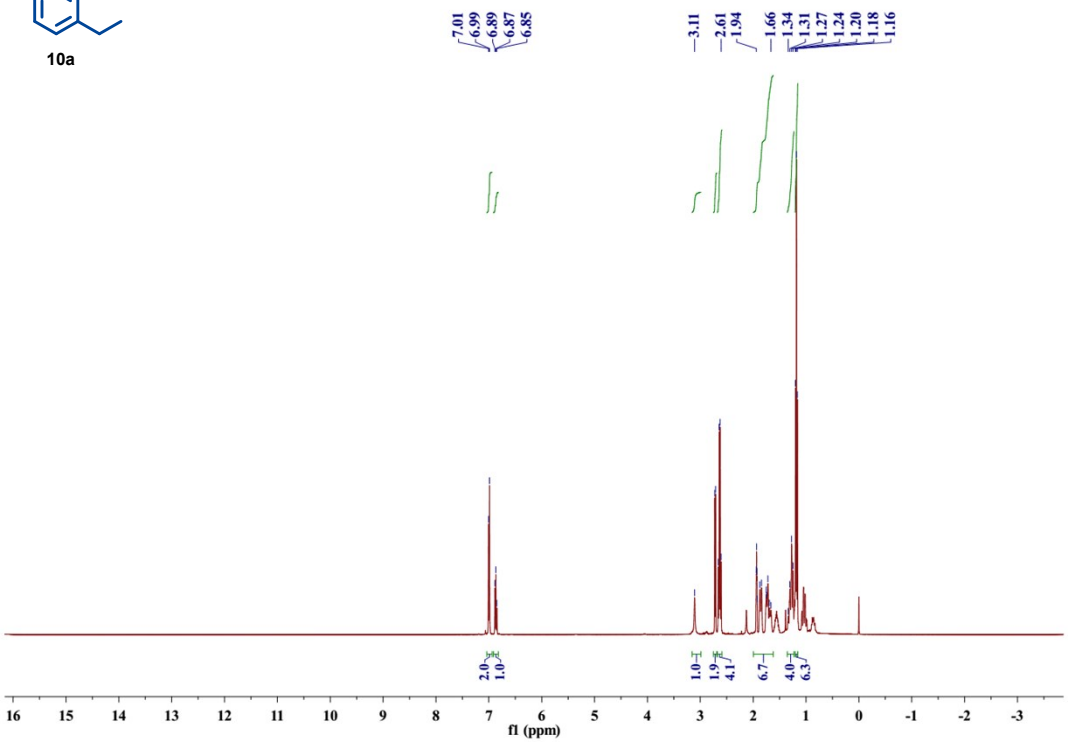

8a
146.64
128.52
127.99
127.35
116.59
110.19
50.52
37.55
31.66
27.01
26.40
24.23
13.18
f1 (ppm)

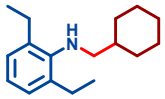

9a
6.91
6.89
6.71
6.69
6.68
3.58
2.72
2.70
2.20
1.67
1.43
1.42
1.42
1.41
1.39
1.36
1.26
1.25
1.23
1.22
1.19
1.17
1.17
1.16
1.15
1.13
1.12
1.11
1.10
1.09
1.08
2.1
1.0
1.0
2.0
6.2
2.1
1.6
4.3
f1 (ppm)


9a
147.01
129.43
128.92
121.34
54.90
38.93
31.26
26.70
26.09
18.80
f1 (ppm)



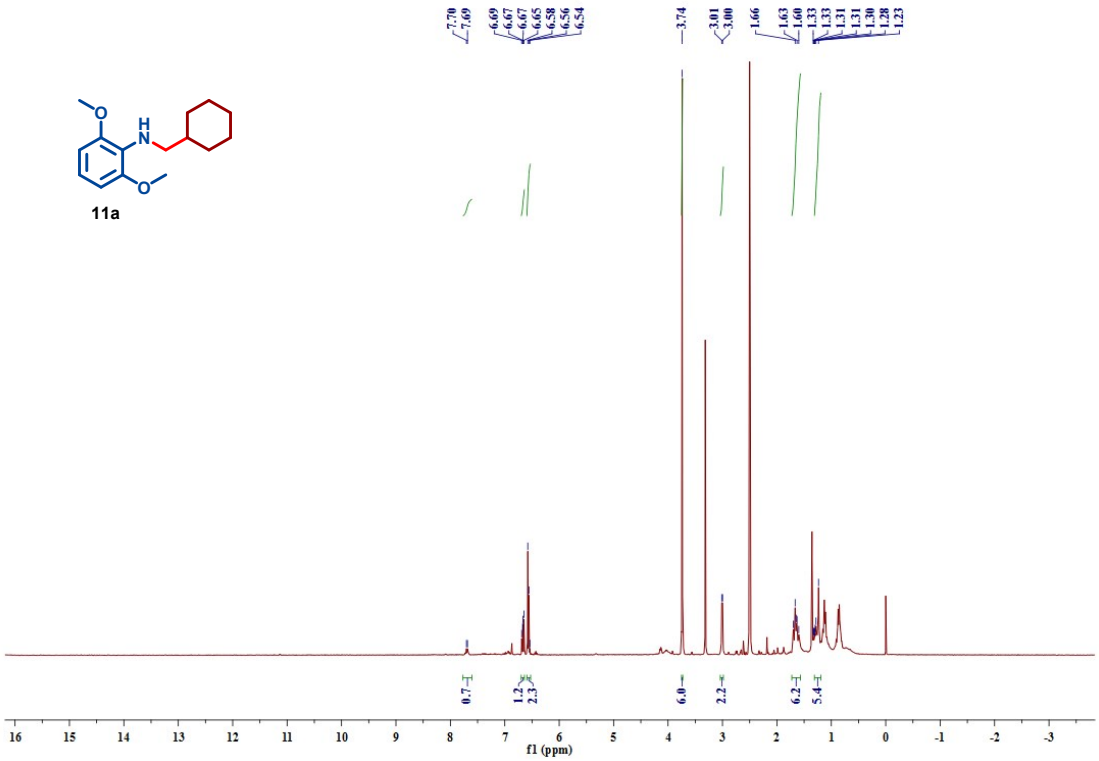
10a

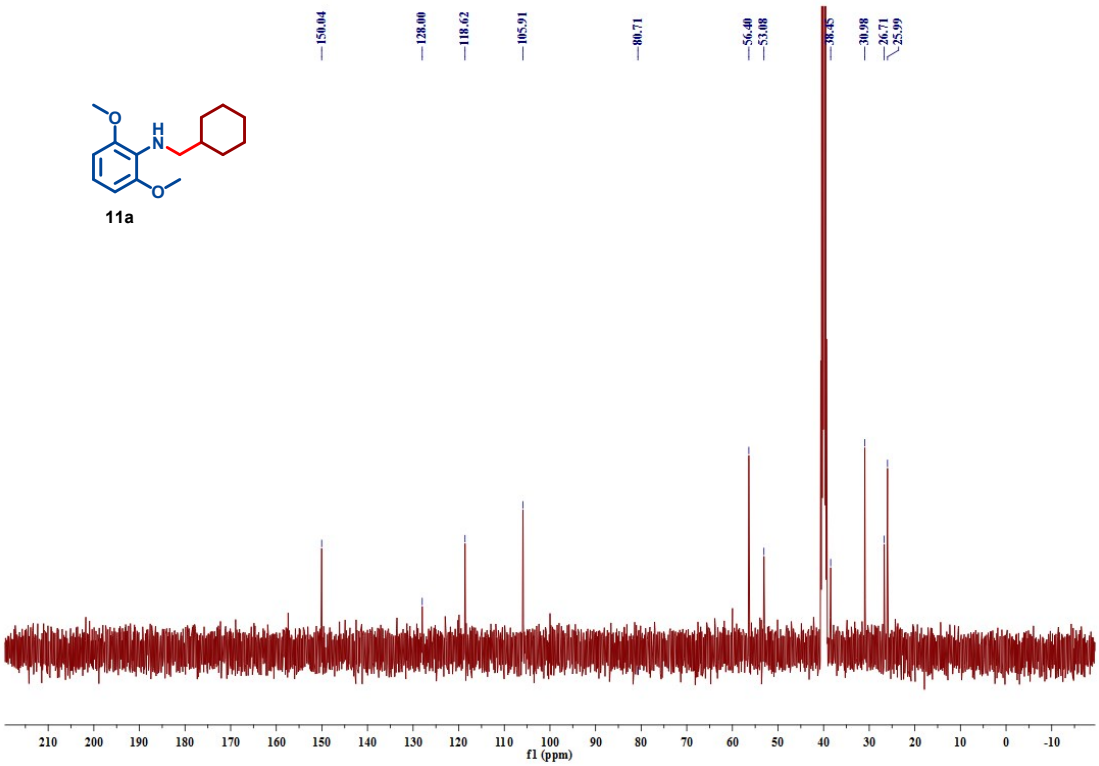

7.01
6.99
6.89
6.87
6.85
3.11
2.61
1.94
1.66
1.34
1.31
1.27
1.24
1.20
1.18
1.16
2.0
1.0
1.0
1.9
4.1
6.7
4.0
6.3
f1 (ppm)

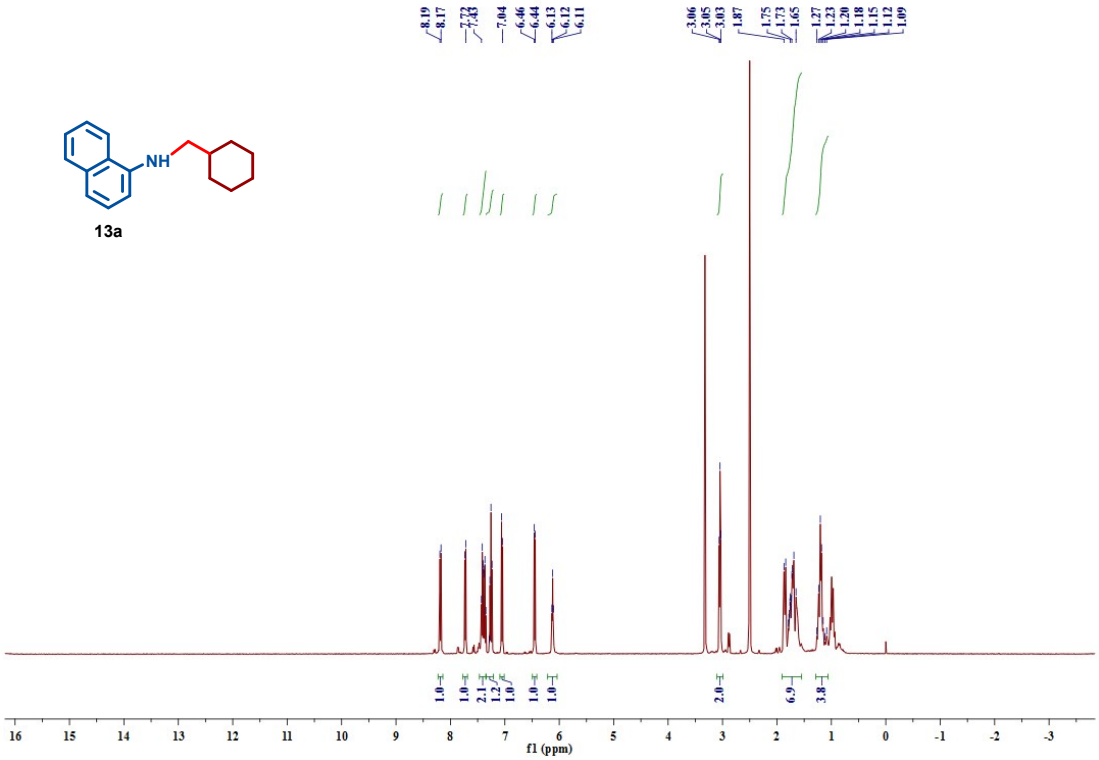


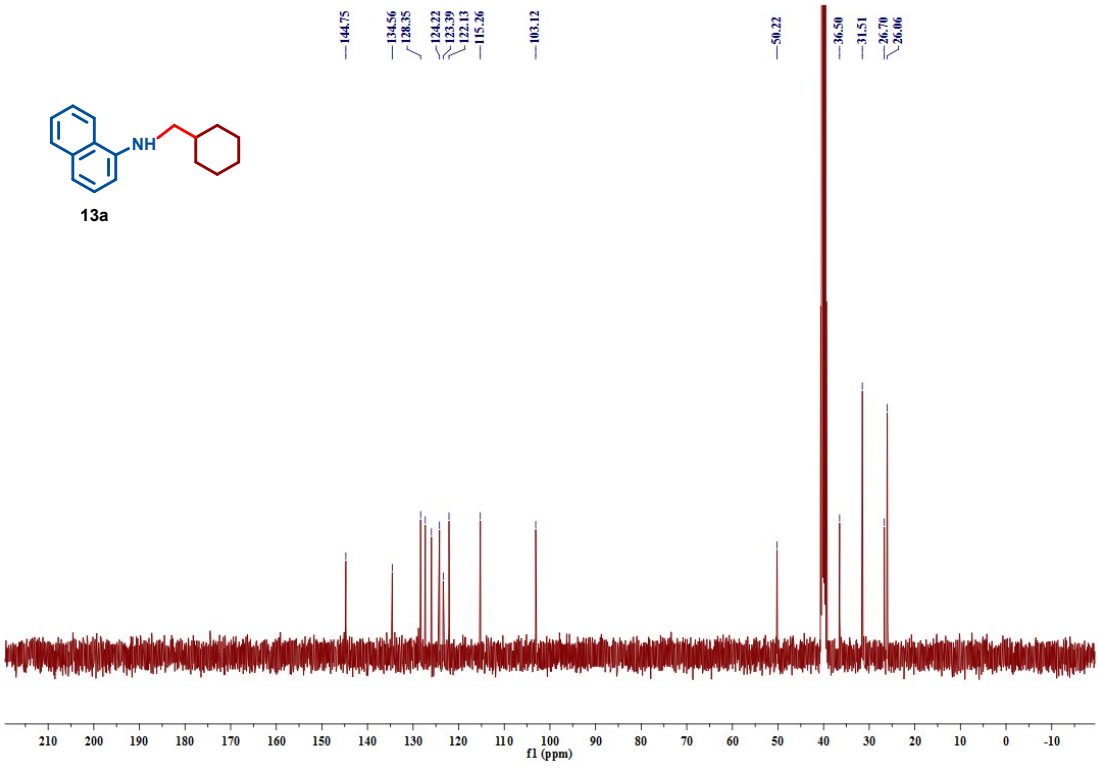
10a

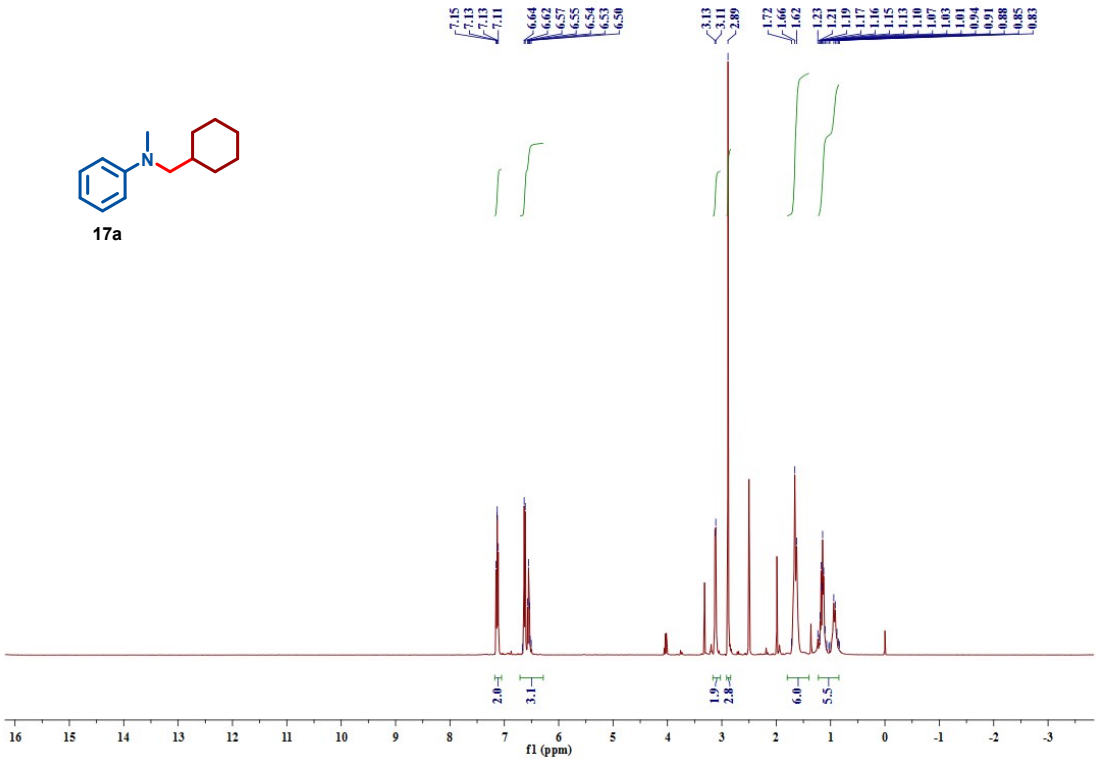
137.10
127.24
122.91
57.37
39.63
31.65
26.46
24.59
15.02
f1 (ppm)

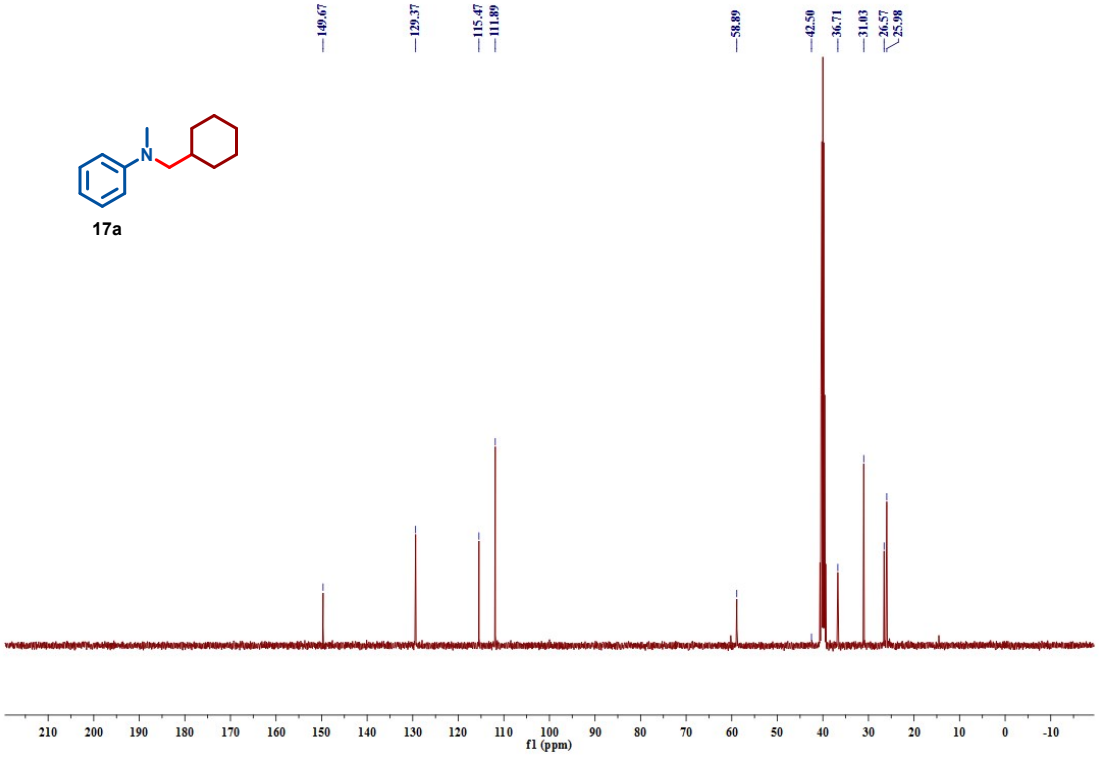

11a
7.70
7.69
6.69
6.67
6.67
6.65
6.58
6.56
6.54
3.74
3.01
3.00
1.66
1.63
1.60
1.33
1.33
1.31
1.31
1.30
1.28
1.23
0.7
1.2
2.3
6.0
2.2
6.2
5.4
f1 (ppm)

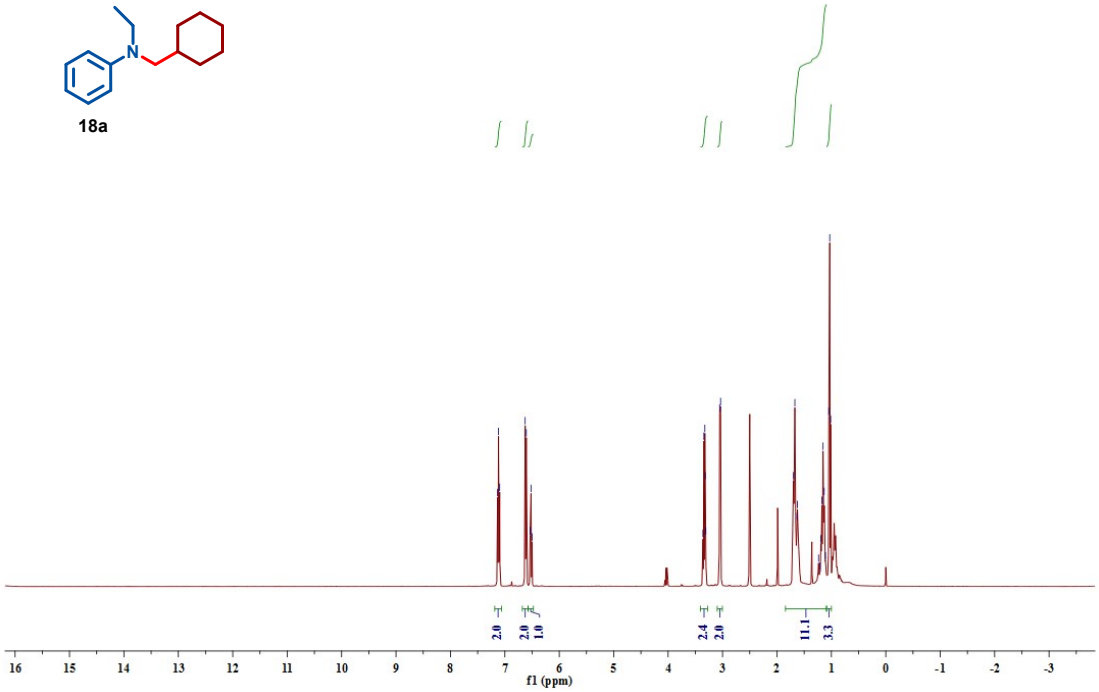

11a
150.04
128.00
118.62
105.91
80.71
56.40
53.08
38.45
30.98
26.71
25.99
f1 (ppm)

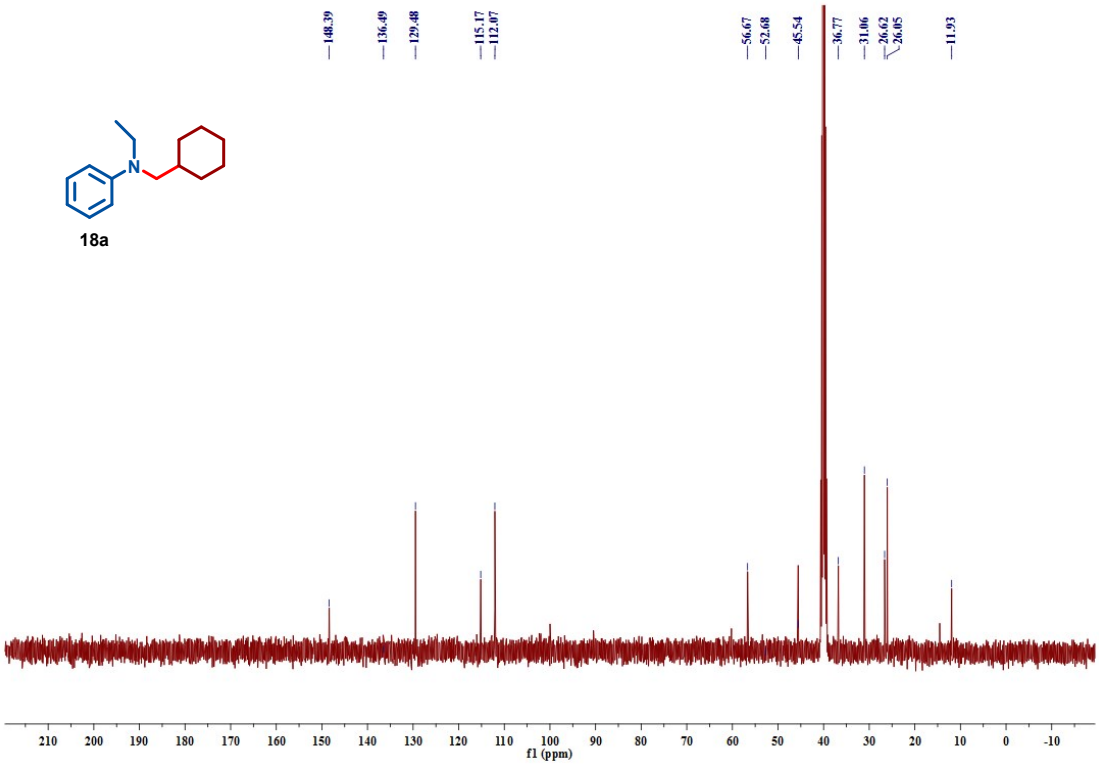

NH
13a
8.19
8.17
7.72
7.43
7.04
6.46
6.44
6.13
6.12
6.11
3.06
3.05
3.03
1.87
1.75
1.73
1.65
1.27
1.23
1.20
1.18
1.15
1.12
1.09
1.0
1.0
2.1
1.2
1.0
1.0
1.0
2.0
6.9
3.8
f1 (ppm)

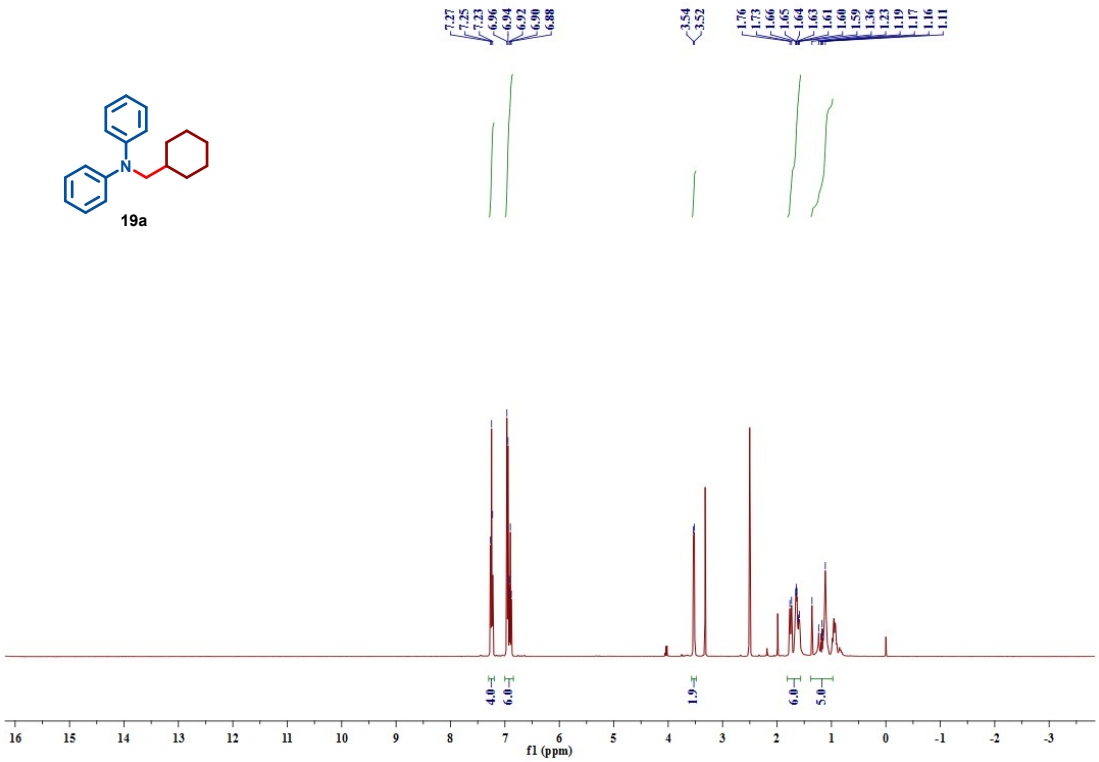

NH
13a
144.75
134.56
128.35
124.22
123.39
122.13
115.26
103.12
50.22
36.50
31.51
26.70
26.06
f1 (ppm)

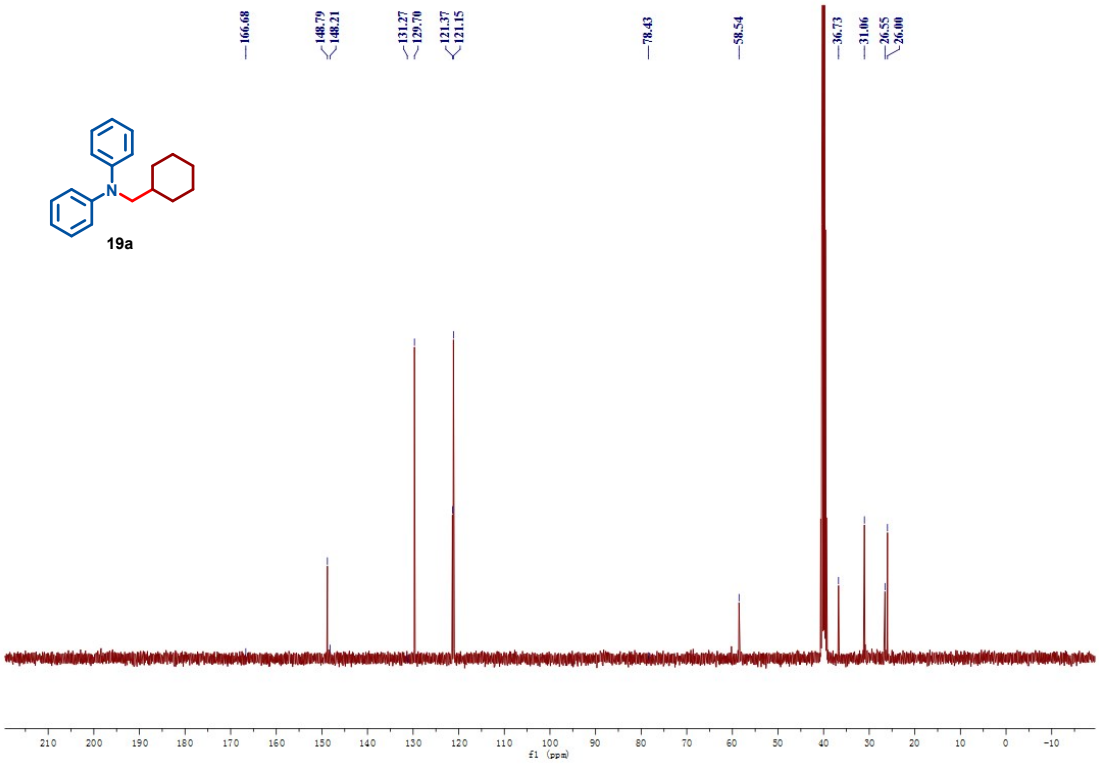

17a
7.15
7.13
7.13
7.11
6.64
6.62
6.57
6.55
6.54
6.53
6.50
3.13
3.11
2.89
1.72
1.66
1.62
1.23
1.21
1.19
1.17
1.16
1.15
1.13
1.10
1.07
1.05
1.01
0.94
0.91
0.88
0.85
0.83
2.0
3.1
1.9
2.8
6.0
5.5
f1 (ppm)

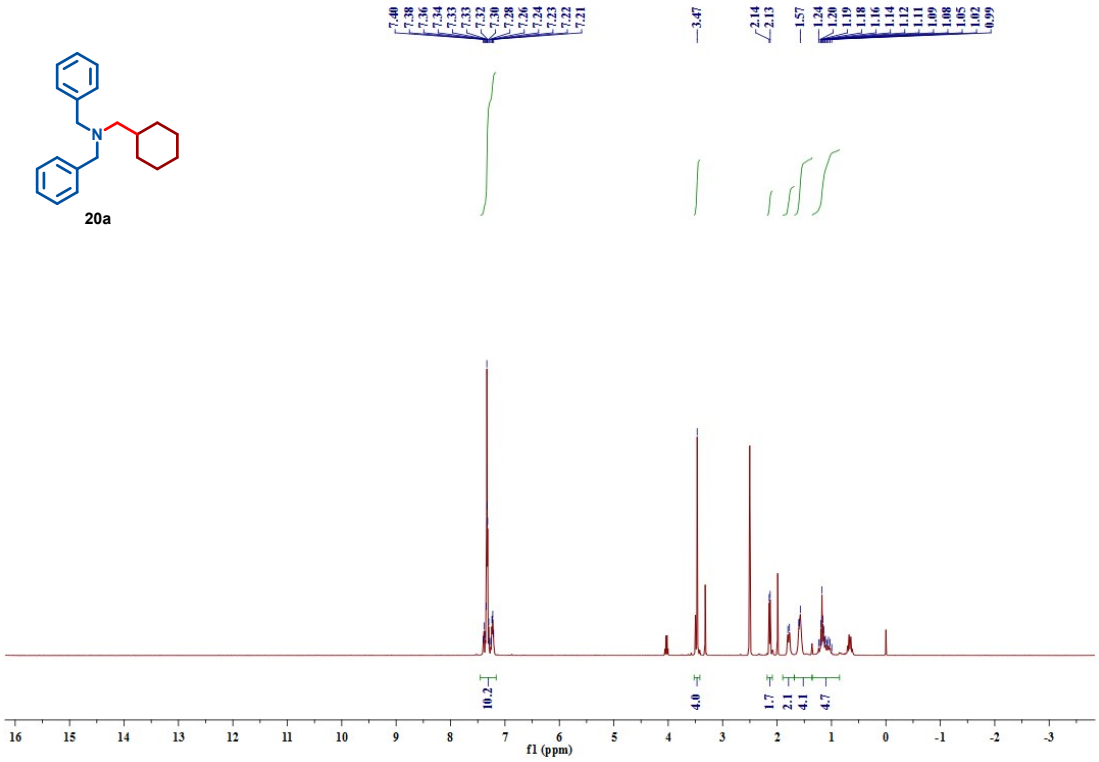

17a
149.67
129.37
115.47
111.89
58.89
42.50
36.71
31.03
26.57
25.98
f1 (ppm)

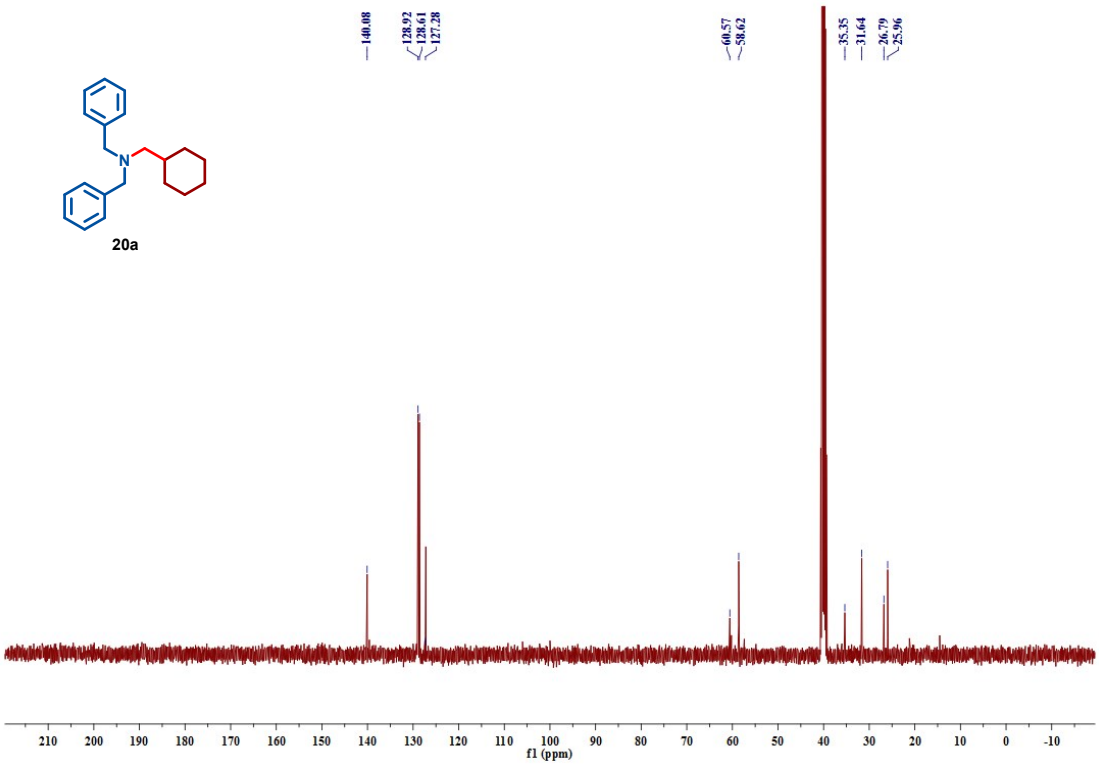

7.13
7.12
7.09
6.63
6.61
6.54
6.52
6.50
3.36
3.34
3.33
3.32
3.31
3.05
3.04
1.67
1.63
1.62
1.24
1.21
1.19
1.17
1.15
1.13
1.11
1.05
1.03
1.01
18a
2.0
2.0
1.0
2.4
2.0
11.1
3.3
f1 (ppm)

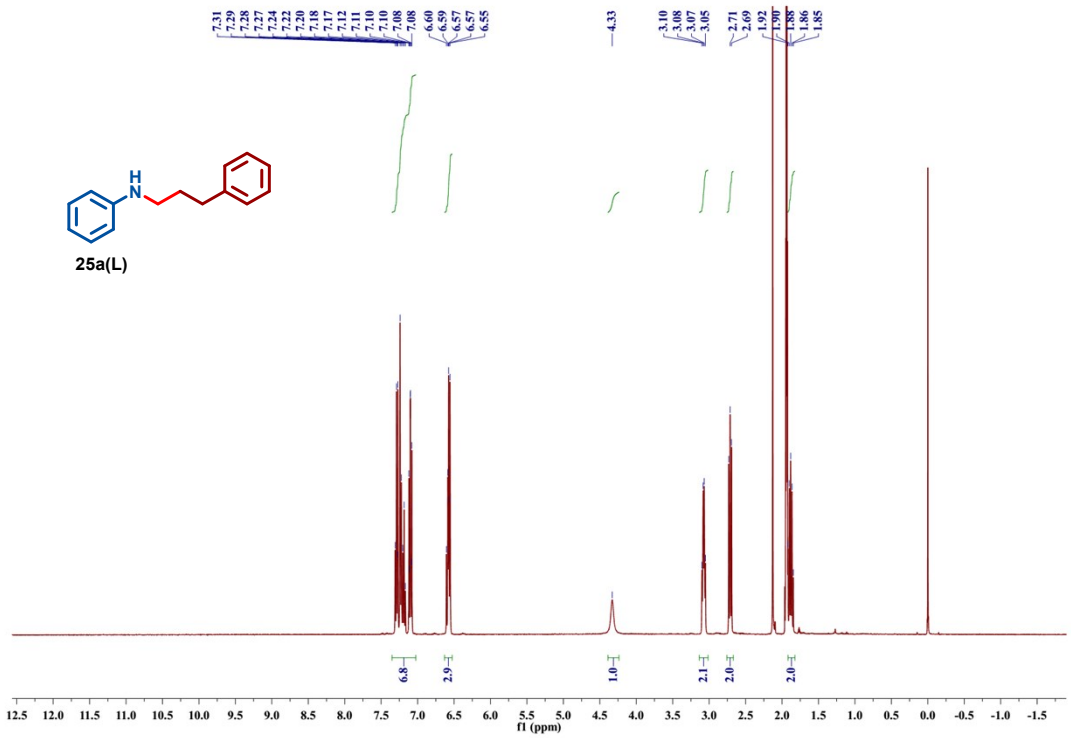

148.39
136.49
129.48
115.17
112.07
56.67
52.68
45.54
36.77
31.06
26.62
26.05
11.93
18a
f1 (ppm)

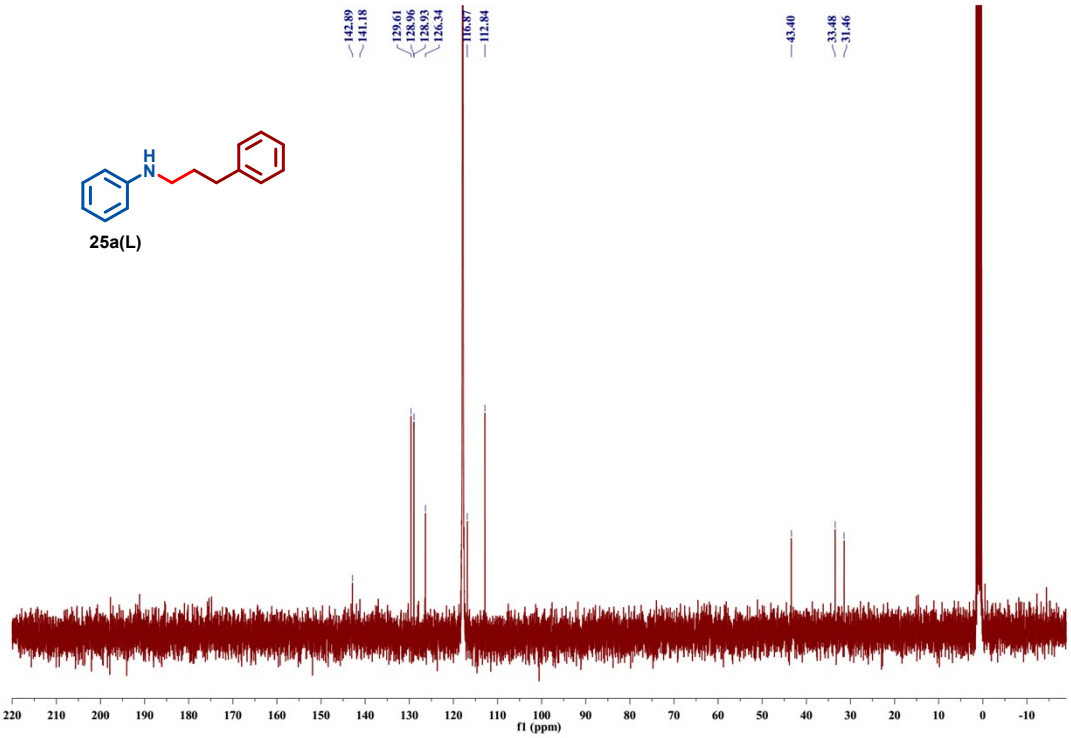

7.27
7.25
7.23
6.96
6.94
6.92
6.90
6.88
3.54
3.52
1.76
1.73
1.66
1.65
1.64
1.63
1.61
1.60
1.59
1.36
1.23
1.19
1.17
1.16
1.11
19a
4.0
6.0
1.9
6.0
5.0
f1 (ppm)

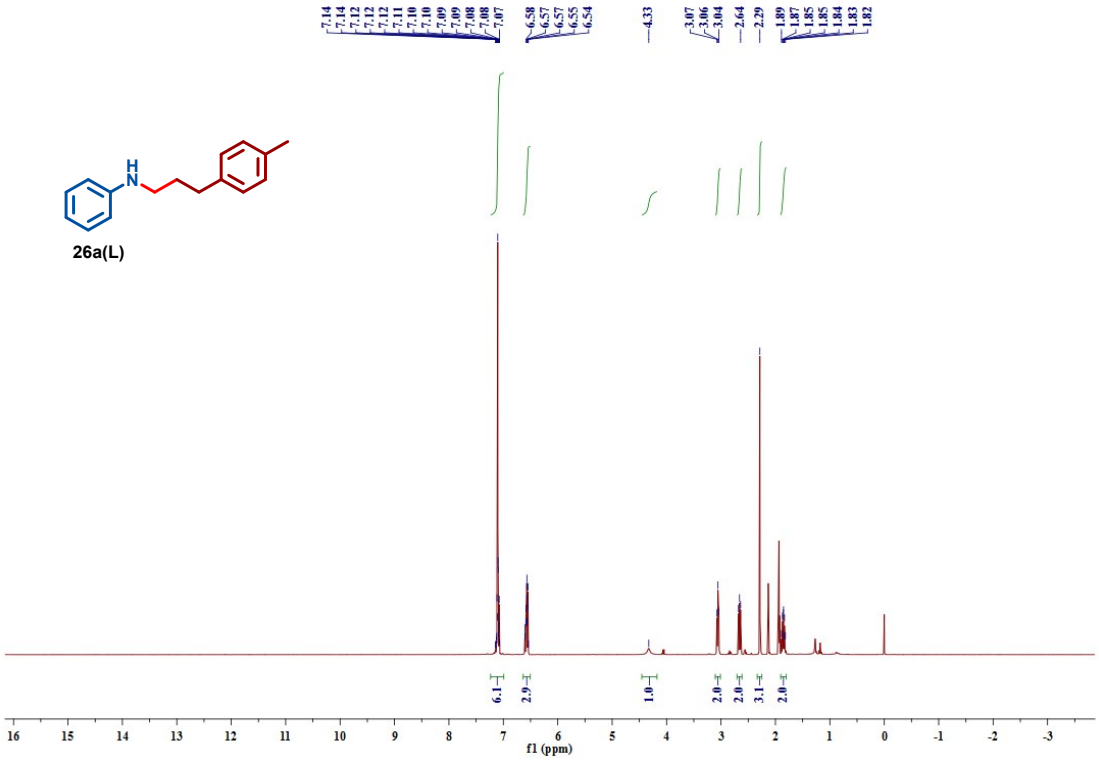

166.68
148.79
148.21
131.27
129.70
121.37
121.15
78.43
58.54
36.73
31.06
26.55
26.00
19a
f1 (ppm)

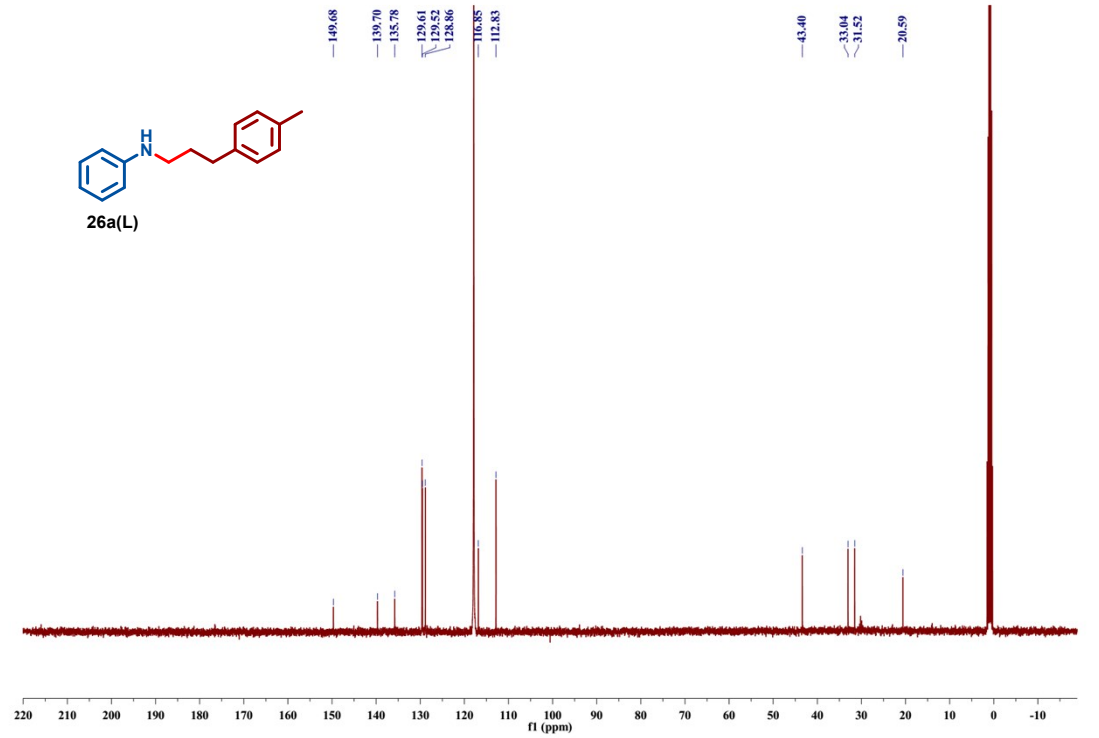

20a
7.40
7.38
7.36
7.34
7.33
7.33
7.32
7.30
7.28
7.26
7.24
7.23
7.22
7.21
3.47
2.14
2.13
1.57
1.24
1.20
1.19
1.18
1.16
1.14
1.12
1.11
1.09
1.08
1.05
1.02
0.99
10.2
4.0
1.7
2.1
4.1
4.7
f1 (ppm)

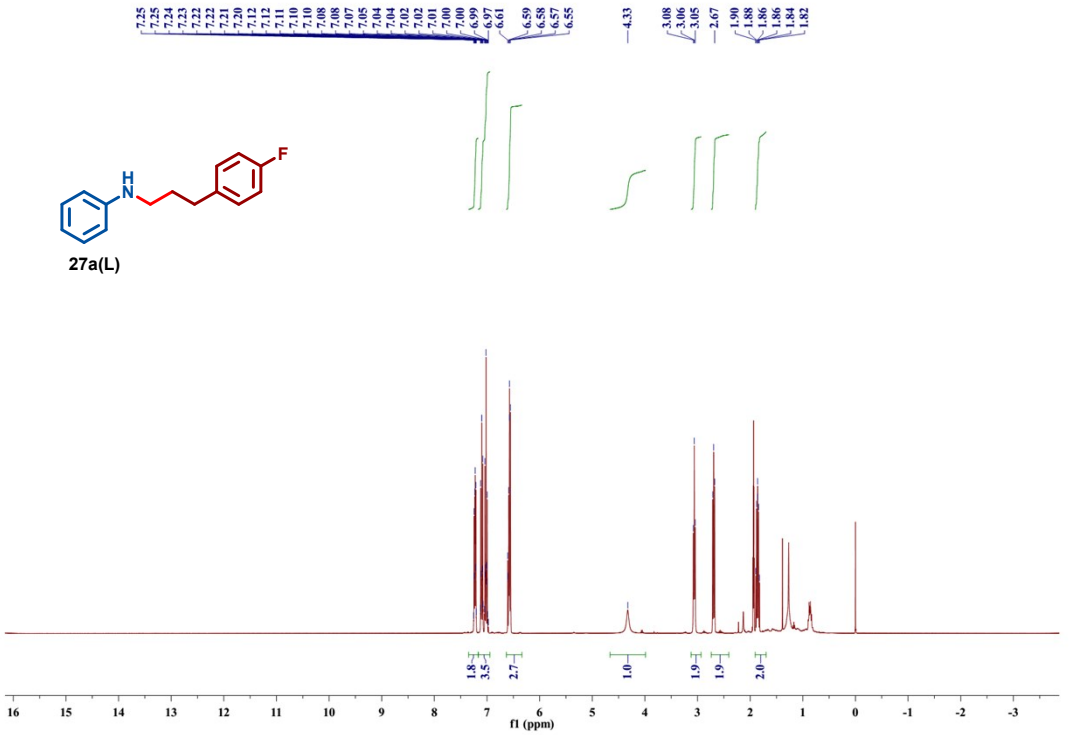

20a
140.08
128.92
128.61
127.28
60.57
58.62
35.35
31.64
26.79
25.96
f1 (ppm)

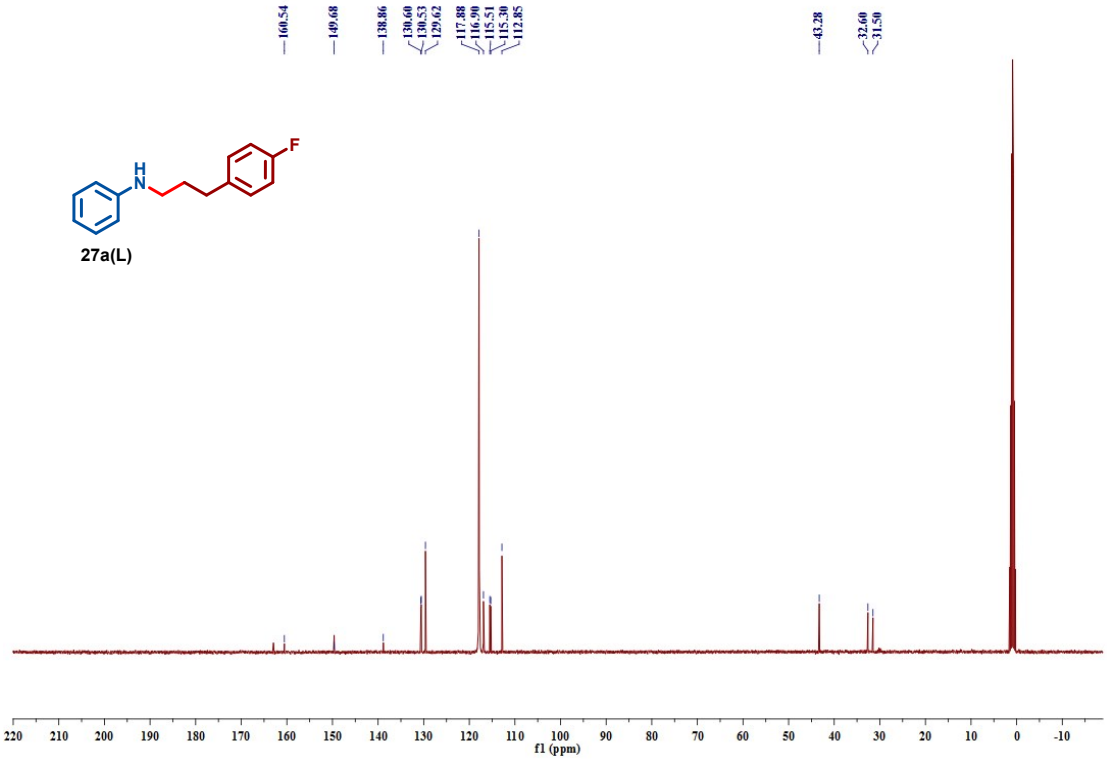

7.31
7.29
7.28
7.27
7.24
7.22
7.20
7.18
7.17
7.12
7.11
7.10
7.10
7.08
7.08
6.60
6.59
6.57
6.57
6.55
4.33
3.10
3.08
3.07
3.05
2.71
2.69
1.92
1.90
1.88
1.86
1.85
H
N
25a(L)
6.8
2.9
1.0
2.1
2.0
2.0
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

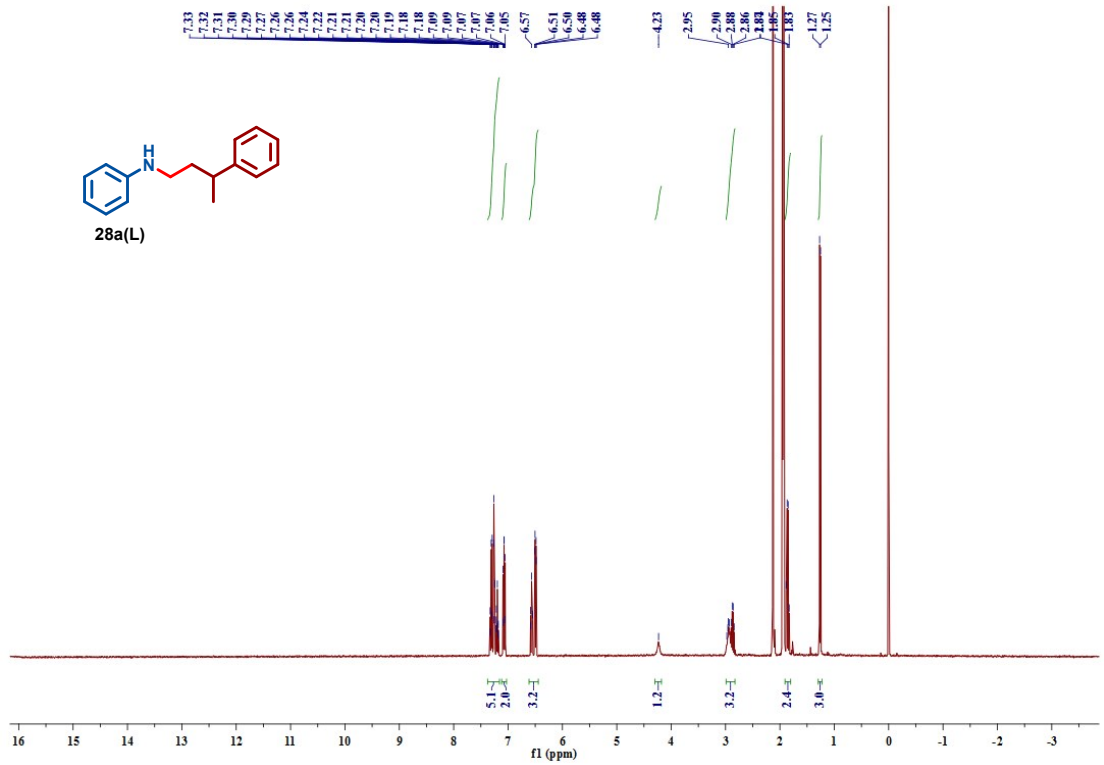

142.89
141.18
129.61
128.96
128.93
126.34
116.87
112.84
43.40
33.48
31.46
H
N
25a(L)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

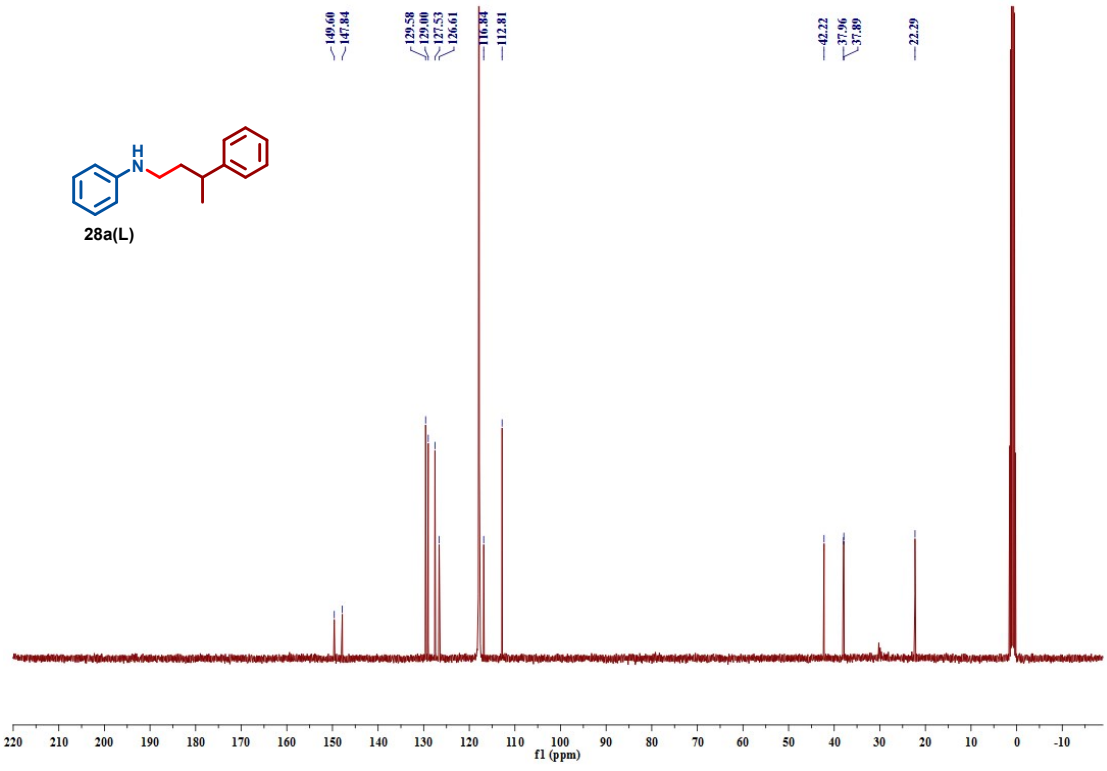

7.14
7.14
7.12
7.12
7.12
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
6.58
6.57
6.57
6.55
6.54
4.33
3.07
3.06
3.04
2.64
2.29
1.89
1.87
1.85
1.85
1.84
1.83
1.82
H
N
26a(L)
6.1
2.9
1.0
2.0
2.0
3.1
2.0
f1 (ppm)

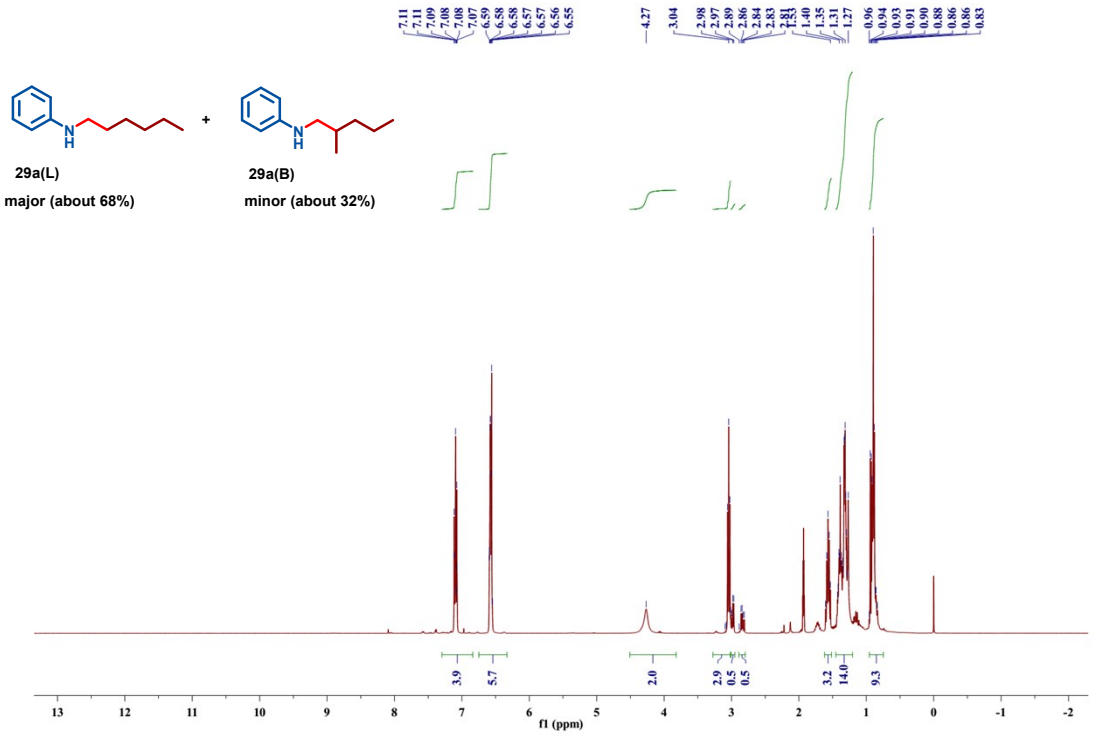

149.68
139.70
135.78
129.61
129.52
128.86
116.85
112.83
43.40
33.04
31.52
20.59
H
N
26a(L)
f1 (ppm)

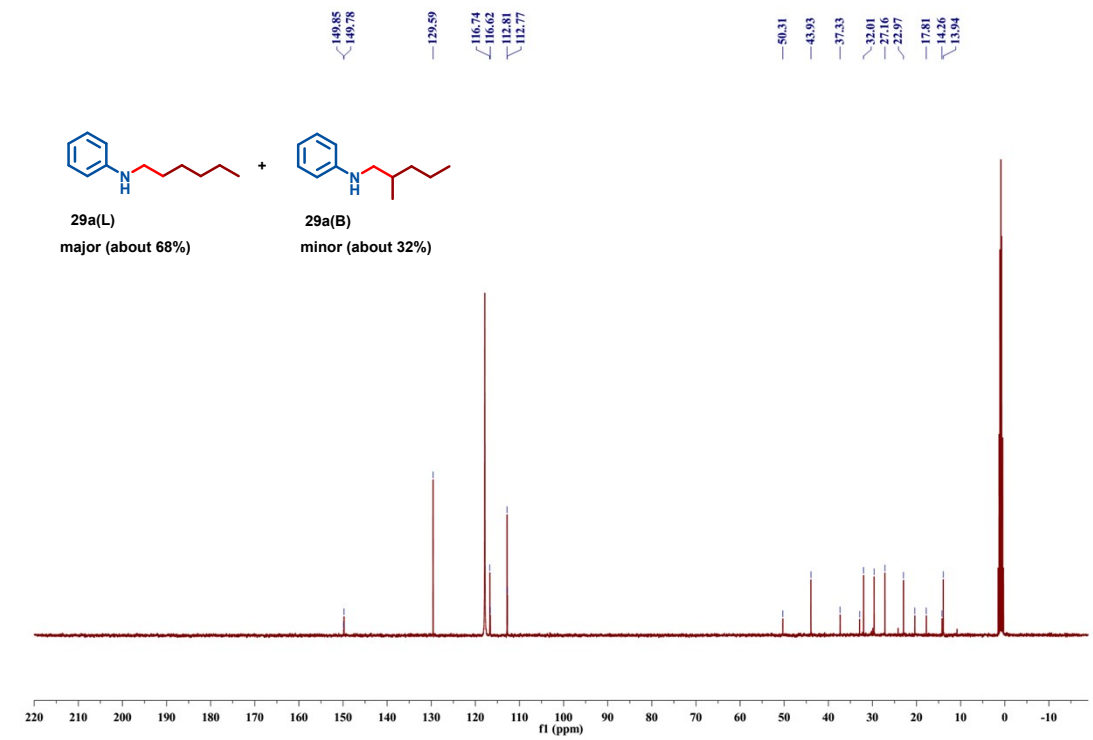

7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.12
7.12
7.11
7.10
7.10
7.08
7.08
7.07
7.05
7.04
7.04
7.02
7.02
7.01
7.00
7.00
6.99
6.97
6.61
6.59
6.58
6.57
6.55
4.33
3.08
3.06
3.05
2.67
1.90
1.88
1.86
1.86
1.84
1.82
H
N
F
27a(L)
1.8
3.5
2.7
1.0
1.9
1.9
2.0
f1 (ppm)

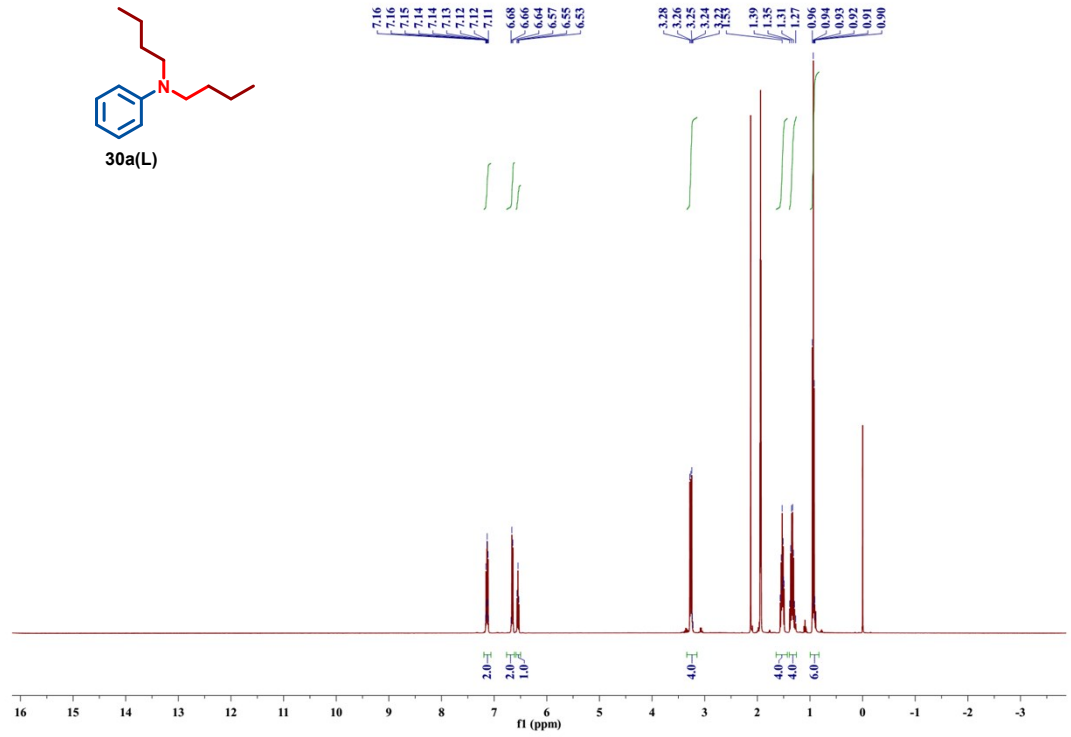

160.54
149.68
138.86
130.60
130.53
129.62
117.88
116.90
115.51
115.30
112.85
43.28
32.60
31.50
H
N
F
27a(L)
f1 (ppm)

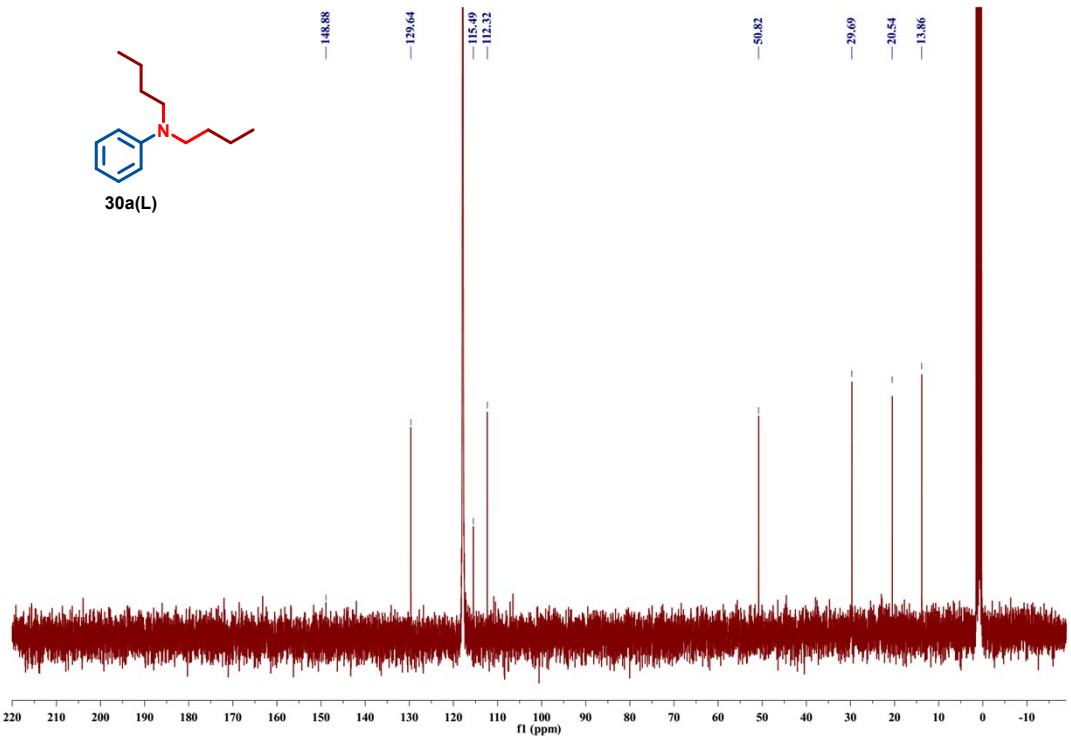

28a(L)
f1 (ppm)

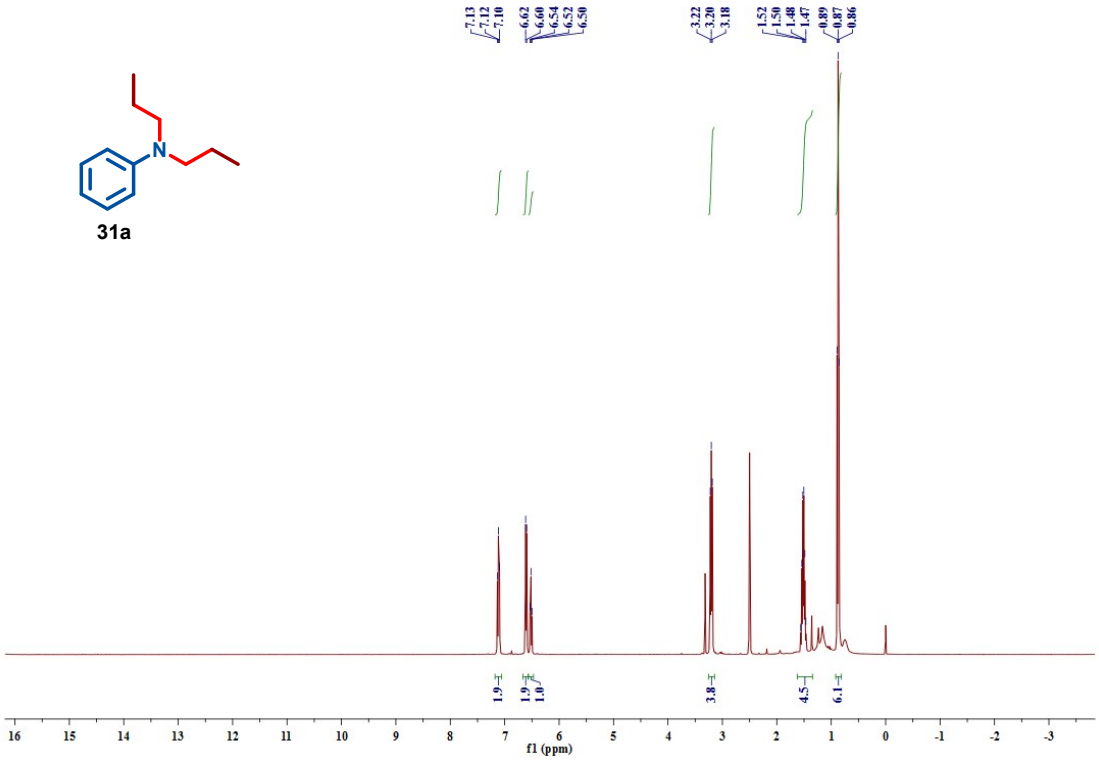

28a(L)
f1 (ppm)

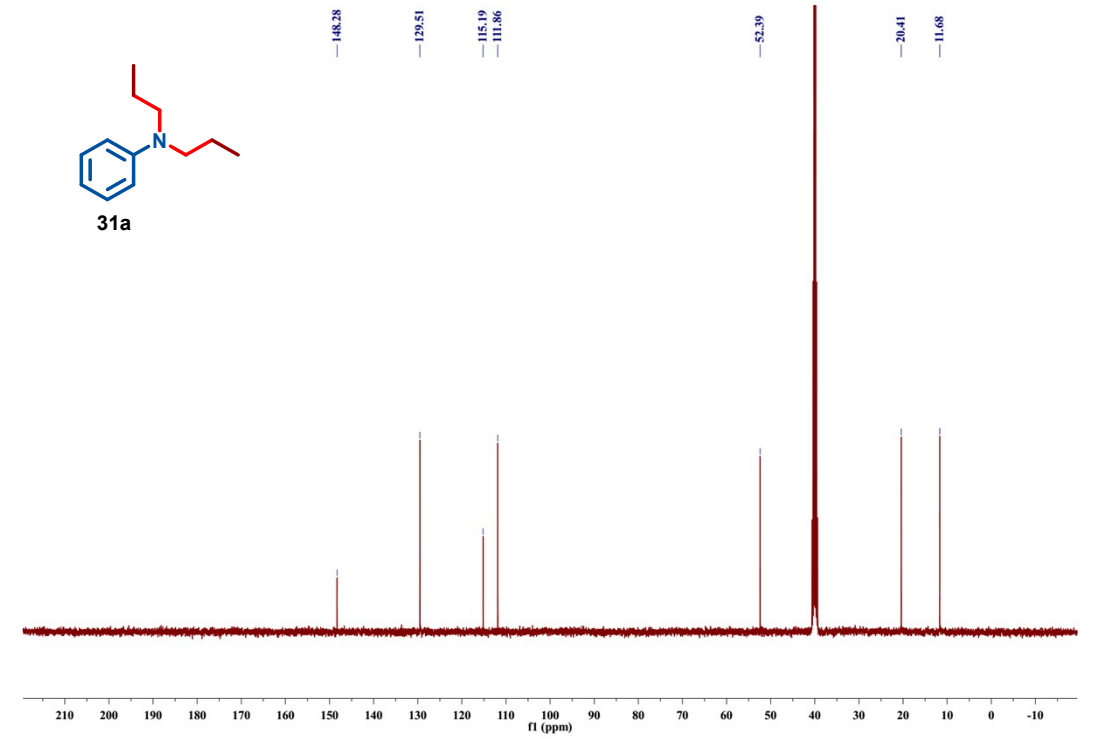

7.11
7.11
7.09
7.08
7.08
7.07
6.59
6.58
6.58
6.57
6.57
6.56
6.55
4.27
3.04
2.98
2.97
2.89
2.86
2.84
2.83
2.81
1.53
1.40
1.35
1.31
1.27
0.96
0.94
0.93
0.91
0.90
0.88
0.86
0.86
0.83
29a(L)
major (about 68%)
29a(B)
minor (about 32%)
3.9
5.7
2.0
2.9
0.5
0.5
3.2
14.0
9.3
f1 (ppm)

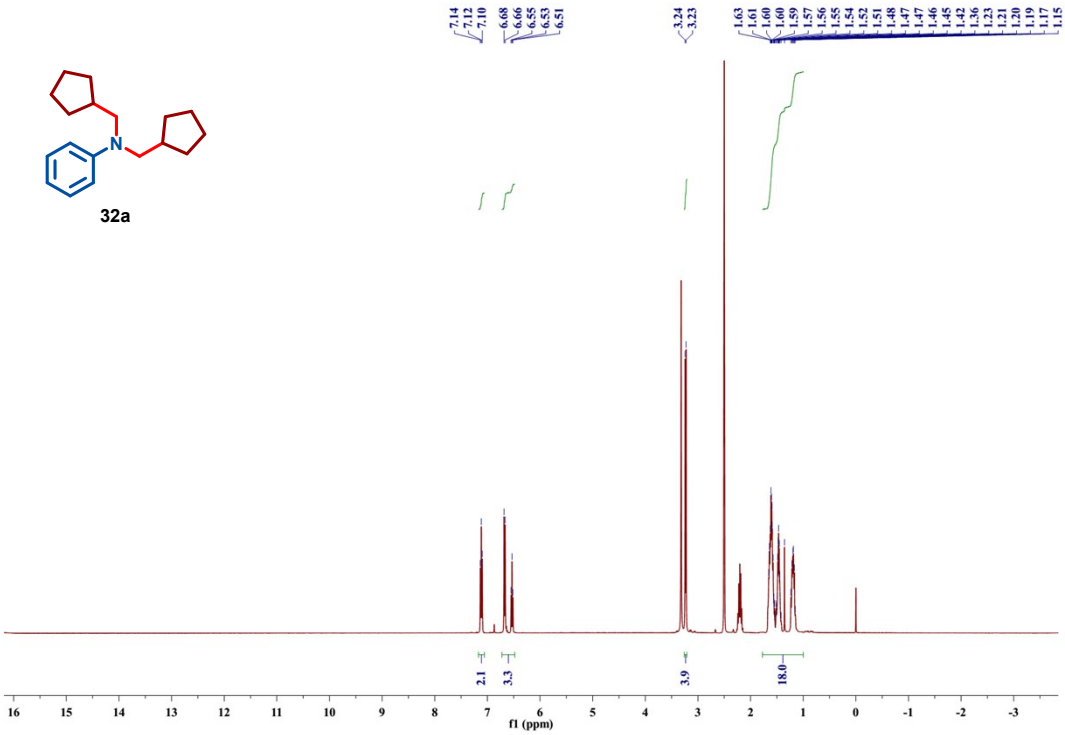

149.85
149.78
129.59
116.74
116.62
112.81
112.77
50.31
43.93
37.33
32.01
27.16
22.97
17.81
14.26
13.94
29a(L)
major (about 68%)
29a(B)
minor (about 32%)
f1 (ppm)

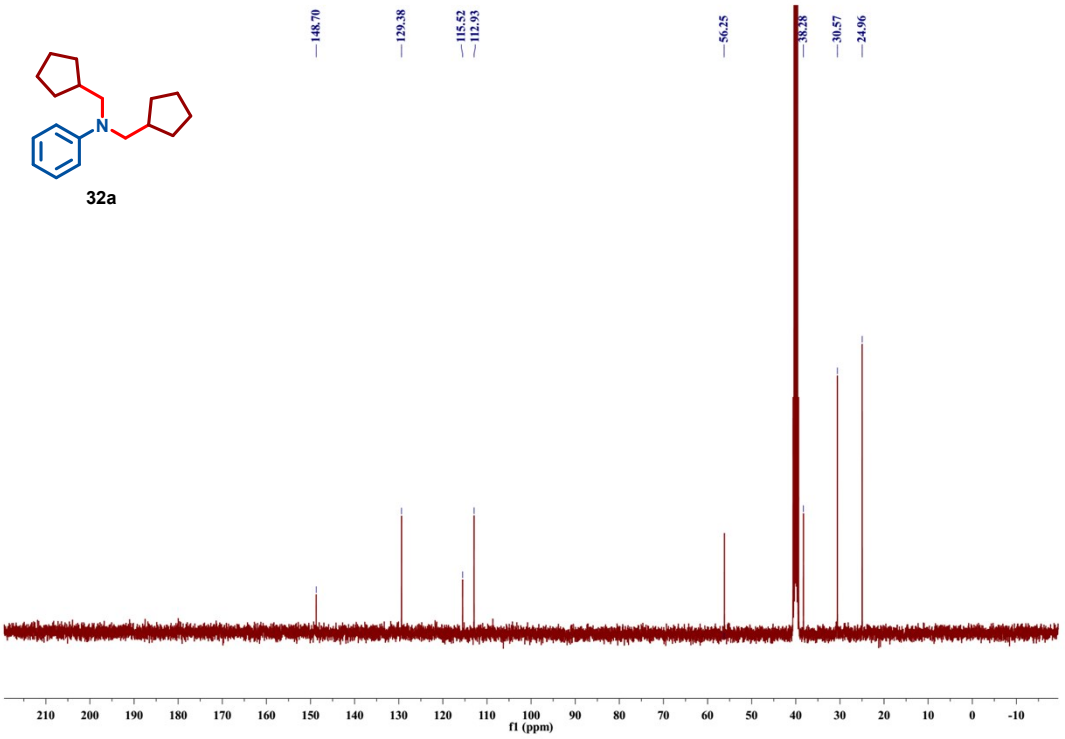

30a(L)
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.11
6.68
6.66
6.64
6.57
6.55
6.53
3.28
3.26
3.25
3.24
1.39
1.35
1.31
1.27
0.96
0.94
0.93
0.92
0.91
0.90
2.0
2.0
1.0
4.0
4.0
4.0
6.0
f1 (ppm)


30a(L)
148.88
129.64
115.49
112.32
50.82
29.69
20.54
13.86
f1 (ppm)


31a
7.13
7.12
7.10
6.62
6.60
6.54
6.52
6.50
3.22
3.20
3.18
1.52
1.50
1.48
1.47
0.89
0.87
0.86
1.9
1.9
1.0
3.8
4.5
6.1
f1 (ppm)


31a
148.28
129.51
115.19
111.86
52.39
20.41
11.68
f1 (ppm)


32a
7.14
7.12
7.10
6.68
6.66
6.55
6.53
6.51
3.24
3.23
1.63
1.61
1.60
1.60
1.59
1.57
1.56
1.55
1.54
1.52
1.51
1.48
1.47
1.47
1.46
1.45
1.42
1.36
1.23
1.21
1.20
1.19
1.17
1.15
2.1
3.3
3.9
18.0
f1 (ppm)


32a
148.70
129.38
115.52
112.93
56.25
38.28
30.57
24.96
f1 (ppm)

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